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

XIV*. SOME ADVANCES IN THE SYNTHESIS OF MIXED POLY(*N*-ALKYLIMINO) DERIVATIVES OF ALUMINUM AND ALKALINE-EARTH METALS

S. CUCINELLA **, G. DOZZI, G. PEREGO and A. MAZZEI

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

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Summary

Crystalline mixed imino derivatives of aluminum and calcium, $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NCa \cdot 3THF)]$ or magnesium $[(t\text{-}C_4H_9AlH)_3(t\text{-}C_4H_9NMg \cdot THF)]$ were obtained by the reaction of a mixture of $Ca(AlH_4)_2$— or $Mg(AlH_4)_2$—tetrahydrofuranate and $AlH_3 \cdot N(CH_3)_3$ with $t\text{-}C_4H_9NH_2$. The molecular structures of these compounds have been fully characterized by X-ray analysis of single crystals. A mixed imino derivative of composition $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NMg \cdot 3THF)]$ was also obtained by direct synthesis from aluminum, magnesium and $t\text{-}C_4H_9NH_2$ in tetrahydrofuran under hydrogen pressure.

Introduction

Preliminary results on the reaction of $Ca(AlH_4)_2$ and $Mg(AlH_4)_2$ with n-butylamine, neopentylamine, butyronitrile and aniline were reported some years ago [1]. With a molar ratio of amine (or nitrile)/alanate = 3/1, mixed polyimino compounds (mixed PIA's) containing both —AlH—NR— and —Ca—NR— (or —Mg—NR—) units were obtained. The derivatives from aliphatic amines were amorphous, whereas aniline yielded crystalline products. However, attempts to isolate crystals suitable for a complete molecular characterization by X-ray analysis were unsuccessful.

In the course of our extensive work on poly(*N*-alkyliminoalanes) [2] (PIA)

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* For part XIII see ref. 10.

** To whom correspondence should be addressed.

TABLE 1

RESULTS OF THE REACTIONS OF $M^1(AlH_4)_2$ WITH RNH_2 IN THE PRESENCE OR IN THE ABSENCE OF $AlH_3 \cdot N(CH_3)_3$ (M^1 = Ca, Mg; R = $i\text{-}C_3H_7$; $t\text{-}C_4H_9$)

Entry	$M^1(AlH_4)_2 \cdot x$THF (mmol)	RNH_2 (mmol)	$AlH_3 \cdot N(CH_3)_3$ (mmol)	Solvent (ml)	Temperature (°C) (time (h))	Fraction		Chemical analysis (Found (calcd.)) (%)						
						Sample[a] (g)	X-ray analysis[b]	Al	M^1	N	H_{act}[c]	$\frac{M^1}{Al}$	$\frac{N}{Al}$	$\frac{H_{act}}{Al}$
1	$Ca(AlH_4)_2 \cdot 3$THF (25.4)	$i\text{-}C_3H_7NH_2$ (50.8)	—	THF (230)	25 (20)	R	A	16.6	13.0	8.8	13.2	0.53	1.02	2.14
2	$Ca(AlH_4)_2 \cdot 3$THF (27.5)	$t\text{-}C_4H_9NH_2$ (55)	—	THF (230)	25 (20)	C(THF, −5)	xx	14.7	7.6	9.7	6.0			
						(1.8)		(14.6)	(7.2)	(10.1)	(5.5)[d]			
						R	A	17.0	12.8	8.2	12.7	0.51	0.93	2.00
3	$Mg(AlH_4)_2 \cdot 5$THF (25.2)	$t\text{-}C_4H_9NH_2$ (50.4)	—	THF (250)	25 (20)	R	xx	15.0	7.0	8.3	10.4	0.52	1.07	1.85
4	$Ca(AlH_4)_2 \cdot 3$THF	$t\text{-}C_4H_9NH_2$	26	THF	−40−25;	C(THF, −5)	xx	14.9	7.6	10.0	5.7			
	(26.0)	(104)		(225)	55(12)	(2.8)		(14.6)	(7.2)	(10.1)	(5.5)[d]			
						R	xx	13.4	6.9	8.9	5.5	0.35	1.28	1.10
5	$Mg(AlH_4)_2 \cdot 5$THF	$t\text{-}C_4H_9NH_2$	25.5	C_6H_6	25(20)	C(tol., −5)	xx	16.5	5.0	12.0	6.3			
	(25.5)	(102)		(280)	50(3)	(1.5)		(17.4)	(5.2)	(12.0)	(6.4)[e]			
						R	xx	17.0	5.0	12.2	7.0			
								(17.4)	(5.2)	(12.0)	(6.4)[e]			

[a] R = solid residue obtained by evaporating under vacuum the reaction solution after separation of C; for entry 5, R indicates the solid residue obtained by evaporating a toluene solution of the reaction product after separating crystals, C(s, x) = crystals separated from the solution in the solvent s at x°C. [b] Results of X-ray powder pattern: A = practically amorphous; xx = crystalline. [c] H_{act} = hydridic hydrogen content indicated as meq/g. [d] Values calculated for $C_{24}H_{55}Al_3CaN_4O_2$. [e] Values calculated for $C_{20}H_{47}Al_3MgN_4O$.

we have briefly reexamined the question of the mixed PIA's, with the objective of confirming the existence of M—NR—Al bonds (M = Mg, Ca) by complete determination of the molecular structure of the crystalline compounds. The feasibility of the direct synthesis of mixed PIA's, from metals and amine, has been also investigated. The results form the subject matter of this paper.

Results and discussion

Our previous results on PIA synthesis [2] showed that, independent of the method of synthesis, pure PIA's of formula $(HAlNR)_n$ with a tetrameric or hexameric molecular cage structure are obtained from isopropyl, s-butyl, t-butyl and cyclohexylamine, n-butylamine and other linear primary amines usually gave a mixture of PIA oligomers. Thus n-butylamine and butyronitrile are now considered unsuitable for producing well-defined mixed PIA's and in reconsidering the synthesis of mixed PIA's from $M^1(AlH_4)_2$ (M^1 = Ca; Mg) and amines we have limited the research to $i\text{-}C_3H_7NH_2$ and $t\text{-}C_4H_9NH_2$.

We previously showed that in the reaction of $Ca(AlH_4)_2$ and aniline [1] in a molar ratio 1/2, reaction 1 occurs

$$Ca(AlH_4)_2 + 2RNH_2 \xrightarrow{THF} \underset{(I)}{Ca(NRAlH_2)_2} + 4H_2 \qquad (1)$$

giving tetrahydrofuran complexes of the imino derivative I (reasonably precursor of the mixed PIA), instead of a mixture of PIA and M^1H_2, as would be expected from the well known reaction 2 [3].

$$M^2AlH_4 + RNH_2 \rightarrow M^2H + \frac{1}{n}(HAlNR)_n + 2H_2 \qquad (2)$$

(M^2 = Li, Na)

The isolation and characterization of the intermediate I from aliphatic primary amines also would have added to the evidence for formation of Al—NR—M^1 bonds, but our recent attempts to separate single crystals of the compound either from isopropyl or t-butylamine have again been unsuccessful. Some typical results are summarized in Table 1 (entries 1—3).

Unexpectedly, in the case of the reaction of $Ca(AlH_4)_2$ with $t\text{-}C_4H_9NH_2$ in THF some crystals which separated from the reaction mixture had a composition agreeing well with the formula $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NCa) \cdot 2THF]$ (II), which corresponds to the replacement of one Al—H group in the tetramer $(t\text{-}C_4H_9NAlH)_4$ by one calcium atom coordinated to two THF molecules. This prompted us to examine the possibilities of forming II and the corresponding derivative containing magnesium, from a mixture of $M^1(AlH_4)_2$, AlH_3 and $t\text{-}C_4H_9NH_2$ by the correct choice of the stoichiometry of the reagents, according to equation 3.

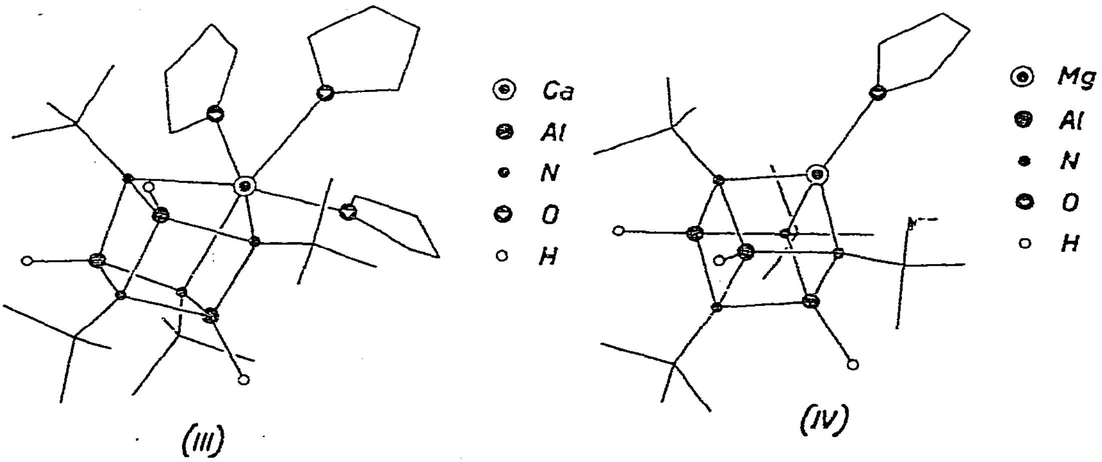
$$M^1(AlH_4)_2 + AlH_3 + 4RNH_2 \rightarrow [(RNAlH)_3(RNM^1)] + 8H_2 \qquad (3)$$

These reactions were carried out in tetrahydrofuran or benzene. In both cases complexes of $Ca(AlH_4)_2$ or $Mg(AlH_4)_2$ with THF molecules and $AlH_3 \cdot N(CH_3)_3$ were used as starting materials. A good yield of the expected tetrameric mixed

PIA is obtained, containing three atoms of aluminum and one atom of alkaline-earth metal (Table 1, entries 4 and 5). Their molecular structures have been fully characterized by X-ray analysis of single crystals. A skeletal representation of the structure of calcium and magnesium derivatives is presented in Fig. 1. The X-ray patterns of the powders are reported in Table 2. A complete discussion of the molecular structure is given in part XV of this series [4]. These mixed PIA's have essentially the typical cubane structure found for the parent tetrameric PIA with the replacement of one Al—H group by one atom of the alkaline-earth metal. For the calcium derivative (III) X-ray analysis indicates hexacoordination of the calcium atom through three bridged NR groups and three THF molecules. Some anomaly is associated with the chemical analysis, which agrees with pentacoordinated calcium (two molecules of THF). However, it must be remembered that the X-ray analysis was performed on crystals separated from the reaction mixture, whereas the chemical analyses were carried out on the product dried under vacuum and the drying changes the coordination number of the calcium. The dried product is also crystalline, but, we did not succeed in isolating single crystals; this material shows one ν(Al—H) band at 1760 cm^{-1}, and it is known [1] that the partial replacement of Al—H groups in a PIA causes a shift of the infrared absorption ν(Al—H); thus [2] $(HAlN\text{-}t\text{-}C_4H_9)_4$ shows one ν(Al—H) band at 1850 cm^{-1}.

When reaction 3 was carried out in benzene, a mixture of crystalline imino derivatives was obtained. These compounds, separated by fractionally crystallizing (4 fractions) a toluene solution at different temperatures, contain calcium and aluminum in a constant atomic ratio 1/2. Nevertheless their compositions ($1.0 \leqslant N/Al \leqslant 1.6$; $1.6 \geqslant H_{att}/Al \geqslant 1.20$) and their X-ray powder patterns are different. This aspect has not been further investigated.

For the magnesium derivative (IV) of Fig. 1, the X-ray analysis and the chemical composition were carried out on the dried product, and reveal a tetracoordinated magnesium through three bridged NR groups and one THF molecule. This compound shows one infrared ν(Al—H) band with a maximum at 1785 cm^{-1} IV was easily obtained from reaction 3 in benzene.



(III) (IV)

Fig. 1. Skeletal representation of the molecular structure of $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NCa \cdot 3THF)]$ and of $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NMg \cdot THF)]$ as determined by X-ray crystallography [4].

TABLE 2

X-RAY POWDER DATA [a] OF POLY(*N*-ALKYLIMINO) DERIVATIVES OF ALUMINUM AND CALCIUM OR MAGNESIUM FROM t-BUTYLAMINE

$[(RNAlH)_3(RNCa\cdot 2THF)]$		$[(RNAlH)_3(RNMg\cdot THF)]$		$[(RNAlH)_3(RNMg\cdot 3THF)]$	
I	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)
w	12.81	ms	8.63	vs	10.16
ms	9.83	s	7.69	s	8.71
vs	8.67	w	7.17	mw	8.04
vs	8.12	w	6.56	ms	7.63
vw	7.63	ms	6.09	ms	6.81
m	6.49	w	5.22	vw	6.35
s	5.91	ms	5.07	w	5.91
w	5.56	m	4.80	w	5.52
ms	4.93	m	4.62	vw	5.22
ms	4.71	mw	4.32	ms	5.00
m	4.19	mw	4.15	s	4.77
m	4.07	w	3.88	w	4.55
m	3.75	mw	3.75	m	4.35
mw	3.46	w	3.55	mw	4.26
w	3.34	w	3.38	w	3.79
w	3.24	w	3.26	w	3.62
m	3.15	mw	3.05	w	3.36
m	2.809	w	2.698	w	3.24
w	2.648	mw	2.410	w	2.58
m	2.553	mw	2.368		
w	2.468	mw	2.298		
mw	2.344	w	2.191		
w	2.270	w	2.151		
mw	2.219	mw	2.036		
mw	2.044				

[a] Visually estimated intensities are reported as: vs = very strong, s = strong, m = medium, ms = medium strong, mw = medium weak, w = weak, vw = very weak (Cu-K_α radiation, λ 1.54178 Å).

Finally, we were able to bring about the direct synthesis of mixed PIA from aluminum, magnesium and t-butylamine. The synthesis occurs under a pressure of hydrogen if an activator is present (reaction 4). Thus at 100°C and a pressure of H_2 of 190 kg/cm^2 in THF a soluble product is obtained, with the atomic

$$3Al + Mg + 4RNH_2 \xrightarrow{THF} \underset{(V)}{[(HAlNR)_3(RNMg - xTHF)]} + \tfrac{5}{2}\,H_2 \qquad (4)$$

ratios Mg/Al = 0.33 and N/Al near 1.3, indicating the formation of a compound of type IV under these conditions also. $NaAlH_4$ was found to be a good activator, as in the direct synthesis of PIA from aluminum and amine [2]. Unlike IV, product V appears to be complexed by more than one THF molecule. Its chemical composition is rather similar to that of a complex containing three molecules of THF. The X-ray pattern of the powder is different from that found for IV (Table 2). It is also different from the X-ray powder pattern of $(HAlN\text{-}t\text{-}C_4H_9)_4$ [5], which can be obtained directly from aluminum and amine [2], as well as of the magnesium amide, recently synthesized from magnesium and amine [6], excluding the formation of a mixture containing these products.

Finally the formation of a mixed PIA is confirmed by the infrared spectrum, which shows one ν(Al—H) band at 1780 cm^{-1}.

Experimental

Reagents and solvents

$Ca(AlH_4)_2$ and $Mg(AlH_4)_2$ were prepared as previously reported [1] by published methods [7,8]. $AlH_3 \cdot N(CH_3)_3$ was obtained from $LiAlH_4$ and $(CH_3)_3N \cdot HCl$ [9].

Powdered magnesium (Eckart—Werke MX31) was used which was deoxygenated before reaction by milling for 20 hours at room temperature with $Al(C_2H_5)_3$ in toluene (molar ratio Al/Mg was 0.02). The $Al(C_2H_5)_3$ was completely removed by filtration, and the milled magnesium was washed several times with toluene and subsequently with THF. Aluminum (Eckart—Werke AS081) was purified in the same manner [2]. Commercial pure amines were dried and purified by distillation over Na or KOH. All solvents were purified and dried by standard methods, and all the syntheses and physico-chemical characterizations were carried out under nitrogen.

Chemical analyses and physicochemical measurements

The chemical analyses were carried out on solutions obtained by decomposition of weighed samples with diluted aqueous acid solutions. The aluminum content was determined by the EDTA $\cdot$ $ZnSO_4$ method. Magnesium was also determined with EDTA at pH 10; in this case the aluminum was first complexed with triethanolamine. Calcium was determined as CaO. For analyses, a Kjeldahl apparatus was used for the nitrogen determination of amines obtained on hydrolysis of weighed samples.

X-ray powder patterns were recorded by a Debye-Scherrer camera (diameter 114.6 mm) with Cu-K_α radiation. IR spectra in Nujol were recorded by a Perkin—Elmer 225 instrument.

Synthesis of mixed polyimino derivatives

Typical methods of synthesis giving well-characterized compounds were as follows:

(a) Synthesis of $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NCa \cdot 2THF)]$ from $Ca(AlH_4)_2$-tetrahydrofuranate, $AlH_3 \cdot N(CH_3)_3$ and $t\text{-}C_4H_9NH_2$. A solution of $t\text{-}C_4H_9NH_2$ (104 mmol) in THF (50 ml) was slowly added dropwise to a stirred solution of $Ca(AlH_4)_2$ (26 mmol) and $AlH_3 \cdot N(CH_3)_3$ (26 mmol) in THF (160 ml) at −40°C. The mixture was allowed to warm to room temperature (H_2 and $N(CH_3)_3$ were evolved) and heated for 12 h at 55°C. Crystals were formed and X-ray analysis, carried out on one of the crystals, freshly separated from the mother solution, gave the molecular structure depicted in Fig. 1. When the crystals were separated from the solution and dried under vacuo (10^{-3} Torr, 8 h at room temperature), a crystalline product (2.8 g) was obtained and analysed (Found: Al, 14.9; Ca, 7.6; N, 10.0%; H_{act}, 5.7 meq/g. $C_{24}H_{55}Al_3CaN_4O_2$ calcd.: Al, 14.6; Ca, 7.2; N, 10.1%; H_{act}, 5.5 meq/g). The remaining solution was evaporated in vacuo and the dried crystalline residue was analyzed (Found: Al, 13.4; Ca, 6.9; N, 10.1%; H_{act}, 5.4 meq/g; Ca/Al = 0.35; N/Al = 1.28; H_{act}/Al = 1.28).

(b) Synthesis of $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NMg \cdot THF)]$ from $Mg(AlH_4)_2 \cdot 5THF$, $AlH_3 \cdot N(CH_3)_3$ and $t\text{-}C_4H_9NH_2$. A solution of $t\text{-}C_4H_9NH_2$ (100 mmol) in benzene (50 ml) was slowly added dropwise to a stirred mixture of $Mg(AlH_4)_2 \cdot 5THF$ (25.5 mmol), $AlH_3 \cdot N(CH_3)_3$ (25.5 mmol) in benzene (220 ml) at 25°C. H_2 and $N(CH_3)_3$ were evolved. The mixture was stirred for 20 h at room temperature and then for 3 h at 50°C. Small amounts of insoluble materials were filtered off and the filtrate was evaporated under vacuo. The solid residue was dissolved in the minimum amount of toluene and the solution was cooled to −5°C. The crystals formed were separated and dried under vacuo (10^{-3} Torr, 8 h at room temperature) and analyzed. (Found: Al, 16.5; Mg, 5.0; N, 12.0%; H_{act}, 6.3 meq/g. $C_{20}H_{47}Al_3MgN_4O$ calcd.: Al, 17.4; Mg, 5.2; N, 12.0%; H_{act}, 6.4 meq/g). The yield was 1.5 g. X-ray analysis of a single crystal directly separated from the mother solution gave the molecular structure shown in Fig. 1. The mother liquor was evaporated in vacuo to give a crystalline residue, which was dried and analyzed (Found: Al, 17.0; Mg, 5.0; N, 12.2%; H_{act}, 7.0 meq/g. $C_{20}H_{47}Al_3MgN_4O$ calcd.: Al, 17.4; Mg, 5.2; N, 12.0%; H_{act}, 6.4 meq/g). X-ray powder pattern demonstrated that this residue has the same molecular structure as the crystals described above.

(c) Synthesis of $[(t\text{-}C_4H_9NAlH)_3(t\text{-}C_4H_9NMg \cdot 3THF)]$ from aluminum, magnesium and t-butylamine. A mixture of powdered magnesium (150 mmol), powdered aluminum (210 mmol), $NaAlH_4$ (10 mmol) and t-butylamine (280 mmol) in THF (400 ml) was introduced into a 1 l autoclave provided with an anchor stirrer. Hydrogen (140 kg cm^{-2}) was introduced and the autoclave was heated at 100°C; the pressure increased to ca. 190 kg cm^{-2}. The mixture was stirred for 48 h, allowed to cool to room temperature, and filtered. The insoluble fraction was washed several times with fresh solvent, and the soluble fractions combined with the mother solution to give 450 ml of a solution, for which analysis gave: Al, 4.4 g-atoms/100 ml; Mg, 1.45 g-atoms; N, 5.55 g-atoms; H_{act}, 3.96 g-atoms; Mg/Al, 0.33; N/Al, 1.26, H_{act}/Al, 0.9. The solution was evaporated to leave a sticky residue, which was washed several times with n-hexane, and dried to give a crystalline product. (Found: Al, 12.5; Mg, 3.8; N, 8.4%; H_{act}, 4.1 meq/g. $C_{28}H_{63}Al_3MgN_4O_3$ calcd.: Al, 13.3; Mg, 4.0; N, 9.1; H_{act}, 4.9 meq/g).

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