Journal of Organometallic Chemistry, 63 (1973) 17–26

MIXED IMINO DERIVATIVES OF ALUMINUM AND ALKALINE EARTH METALS

S CUCINELLA, G DOZZI and A MAZZEI

SNAM Progetti S p A, Direzione Ricerca e Sviluppo, Laboratori Ricerche Polimeri S Donato Milanese, Milano (Italy)

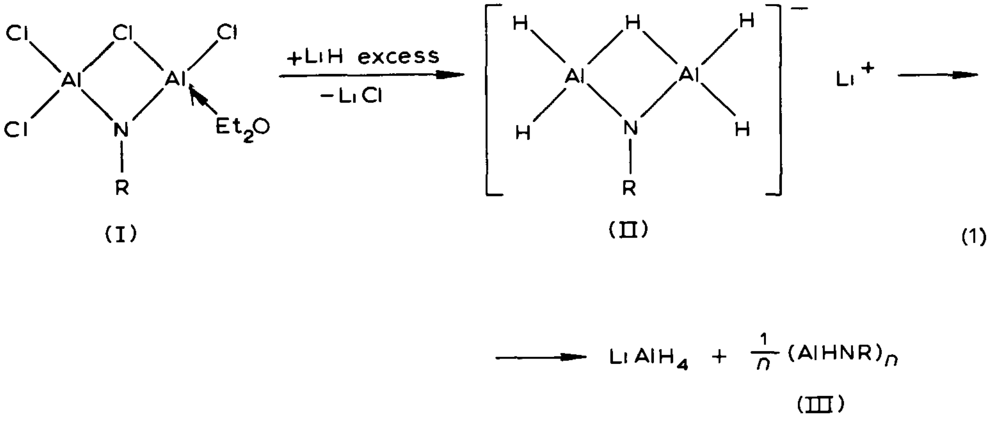
(Received March 10th, 1973, in revised form April 26th, 1973)

SUMMARY

The reactions of $Ca(AlH_4)_2$ and $Mg(AlH_4)_2$ with primary amines or organic nitriles have been investigated. For amine (or nitrile)/alanate ratios of 3/1, mixed polyimino compounds containing –AlH–NR– and –Ca–NR– (or –Mg–NR–) units are formed, whereas for lower molar ratios definite compounds cannot be isolated, except in the reaction of $Ca(AlH_4)_2$ with aniline, from which crystals of calcium *N*-phenyliminodialane have been obtained.

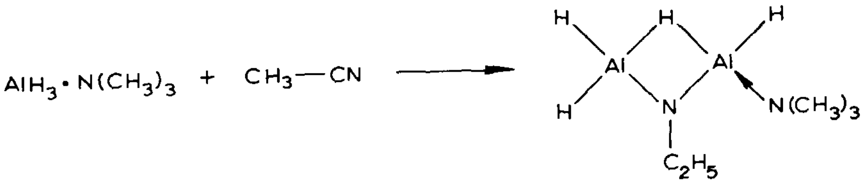
INTRODUCTION

We previously described the formation of $LiAlH_4$ and poly-*N*-butyliminoalane as decomposition products in an attempted synthesis of *N*-butyliminodialanes according to Eqn. (1)[1].



(I) (II) (III) (1)

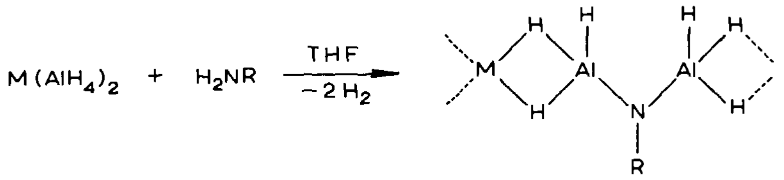
In attempting to reproduce the reaction reported by Ehrlich and Young[2] we have obtained a mixture of poly-*N*-ethyliminoalane and $AlH_3 \cdot 2N(CH_3)_3$[3] which confirmed the difficulty encountered in obtaining *N*-alkyliminodialanes in a stable form [eqn. (2)]



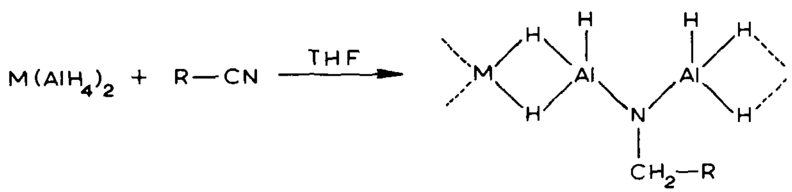
(2)

(IV)

In line with this result the reaction of $Ca(AlH_4)_2$ or $Mg(AlH_4)_2$ with primary amines or organic nitriles was expected to yield poly-*N*-alkyliminoalanes according to eqn. (3):

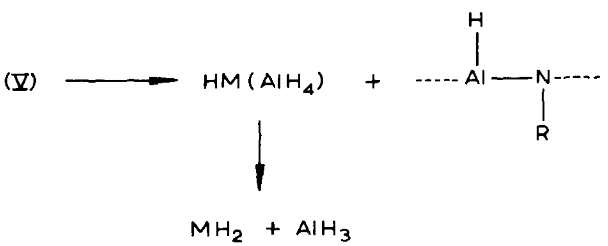


(V)



(3)

(V)



On the contrary, we have found no evidence for the presence of poly-*N*-alkyliminoalanes as products of reaction of $M(AlH_4)_2$ species with ethylamine, n-butylamine, aniline, and various organic nitriles in a molar ratio 1/1 and this finding has prompted us to investigate the reaction in greater detail.

RESULTS AND DISCUSSION

When n-butylamine is added to a tetrahydrofuran solution of $Ca(AlH_4)_2$ or

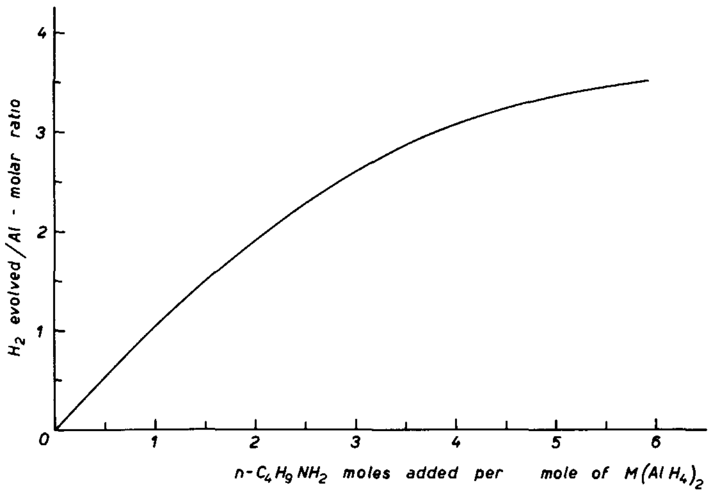
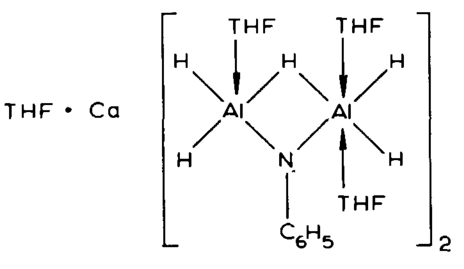


Fig 1 Hydrogen evolution observed in the reaction of $Ca(AlH_4)_2$ or $Mg(AlH_4)_2$ with $n\text{-}C_4H_9NH_2$ Reaction conditions a 5 07 *M* solution of $n\text{-}C_4H_9NH_2$ in THF is added to 5.5 mmoles of $Ca(AlH_4)_2$ or $Mg(AlH_4)_2$ in 150 ml of THF at 22° (the addition rate is ca 0.25 ml/6 min)

suspension of $Mg(AlH_4)_2$, facile hydrogen evolution occurs (Fig. 1). A similar trend was observed for other amines. Generally for an amine (or nitrile)/$M(AlH_4)_2$ molar ratio of 2/1, the reaction products, except those obtained from $Mg(AlH_4)_2$ and aniline, were completely soluble in THF.

In every case the absence of poly-*N*-alkyliminoalane as well as unreacted starting alanate was demonstrated by infrared spectroscopy and by X-ray analysis respectively. It is noteworthy that concentration of the solution obtained from the reaction of $Ca(AlH_4)_2$ with aniline gave an easily separable crystalline intermediate whose composition agreed with a dialane structure:



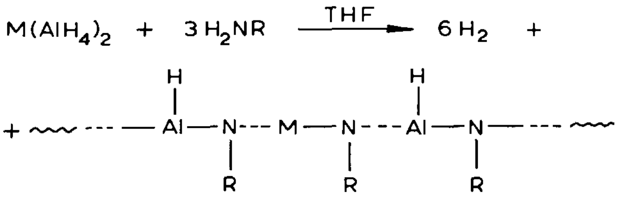
(VI)

The infrared analysis in nujol showed two bands ascribed to $\nu(Al{-}H)$ absorptions at 1760 and 1675 cm^{-1}, corresponding to penta- and hexa-coordinated aluminum atoms respectively. In THF solution only one band maximum at 1750 cm^{-1} is observed.

Molecular weight measurements carried out by ebulliometry in THF show a value of 415 ± 15 instead of 845.17 and in our opinion dissociation takes place in THF solution. Furthermore the discrete complex $Ca(AlH_4)_2 \cdot 4THF$, in THF solution has a molecular weight equal to 205 ± 10 instead of 390.5

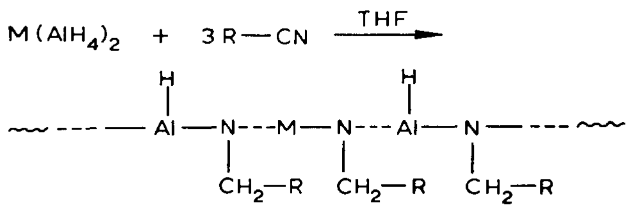
The nature of the products derived from the reaction of amines other than aniline were not at all clear

Finally at a primary amine (or nitrile)/$M(AlH_4)_2$ ratio of 3/1 analysis of all products (M = Ca or Mg) with different amines (or nitriles) polyimino compounds containing (–AlH–NR–) groups (VII) linked to (–M–NR–) units (VIII) were formed according to schemes (4) and (5):



(4)

(IX)



(5)

(IX)

On the basis of experimental evidence, described below, it can be assumed that different imino units such as (VII) and (VIII) are not distributed in a regularly alternate way in the polyimino chain.

All derivatives are completely soluble in tetrahydrofuran except in the case of aniline, where an insoluble fraction is formed which has the same composition as the soluble fraction. In every case the solubility is poor in ether and very low in hydrocarbons.

Solid products were isolated by removing the solvent under vacuum or by precipitation with an excess of n-heptane.

Generally in the products obtained from reactions (4) and (5) the M/Al ratio is similar to the value observed for the starting $M(AlH_4)_2$ species, which, synthesized following the methods reported in the literature[4 5], show a little excess of the alkali earth metal. Probably $HM(AlH_4)$ together to $M(AlH_4)_2$ species were present, although attempts to prepare $HMgAlH_4$ in a pure state failed[6].

We have no evidence as to the exact nature of terminal groups in (IX), namely –NHR, $-AlH_2$ or –MH; however presence of the latter group would be favoured because of its probable non-reactivity with amines[7].

Chemical analyses indicate the presence of coordinated tetrahydrofuran molecules, the number of which depends upon the nature of the hydrocarbon radical in the starting amine or of the alkaline earth metal. Thus with butyl- and neopentylamine derivatives one THF molecule per two atoms of aluminum is present. The presence of only one infrared ν(Al–H) band, which excludes two different coordinative environments for aluminum, shows that in our opinion the THF molecules are complexed to the alkaline earth metal atoms. In the aniline derivatives the number of coordinated THF molecules increases owing to electron withdrawal in the aniline group. In such cases the THF/Al ratios are ca. 2/1 or 1/1 for the calcium or magnesium derivatives respectively; and for calcium THF coordination to aluminum also probably occurs.

The derivatives from aliphatic amines are amorphous whereas the aniline derivatives are crystalline.

The infrared spectra show ν(Al–H) absorption bands shifted to lower frequency with respect to the corresponding simple polyiminoalanes[8], according to charge displacement within the ⟩Al–H bonds due to the partial replacement of aluminum atoms with more electropositive elements (Table 1). However the frequencies (measured in nujol) indicate a tetracoordinated environment of aluminum atoms which is probably due to N → Al coordination.

TABLE 1

INFRARED ν(Al–H) ABSORPTIONS FOR POLYIMINO DERIVATIVES OF ALUMINUM AND ALKALINE EARTH METALS AND CORRESPONDING POLYIMINOALANES

Compound	*ν(Al–H) maximum (cm⁻¹)*	
	In nujol	*In THF*
Poly-*N*-butyliminoalane	1853	1860
Poly-*N*-butylimino derivative of aluminum and calcium	1720–1750	1730
Poly-*N*-butylimino derivativeof aluminum and magnesium	1760–1770	1760–1770
Poly-*N*-phenyliminoalane	1905	
Poly-*N*-phenylimino derivative of aluminum and calcium	1750	
Poly-*N*-phenylimino derivative of aluminum and magnesium	1800	

TABLE 2

TYPICAL FRACTIONATION RESULTS OF POLY-*N*-BUTYLIMINO DERIVATIVES OF ALUMINUM AND CALCIUM

Product	*Heptane[a] added (ml)*	*Precipitate*									
		g	*Chemical composition*							*ν(Al–H) (cm⁻¹)*	
			Al(%)	*Ca(%)*	*N(%)*	H_{act}/Al	*Ca/Al*	*N/Al*		*In nujol*	*In THF*
Initial product			13 90	13 17	10 20	1 17	0 64	1 42		1720	1720–1750
1st fraction	120	3 3	13 60	14 70	10 10	1 38	0 73	1 43		1720	1720–1750
2nd fraction	25	4 7	13 25	13 77	10 85	1 37	0.70	1 57		1720	1720–1750
3rd fraction	30	1 4	12 97	13.00	10.31	1 25	0 67	1 53		1705	1740
4th fraction	45	1 0	10 72	13 00	8 6	n.d	0 81	1 55			1720–1750
Residue		2 5	14 50	8 9	12	1 13	0 41	1 59		1720	

[a] For the starting solution 13 5 g of initial product were dissolved in 80 ml of THF After the addition of the indicated amount of n-heptane the mixture was cooled at −78°; the precipitated fraction was isolated by decantation

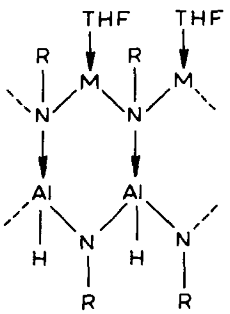
Molecular weight measurements in THF give irreproducible values, which are less than those expected for polymeric compounds of composition corresponding to (IX). Probably in this case also the measurements are influenced by dissociation.

The formation of compounds containing both aluminum and alkaline-earth atoms in the same polyimino chain is supported by the composition of the products separated by fractional precipitation carried out by adding n-heptane to a THF solution of the product. The data reported in Tables 2 and 3 indicate that for either the magnesium or calcium derivatives, all fractions contain aluminum and alkaline-earth metal atoms.

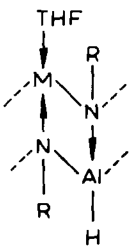
Because of the good solubility of the simple poly-*N*-butyliminoalane[8] in n-heptane, the M/Al atomic ratio in the soluble residue is less than in the precipitated fractions.

The composition of the different separated fractions indicate a more homogeneous distribution of the different monomer units (VII) and (VIII) in the polyimino chain for derivatives of $Ca(AlH_4)_2$. In every case the fractionation data exclude a perfectly alternate distribution.

In our opinion, the formation of simple mechanical mixtures or complexes between polyiminoalane and alkaline-earth metal hydrides as well as of nitrogen-bridged complexes between polymeric chains containing the two different metals separately, such as (X) or (XI) for example, can be excluded not only on the basis of the



(X)



(XI)

aforesaid fractionation, but also because the addition of strong Lewis bases (dioxane, trimethylamine, triethylenediamine) or acids (diborane) did not lead to separation of the two different polyimino chains. Furthermore, by admitting the formation of complexes such as (X) or (XI), the presence of $\approx 50\%$ of free poly-*N*-alkyliminoalane would be expected. This would correspond to the appearance of two distinct infrared ν(Al–H) absorptions which have not been found experimentally.

We also exclude the formation of complexes between polyiminoalanes and alkaline earth metal hydrides because it proved impossible to obtain compounds containing atoms of the different metals either by milling CaH_2 in THF solutions of poly-*N*-butyliminoalane or by reacting AlH_3 with butylamine in the presence of CaH_2. In every case all CaH_2 was recovered.

Finally, by adding n-butylamine to the product freshly obtained by the reaction of ZnI_2 with $LiAlH_4$, we were unable to isolate products such as (IX) containing zinc.

TABLE 3

TYPICAL FRACTIONATION RESULTS OF POLY-*N*-BUTYLIMINO DERIVATIVES OF ALUMINUM AND MAGNESIUM

Product	*Heptane*[a] *added* (*ml*)	*Precipitate*						ν(*Al–H*) (*cm*$^{-1}$) *in THF*
		g	*Chemical composition*					
			Al(%)	*Mg*(%)	*N*(%)	*Mg/Al*	*N/Al*	
Initial product			15 12	7 46	11 8	0 55	1 50	1780
1st fraction	70	3 0	15 02	9 74	11 56	0 72	1 48	1770–1790
2nd fraction	20	1 3						1800
3rd fraction	75	0 7	13 36	16 55	9 75	1 37	1 40	1770–1780
Residue		7 1	16.39	4 02	13 18	0 27	1 55	1780

[a] For the starting solution 12 5 g of initial product were dissolved in 80 ml of THF After the addition of the indicated amount of n-heptane the mixture was cooled at −78° and the precipitated fraction was isolated by decantation

In different attempts ZnH_2 was separated by filtration from a solution of the polyimino-alanes and this is probably due to the instability of the intermediate $Zn(AlH_4)_2$[9]. The stability of the starting alanate seems to be very important for the formation of mixed polyimino derivatives, which arise as a result of gradual substitution of hydridic hydrogens within $[AlH_4]^-$ by >NR groups.

EXPERIMENTAL

Reagents and solvents

Lithium hydride (Degussa), aluminum trichloride (Fluka) and calcium hydride (Merck) were used. Activation of CaH_2 was performed by milling a toluene suspension containing 1–2 % of $ZnEt_2$ or $AlEt_3$. Before use it was recovered by filtration, washed by toluene and dried *in vacuo*. $Ca(AlH_4)_2$ was prepared by reacting $AlCl_3$ with an excess of activated CaH_2 in THF as described in the literature[4], the reaction being facilitated by the addition of a trace of iodine. $AlCl_3$ was added slowly to the CaH_2 suspension with stirring. The reaction was then held at the reflux temperature, until the disappearance of chlorine was complete and $Ca(AlH_4)_2$ was separated as THF complex by cooling. Generally the chemical analysis showed a Ca/Al atomic ratio in the range 0.5 to 0.56. MgI_2 was prepared by Mg and I_2 in diethylether; its insoluble complex with THF was used for the synthesis of $Mg(AlH_4)_2$. $LiAlH_4$ was prepared by reduction of $AlCl_3$ with LiH[10] in diethylether. For reaction with MgI_2, the solvent was removed *in vacuo* and the residue dissolved in THF. Solvent was then removed and further THF was added. $Mg(AlH_4)_2$ was prepared by reduction of MgI_2 with $LiAlH_4$ in THF as reported by Ashby and coworkers[5]. Commercially pure amines and organic nitriles were dried and purified by distillation from Na or from KOH. All solvents were purified and dried by the known methods and all syntheses were carried out in argon atmosphere.

Chemical analyses and physico-chemical measurements

Chemical analyses were carried out on solutions obtained by decomposition of weighed samples with dilute aqueous acid. The aluminum content was evaluated by the EDTA/$ZnSO_4$ method[11]. Magnesium was also determined by EDTA at pH 10; in this case the aluminum present was complexed by triethanolamine[12]. Calcium was determined as CaO; Kjeldahl or Dumas methods were used for nitrogen, depending on the nature of the products.

IR spectra were recorded on a Perkin–Elmer 225 model instrument.

Synthesis of Poly-N-butylimino derivatives of aluminum and calcium

(*a*). When a soln. of n-butylamine (330 mmoles) in 70 ml of THF was added slowly to a stirred solution of $Ca(AlH_4)_2$ (110 mmoles) in 400 ml of THF at room temp., hydrogen evolution took place immediately. After 18 h the solution was filtered from traces of insoluble material and evaporated *in vacuo*. The white solid residue was dried (6 h, room temp., 10^{-3} mmHg) and analyzed. (Found: C, 47.20; H, 9.90; N, 10.14; Al, 13.17; Ca, 12.32%; H_{active}/Al, 1.30.)

The data are in accord with a polyimino derivative, with a Ca/Al ratio of 0.62, corresponding to the average composition

$$[AlHN(C_4H_9)]_{2x}[CaN(C_4H_9)\ THF]_x[CaH\cdot THF]$$

(Calcd. for $x=4$: C, 49.82; H, 9.70; N, 10.25; Al, 13.16; Ca, 12.22%; H_{active}/Al, 1.25.)

The IR spectrum in nujol showed a broad ν(Al–H) band with maximum at 1720–1750 cm^{-1}; in THF solution the maximum appears at 1730 cm^{-1}.

(*b*). Butyronitrile (57.75 mmoles) was added slowly to a solution of 19.25 mmoles of $Ca(AlH_4)_2$ in 200 ml of tetrahydrofuran. The reaction mixture was stirred at room temp. overnight and after filtration from traces of insoluble material, the solution was evaporated *in vacuo* and the solid residue dried (10^{-3} mmHg, 6 h, room temp.) and analyzed. (Found: N, 10.28; Al, 12.74; Ca, 12.06%; H_{active}/Al, 1.25. Calcd. for

$$[AlHN(C_4H_9)]_{2x}[CaN(C_4H_9)\ THF]_x[CaH\cdot THF]$$

in which $x=4$: N, 10.25; Al, 13.16; Ca, 12.22%; H_{active}/Al, 1.25.)

The IR spectrum in THF shows a ν(Al–H) band with a broad maximum at 1730 cm^{-1}.

Synthesis of poly-N-butylimino derivative of aluminum and magnesium

A suspension of $Mg(AlH_4)_2$ (6.75 mmoles) in 100 ml of THF was reacted with 20.25 mmoles of n-butylamine in 50 ml of THF. After the removal of traces of insoluble materials, evaporation of the solution *in vacuo* gave a white solid, which was dried as reported above and analyzed. (Found: C, 50.72; H, 9.50; N, 11.22; Al, 13.59; Mg, 7.08%; H_{active}/Al, 1.09. Calcd. for

$$[AlHN(C_4H_9)]_{2x}[MgN(C_4H_9)\cdot THF]_x[MgH\cdot THF]$$

in which $x=11$: C, 52.44; H, 10.19; N, 11.22; Al, 14.39; Mg, 7.08%; H_{active}/Al, 1.09.)

The IR spectra showed a maximum for ν(Al–H) at 1760–1770 cm^{-1} in either nujol or in THF.

Synthesis of Poly-N-neopentylimino derivative of aluminum and calcium

$Ca(AlH_4)_2$ (27.25 mmoles) and pivalonitrile (81.75 mmoles) were reacted in 225 ml of THF at room temp. with stirring overnight. After filtration from traces of insoluble material, the solution was evaporated *in vacuo* and the yellow solid residue was dried (10^{-3} mmHg, 6 h, room temp.) and analyzed. (Found: C, 52.50; H, 10.39; N, 9.40; Al, 11.42; Ca, 9.63%. Calcd. for

$$[AlH\,N(R)]_{2x}[Ca\,N(R)\cdot THF]_x[CaH\cdot THF]$$

in which $x=7$ and $R=-CH_2-C(CH_3)_3$: C, 53.43; H, 10.18; N, 9.55; Al, 12.26; Ca, 10.41%.)

IR spectrum in nujol: ν(Al–H) at 1760 cm^{-1}.

Synthesis of poly-N-phenylimino derivative of aluminum and calcium

Aniline (75 mmoles) in 40 ml of THF was added slowly to $Ca(AlH_4)_2$ (25 mmoles) in 150 ml of THF. The reaction mixture was stirred overnight at room temp. A precipitate was formed; it was separated by filtration and dried (6 h, 10^{-3} mmHg, room temp.) to give 10.5 g of product. (Found: C, 62.10; H, 7.50; N, 5.94; Al, 8.21; Ca, 6.65%. Calc. for

$$[AlH\,N(C_6H_5)\cdot THF]_{2x}[CaN(C_6H_5)\cdot 2THF]_x[CaH\cdot 2THF]$$

in which $x=8$: C, 61.73; H, 7.52; N, 6.16; Al, 7.92; Ca, 6.62%.)

IR spectrum in nujol: ν(Al–H) at 1750 cm^{-1}.

The remaining solution was evaporated and the residue dried and analyzed (Found: N, 6.43; Al, 8.26; Ca, 6.96%.)

IR spectrum in nujol: ν(Al–H) at 1750 cm^{-1}.

Synthesis of poly-N-phenylimino derivative of aluminum and magnesium

Aniline (32.1 mmoles) was added slowly to $Mg(AlH_4)_2$ (10.7 mmoles) in 200 ml of THF. The mixture was stirred overnight. The obtained insoluble product was separated by filtration, dried (10^{-3} mmHg, 6 h, room temp.) and analyzed. The yield was ≈70%. (Found: C, 62.15; H, 8.40; N, 7.70; Al, 10.25; Mg, 5.00%; H_{active}/Al, 0.96. Calcd. for

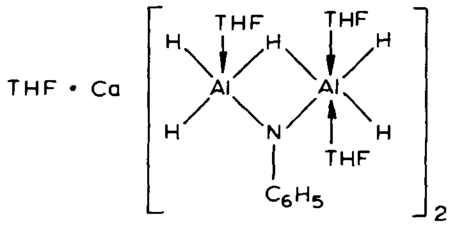
$$\ldots[AlH\,N(C_6H_5)]_2\ldots[Mg\,N(C_6H_5)\cdot 2THF]\ldots$$

C, 62.70; H, 6.70; N, 8.44; Al, 10.82; Mg, 4.98%; H_{active}/Al, 1.)

IR spectrum in nujol: ν(Al–H) at 1800 cm^{-1}.

Intermediate product from the reaction between $Ca(AlH_4)_2$ and aniline at molar ratio 1/2.

A solution of aniline (50.6 mmoles) in 30 ml of THF was added to a stirred solution of $Ca(AlH_4)_2$ (25.3 mmoles) in 200 ml of THF. The reaction mixture was stirred 24 h. After filtration from traces of insoluble material, the solution was concentrated and cooled at −10°. The separation of white crystals was observed. They were isolated by filtration, washed with cooled THF and dried (6 h, 10^{-3} mmHg, room temp.). White product (7 g) was obtained. (Found: C, 54.07; H, 7.90, N, 3.28; Al, 12,75; Ca, 4.81%; H_{active}/Al, 2.51. Calcd. for (VI), C, 56 84; H, 9.06; N, 3.31; Al, 12.76; Ca, 4.74%; H_{active}/Al, 2.50.)



(VI)

The IR spectrum in THF shows a ν(Al–H) band with maximum at 1750 cm^{-1}; in nujol two maxima appear at 1760 and 1675 cm^{-1}, according to the two different coordinative environments of the aluminum atoms

The mol. wt. by ebulliometry in THF was found 415±15 (theoretical value 845.17).

ACKNOWLEDGEMENT

Permission to publish this paper by SNAM Progetti, Laboratorio Ricerche Polimeri, is gratefully acknowledged.

REFERENCES

1 A Mazzei, S Cucinella and W Marconi, *Inorg Chim Acta*. 2 (1968) 305
2 R Ehrlich and A R Young II, *J Inorg Nucl Chem*, 30 (1968) 53
3 S Cucinella, A Mazzei and W Marconi, *Inorg Chim Acta Rev*, 4 (1970) 51
4 A E Finholt, *U S Pat*, 2 550 985 (1951), W Schwab and K Wintersberger, *Z Naturforsch*, *B*, 8 (1953) 690, E C. Ashby, *Advan Inorg Chem Radiochem*, 8 (1966) 327
5 E C Ashby, R D Schwartz and B D James, *Inorg Chem*, 9 (1970) 325
6 E C Ashby and R D Schwartz, *Inorg Chem*, 11 (1972) 925
7 E C Ashby and R G Beach, *Inorg Chem*, 10 (1971) 906
8 A Mazzei, S Cucinella and W Marconi, *Makromol Chem*, 122 (1969) 168
9 E Wiberg, W. Henle and R Bauer, *Z Naturforsch*, 66 (1951) 393
10 A E Finholt, A C Bond Jr and H I Schlesinger, *J Amer Chem Soc*, 69 (1947) 1199
11 E Vanninen and A Ringbom, *Anal Chim Acta*, 12 (1955) 308
12 R Pribil, *Chem Listy*, 48 (1954) 382