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

IX *. HEXAMERIC ORGANOALUMINUM IMIDES BY REACTION OF $(HAlN\text{-iso-}C_3H_7)_6$ WITH TRIALKYLALUMINUMS

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Summary

$(HAlN\text{-iso-}C_3H_7)_6$ reacts with $Al(CH_3)_3$ or $Al(C_2H_5)_3$ to give compounds in which the hydridic hydrogens are partially or completely replaced by alkyl groups. The degree of alkylation depends on the reaction conditions and on the nature of the trialkylaluminum. Pure crystalline $(CH_3AlN\text{-iso-}C_3H_7)_6$, its crystallization product with $[(CH_3AlN\text{-iso-}C_3H_7)_5(HAlN\text{-iso-}C_3H_7)]$ and a mixture of $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$ isomers have been isolated. The reaction of $Al(CH_3)_3$ or $Al(C_2H_5)_3$ with iso-$C_3H_7NH_2$ gives tetramers $(CH_3AlN\text{-iso-}C_3H_7)_4$ and $(C_2H_5AlN\text{-iso-}C_3H_7)_4$.

Introduction

For many years, work in our laboratories has aimed at a deeper knowledge of poly(*N*-alkyliminoalanes) (PIA). Progress has been made in the synthesis of this class of compounds [1—3] and in the characterization of the molecular structure of several PIA [4—7]. More recently we began to investigate the substitution of different ligands for the hydridic hydrogens and the molecular features of the product compounds. For example, partially or completely chlorinated PIA have been obtained [8], which retain the cage structure of the starting PIA. This paper deals with the replacement of hydridic hydrogens of $(HAlN\text{-iso-}C_3H_7)_6$(i-PrPIA-Hex) by methyl or ethyl groups.

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TABLE 1

RESULTS OBTAINED FOR THE REACTION OF $(HAlN\text{-}iso\text{-}C_3H_7)_6$(i-PrPIA-Hex) WITH $Al(CH_3)_3$ OR $Al(C_2H_5)_3$ AT 24°C IN BENZENE[a]

AlR_3	Molar ratio AlR_3 / i-PrPIA-Hex	Results from physicochemical measurements[b]	
		Alkylation degree[c]	Reaction products[d]
$Al(CH_3)_3$	0.33	1.0	[(MeAlN-iPr)(HAlN-iPr)$_5$] (predominant), [(MeAlN-iPr)$_2$(HAlN-iPr)$_4$],
	0.66	1.3	[(MeAlN-iPr)$_3$(HAlN-iPr)$_3$] besides unreacted i-PrPIA-Hex
	1.00	2.0	
	1.33	>2.0	[(MeAlN-iPr)(HAlN-iPr)$_5$], [(MeAlN-iPr)$_2$(HAlN-iPr)$_4$] (predominant),
	1.66	2.5	[(MeAlN-iPr)$_3$(HAlN-iPr)$_3$], [(MeAlN-iPr)$_4$(HAlN-iPr)$_2$]
	2.00	2.5	
$Al(C_2H_5)_3$	0.66		[EtAlN-iPr)(HAlN-iPr)$_5$], [(EtAlN-iPr)$_2$(HAlN-iPr)$_4$] besides unreacted i-PrPIA-Hex
	1.66		[(EtAlN-iPr)(HAlN-iPr)$_5$], [(EtAlN-iPr)$_2$(HAlN-iPr)$_4$] (dominant),
	2.00		[(EtAlN-iPr)$_3$(HAlN-iPr)$_3$] besides unreacted i-PrPIA-Hex

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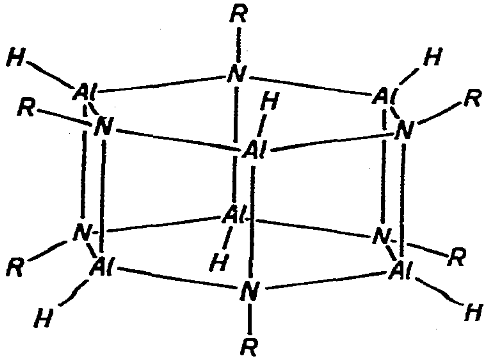
[a] For both reactants, solutions with concentrations of 2 g atoms of aluminum per liter were used. [b] Physicochemical measurements were carried out on reaction mixtures 24 h old at 24°C. [c] Number of alkyl groups substituting hydridic hydrogens of i-PrPIA-Hex, measured by ^{1}H NMR. [d] Mass spectrometry measurement.

Results and discussion

A. The reactions of hexakis(N-isopropyliminoalane) (i-PrPIA-Hex) with trialkylaluminum

A. 1 Reaction of i-PrPIA-Hex with stoichiometric amounts of trialkylaluminum. We began by examining the exchange reactions between i-PrPIA-Hex (I) [4] and $Al(CH_3)_3$ or $Al(C_2H_5)_3$, according to eq. 1.



$$(HAlNR)_6 + y AlR'_3 \rightarrow [(R'AlNR)_z(HAlNR)_{6-z}] + y AlR'_{3-x}H_x \quad (1)$$

$z = y.x$; R = iso-C_3H_7; R' = CH_3, C_2H_5

The reaction is rapid in benzene solution at room temperature. At $Al(CH_3)_3$/i-PrPIA-Hex molar ratios ranged from 0.33 to 2.00, the reaction yields soluble alkylated derivatives of i-PrPIA-Hex and a white insoluble product. This product probably consists of alkylaluminum hydrides $Al(CH_3)_{3-x}H_x$, with $x > 1$, which slowly decompose to aluminum metal. The similar reaction with $Al(C_2H_5)_3$ yields analogous partially ethylated derivatives of i-PrPIA-Hex, although the reaction occurs less easily than with $Al(CH_3)_3$.

The results obtained are reported in Table 1. Mass spectrometry and ^1H NMR provide evidence for the formation of hexamers derived from partial alkylation of i-PrPIA-Hex. The most abundant peaks in the mass spectra of methyl derivatives correspond to $(M - CH_3)^+$ ions, as in mass spectra of PIA [1] and their chlorinated derivatives [8]. These peaks could be used to evaluate the number of substituent methyl groups in I even though we are unable to decide between the loss of one methyl group bonded to aluminum and that of one methyl group of the isopropyl radical. The ambiguity could be eliminated by preparing a derivative of i-PrPIA-Hex from deutero-isopropylamine or from deutero-trimethylaluminum. In the mass spectra of the hexameric ethyl derivatives from I, the most abundant peaks correspond to $(M - C_2H_5)^+$ ions clearly due to Al—C cleavage, but there is competition between the loss of the ethyl and that of the methyl group. The $(M - Et)^+/(M - Me)^+$ ratio was near 2 for $[(C_2H_5AlN\text{-iso-}C_3H_7)(HAlN\text{-iso-}C_3H_7)_5]$, near 4 for $[(C_2H_5AlN\text{-iso-}C_3H_7)_2(HAlN\text{-iso-}C_3H_7)_4]$, near 5 for $[(C_2H_5AlN\text{-iso-}C_3H_7)_3(HAlN\text{-iso-}C_3H_7)_3]$ and greater than 10 for $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$. At AlR_3/i-PrPIA-Hex $\leqslant 1.33$, the ^1H NMR spectra of the benzene reaction solution exhibit, in the chemical shift range expected for the CH_3 protons of the isopropyl groups, one doublet at τ 8.49 assigned to I, plus other signals. The number of these signals increases with the proportion of AlR_3 taken. They are assigned to hexameric species derived from the partial replacement of hydridic hydrogens of I by alkyl groups; this is connected with the loss of the magnetic equivalence of iso-propyl groups. At AlR_3/i-PrPIA-Hex $\geqslant$ 1.66, the typical doublet at τ 8.49 of I disappears. Furthermore, the ^1H NMR spectra show a signal at ca. τ 10.13 which is assigned to protons of the CH_3 groups bonded to aluminum in the alkylated hexamer derived from I and $Al(CH_3)_3$. The relative intensity of these signals and those of the *N*-iso-C_3H_7 groups allows an evaluation of the extent of methyl-substitution in the product.

For the products from reaction with $Al(C_2H_5)_3$, on the other hand, the CH_3 triplet of the C_2H_5 groups appears in the range of signals due to CH_3 of the isopropyl groups. Furthermore, CH_2 quartets of unreacted $Al(C_2H_5)_3$ and its derivatives partially mask a quartet at τ 9.43 assigned to signals of CH_2 bonded to aluminum of alkylated i-PrPIA-Hex. In this case, the evaluation of the extent of substitution of hydridic hydrogens by ethyl groups is impossible.

At AlR_3/i-PrPIA-Hex = 2, increased reaction temperature (70°C) did not significantly increase alkylation of I. In every case, when the reaction mixture was concentrated and cooled, a product separated which again consisted of a mixture of compounds with different degrees of alkylation.

A. 2 Reactions of i-PrPIA-Hex with excess trimethylaluminum. The synthesis of hexa-μ_3-isopropylimido-pentakis (methylaluminum)-mono(aluminumhydride), $[(CH_3AlN\text{-iso-}C_3H_7)_5(HAlN\text{-iso-}C_3H_7)]$ (II) and of hexa-μ_3-isopropylimido-hexakis(methylaluminum), $(CH_3AlN\text{-iso-}C_3H_7)_6$ (III) were achieved by treating i-PrPIA-Hex with an excess of trimethylaluminum in refluxing benzene. The reaction conditions can influence the nature of products.

The addition of a solution of i-PrPIA-Hex in benzene to a solution of a large excess of trimethylaluminum at 50°C (AlR_3/i-PrPIA-Hex was 25) causes crystal formation. Chemical composition and mass spectra (Table 2) indicate the product is III. The DTA trace (Fig. 1B) exhibits an endothermic effect at 263°C, which was found to be reversible on cooling with an exothermic effect at 228°C). As shown by the decomposition temperature of 375°C, this compound is highly stable thermally. The comparison with the DTA trace (Fig. 1A) of i-PrPIA-Hex shows the increased thermal stability resulting from substitution of hydridic hydrogens by methyl groups. Thus i-PrPIA-Hex decomposes at 245°C; endothermic effects at lower temperatures are probably due to crystalline transitions. In particular, the effect at 44°C, which is very slowly reversible, was found to be due to a crystalline transition $A_3B \rightarrow B$, where A is a conformer of i-PrPIA-Hex with symmetry $\bar{3}$ and B is a more asymmetric conformer related to A by a 120° rotation of one isopropyl group around the N—C bond [10]. It is noteworthy that exposure to the air for 5 min had no effect on the thermal trace of III, thus indicating unusual chemical stability of the Al—C bond in III. Under the same conditions i-PrPIA-Hex quickly decomposes.

The addition of a slight excess of $Al(CH_3)_3$ to a i-PrPIA-Hex solution ($AlMe_3$/i-PrPIA-Hex = ca. 6) followed by several hours at reflux leads to separation of colorless crystals, which mass spectrometry shows to consist of equimolar amounts of II and III. The DTA trace (Fig. 1C), showing a reversible endotherm-

TABLE 2

MOST ABUNDANT IONS OF MASS SPECTRA OF HEXAMERIC ORGANOALUMINUM IMIDES DERIVED FROM THE REACTION OF $(HAlN\text{-iso-}C_3H_7)_6$ WITH $Al(CH_3)_3$ OR $Al(C_2H_5)_3$

Methylation degree [a]	$(M - Me)^+$ m/e	Ethylation degree [a]	$(M - Me)^+$ m/e	$(M - Et)^+$ m/e
0	495	0	495	
1	509	1	523	509
2	523	2	551	537
3	537	3	579	565
4	551	4	607	593
5	565			
6	579			

[a] Number of methyl or ethyl groups substituting hydridic hydrogens of $(HAl\text{-iso-}C_3H_7)_6$.

ic effect at 233°C and a decomposition temperature of 340°C, suggests a co-crystallization product of these species.

A. 3 Reactions of i-PrPIA-Hex with excess $Al(C_2H_5)_3$. By treating i-PrPIA-Hex with excess $Al(C_2H_5)_3$ ($AlEt_3$/i—PrPIA-Hex was near 6) in refluxing benzene we were unable to achieve the complete replacement of hydridic hydrogens by ethyl groups. Only hexa-μ_3-isopropylimido-tetrakis (ethylaluminum)bis(aluminum hydride), $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$ (IV) was formed. This crystalline, soluble compound was detected by mass spectrometry (Table 2)

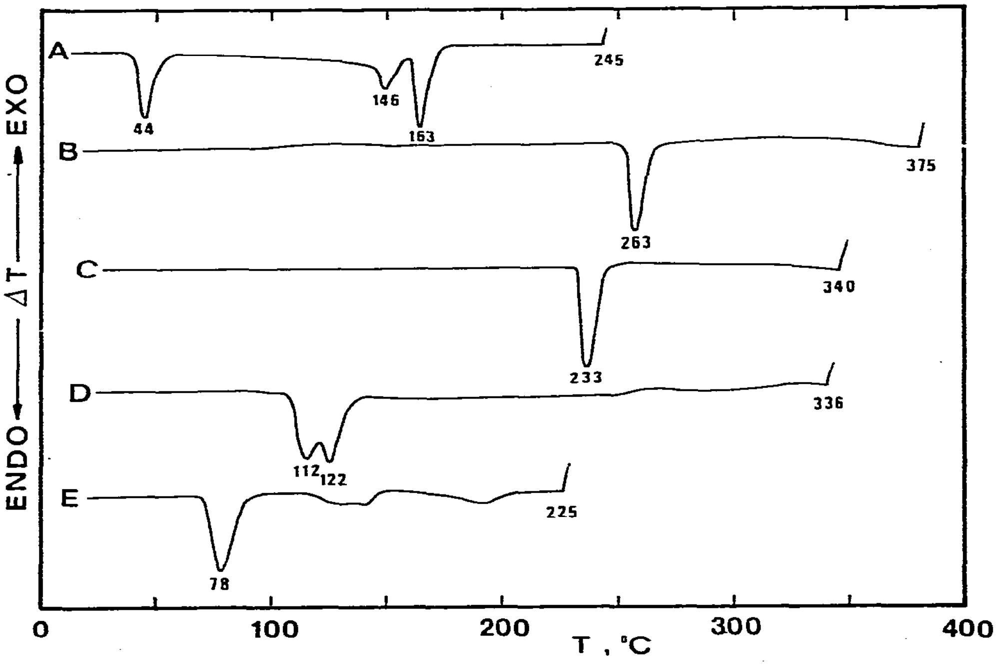


Fig. 1. DTA traces of $(HAlN\text{-iso-}C_3H_7)_6$ and of the products derived by replacement of hydridic hydrogens by alkyl groups. A, $(HAlN\text{-iso-}C_3H_7)_6$; B, $(CH_3AlN\text{-iso-}C_3H_7)_6$; C, co-crystallization product of $(CH_3AlN\text{-iso-}C_3H_7)_6$ with $[(CH_3AlN\text{-iso-}C_3H_7)_5(HAlN\text{-iso-}C_3H_7)]$; D, $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$; E, $(CH_3AlN\text{-iso-}C_3H_7)_4$.

and ^{1}H NMR. The NMR spectrum (Fig. 2) exhibits three doublets at τ 8.36, τ 8.54 and τ 8.56 ppm assigned to CH_3 of isopropyl groups, one quartet at τ 9.45 assigned to CH_2 protons and one triplet at τ 8.51 due to CH_3 protons of ethyl groups. The multiplicity of signals due to CH_3 of isopropyl groups excludes the formation of the single isomer of IV characterized by a symmetric arrangement of ethyl groups in the hexamer cage. Attempts to isolate different isomers by crystallization were unsuccessful. The decomposition temperature of 340°C (Fig. 1D) confirms the enhanced thermal stability arising from replacement of hydridic hydrogens of I by alkyl groups.

The reaction of i-PrPIA-Hex with a larger excess of $Al(C_2H_5)_3$ ($AlEt_3$/i-PrPIA-Hex = 25) yields IV plus some decomposition products.

B. Reactions of chloro-hexakis(N-isopropyliminoalanes) with lithium alkyls

Previously we reported both partial and complete substitution of hydridic hydrogens of i-PrPIA-Hex with chlorine by reaction with HCl or $TiCl_4$ [8]. The products retain the cage structure of starting i-PrPIA-Hex [9]. We have now observed that the reaction of these chlorinated products with lithium alkyls allows replacement of chlorine by alkyl groups according to eq. 2.

$$\text{alCl} + \text{LiR} \rightarrow \text{alR} + \text{LiCl} \qquad (2)$$

$$\text{al} = 1/3\ \text{Al}$$

The products are partially or completely alkylated hexamers from i-PrPIA-Hex. In particular, in accord with eq. 2, a mixture of $[(C_2H_5AlN\text{-iso-}C_3H_7)(HAl\text{-}N\text{-iso-}C_3H_7)_5]$ and $[(C_2H_5AlN\text{-iso-}C_3H_7)_2(HAlN\text{-iso-}C_3H_7)_4]$ was obtained from a mixture of $[(ClAlN\text{-iso-}C_3H_7)(HAlN\text{-iso-}C_3H_7)_5]$ and $[(Cl_2AlN\text{-iso-}C_3H_7)_2(HAlN\text{-iso-}C_3H_7)_4]$. The reaction of insoluble $(ClAlN\text{-iso-}C_3H_7)_6$ with an excess of $LiCH_3$ occurs slowly. However, in refluxing ether we obtained a mixture containing $(CH_3AlN\text{-iso-}C_3H_7)_6$, with traces of $[(CH_3AlN\text{-iso-}C_3H_7)_5(ClAlN\text{-iso-}C_3H_7)]$, $[(CH_3AlN\text{-iso-}C_3H_7)_4(ClAlN\text{-iso-}C_3H_7)_2]$ plus unreacted $(ClAlN\text{-iso-}C_3H_7)_6$. The mass spectra (Table 2) show the fragments from $(CH_3AlN\text{-iso-}C_3H_7)_6$ and $(ClAlN\text{-iso-}C_3H_7)_6$ [8] as well as the weak ions at m/e 599, 601 and at m/e 619, 621, 623 assigned to $(M - CH_3)^+$ from mono- and dichloro-derivatives.

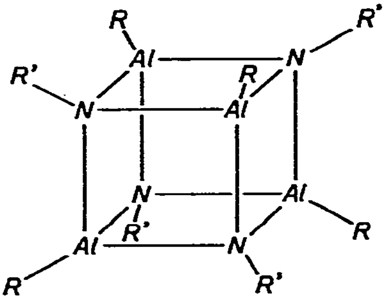
C. Reactions between trialkylaluminums and isopropylamine

The synthesis of organoaluminum imides $(RAlNR')_n$ by reaction of trialkylaluminum with primary amines other than isopropylamine (eq. 3) is well known.

$$n\ AlR_3 + n\ R'NH_2 \rightarrow (RAlNR')_n + 2\,nRH \qquad (3)$$

By this route $(C_6H_5AlNC_6H_5)_4$ [11], $(C_2H_5AlNC_6H_5)_4$ [12], $(C_2H_5AlNCH_3)_8$ [13], $(C_2H_5AlN\text{-tert-}C_4H_9)_4$ and $(CH_3AlNCH_3)_7$ [14] have been synthesized. We have now extended eq. 3 to $Al(CH_3)_3$ or $Al(C_2H_5)_3$ and iso-$C_3H_7NH_2$ in toluene at 200°C to yield the tetramers $(CH_3AlN\text{-iso-}C_3H_7)_4$ (V) and $(C_2H_5AlN\text{-iso-}C_3H_7)_4$ (VI) respectively. This route gives compounds different from those formed in the reaction of i-PrPIA-Hex with trialkylaluminum. Furthermore, the preparation of V and VI is somewhat unexpected, since AlH_3 and isopropylamine give a hexamer (I) [1].

The tetrameric structure of V and VI is shown by mass spectrometry, The spectra exhibit weak molecular ions at m/e 396 and at m/e 452 respectively with most abundant ions $(M - CH_3)^+$ at m/e 381 and at m/e 437. Furthermore, the spectrum of VI shows a peak at m/e 423 corresponding to $(M - C_2H_5)^+$. The ^1H NMR spectrum of V in benzene has one singlet at τ 10.13 due to Al—CH_3 protons, one doublet at τ 8.77 and one septet at τ 6.73 assigned to CH_3 and CH protons of isopropyl group respectively. In the case of VI, the spectrum contains one quartet at τ 9.47 and one triplet at τ 8.54 assigned to the CH_2 and CH_3 protons of the ethyl group; the signals from the isopropyl group are at τ 8.74 and τ 6.60. The magnetic equivalence of all Al—R and of all N-iso-C_3H_7 groups is evident. The latter was found in the cubic cage of (HAlN-iso-$C_3H_7)_4$ [3,14] and in other typical cage structures of PIA [1,3]. Therefore, a cubic structure VII is reasonable for V and VI. An X-ray study of V, crystals of which separate easily from hexane, is in progress. The trace of V, (Fig. 1E), shows a lower thermal stability of the tetrameric structure $(CH_3AlN\text{-iso-}C_3H_7)_4$ with respect to the hexameric species $(CH_3AlN\text{-iso-}C_3H_7)_6$.



D. Observations on the chemical stability of $(RAlN\text{-iso-}C_3H_7)_4$

In our investigations on the chemical properties of PIA, we observed that the rapid addition of iso-$C_3H_7NH_2$ to an equimolar amount of $AlH_3.N(CH_3)_3$ in the presence of (HAlN-iso-$C_3H_7)_4$ (i-PrPIA-Tet) in diethyl ether at —40°C completely transforms i-PrPIA-Tet into i-PrPIA-Hex. This result was explained on the basis of two assumptions. First the rapid addition of amine to AlH_3 causes the formation of amidoalane VIII (eq. 4), which in this case is intermediate in the synthesis of i-PrPIA-Hex (eq. 5). This hypothesis is supported by the tendency towards evolution of hydrogen as the reaction between AlH_3 and iso-$C_3H_7NH_2$ proceeds in the absence of other reagent (Fig. 3). Second, the reaction of VIII with i-PrPIA-Tet gives the more stable i-PrPIA-Hex (eq. 6).

$$AlH_3 + \text{iso-}C_3H_7NH_2 \rightarrow 1/n\ (H_2AlNH\text{-iso-}C_3H_7)_n + H_2 \qquad (4)$$

$$\text{(VIII)}\ n = 2 \text{ or } 3$$

$$6/n\ (H_2AlNH\text{-iso-}C_3H_7)_n \rightarrow (HAlN\text{-iso-}C_3H_7)_6 + 6\ H_2 \qquad (5)$$

$$(HAlN\text{-iso-}C_3H_7)_4 + 2/n\ (H_2AlNH\text{-iso-}C_3H_7)_n \rightarrow (HAlN\text{-iso-}C_3H_7)_6 + 2\ H_2 \qquad (6)$$

We therefore wondered whether the reaction with VIII could transform tetrameric $(CH_3AlN\text{-iso-}C_3H_7)_4$ (V) and $(C_2H_5AlN\text{-iso-}C_3H_7)_4$ (VI) into hexameric

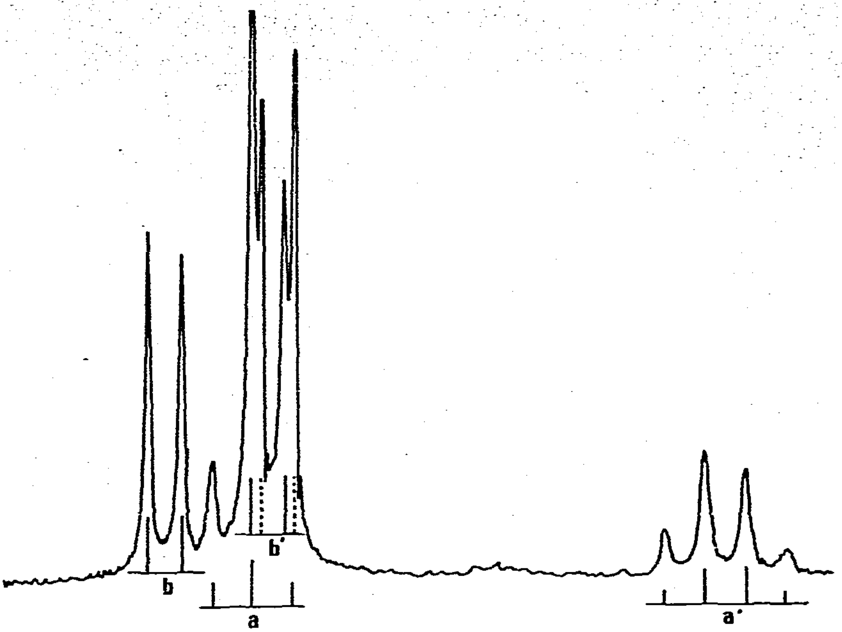


Fig. 2. ^{1}H NMR spectrum of [$(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_4H_7)_2$] in benzene; a,a' = signals assigned to CH_3 and CH_2 protons of Al—C_2H_5 groups; b,b' = signals assigned to CH_3 protons of iso-C_3H_7N—groups.

organoaluminum imides such as [$(RAlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2$] (eq. 7).

$$(RAlN\text{-iso-}C_3H_7)_4 + 2/n\ (H_2AlNH\text{-iso-}C_3H_7)_n \rightarrow$$
$$[(RAlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2] + 2\ H_2 \qquad (7)$$

Thus, iso-$C_3H_7NH_2$ was added to an ethereal solution of $AlH_3 \cdot N(CH_3)_3$ and of V (or VI) at —40°C, with the reaction completed at room temperature (the molar ratios of reactants were V (or VI)/AlH_3/RNH_2 = 1 : 12 : 12). In the case of V, physicochemical investigation of the products indicated a mixture consisting essentially of reactant V and $(HAlN\text{-iso-}C_3H_7)_6$, plus minor uncharacterized species non-attributable to the transformation of V into hexameric organoaluminum imides. For VI the reaction mixture contained exclusively unreacted VI and $(HAlN\text{-iso-}C_3H_7)_6$. Therefore, tetrameric organoaluminum imides $(RAlN\text{-iso-}C_3H_7)_4$ appear to be more stable than tetra(*N*-isopropyliminoalane) $(HAlN\text{-iso-}C_3H_7)_4$ regarding transformation into hexameric structures. Furthermore, in conformation of the chemical stability of these new products, we have not observed exchange reactions between $(CH_3AlN\text{-iso-}C_3H_7)_4$ and $(HAlN\text{-iso-}C_3H_7)_6$ in refluxing diethyl ether.

Conclusions

The reaction of $(HAlN\text{-iso-}C_3H_7)_6$ (i-PrPIA-Hex) with variable amounts of $Al(CH_3)_3$ or $Al(C_2H_5)_3$ leads to ther partial or the complete replacement of

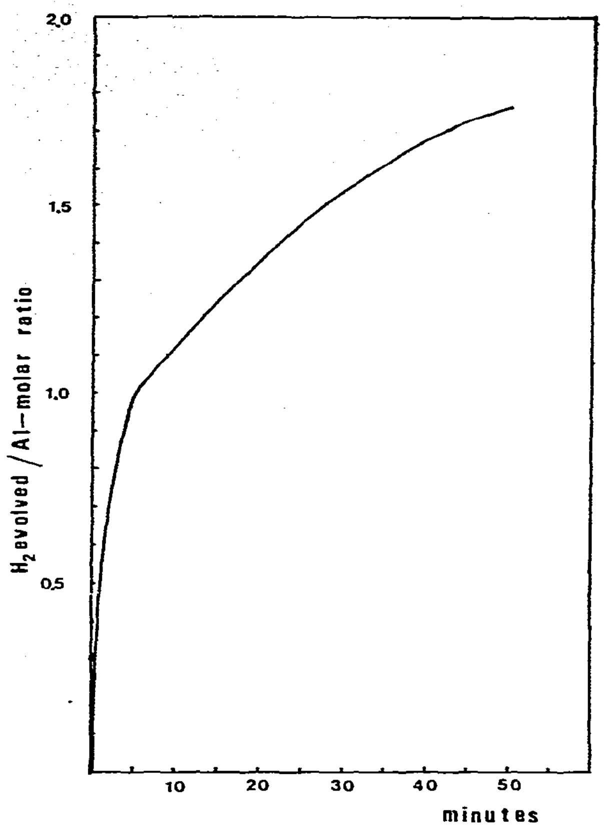


Fig. 3. Hydrogen evolution in the reaction of $AlH_3 \cdot N(CH_3)_3$ with iso-$C_3H_7NH_2$. Reaction conditions: a solution of iso-$C_3H_7NH_2$ (10 mmol) in diethyl ether (15 ml) was added at once to a solution of $AlH_3 \cdot N(CH_3)_3$ in diethyl ether (250 ml), using the apparatus previously described [18].

hydridic hydrogens by alkyl radicals with formation of hexameric organoimido aluminum species. The bulk of the alkyl group of the trialkylaluminum affects the reaction. Thus $(CH_3AlN\text{-iso-}C_3H_7)_6$ and other hexameric species derived from partially substituted $(HAlN\text{-iso-}C_3H_7)_6$ have been obtained with $Al(CH_3)_3$ but when $Al(C_2H_5)_3$ was used the most alkylated organoimido compound was $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$. A hexameric cage structure of i-PrPIA-Hex type is suggested for these new compounds. The substitution of hydridic hydrogens of i-PrPIA-Hex can be achieved also by chlorination and subsequent reaction with alkyllithium. As shown by the reaction of $Al(CH_3)_3$ or $Al(C_2H_5)_3$ with iso-$C_3H_7NH_2$ to yield tetramers $(RAlN\text{-iso-}C_3H_7)_4$, the synthesis route affects the structure of the product. Furthermore, in the compounds $(XAlNR)_n$, the nature of the ligand X (X = hydrogen, halogen or alkyl) as well as that of R, influences the molecular structure [1,3,16], as shown by a comparison with two other reactions: that of $AlH_3 \cdot B$ (B = $N(CH_3)_3$, THF) and iso-$C_3H_7NH_2$ to yield hexamers [1,16], and that of $AlH_2Cl \cdot N(CH_3)_3$ and iso-$C_3H_7NH_2$ to yield pentamers [17].

Experimental

Reagents and solvents

Pure $Al(CH_3)_3$ (Texas Alkyls) and pure $Al(C_2H_5)_3$ (Schuchardt) were used without further purification. The diethyl ether solution of $LiCH_3$ was a Merck product. The diethyl ether solution of LiC_2H_5 was prepared by substituting the solvent in the benzene suspension of the Fluka product. $AlH_3 \cdot N(CH_3)_3$ [19] and $(HAlN\text{-iso-}C_3H_7)_6$ [2] were prepared by published methods. Commercial isopropylamine was dried by distillation from KOH. All solvents were purified and dried by standard methods and all syntheses were carried out under nitrogen.

Chemical analyses and physicochemical measurements

The measurements were carried out as previously described [1]. DTA measurements were carried out on a Du Pont Mod. 900 instrument. The heating rate was 10°C/min; glass was used as standard. The hydrogen development of the reaction between $AlH_3 \cdot N(CH_3)_3$ and $iso\text{-}C_3H_7NH_2$ was measured by using the apparatus previously reported [18].

Synthesis reactions

The syntheses of products which could be isolated and characterized in a pure form are described below.

Synthesis of $(CH_3AlN\text{-iso-}C_3H_7)_6$. $(HAlN\text{-iso-}C_3H_7)_6$ (3.3 mmol) in benzene (30 ml) was added slowly to a stirred solution of $Al(CH_3)_3$ (82.5 mmol) in benzene (70 ml) at 50°C. The mixture was refluxed 7 h and stirred for 18 h at 24°C. A crystalline product was prepared, and was filtered off and dried in vacuo (10 h, 10^{-3} torr, room temp.). (Found: Al, 26.6; N, 13.3, $C_4H_{10}AlN$ calcd.: Al, 27.2; N, 14.1%). The yield was 1.7 g.

Synthesis of the co-crystallization product of $(CH_3AlN\text{-iso-}C_3H_7)_6$ *with* $[(CH_3AlN\text{-iso-}C_3H_7)_5(HAlN\text{-iso-}C_3H_7)]$. $Al(CH_3)_3$ (10 mmol) in benzene (25 ml) was added dropwise to a stirred solution of $(HAlN\text{-iso-}C_3H_7)_6$ (1.7 mmol) in benzene (25 ml) at 24°C. The mixture was refluxed for 9 h and left overnight. The crystals which formed were separated by filtration, and dried in vacuo. (Found: Al, 26.9; N, 14.1. $C_{47}H_{118}Al_{12}N_{12}$ calcd.: Al, 27.5; N, 14.3%). The yield was 0.9 g.

Synthesis of $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$. $Al(C_2H_5)_3$ (10 mmol) in benzene (25 ml) was added to a stirred solution of $(HAlN\text{-iso-}C_3H_7)_6$ (1.7 mmol) in benzene (25 ml) at 24°C. The mixture was refluxed for 9 h and left overnight. Mass spectrometry showed the presence of $[(C_2H_5AlN\text{-iso-}C_3H_7)_4(HAlN\text{-iso-}C_3H_7)_2]$ in the solution. Crystals were separated by cooling the hexane (15 ml) solution of the products at —5°C. They were separated by filtration, and dried in vacuo. (Found: Al, 26.1; N, 12.6. $C_{26}H_{64}Al_6N_6$ calcd.: Al, 26.0; N, 13.5%).

Synthesis of $(CH_3AlN\text{-iso-}C_3H_7)_4$. A solution of $Al(CH_3)_3$ (370 mmol) in toluene (300 ml) was introduced into 1 l autoclave followed by a solution of $iso\text{-}C_3H_7NH_2$ (370 mmol) in toluene (50 ml). The mixture was stirred with magnetic stirrer at 210°C for 50 h. Mass spectrometry indicated the formation of $(CH_3AlN\text{-iso-}C_3H_7)_4$ as the only product present in the solution. Crystals were formed from the hexane solution of the reaction product. They were separated by filtration, and dried under vacuum. (Found: Al, 26.8; N, 14.0. $C_4H_{10}AlN$ calcd.: Al, 27.2; N, 14.1%).

Synthesis of $(C_2H_5AlN\text{-}iso\text{-}C_3H_7)_4$. A solution of $Al(C_2H_5)_3$ (300 mmol) in toluene (250 ml) and a solution of iso-$C_3H_7NH_2$ (300 mmol) in toluene (50 ml) were introduced consecutively into a 1 l autoclave. The mixture was stirred with a magnetic stirrer at 210°C for 50 h. Mass spectrometry indicated the formation of $(C_2H_5AlN\text{-iso-}C_3H_7)_4$ as the only product in the solution. The solvent was evaporated in vacuo and the residue was dissolved in hexane (250 ml). The hexane solution was cooled at —78°C and the precipitate was separated by decantation and dried in vacuo. (Found: Al, 23.7; N, 12.5. $C_5H_{12}AlN$ calcd.: Al, 23.8; N, 12.4%). The yield was 3.1 g.

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References

1 S. Cucinella, T. Salvatori, C. Busetto, G. Perego and A. Mazzei, J. Organometal. Chem., 78 (1974) 185.
2 S. Cucinella, A. Mazzei and G. Dozzi, J. Organometal. Chem., 84 (1975) C19.
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 G. Perego, M. Cesari, G. Del Piero, A. Balducci and E. Cernia, J. Organometal. Chem., 87 (1975) 33.
6 M. Cesari, G. Perego, G. Del Piero and M. Corbellini, J. Organometal. Chem., 87 (1975) 43.
7 G. Perego, G. Del Piero, M. Cesari, A. Zazzetta and G. Dozzi, J. Organometal. Chem., 83 (1975) 53.
8 S. Cucinella, T. Salvatori, C. Buseto and A. Mazzei, J. Organometal. Chem., 108 (1976) 13.
9 M. Cesari, G. Perego and G. Del Piero, to be published.
10 M. Cesari, G. Del Piero and G. Perego, private communication.
11 J.I. Jones and W.S. McDonald, Proc. Chem. Soc., (1962) 366.
12 J.K. Gilbert and J.D. Smith, J. Chem. Soc. A, (1968) 233.
13 K. Gosling, I.D. Smith and D.H. Wharmby, J. Chem. Soc. A, (1969) 1738.
14 P.B. Hitchcock, G.M. McLaughlin, I.D. Smith and K.M. Thomas, J. Chem. Soc. Chem. Commun., (1973) 934.
15 M. Cesari, G. Perego and G. Del Piero, to be published.
16 G. Dozzi, S. Cucinella, A. Mazzei and T. Salvatori, Inorg. Chim. Acta, 15 (1975) 179.
17 Our unpublished results.
18 S. Cucinella, G. Dozzi, M. Bruzzone and A. Mazzei, Inorg. Chim. Acta, 13 (1975) 73.
19 J.K. Ruff and M.F. Hawthorne, J. Amer. Chem. Soc., 82 (1960) 2141.
20 S. Cucinella, G. Dozzi, C. Busetto,and A. Mazzei, J. Organometal. Chem., 113 (1976) 233.