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

VII *. THE CHLORINATION OF POLY(*N*-ALKYLIMINOALANES)

S. CUCINELLA **, T. SALVATORI, C. BUSETTO and A. MAZZEI

Snamprogetti S.p.A., Direzione Ricerca e Sviluppo, 20097 San Donato Milanese, Milano (Italy)

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Summary

Reactions of poly(*N*-alkyliminoalanes) (PIA) such as $(HAlN\text{-t-Bu})_4$, $(HAlN\text{-i-Pr})_4$, $(HAlN\text{-i-Pr})_6$ and $(HAlN\text{-n-Pr})_8$ with HCl, $HgCl_2$ and $TiCl_4$ have been investigated.

Two reaction paths are observed which involve either the simple substitution of hydridic hydrogens with chlorine or the same reaction accompanied by the cleavage of Al—N bonds with subsequent rearrangement of the molecular structure of the PIA. In both cases the reaction depends on the chlorination agent and the molecular features of the poly(*N*-alkyliminoalanes).

Poly(*N*-alkyliminoalanes) have been obtained with partial and complete chlorination that include $(ClAlN\text{-t-Bu})_4$, $(ClAlN\text{-i-Pr})_4$, $(ClAlN\text{-i-Pr})_6$, which were separated as crystalline products and fully characterized.

Introduction

The substitution of hydridic hydrogens with chlorine atoms by reaction of some alane derivatives with mercury chloride (reaction 1) or hydrochloric acid (reaction 2) is well-known in the literature. For example, complexes of chloro-

$$\equiv Al{-}H + \tfrac{1}{2}\, HgCl_2 \rightarrow \equiv Al{-}Cl + \tfrac{1}{2}\, Hg + \tfrac{1}{2}\, H_2 \qquad (1)$$

$$\equiv Al{-}H + HCl \rightarrow \equiv Al{-}Cl + H_2 \qquad (2)$$

alane with Lewis bases [1] or chlorodialkylaminoalanes [1,2] are obtained from complexes of alane or dialkylaminoalanes. In the course of these investigations

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[*] For part VI see ref. 6.

[**] To whom correspondence should be addressed.

on poly(*N*-alkyliminoalanes) (PIA) [3—7] reactions 1 and 2 have been extended to this class of compounds. In addition, reactions with $TiCl_4$ have also been investigated, to obtain information on the catalytic behaviour of the PIA—$TiCl_4$ systems in diolefin polymerization [8]. This paper describes the results obtained and shows how the chlorination reaction is influenced by both the chlorinating agent and the nature of the PIA.

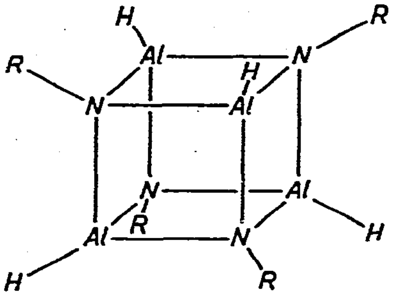
Results and discussion

1. *The chlorination of poly(N-t-butyliminoalane)*

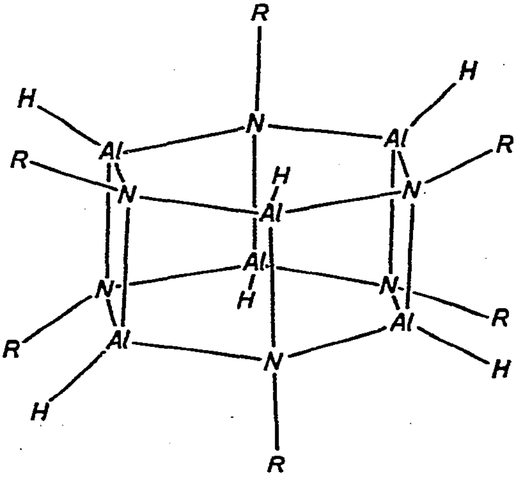
Poly(*N*-t-butyliminoalane), (t-BuPIA), is a tetramer which can be synthesised by more than one method [3,6]. The results of its reactions with different chlorinating agents are given in Table 1. The partial chlorination (eq. 3) does not

$$(HAlNR)_4 + HCl \xrightarrow{Et_2O} [(HAlNR)_3\,(ClAlNR)_1] + H_2 \qquad (3)$$

yield monochlorinated t-BuPIA as the sole product but gives a mixture of mono- and di-chlorinated PIA tetramers, together with unreacted t-BuPIA, as shown by mass spectrometry, which gives the ions $(M - CH_3)^+$ at m/e 415, 417 and at m/e 449, 451, 453 respectively together with the ions $(M - CH_3)^+$ at m/e 381. Its ^1H NMR spectrum in benzene solution (Fig. 1), exhibits four signals at τ 8.50, 8.54, 8.61 and 8.63 ppm together with a signal at τ 8.56 ppm assigned to the t-butyl group protons of t-BuPIA with a cubic structure (I) [3].These data indicate that after this partial chlorination t-BuPIA retains a cubic



(I)



(II)

structure. The signals at τ 8.54 and 8.63 ppm, which have relative intensities of 3 : 1, can be attributed to the alkyl groups of a monochlorinated cubic t-BuPIA, i.e. to the alkyl groups attached to the nitrogen atoms adjacent to the Al—Cl group and to alkyl groups attached to nitrogen atoms bonded to three Al—H groups respectively. The signals at τ 8.50 and 8.61 ppm, have the same intensity and have been assigned to the alkyl groups on nitrogen atoms of a dichlorinated t-BuPIA. The substitution in I of two hydridic hydrogens with chlorine

TABLE 1

CHLORINATION OF $(HAlN\text{-}t\text{-}Bu)_4$

$(HAlN\text{-}t\text{-}Bu)_4$ (mmol)	Chlorinating agent (mmol)	Reaction conditions			Reaction product					
		Solvent (ml)	Time (h)	Temp. (°C)	g	Analysis: Found (calcd.) (%)				Physicochemical data suggested
						Al	Cl	N	H_{act}[a]	
7.5	HCl (7.5)	Et_2O (100)	20	ca. 22	3.1 [b]	24.7 (25.1)	7.2 (8.2)	13.1 (13.0)	6.8 (7.0) [d]	non-, mono- and di-chloro tetramers
5.25	HCl (21)	Et_2O (100)	2	reflux temp.	2.6 [b]	19.2 (20.2)	23.0 (26.6)	9.3 (10.5) [e]	— —	tetrachloro tetramer
5.5	$HgCl_2$ (30)	Et_2O (100)	8	reflux temp.	2.9 [b]	18.2 (20.2)	27.1 (26.6)	9.2 (10.5) [e]	— —	tetrachloro tetramer
12.6	$TiCl_4$ (50.4)	n-heptane (400)	0.5	25—30	6.0 [c]	19.1 (20.2)	25.2 (26.6)	10.0 (10.5) [e]	— —	tetrachloro tetramer

[a] Hydridic hydrogen content indicated as meq/g. [b] Solid product obtained by evaporation of reaction solution in vacuo. [c] Solid product obtained by evaporation of solution separated from insoluble brown $TiCl_3$. [d] Calcd. for $C_{16}H_{39}Al_4ClN_4$. [e] Calcd. for C_4H_9AlClN.

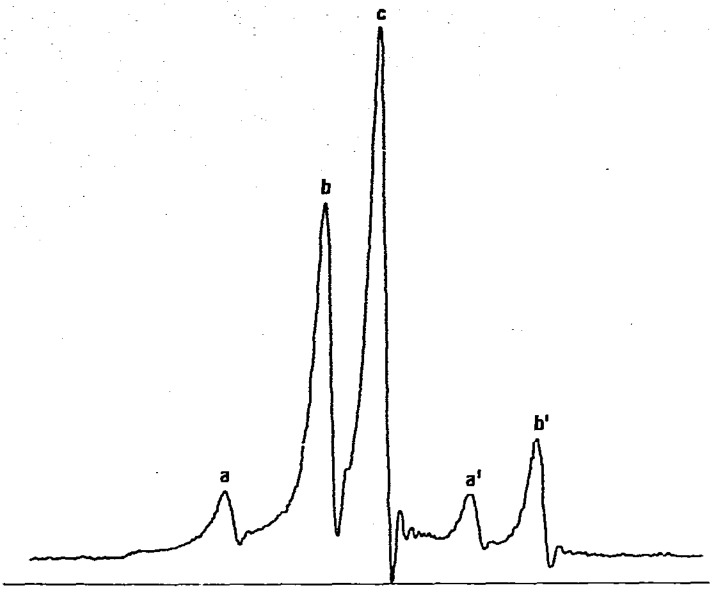


Fig. 1. ^{1}H NMR spectrum in benzene of partially chlorinated poly(N-t-butyliminoalane) (t-BuPIA). a,a' signals at τ 8.50 and 8.61 ppm assigned to alkyl groups of dichlorinated t-BuPIA; b,b' signals at τ 8.54 and 8.63 ppm assigned to alkyl groups of monochlorinated t-BuPIA; c signal at τ 8.56 ppm assigned to alkyl groups of non-chlorinated t-BuPIA.

atoms causes a distinction between alkyls on nitrogen atoms bonded to two Al—Cl and one Al—H groups, and alkyls on nitrogen atoms bonded to one Al—Cl and two Al—H.

The complete chlorination of t-BuPIA (reactions 4—6), has been achieved using different chlorinating agents (Table 1).

$$(\mathrm{HAlNR})_n + n\,\mathrm{HCl} \xrightarrow{\mathrm{Et_2O}} (\mathrm{ClAlNR})_n + n\,\mathrm{H_2} \qquad (4)$$

$$(\mathrm{HAlNR})_n + n/2\,\mathrm{HgCl_2} \xrightarrow{\mathrm{Et_2O}} (\mathrm{ClAlNR})_n + n/2\,\mathrm{Hg} + n/2\,\mathrm{H_2} \qquad (5)$$

$$(\mathrm{HAlNR})_n + n\,\mathrm{TiCl_4} \xrightarrow{\text{n-heptane}} (\mathrm{ClAlNR})_n + n\,\mathrm{TiCl_3} + n/2\,\mathrm{H_2} \qquad (6)$$

In every case a soluble compound was obtained from which chemical and physicochemical evidence suggests the formation of tetrachlorotetra(*N*-butyliminoalane). Its mass spectrum shows abundant ions $(M-\mathrm{CH_3})^+$ at m/e 517, 519, 521 and 523 with relative intensities corresponding to the presence of four chlorine atoms. The ^{1}H NMR spectrum in benzene exhibits one signal due to the t-butyl groups at τ 8.49 ppm, indicating the retention of a cubic structure. The product is a crystalline solid; its X-ray powder pattern is reported in Table 2.

2. *The chlorination of poly(N-isopropyliminoalanes)*

The syntheses of $(\mathrm{HAlN\text{-}i\text{-}Pr})_6$ (i-PrPIA-Hex) [3,5,6] and $(\mathrm{HAlN\text{-}i\text{-}Pr})_4$ (i-PrPIA-Tet) [6] have previously been reported; single crystal X-ray analysis demonstrated hexameric (II) [4] and cubic (I) [9] cage molecular structures, respectively. The partial and the complete substitution of hydridic hydrogens with

TABLE 2

X-RAY POWDER DATA FOR CHLOROPOLY(*N*-ALKYLIMINOALANES)

$(ClAlN\text{-}t\text{-}Bu)_4$		$(ClAlN\text{-}i\text{-}Pr)_6$		$(ClAlN\text{-}i\text{-}Pr)_4$	
I	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)
w	9.12	m	8.67	m	9.16
vs	8.23	vs	8.04	w	7.69
ms	7.69	m	5.89	vw	6.81
w	6.86	mw	4.93	mw	6.44
w	6.51	mw	4.59	vw	5.36
vw	6.07	ms	4.28	mw	4.41
vw	5.79	mw	4.03	w	4.18
w	5.34	vw	3.79	mw	3.41
m	4.67	ms	3.65	s	3.25
m	4.45	s	3.22	vw	3.10
m	4.29	m	3.13	vw	2.969
m	4.08	vw	3.01	mw	2.809
mw	3.78	m	2.936	w	2.751
w	3.60	m	2.844	w	2.675
m	3.37	w	2.681	vw	2.585
m	3.27	w	2.567	mw	2.368
m	3.14	w	2.522	vw	2.259
m	3.06	w	2.423	mw	2.212
mw	2.894	ms	2.374	mw	2.127
vw	2.809	m	2.276	w	2.074
mw	2.734	w	2.206	w	1.907
w	2.603	w	2.129	mw	1.804
vw	2.546	w	2.065	w	1.762
vw	2.485	mw	1.961	w	1.637
mw	2.411	w	1.911		
vw	2.353	w	1.864		
vw	2.301	mw	1.822		
mw	2.259	mw	1.707		
mw	2.196	w	1.639		
w	2.090	w	1.612		
w	2.045	w	1.585		
w	1.989	w	1.528		
vw	1.929				
vw	1.857				
mw	1.831				
mw	1.781				
vw	1.743				
w	1.710				
w	1.694				

chlorine has now been attempted with these compounds and the results are reported in Table 3.

The average substitution of one hydridic hydrogen by chlorine in i-PrPIA-Hex, with the stoichiometry of reactions 7 and 8, seems to occur without rearrangement of the molecular cage structure.

$$(HAlNR)_6 + \tfrac{1}{2}\,HgCl_2 \xrightarrow{Et_2O} [(ClAlNR)(HAlNR)_5] + \tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,Hg \qquad (7)$$

$$(HAlNR)_6 + HCl \xrightarrow{Et_2O} [(ClAlNR)(HAlNR)_5] + H_2 \qquad (8)$$

Mass spectra show the presence of mono- and di-chloro-hexakis(*N*-isopropyliminoalane) $[(M - CH_3)^+$ at *m/e* 529, 531 and at *m/e* 563, 565, 567 respec-

TABLE 3

CHLORINATION OF POLY(*N*-PROPYLIMINOALANES)

PIA (mmol)	Chlorinating agent (mmol)	Reaction conditions		Reaction product									
		Solvent (ml)	Temp. (°C) (Time (h))	Sample [b]	g	Analysis: Found (calcd.) (%)							Physico-chemical data suggested
						Al	Cl	N	H_{act} [a]	Cl/Al	N/Al	H_{act}/Al	
$(HAlN\text{-}i\text{-}Pr)_6$ (9.55)	HCl (9.55)	Et_2O (70)	ca. 22 (20)	E	5.5	27.8 (29.7)	5.8 (6.5)	15.0 (15.4)	8.4 (9.2) [c]	0.16	1.03	0.82	non-, mono- and di-chloro hexamers
$(HAlN\text{-}i\text{-}Pr)_6$ (10.2)	$HgCl_2$ (5.2)	Et_2O (120)	ca. 22 (15)	P_1/—78	2.8	29.1 (29.7)	5.9 (6.5)	15.9 (15.4)	9.5 (9.2) [c]	0.15	1.05	0.87	non-, mono- and di-chloro hexamers
				R	—	26.3 (29.7)	5.4 (6.5)	14.4 (15.4) [c]	— —	0.15	1.05	—	non-, mono- and di-chloro hexamers
$(HAlN\text{-}i\text{-}Pr)_6$ (18)	$HgCl_2$ (60)	Et_2O (300)	reflux temp., ca. 22 (11,16)	P	1.3	22.5	20.8	11.1	—	0.70	0.95	—	chlorinated oligomers mixture (see Table 4)
				R	—	16.8	25.9	8.9	—	1.17	1.02	—	
$(HAlN\text{-}i\text{-}Pr)_6$ (9)	HCl (54)	Et_2O (150)	reflux temp., ca. 22 (2,20)	P	0.6	24.4	20.1	12.7	—	0.63	1.00	—	chlorinated oligomers mixture (see Table 4)
				P_1/—5	1.8	20.8	23.9	11.5	—	0.87	1.06	—	
				P_2/—5	1.0	17.9	23.4	9.8	—	0.99	1.05	—	
				P_3/—5	0.9	18.6	31.7	11.0	—	1.30	1.03	—	

$(HAlN\text{-}i\text{-}Pr)_6$ (14.5)	$TiCl_4$ (87)	n-heptane (400)	25—30 (0.5)	X	7.0	21.8 (22.6)	29.4 (29.7)	11.5 (11.7)[d]	— —	1.02	1.02	—	hexachloro hexamers
$(HAlN\text{-}i\text{-}Pr)_4$ + $(HAlN\text{-}i\text{-}Pr)_6$ (5.8 + 11.6)	HCl (15.5)	Et_2O (150)	ca. 22 (0.5)	E	8.5	28.4 (29.7)	6.3 (6.5)	15.0 (15.4)	9.0 (9.2)[c]	0.16	1.01	0.85	non-, mono- and di-chloro hexamers
$(HAlN\text{-}i\text{-}Pr)_4$ + $(HAlN\text{-}i\text{-}Pr)_6$ (4.6 + 9.2)	$TiCl_4$ (73.6)	n-heptane (200)	25—30 (0.5)	Cr	1.3	21.9 (22.6)	28.9 (29.7)	10.9 (11.7)[d]	— —	1.00	0.96	—	tetrachloro tetramer
				X	—	21.8 (22.0)	29.3 (29.7)	11.2 (11.7)[d]	— —	1.02	0.99	—	hexachloro hexamer
$(HAlN\text{-}n\text{-}Pr)_8$ (3)	$TiCl_4$ (24)	n-heptane (150)	25—30 (0.5)	E	2.5	20.8 (22.6)	26.9 (29.7)	11.2 (11.7)[d]	— —	0.98	1.04	—	completely chlorinated hexamer, octamer, decamer

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[a] H_{act} = hydridic hydrogen content indicated as meq/g. [b] E = solid from evaporation of the reaction solution; P = insoluble fraction from the reaction mixture; P_n/x is the solid separated at x°C by gradual concentration of the ethereal solution of the reaction product; R = solid from evaporation of the remaining solution after separation of P or Cr; Cr = crystals from reaction solution; X = crystalline compound extracted with boiling benzene from the reaction product. [c] Calcd. for $C_{18}H_{47}Al_6ClN_6$. [d] Calcd. for C_3H_7AlClN.

TABLE 4

MASS SPECTRA OF COMPOUNDS OBTAINED FROM THE CHLORINATION OF $(HAl\text{-}N\text{-}i\text{-}Pr)_6$ WITH HCl OR $HgCl_2$ [a]

m/e	Cl atoms	Assignment	
		Ion [b]	Compound
563, 565	2	$[(H_4{}^{*}Cl_2Al_6N_6Pr_6) - Me]^+$	Closed dichloro hexamer
597, 599, 601	3	$[(H_3{}^{*}Cl_3Al_6N_6Pr_6) - Me]^+$	Closed trichloro hexamer
631, 633, 635	4	$[(H_2{}^{*}Cl_4Al_6N_6Pr_6) - Me]^+$	Closed tetrachloro hexamer
665, 667, 669	5	$[(H^{*}Cl_5Al_6N_6Pr_6) - Me]^+$	Closed pentachloro hexamer
582, 584, 586	5	$[(H^{*}Cl_5Al_5N_5HPr_5) - Me]^+$	Open pentachloro pentamer
616, 618, 620, 622	6	$[(Cl_6Al_5N_5HPr_5) - Me]^+$	Open hexachloro pentamer
461, 463, 465	4	$[(Cl_4Al_4N_4Pr_4) - Me]^+$	Closed tetrachloro tetramer
497, 499, 501	5	$[(Cl_5Al_4N_4HPr_4) - Me]^+$	Open pentachloro tetramer
295, 297, 299	4	$[(Cl_4Al_2N_2H_2Pr_2) - Me]^+$	$(Cl_2AlNH\text{-}i\text{-}Pr)_2$

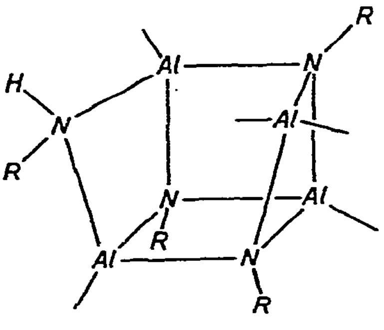
[a] As obtained while attempting the complete chlorination according to the conditions of Table 3. [b] H^{*} indicate hydridic hydrogens.

tively] together with unreacted i-PrPIA-Hex $[(M - CH_3)^+$ at *m/e* 495]. The ^1H NMR spectrum in benzene is rather complex and it is not possible to assign signals due to the differently chlorinated species. However, as with the partially-chlorinated t-BuPIA, the spectrum consists of the typical signals of the starting i-PrPIA-Hex [3], together with other signals due to the isopropyl protons of the chlorinated species.

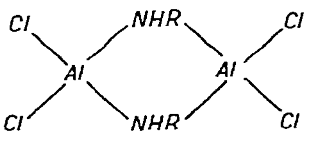
When complete chlorination with $HgCl_2$ or HCl was attempted (eq. 4-5), the reaction was found to be quite complicated. In fact, besides the expected product $(ClAlN\text{-}i\text{-}Pr)_6$ (III), mass spectrometry showed the formation of a mixture of hexameric i-PrPIA with different degrees of chlorination, together with chlorinated pentamers and tetramers and more simple species such as $(Cl_2AlNH\text{-}i\text{-}Pr)_2$, evidently due to degradation reactions.

In Table 4, the more abundant ions in mass spectra are reported. It is not at present possible to suggest a reasonable structure for the pentamer species. The chlorinated open tetramer species can be regarded as derived from IV. The possibility of a similar structure was previously supported by ^1H NMR for a PIA obtained from t-butylamine [3].

The formation of a complex with nitrogen bridges (V) appears to be very probable for $(Cl_2AlNH\text{-}i\text{-}Pr)_2$.



(IV)



(V)

The ^{1}H NMR spectra of benzene solutions of the reaction products are characterized by the presence of doublets and septets in the range of CH_3 and CH protons in accordance with the different species derived from structural rearrangements of the starting i-PrPIA-Hex. In addition, a doublet at τ 9.12 ppm was assigned to the CH_3 protons of V.

The separation of the pure compounds from the reaction products of the completely-chlorinated i-PrPIA-Hex with HCl and $HgCl_2$ was attempted by fractionation, either by gradual concentration or by the cooling of their solution in diethyl ether. Although changes in composition of the different fractions occurred (Cl/Al increases from 0.63 to 1.30 with the solubility), it was not possible to separate the pure species (Table 3). On the other hand, the reaction of i-PrPIA-Hex with a stoichiometric quantity of $TiCl_4$ in n-heptane gave only the chlorinated hexamer III (reaction 6). This product is only slightly soluble in the hydrocarbon reaction medium and coprecipitates with β-$TiCl_3$. From this mixture, III is separated as a crystalline solid by continuous extraction with refluxing benzene. The molecular structure was determined by a single crystal X-ray analysis [9], and showed that III maintains the cage hexamer structure II of the starting i-PrPIA-Hex. The corresponding X-ray powder pattern is reported in Table 2.

When a mixture of i-PrPIA-Hex and i-PrPIA-Tet (molar ratio 2 : 1), as obtained from the reaction between $LiAlH_4$ and i-$PrNH_2$ [6], was allowed to react with HCl at a ratio HCl/Al—H = 1 : 6, only hexameric chlorinated i-PrPIA was found as the reaction product (Table 3). The mass spectrum exhibits the above ions from mono- and di-chlorinated hexakis(*N*-isopropyliminoalanes) together with ions from i-PrPIA-Hex. The ^{1}H NMR spectrum in benzene is very similar to that observed for the product of the partial chlorination of i-PrPIA-Hex.

However, the reaction of the mixture of i-PrPIA-Hex and i-PrPIA-Tet with $TiCl_4$ (Al/Ti = 1) in n-heptane gave the corresponding mixture of $(ClAlN\text{-}i\text{-}Pr)_4$ (VI) and III. Unlike III compound VI is soluble in the reaction medium, from which it can be easily obtained as prismatic crystals by standing or by concentration and cooling. A single crystal X-ray investigation is in progress and preliminary data indicate that VI retains the cubic molecular structure of the starting i-PrPIA-Tet [9]. Its X-ray powder pattern is reported in Table 2. The mass spectrum confirms the presence of abundant ions at *m/e* 461, 463 and 465 from the tetrachlorinated tetramer. The ^{1}H NMR spectrum in benzene shows a doublet at τ 8.64 ppm and a septet at τ 6.63 ppm, in accordance with the magnetic equivalence of the isopropyl groups of the nitrogen atoms.

3. *The chlorination of poly(N-n-propyliminoalane)*

The investigation was limited to the interaction of $TiCl_4$ with octakis(*N*-n-propyliminoalane) (n-PrPIA), which is obtainable in a pure form by direct synthesis from aluminium and the amine in the presence of hydrogen [5]. For this compound, the single crystal X-ray analysis indicates as a preliminary result a cage molecular structure [10] as in Fig. 2. Its reaction with $TiCl_4$ at Al/Ti = 1 (Table 3) seems to proceed with some structural rearrangements. The mass spectrum shows the presence of some ions $(M - Et)^+$ at *m/e* 685, 687, 689, 691 from $(ClAlN\text{-}n\text{-}Pr)_6$, at *m/e* 1161, 1163, 1165, 1167 from $(ClAlN\text{-}n\text{-}Pr)_{10}$ together with ions from the expected $(ClAlN\text{-}n\text{-}Pr)_8$ at *m/e* 923, 925, 927, 929. The ^{1}H NMR

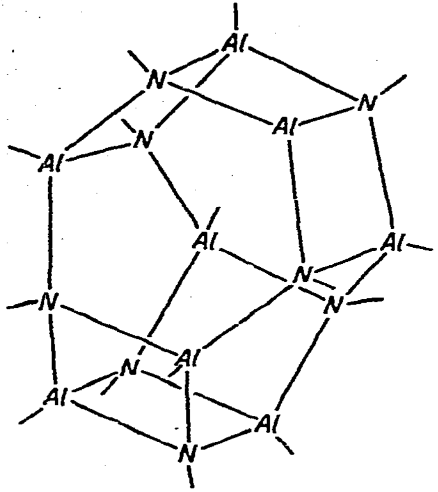


Fig. 2. A skeletal representation of the octameric cage molecule $(HAlN\text{-}n\text{-}Pr)_8$ as determined by X-ray crystallography.

spectrum in benzene is complicated by a multiplicity of signals in accordance with the presence of different molecular species.

4. Observations on the mechanism of chlorination

The above results indicate that the chlorination of PIA occurs via two reactions: (i) the substitution of hydridic hydrogen with chlorine, where the chlorinated PIA retains its original molecular structure. This reaction is favoured when the PIA is chlorinated with $TiCl_4$; (ii) the cleavage of Al—N bonds. In this case chlorinated species are obtained which are structurally different with respect to the starting PIA. This reaction is more probable with HCl or $HgCl_2$. The latter reagent could cause the formation of HCl (reactions 9 and 10).

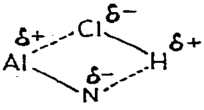
$$\equiv Al{-}H + HgCl_2 \rightarrow \equiv Al{-}Cl + HgHCl \quad (9)$$

$$HgHCl \rightarrow Hg + HCl \quad (10)$$

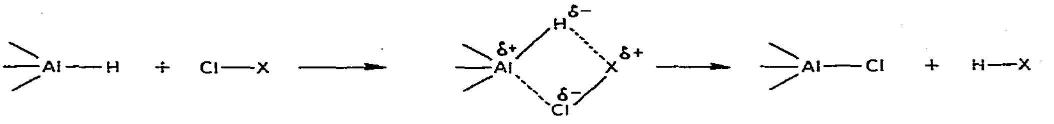
An example of this cleavage was previously reported [11] for reaction 11.

$$(C_2H_5Al{-}NC_6H_5)_4 + 4\,HCl \rightarrow 2\,(C_2H_5ClAl{-}NHC_6H_5)_2 \quad (11)$$

The molecular structure of the PIA and the steric hindrance of the alkyl groups of the nitrogen atoms, seem to influence the occurrence of the substitution or cleavage reactions, which occurs as follows.

4.1. The high steric hindrance of the t-butyl group would prevent the predictable intermediate interaction  and the cleavage reaction is thus very improbable.

The substitution occurs via reaction 12 with production of chlorinated species retaining the cubic structure of the starting PIA, and this does not depend on the degree of chlorination or the chlorinating agent (in the case of $TiCl_4$ the final formation of $TiCl_3$ could result from the decomposition of the unstable intermediate $HTiCl_3$).



(12)

(X = H, HgCl, $TiCl_3$)

4.2. The lower steric hindrance of alkyl groups is probably responsible for the Al—N cleavage by HCl or $HgCl_2$ even in the case of the partial chlorination of $(HAlN\text{-i-Pr})_4$ with rearrangement of the resulting frameworks to the more stable hexamers. On the other hand, the intermediate formation of complexes PIA · $TiCl_4$ by reaction 12 could control the complete chlorination without structural rearrangements.

The more stable hexamer structure would favour the partial chlorination of $(HAlN\text{-i-Pr})_6$ by a substitution reaction. The increased chlorination would then deactivate the remaining hydridic hydrogens with respect to their substitution by chlorine and this, in the case of i-PrPIA-Hex, would correspond to the possibility of Al—N bond cleavage at high degrees of chlorination. The final result after attempting complete chlorination with HCl or $HgCl_2$ is the formation of species deriving from structural degradation together with chlorinated hexamers. The formation of $(Cl_2AlNH\text{-i-Pr})_2$ instead of $(ClHAlNH\text{-i-Pr})_2$ (VII) which would be expected from reaction 13, as with reaction 11, could be due to a further chlorination of VII. The complete chlorination of i-PrPIA-Hex with $TiCl_4$ gives only the

$$(HAlNR)_n + n\ HCl \rightarrow n/2\ (ClHAlNHR)_2 \tag{13}$$

hexamer $(ClAlN\text{-i-Pr})_6$ confirming the results obtained with i-PrPIA-Tet.

4.3. The results obtained for $(HAlN\text{-n-Pr})_8$ indicate that Al—N bond cleavage is also possible when $TiCl_4$ is used. By investigating the products from complete chlorination, it can be shown that disproportionation (eq. 14) has occurred together with the simple substitution of Cl for H. X represents either H or Cl, and

$$2\ (XAlNR)_8 \rightarrow (XAlNR)_6 + (XAlNR)_{10} \tag{14}$$

it is not known at which degree of chlorination reaction 14 occurs.

Conclusions

In the reaction of PIA with some chlorinating agents, such as HCl, $HgCl_2$ or $TiCl_4$, simple substitution of hydridic hydrogen by chlorine as well as Al—N cleavage can take place, depending on the nature of both reagents. From the simple substitution, chlorinated PIA are obtained which maintain the molecular cage structure of the starting material. The cleavage reaction leads to structural rearrangement, yielding chlorinated PIA with different molecular cage structures and eventually *N*-alkylaminoalane dimers. Simple substitution seems more favoured with $TiCl_4$ and for PIA derived from amines having alkyl groups with higher steric hindrance.

Experimental

Reagents and solvents

The preparation of pure PIA was carried out as previously reported [3,5,6]. $HgCl_2$ and $TiCl_4$ were RP Erba products. All solvents were purified and dried by known methods and all syntheses were carried out under an atmosphere of nitrogen.

Chemical analyses and physicochemical measurements

Chemical analyses and physicochemical measurements were carried out by using the methods and the apparatus previously reported [3].

Chlorination of poly(N-alkyliminoalanes)

Some typical chlorination reactions are described only for hexakis(*N*-isopropyliminoalane), with different chlorinating agents. The other PIA were chlorinated by similar methods, under the conditions given in Tables 1 and 3.

(a) A solution of HCl (0.72 *N*, 9.55 mmol) in diethyl ether (13.3 ml) was added dropwise to a stirred solution of i-PrPIA-Hex (9.55 mmol) in diethyl ether (57 ml) at room temperature (ca. 22° C). Hydrogen evolution took place, and the reaction mixture was stirred for 1 h and then left overnight. The solvent was then removed by evaporation in vacuo. The white solid residue was dried (10 h, room temp., 10^{-3} mmHg) and analyzed (Found: Al, 27.8; Cl, 5.8; N, 15.0%; H_{act}, 8.4 meq/g. $C_{18}H_{47}Al_6ClN_6$ calcd.: Al, 29.7; Cl, 6.5; N, 15.4%; H_{act}, 9.2 meq/g).

(b) $HgCl_2$ (60 mmol) was added to a stirred solution of i-PrPIA-Hex (18 mmol) in diethyl ether (300 ml) at ca. 22° C. Evolution of hydrogen took place immediately, while the colour of the reaction mixture became black. The reaction mixture was allowed to reflux for 11 h and then left overnight. The reaction mixture was separated from drops of mercury which had collected on the bottom of the flask and filtered. The insoluble material was dried and analyzed (Found: Al, 22.5; Cl, 20.8; N, 11.1%; Cl/Al, 0.70; N/Al, 0.95) (Yield 1.3 g). The solid from evaporation of the remaining solution was dried and analyzed (Found: Al, 16.8; Cl, 25.9; N, 8.9%; Cl/Al, 1.17; N/Al, 1.02).

(c) A solution of HCl (0.7 *N*, 54 mmol) in diethyl ether (77.2 ml) was added to a stirred solution of i-PrPIA-Hex (9 mmol) in diethyl ether (78 ml) at room temperature (ca. 22° C). Evolution of hydrogen took place and the reaction mixture was stirred for 2 h and then left overnight. Traces of impurities were removed by filtration and the solution was evaporated in vacuo to obtain a semisolid material. By addition of a smaller amount of diethyl ether (100 ml), this material did not dissolve completely. The insoluble substance was separated by filtration, dried and analyzed (Found: Al, 24.4; Cl, 20.1; N, 12.7%; Cl/Al, 0.63; N/Al, 1.00) (Yield 0.6 g). The ethereal solution was concentrated and cooled to —5° C. The precipitated material was separated, dried and analyzed (Found: Al, 20.8; Cl, 23.9; N, 11.5%; Cl/Al, 0.87; N/Al, 1.06) (Yield 1.8 g). Further concentration allows the separation of other insoluble material at —5° C (Al, 17.9; Cl, 23.4; N, 9.8%; Cl/Al, 0.99; N/Al, 1.05) (Yield 1 g). Finally the remaining solution was further concentrated to 15 ml; the separated insoluble material at —5°C was dried and analyzed (Al, 18.6; Cl, 31.7; N, 11.02%; Cl/Al, 1.30; N/Al, 1.03) (Yield 0.9 g).

(d) i-PrPIA-Hex (14.5 mmol) in n-heptane (170 ml) was added slowly to a stirred solution of $TiCl_4$ (87 mmol) in n-heptane (400 ml). The reaction is exothermic and the reaction temperature was maintained at 25—30° C, by controlling the rate of addition of PIA. Hydrogen evolution took place and the reaction mixture was stirred 0.5 h and then filtered. The brown insoluble product was washed several times with n-heptane, benzene and n-hexane, dried, and then subjected to extraction with refluxing benzene for 35 h. Crystals were separated from the benzene solution which were filtered, dried and analyzed (Found: Al, 21.8; Cl, 29.4; N, 11.5%; C_3H_7AlClN calcd.: Al, 22.6; Cl, 29.7; N, 11.7%) (Yield 7 g).

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