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

VIII *. THE DIRECT SYNTHESIS OF POLY(*N*-ALKYLIMINOALANES)

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Summary

Poly(*N*-alkyliminoalanes) have been synthesized directly from aluminum and primary amines under hydrogen pressure. In particular, hexamers $(HAlNR)_6$ were obtained from iso-$C_3H_7NH_2$, sec-$C_4H_9NH_2$ and cyclohexylamine, octamers $(HAlNR)_8$ from n-$C_3H_7NH_2$, and a mixture of oligomers from $C_2H_5NH_2$ and n-$C_4H_9NH_2$. Tetramer $(HAlNR)_4$ has been isolated from a mixture of various imino derivatives, starting from tert-$C_4H_9NH_2$. The reaction was induced by an activator. A number of activators have been screened for the synthesis of (HAlN-iso-$C_3H_7)_6$, with the result that Na and $NaAlH_4$ have been formed to be the most active.

The mechanism of the reaction is discussed; aluminum amides [Al(NH-iso-$C_3H_7)_3]_2$ and (iso-C_3H_7NH—AlN-iso-$C_3H_7)_4$ are intermediates in the synthesis of (HAlN-iso-$C_3H_7)_6$.

Introduction

In a preliminary communication [1] we reported the novel synthesis of poly(*N*-alkyliminoalanes) (PIA) by the one-step reaction 1 from powdered aluminum and primary amines, under hydrogen pressure in hydrocarbon solvents:

$$Al + RNH_2 \rightarrow 1/n\,(HAlNR)_n + \tfrac{1}{2}\,H_2 \qquad (1)$$

In particular, by this route we achieved the synthesis of (HAlN-iso-$C_3H_7)_6$ from iso-$C_3H_7NH_2$ and of (HAlN-n-$C_3H_7)_8$ from n-$C_3H_7NH_2$. Starting from tert-$C_4H_9NH_2$, tetramer (HAlN-tert-$C_4H_9)_4$ was separated from a mixture of iminoalane derivatives [1]. Subsequently, we have studied different linear and branched primary amines, as well as modified reaction conditions.

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* For part VII see ref. 8.

TABLE 1

RESULTS OBTAINED FOR THE DIRECT SYNTHESIS OF POLY(*N*-ALKYLIMINOALANES) FROM ALUMINUM AND DIFFERENT PRIMARY AMINES [a]

Amine	Solvent	Reaction conditions			Atomic [b] ratio N/Al	PIA [c,e] yield	Chemical composition [e] found (calcd.)			Physico-chemical results
		t (h)	*T* (°C)	*P*(H_2) (kg cm^{-2})			Al (%)	N (%)	H_{active} (meq/g)	
$C_2H_5NH_2$	Toluene	16	170	175	0.99	quant.	37.4 (38.0)	19.2 (19.7)	12.2 (14.1)	Mixture of $(HAlNR)_6$, $(HAlNR)_7$, $(HAlNR)_8$ (predominant), $(HAlNR)_{10}$ and other unidentified species
$C_2H_5NH_2$	Diethyl ether	50	120	160	1.6					
n-$C_3H_7NH_2$	Toluene	16	180	200	1.04	quant.	29.5 (31.7)	15.9 (16.5)	10.7 (11.7)	Practically pure $(HAlNR)_8$
n-$C_3H_7NH_2$	Diethyl ether	36	120	165	1.01	quant.	29.3 (31.7)	15.3 (16.5)	12.0 (11.7)	Mixture of $(HAlNR)_6$, $(HAlNR)_8$ and other unidentified species
n-$C_4H_9NH_2$	Toluene	24	175	210	1.04	quant.	25.7 (27.2)	13.8 (14.1)	9.5 (10.1)	Mixture of $(HAlNR)_6$ (predominant), $(HAlNR)_7$ and $(HAlNR)_8$
n-$C_4H_9NH_2$	Diethyl ether	16	100	160	1.98					$(RNH\text{-}AlNR)_6$
iso-$C_3H_7NH_2$	Toluene	10	180	200	1.02	quant.	30.5 (31.7)	16.4 (16.5)	11.5 (11.7)	$(HAlNR)_6$
iso-$C_3H_7NH_2$	Diethyl ether	4	100	170	0.98	quant.	30.8 (31.7)	15.6 (16.5)	12.2 (11.7)	$(HAlNR)_6$
sec-$C_4H_9NH_2$	Toluene	15	170	180	1.01	quant.	27.4 (27.2)	14.0 (14.1)	10.2 (10.1)	$(HAlNR)_6$
$C_6H_{11}NH_2$	Toluene	50	170	185	1.06	40%	20.8 (21.6)	11.4 (11.2)	8.1 (8.0)	$(HAlNR)_6$
tert-$C_4H_9NH_2$	Toluene	16	180	200	1.5	ca. 25% [d]	27.0 (27.2)	15.1 (14.1)	9.7 (10.1)	$(HAlNR)_4$ and other imino species
tert-$C_4H_9NH_2$	Diethyl ether	16	120	160	2.8					

[a] Generally the following amounts were used: Al (200 mmol), amine (180 mmol), $NaAlH_4$ (9–10 mmol) solvent (280 ml). [b] Atomic ratio N/Al measured in the reaction solution. [c] PIA yield calculated with respect to the starting amine. [d] Yield and chemical composition of tetramer PIA obtained by crystallization from the reaction solution. [e] Yield and chemical composition of the product recovered from evaporation of the reaction solution.

The reaction of isopropylamine has been examined in detail; the isolation and characterization of some reaction intermediates have led to a proposed reaction mechanism. This paper will discuss these recent results.

Results and discussion

Influence of the amine

In Table 1, the results of the reaction of several amines are reported, using $NaAlH_4$ as activator. The reaction of an amine with a secondary carbon atom in the α-position, e.g. iso-$C_3H_7NH_2$, sec-$C_4H_9NH_2$, or cyclohexylamine, yields a very pure PIA hexamer, $(HAlNR)_6$. These data are consistent with the general behaviour of such amines to give PIA hexamers, independent of the method of synthesis [2,3]. Mass spectrometry, ^1H NMR and X-ray measurements on these products are identical with those of PIA prepared by different routes [2,3]. In the case of $(HAlN\text{-iso-}C_3H_7)_6$ (I), the replacement of hydrocarbon solvent with diethyl ether noticeably accelerates the reaction, with no effect on the structure and purity of the final product. The molecular structure is again the typical closed hexameric cage [4]. For cyclohexylamine, if the PIA is recovered by simple evaporation of the filtered reaction mixture, the yield is not quantitative, because of its only partial solubility in hydrocarbons and some $(HAlN\text{-}C_6H_{11})_6$ is removed with the excess of unreacted aluminum powder. However, the PIA may be recovered quantitatively by extraction with boiling benzene.

From n-$C_3H_7NH_2$ in toluene, reaction 1 yields practically pure PIA octamer, $(HAlN\text{-n-}C_3H_7)_8$ (II), purified by crystallization from hexane. Single crystal X-ray analysis reveals a closed cage structure [5]. In contrast to n-propylamine, other linear amines, such as ethylamine and n-butylamine, give a mixture of PIA oligomers $(HAlNR)_n$ with n variable between 6 and 10. These products, characterized by mass spectrometry and ^1H NMR, are similar to those already obtained from complexes of AlH_3 and ethyl, n-propyl, or n-butylamine [2].

In the case of linear amines, the substitution of toluene by diethyl ether does not benefit the reaction rate and it also influences the structure of the PIA obtained from n-$C_3H_7NH_2$, giving a mixture of various PIA oligomers. Starting from ethyl- or n-butylamine in ether solvent, products with an atomic ratio $N/Al > 1$ are obtained, indicating a very slow reaction which does not reach completion under our experimental conditions. The isolated compounds are, in fact, intermediates in the PIA synthesis. For example, employing n-butylamine we have isolated a hexamer $(RNH{-}AlNR)_6$ (III). The more abundant ions in its mass spectrum, *m/e* 1020 and 977, are assigned to the ions $M^{+\cdot}$ and $(M - C_3H_7)^+$, respectively. The fragmentation of the C—C bond adjacent to nitrogen, responsible for the fragment at *m/e* 977, is a previously-noted characteristic of the mass spectrum of PIA [2]. III reacts easily with $AlH_3 \cdot N(CH_3)_3$ in ether to give a mixture of PIA oligomers (prevailing hexamer), according to reaction 2.

$$(RNH{-}AlNR)_6 + 6\ AlH_3 \cdot N(CH_3)_3 \rightarrow 12/n\ (HAlNR)_n + 6\ H_2 \qquad (2)$$

tert-$C_4H_9NH_2$ displays an even lower reactivity with aluminum in toluene. We have reported previously that the reaction gives a mixture of imino derivatives with an atomic ratio $N/Al > 1$; from this mixture, a pure tetramer (HAlN-tert-

$C_4H_9)_4$ has been separated by fractionation [1]. The reaction in diethylether yields a product having an atomic ratio N/Al = 2.8, probably aluminum trisamide.

Reaction conditions

The effect of varying reaction conditions on the synthesis of $(HAlN\text{-iso-}C_3H_7)_6$ was studied owing to its interest as a polymerization catalyst [6].

In the absence of an activator, no reaction occurs between iso-$C_3H_7NH_2$ and Al at high temperature and under a pressure of hydrogen, either in aromatic solvent (p = 200 kg cm^{-2}, 180°C) or in diethyl ether (p = 180 kg cm^{-2}, 110°C).

In Table 2 some results are reported relating to the use of various activators (5 mole % with respect to the amine) under the same experimental conditions. Although many activators promote reaction 1, the reaction rates differ. The highest activity is shown by Na or $NaAlH_4$.

If a very large excess of aluminum with respect to amine is used (in the presence of an activator for the first run), unreacted aluminum may be utilized for subsequent syntheses of $(HAlN\text{-iso-}C_3H_7)_6$, after the product solution is decanted. Further addition of an activator is unnecessary, because of the promoting effect of the small amount of $(HAlN\text{-iso-}C_3H_7)_6$ remaining with the unreacted aluminum. In such a case, in diethyl ether under the conditions reported in Table 1, the synthesis of $(HAlN\text{-iso-}C_3H_7)_6$ requires less than 1 h.

TABLE 2

THE INFLUENCE OF DIFFERENT ACTIVATORS ON THE REACTION OF ALUMINUM WITH ISO-PROPYLAMINE [a]

Activator (mmol)	Solvent (ml)	Reaction conditions			Atomic ratio N/Al in the reaction solution
		t (h)	T (°C)	$P(H_2)$ (kg cm^{-2})	
Na (10.9)	Heptane (280)	12	175	200	1.10
Na sand (10)	Toluene (280)	10	180	200	1.06
$LiAlH_4$ (10)	Toluene (280)	10	180	200	2.00
$NaAlH_4$ (9.4)	Toluene (280)	10	180	200	1.02
$NaAlH_4$ (10)	Diethyl ether (280)	4	100	170	0.98
$AlEt_3$ (10)	Toluene (280)	10	180	200	1.70
$AlH_3 \cdot N(CH_3)_3$ (10)	Toluene (280)	10	180	200	1.98
$(HAlN\text{-i-Pr})_6$ (1.6)	Toluene (280)	10	180	200	2.00
$(HAlN\text{-i-Pr})_6$ (1.7)	Toluene (280)	16	180	200	1.12
$[Al(NH\text{-i-Pr})_3]_2$ [b] (50)	Toluene (280)	16	180	210	1.76

[a] Generally the following amounts were used: aluminum (200 mmol), iso-$C_3H_7NH_2$ (180 mmol). [b] Aluminum (250 mmol) was used in the absence of iso-$C_3H_7NH_2$.

Reaction mechanism

Study was again focused on the reaction with isopropylamine. The reaction between aluminum and the amine does not occur in the absence of hydrogen, even at high temperature (200°C) and in the presence of an activator ($NaAlH_4$). It is therefore reasonable to postulate that the formation of a transient hydridic species of aluminum (i.e., AlH_3) is responsible for the reaction with the amine. The activator, or its derivatives from reaction, contribute to the formation of this transient species by stabilization (i.e. by complexation) for the limited time of the reaction.

If the reaction is quenched at an atomic ratio N/Al = 2 in solution, or if less efficient activators are used, a tetramer $(RNH{-}AlNR)_4$ (IV) is isolated as sole product. The more abundant ions in its mass spectrum, *m/e* 568, 553 and 509, are assigned to the molecular ions $(M^{+\cdot})$, $(M - CH_3)^+$ and $(M - RNH_2)^+$, respectively. The ^1H NMR spectrum (Fig. 1) is characterized by three sets of lines with relative intensities 2 : 12 : 1. The set with relative intensity 12 consists of two equal intensity doublets at τ 8.53 and τ 8.67. The set with intensity 2 consists of three septets centered at τ 6.46, τ 6.54 and τ 6.50, with the last septet double in intensity with respect to the other two. Finally, a doublet of relative intensity 1 is observed at τ 9.76.

These results suggest for IV a cubic structure (V). This structure is confirmed by spin-decoupling experiments which show that signals at τ 6.46 and at τ 6.54 consist of a doublet of septets due to the CH protons of the isopropylamino groups outside the cage coupled with adjacent CH_3 (τ 8.67) and NH (τ 9.76). The coupling constants are $J(CH_3{-}CH{-}) = 6.4$ Hz, and $J({-}CH{-}NH{-}) = 8.5$ Hz. The doublet at τ 8.53 and the septet at τ 6.50 have been assigned to CH_3 and CH components of isopropyl imino groups.

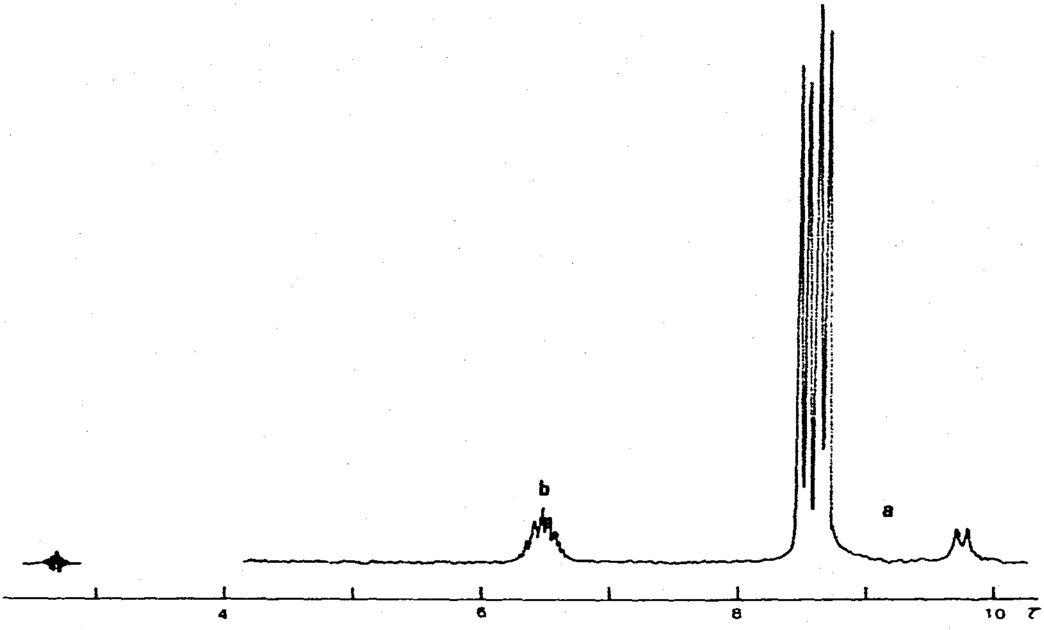
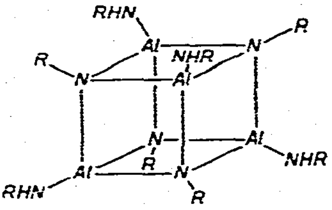


Fig. 1. ^1H NMR spectrum in benzene of $(iso\text{-}C_3H_7NH{-}AlN\text{-}iso\text{-}C_3H_7)_4$.



(V)

Crystals of IV are easily formed from the hydrocarbon or diethyl ether solutions and its molecular structure is now under single crystal X-ray investigation.

The hypothesis that IV is an intermediate of the reaction leading to $(\mathrm{HAlN\text{-}iso\text{-}C_3H_7})_6$ is confirmed by the reaction of IV with aluminum under H_2 pressure (200 kg cm^{-2}) in toluene at 180° C to give I as sole product (reaction 3). This reaction is accelerated by $NaAlH_4$. Furthermore IV reacts with $AlH_3 \cdot NR_3$ to form I (reaction 4), while IV is formed from I in the presence of iso-$C_3H_7NH_2$ (reaction 5).

$$\underset{\text{(IV)}}{3\,(\mathrm{RNH{-}AlNR})_4} + 12\,\mathrm{Al} + 6\,\mathrm{H_2} \rightarrow \underset{\text{(I)}}{4\,(\mathrm{HAlNR})_6} \qquad (3)$$

$$\underset{\text{(IV)}}{3\,(\mathrm{RNH{-}AlNR})_4} + 12\,\mathrm{AlH_3 \cdot N(CH_3)_3} \rightarrow \underset{\text{(I)}}{4\,(\mathrm{HAlNR})_6} + 12\,\mathrm{H_2} + 12\,\mathrm{N(CH_3)_3} \qquad (4)$$

$$\underset{\text{(I)}}{2\,(\mathrm{HAlNR})_6} + 12\,\mathrm{RNH_2} \rightarrow \underset{\text{(IV)}}{3\,(\mathrm{RNH{-}AlNR})_4} + 12\,\mathrm{H_2} \qquad (5)$$

Finally, the reaction of IV with iso-$C_3H_7NH_2$ gives dimer $[\mathrm{Al(NH\text{-}iso\text{-}C_3H_7)_3}]_2$ (VI) (reaction 6).

$$\underset{\text{(IV)}}{(\mathrm{RNH{-}AlNR})_4} + 4\,\mathrm{RNH_2} = \underset{\text{(VI)}}{2\,[\mathrm{Al(NHR)_3}]_2} \qquad (6)$$

The mass spectrum of the dimer shows abundant fragments at *m/e* 344, 286 and 284 assigned to $(M - \mathrm{NHR})^+$, $(M - 2\mathrm{NHR})^+$ and $(M - 2\mathrm{RNH_2})^+$, respectively, plus the low intensity molecular ion at *m/e* 402. Its ^{1}H NMR spectrum consists of three sets of lines with relative intensities 1 : 6 : 1 and chemical shifts similar to those of IV. These signals are thus assigned to the —CH—, CH_3— and —NH— groups, respectively, of the isopropylamine radicals.

As in IV, CH is coupled with NH in VI, with $J(\text{—CH—NH—}) = 12$ Hz. However, the NH doublets in VI indicate at least three magnetically non-equivalent sites. Furthermore, the multiplicity of the CH, CH_3 and NH signals (Fig. 2) suggests a more complicated situation for these groups in VI. At low temperature, signals due to CH_3 protons tend toward two sets of bands at τ 8.63 and at τ 8.77. On the basis of the relative intensities, they are assigned to CH_3 in external and bridged NHR groups, according to structure VII. Probably different conformers are possible for VII, due to rotation of isopropyl groups around the N—C bond.

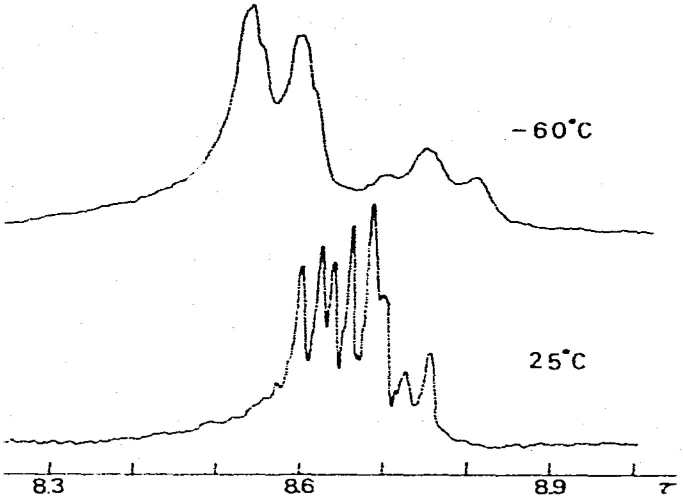
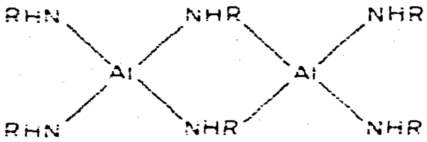


Fig. 2. The temperature effect on the CH_3 signals of ^1H NMR spectrum of $[Al(NH\text{-iso-}C_3H_7)_3]_2$ in toluene.



(VII)

(Note that, according to reaction 6, VI gives IV under conditions which remove amine from the reaction mixture.)

The assumption that VI is an intermediate in the formation of IV is supported by the following chemical observations. VI reacts with Al under pressure of H_2 to give IV, (reaction 7), ($p(H_2)$ = 200 kg cm^{-2}, 180°C, without other activators):

$$4\,[Al(NHR)_3]_2 + 4\,Al \xrightarrow{H_2} 3\,(RNH{-}AlNR)_4 + 6\,H_2 \qquad (7)$$

(VI) (IV)

In the absence of hydrogen, reaction 7 does not occur. Furthermore, VI reacts with an equimolecular amount of $AlH_3 \cdot N(CH_3)_3$ to give IV, or with an excess to give I (reactions 8 and 9):

$$4\,[Al(NHR)_3]_2 + 4\,AlH_3 \cdot N(CH_3)_3 \rightarrow 3\,(RHN{-}AlNR)_4 + 12\,H_2 + 4\,N(CH_3)_3 \qquad (8)$$

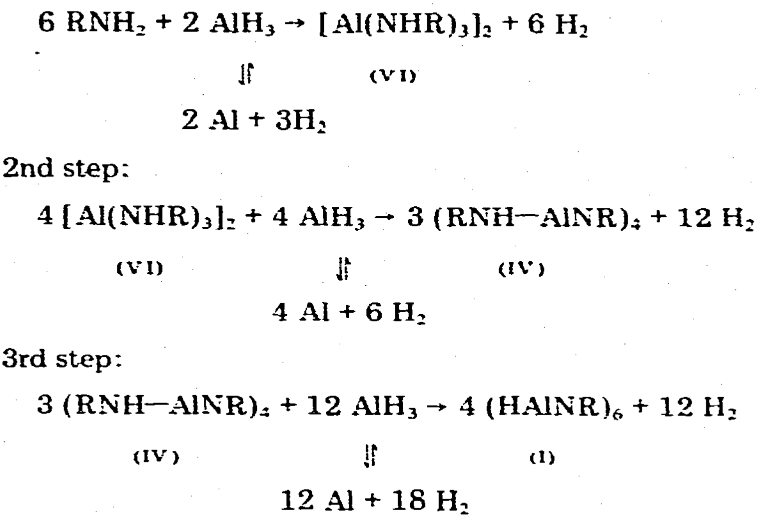
(VI) (IV)

$$[Al(NHR)_3]_2 + 4\,AlH_3 \cdot N(CH_3)_3 \rightarrow (HAlNR)_6 + 6\,H_2 + 4\,N(CH_3)_3 \qquad (9)$$

(VI) (I)

The synthesis of PIA from aluminum tris-amides and AlH_3 has previously been reported [7]. We have now verified that PIA formed in reaction 9 is a hexameric closed cage $(HAlN\text{-iso-}C_3H_7)_6$.

On the basis of the above experimental evidence, the general mechanism for the formation of $(HAlN\text{-iso-}C_3H_7)_6$ from aluminum and isopropylamine may be reasonably postulated as follows.



1st step:

$$6\,RNH_2 + 2\,\underset{\substack{\upharpoonleft\downharpoonright\\ 2\,Al + 3H_2}}{AlH_3} \rightarrow \underset{(VI)}{[Al(NHR)_3]_2} + 6\,H_2$$

2nd step:

$$4\,\underset{(VI)}{[Al(NHR)_3]_2} + 4\,\underset{\substack{\upharpoonleft\downharpoonright\\ 4\,Al + 6\,H_2}}{AlH_3} \rightarrow 3\,\underset{(IV)}{(RNH{-}AlNR)_4} + 12\,H_2$$

3rd step:

$$3\,\underset{(IV)}{(RNH{-}AlNR)_4} + 12\,\underset{\substack{\upharpoonleft\downharpoonright\\ 12\,Al + 18\,H_2}}{AlH_3} \rightarrow 4\,\underset{(I)}{(HAlNR)_6} + 12\,H_2$$

Experimental

Reagents and solvents

Powdered aluminum Walter Marx A9 and Eckart Werke AS 081 were used with the same results. As a precaution, commercial aluminum was deoxygenated before reaction by milling 20 h at room temperature with 2% mole of $Al(C_2H_5)_3$ in toluene or heptane. Before use, $Al(C_2H_5)_3$ was completely removed by filtration. The milled aluminum was then washed several times with toluene or heptane and with the reaction solvent. However, syntheses of PIA carried out with commercially fresh samples of aluminum showed this treatment to be unnecessary.

Commercial samples of pure amines were dried by distillation from KOH. All solvents were purified and dried by standard methods and all syntheses and physico-chemical characterizations were carried out under nitrogen.

Chemical analyses and physico-chemical measurements

Methods previously reported have been used [2]. In particular, for the analysis of nitrogen, the Kjeldahl apparatus was used for direct determination of more volatile amines obtained on hydrolysis of a tared sample.

Synthesis of poly(N-alkyliminoalanes)

A typical preparation is the following. A mixture of powdered aluminum

(200 mmol), purified as reported above, toluene (280 ml), $NaAlH_4$ (9.4 mmol) and isopropylamine (180 mmol) were introduced into a one liter autoclave furnished with an anchor stirrer. H_2 (135 kg cm^{-2}) was then introduced and the autoclave was heated at 180° C; the pressure rose to ca. 200 kg cm^{-2}. The reaction mixture was heated at these conditions for 10 h; the autoclave was then allowed to cool to room temperature. After removal of hydrogen, the reaction solution was filtered to remove excess aluminum. In this solution the N/Al atomic ratio was 1.02. The solvent was removed by evaporation in vacuo. The solid white residue was dried (10 h, room temp., 1 × 10^{-3} Torr) and analyzed (Found: Al, 30.5; N, 16.4%; H_{active} 11.5 meq/g. C_3H_8AlN calcd.: Al, 31.7; N, 16.5%; H_{active} 11.7 meq/g).

Synthesis of [Al(NH-iso-C_3H_7)$_3$]$_2$

iso-$C_3H_7NH_2$ (32 mmol) in benzene (15 ml) was added to a stirred solution of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$ (4 mmol; 16 mg-at. of aluminum) in benzene (25 ml). The reaction mixture was refluxed for 7 h and left overnight. Then the solvent was evaporated under vacuum. The oily residue was dried and analyzed (Found: Al, 13.5; N, 19.6. $C_9H_{24}AlN_3$ calcd.: Al, 13.6; N, 21.2%). By heating at 140° C and at 1 × 10^{-2} Torr this compound decomposed into amine and starting (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$.

Synthesis of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$

(a) A mixture of powdered aluminum (200 mmol) purified as reported above, toluene (280 ml), $AlH_3 \cdot N(CH_3)_3$ (10 mmol) and iso-$C_3H_7NH_2$ (180 mmol) was introduced into a one liter autoclave furnished with an anchor stirrer. Hydrogen (140 kg cm^{-2}) was introduced and the autoclave was heated at 175° C, while the pressure rose to ca. 200 kg cm^{-2}. The reaction mixture was stirred at these conditions for 8 h, then the autoclave was allowed to cool to room temperature. The reaction solution was filtered and the solvent was removed in vacuo.

In the solid residue the atomic ratio N/Al was 2.0; mass spectrometry and ^{1}H NMR indicated the formation of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$ as sole product. Crystals of this compound separated easily from hydrocarbon solution cooled to 0° C; they were recovered by decantation, dried under vacuum (10 h, room temp., 10^{-3} Torr) and analyzed (Found: Al, 19.3; N, 20.0. $C_6H_{15}AlN_2$ calcd.: Al, 19.0; N, 19.7%).

(b) A mixture of powdered aluminum (200 mmol), purified as reported above, toluene (280 ml), [Al(NH-iso-C_3H_7)$_3$]$_2$ (50 mmol; 100 mg-at. of Al) was introduced in one liter autoclave furnished with an anchor stirrer. Hydrogen (140 kg cm^{-2}) was introduced and the autoclave was heated to 175° C, while pressure rose to ca. 200 kg cm^{-2}. The reaction mixture was stirred for 2 h at these conditions, then the autoclave was allowed to cool to room temperature. The atomic N/Al ratio in the solution was 2, and the mass spectrometry and ^{1}H NMR indicated the formation of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$.

The solvent was evaporated in vacuo and the solid residue was dried under vacuum and analyzed (Found: Al, 18.9; N, 19.5. $C_6H_{15}AlN_2$ calcd.: Al, 19.0; N, 19.7%).

(c) iso-$C_3H_7NH_2$ (100 mmol) in toluene (50 ml) was added to a stirred solution of (HAlN-iso-C_3H_7)$_6$ (16.5 mmol) in toluene (250 ml) and the reaction mix-

ture was introduced in a one liter autoclave furnished with an anchor stirrer. The mixture was stirred at 170°C for 9 h. After 9 h, mass spectra of the reaction solution contained intense ions due to (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$ as well as other species (i.e. ions at *m/e* 344). The ^{1}H NMR spectrum agreed with a predominance of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$, which was separated in the pure form from the crude oil product (N/Al = 2) by sublimation (140°C; 5×10^{-4} Torr). In ca. 2 h the sublimed compound was recovered in 58% yield with respect to the aluminum content of the crude product and analyzed (Found: Al, 19.1; N, 19.1. $C_6H_{15}AlN_2$ calcd.: Al, 19.0; N, 19.7%). Its ^{1}H NMR spectrum showed pure (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$. In the residue from sublimation (containing 39% of aluminum of the crude product) the atomic N/Al ratio was 1.66, indicating partial decomposition with formation of amine. ^{1}H NMR again shows typical signals of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$. The more volatile oil fraction (containing 3% of aluminum of crude product) consisted of [Al(NH-iso-C_3H_7)$_3$]$_2$ (N/Al was 3.03).

(d) [Al(NH-iso-C_3H_7)$_3$]$_2$ (33.5 mmol; 67 mg-at. of aluminum) in toluene (50 ml) was dropped slowly into a stirred solution of $AlH_3 \cdot N(CH_3)_3$ (33.5 mmol) in toluene (50 ml). The reaction mixture was refluxed for 15 h. Then the reaction solvent was evaporated in vacuo. The solid residue was shown to be pure (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$ by its ^{1}H NMR spectrum.

Synthesis of (HAlN-iso-C_3H_7)$_6$ from (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$

(a) $AlH_3 \cdot N(CH_3)_3$ (12 mmol) in toluene (30 ml) was added slowly to a stirred solution of (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$ (3 mmol; 12 mg-at. of aluminum) in toluene (70 ml). The reaction mixture was stirred at room temperature (24°C) 3 h and was then refluxed for 1 h. The reaction solution was filtered to remove traces of aluminum powder and the solvent was evaporated in vacuo. The solid residue was dried under vacuum and analyzed (Found: Al, 31.1; N, 15.9%; H_{active} 12.0 meq/g. C_3H_8AlN calcd.: Al, 31.7; N, 16.5%; H_{active} 11.7 meq/g). Mass spectrometry and ^{1}H NMR showed the formation of pure (HAlN-iso-C_3H_7)$_6$.

(b) A mixture of powdered aluminum (120 mmol), purified as above reported, toluene (280 ml), (iso-C_3H_7NH—AlN-iso-C_3H_7)$_4$ (25 mmol; 100 mg-at. of aluminum) and $NaAlH_4$ (10 mmol) was introduced into a one liter autoclave furnished with an anchor stirrer. Hydrogen (135 kg cm^{-2}) was introduced and the autoclave was heated to 180°C, while the pressure rose to ca. 200 kg cm^{-2}. The reaction mixture was stirred in these conditions for 10 h; then the autoclave was allowed to cool to room temperature. In the reaction solution the atomic ratio N/Al was 1.03. The solvent was removed in vacuo; the solid residue was dried under vacuum and analyzed (Found: Al, 31.0; N, 16.0%; H_{active} 11.5 meq/g. C_3H_8AlN calcd.: Al, 31.7; N, 16.5%; H_{active} 11.7 meq/g). Mass and ^{1}H NMR spectra indicated the formation of pure (HAlN-iso-C_3H_7)$_6$.

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References

1 S. Cucinella, A. Mazzei and G. Dozzi, J. Organometal. Chem., 84 (1975) C19.
2 S. Cucinella, T. Salvatori, C. Busetto, G. Perego and A. Mazzei, J. Organometal. Chem., 78 (1974) 185; G. Dozzi, S. Cucinella, A. Mazzei and T. Salvatori, Inorg. Chim. Acta, 15 (1975) 179.
3 S. Cucinella, G. Dozzi, A. Mazzei and T. Salvatori, J. Organometal. Chem., 90 (1975) 257.
4 M. Cesari, G. Perego, G. Del Piero, S. Cucinella and E. Cernia, J. Organometal. Chem., 78 (1974) 203.
5 M. Cesari, G. Perego and G. Del Piero, Results to be published.
6 A. Balducci, M. Bruzzone, S. Cucinella and A. Mazzei, Rubber Chem. Technol., 48 (1975) 736.
7 A. Mazzei, S. Cucinella and W. Marconi, Makromol. Chem., 122 (1969) 168.
8 S. Cucinella, T. Salvatori, C. Busetto and A. Mazzei, J. Organometal. Chem., 108 (1976) 13.