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A Contribution to the Chemistry of N-Alkylalazanes*

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By reaction of a primary amine with halogenalanes (mole ratio 1:2), derivatives such as $Cl_2Al-N(R)-AlCl_2.O(C_2H_5)_2$ are obtained. Reducing these compounds with LiH, a mixture of $LiAlH_4$ and polymeric $(-HAl-NR)_n$ is obtained, instead of the expected $H_2Al-NR-AlH_2$. When halogenalanes were reacted with aluminum amides (mole ratio 3:1) compounds of type $Al(NR-AlCl_2)_3$ resulted. Also it is possible to synthesize these complexes reacting halogenalanes with primary amine and then with aluminum-hydride. They were isolated as complexes with Lewis bases such as diethyl ether, tetrahydrofuran, trialkylamines. Reduction of these complexes in suitable conditions gives stable aluminum tris-(N-alkylalazanes) $Al(NR-AlH_2)_3$. A possible structure is suggested for these compounds.

Introduction

Different classes of compounds derived from aluminum hydride and tertiary, secondary and primary amines are known:

(1) $AlH_3 . NR_3$ trialkylamine alane[1]

(2) AlH_2NR_2 dialkylamino alane[2]

(3)  poly(N-alkyliminoalane)[3]

$$-\!\left[\underset{H}{Al}-\underset{R}{N}\right]_n\!-$$

Also derivatives obtained by substitution of hydrogen atoms with halogen atoms or $-NR_2$, $-OR$, $-SR$ groups in the compounds of classes 1 and 2, have been synthesized.[2,4]

Their catalytic activity in the polymerization of diolefins has been previously reported;[5] in particular the use of poly (N-alkyliminoalanes) gives isoprene polymers of high 1,4 *cis* content and very high molecular weight.[6]

Such results prompted us to investigate on the synthesis of poly(iminoalanes). In addition to the known methods,[3] we found that it is possible to prepare poly(iminoalanes) from aluminum amides in different ways:[6]

(a) $$2AlH_3 . N(CH_3)_3 + Al(NHR)_3 \longrightarrow 3\frac{1}{n}(-HAl-NR-)_n + 3H_2 + 2N(CH_3)_3$$

(b) $$AlX_3 . O(C_2H_5)_2 + 2Al(NHR)_3 \longrightarrow 3AlX(NHR)_2 + O(C_2H_5)_2$$

$$AlX(NHR)_2 + LiAlH_4 \longrightarrow 2\frac{1}{n}(-HAl-NR-)_n + LiX + 2H_2$$

(c) $$2AlX_3 + Al(NHR)_3 \longrightarrow 3AlX_2NHR \xrightarrow[-LiX]{+LiH} 3\frac{1}{n}(-HAl-NR-)_n + 3H_2$$

where X = halogen and R can be $i-C_3H_7$, $n-C_4H_9$, $-C_6H_5$.

In the course of our research work on the same subject, we have attempted to synthesize more simple imino-derivatives of aluminum hydride such as: $H_2Al-NR-AlH_2$ and $Al(NR-AlH_2)_3$, where R is n-butyl (if R is lower than $-C_4H_9$ some difficulties could occur for the solubility of the obtained complex).

Results and Discussion

*N-Alkyl-Dialazanes.** Similar derivatives from aluminum alkyls were reported but not fully characterized:[7]

$R_2Al-NR'-AlR_2$ $\qquad$ $Li[R_2Al-NR'-AlR_3]$

We attempted to synthesize compounds such as $H_2Al-NR-AlH_2$ by the following reactions:

(1) In toluene

$$H_2NR \xrightarrow[-H_2]{+AlHCl_2} Cl_2AlNHR \xrightarrow[-H_2]{+AlHCl_2} Cl_2Al-NR-AlCl_2$$

(*) Based on a lecture presented by S. Cucinella at EUCHEM Conference on the Chemistry of Metal Hydrides, Bristol, April 1966.

(1) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, *82*, 2141 (1960); J. K. Ruff and M. F. Hawthorne, *ibid.*, *83*, 535 (1961).

(2) E. Wiberg and A. May, *Z. Naturforsch.*, *10b*, 234 (1955); J. K. Ruff, *J. Am. Chem. Soc.*, *83*, 2835 (1961); W. Marconi, A. Mazzei, F. Bonati, and M. De Maldè, *Gazz. Chim. Ital.*, *92*, 1062 (1692).

(3) E. Wiberg and A. May, *Z. Naturforsch.*, *10b*, 232 (1955); E. Ehrlich, A. R. Young II, B. M. Lichstein, and D. D. Perry, *Inorg. Chem.*, *3*, 628 (1964); R. F. Lang, *Makrom. Chem.*, *83*, 274 (1965).

(4) J. K. Ruff, *J. Am. Chem. Soc.*, *83*, 1798 (1961); W. Marconi, A. Mazzei, F. Bonati, and M. De Maldè, *Z. Naturforsch.*, *18b*, 3 (1963); Belg. Pat. 637.763.

(5) W. Marconi, A. Mazzei, S. Cucinella, and M. De Maldè, *Makromol. Chem.*, *71*, 118 and 134 (1964); W. Marconi, A. Mazzei, M. Araldi, and M. De Maldè, *J. Polymer Sci.*, *A3*, 735 (1965).

(6) Our data to be published.

(*) Name proposed by authors, according to the referee's suggestion.

(7) C. Longiave and R. Castelli, *J. Polymer Sci.*, *4C*, 387 (1963); H. Tani and N. Oguni, *J. Polymer Sci.*, *B3*, 123 (1965).

(2) In ethyl-ether or toluene-ether mixture

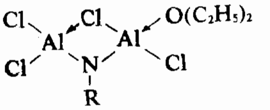
$$Cl_2Al{-}NR{-}AlCl_2 \xrightarrow[-LiCl]{+LiH} H_2Al{-}NR{-}AlH_2$$

Although it is reported[8] that halogenalanes do not react with primary amines, Mödritzer found[9] that dichloroalane reacts with methylamine with evolution of hydrogen:

$$Cl_2AlH + H_2NMe \longrightarrow 1/2[Cl_2Al(NHMe)]_2 + H_2$$

According to this reaction we have found that $AlHCl_2.O(C_2H_5)_2$ reacts with an equimolar amount of n-butylamine and an intermediate soluble in ethers and aromatic hydrocarbons is obtained. The disappearance of active hydrogen bonded to aluminum is observed; the evolution of hydrogen takes place even at very low temperature (−60°C). In order to react completely the second mole of $AlHCl_2.O(C_2H_5)_2$ a temperature in the range of 80 ÷ 100°C is necessary.

The final product of reaction (1) retains a complexed diethyl ether molecule. Using the cryoscopic method in benzene, molecular weight measurements indicate a monomeric form for the n-butyl derivative, for which the following structure is suggested:



(1)

Molecular weight determinations by ebullioscopy in diethyl ether gave values corresponding to a monomeric form too. By reduction of the chloro-butylimino compound with an excess of LiH in the presence of diethyl ether we obtained a substance for which elemental analysis indicated Al:N:Li ratios of 2:1:1.

The infrared spectrum of the ether dry substance shows a large absorption νAl–H at 5.55 ÷ 5.85 μ. In diethyl ether two bands at 5.55 μ and 5.80 μ were observed and by addition of tetrahydrofuran these bands shift to ∼5.65 μ and 5.95 μ. These bands correspond to the absorption of a mixture of poly (N-butyliminoalane) and $LiAlH_4$ in equimolecular ratios. Furthermore $LiAlH_4$ is separated adding toluene to the dry reduced product. These facts would suggest the following disproportionation reactions:

$$Cl_2Al{-}N(C_4H_9){-}AlCl_2 \xrightarrow[-LiCl]{+LiH} [H_2Al{-}N(C_4H_9){-}AlH_3]Li \longrightarrow$$

$$LiAlH_4 + \frac{1}{n}[HAl{-}N(C_4H_9){-}]_n$$

*Aluminum Tris-(N-Alkylalazanes).** Complexes of these compounds with Lewis bases were obtained by the following methods:

(1a) In toluene

$$AlHCl_2 + H_2NR \longrightarrow AlCl_2NHR + H_2$$

$$3AlCl_2NHR + AlH_3 \longrightarrow Al(NR{-}AlCl_2)_3 + 3H_2$$

(1b)

$$Al(NHR)_3 + 3AlHCl_2 \longrightarrow Al(NR{-}AlCl_2)_3 + 3H_2$$

(2) In diethyl-ether or tetrahydrofuran:

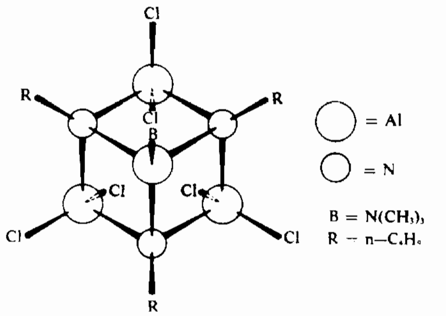
$$Al(NR{-}AlCl_2)_3 \xrightarrow[-LiCl]{+LiH} Al(NR{-}AlH_2)_3$$

For the reaction (1a), $AlHCl_2.O(C_2H_5)_2$ and $AlH_3.N(CH_3)_3$ were employed. To complete the second step of this reaction a rather elevated temperature (about 70°C) is necessary.

The final product, dried under high vacuum, retains a complexed trimethylamine molecule, and is soluble in diethyl ether and aromatic solvents.

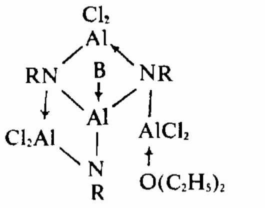
In the reaction (1b), $AlHCl_2.N(CH_3)_3$ was used From the reaction mixture crystals of $Al(NR{-}AlCl_2)_3.2N(CH_3)_3$ separate initially on cooling, and then, under high vacuum, one $N(CH_3)_3$ molecule is lost, to give the same complex as in reaction (1a).

Molecular weight measurements by ebulliometry in benzene indicate a monomeric form for $Al(NC_4H_9{-}AlCl_2)_3.N(CH_3)_3$, for which the following structure is suggested according to a tetracoordinated environment around all the aluminum atoms:



(II)

Similar values of the molecular weight were obtained following the ebullioscopic method in diethyl ether. An attempt to obtain again a complex with two NR_3 molecules from the ether solution of (II), using an excess of trimethylamine, gave monomeric $Al(NC_4H_9{-}AlCl_2)_3.O(C_2H_5)_2.N(CH_3)_3$. The structure of this compound would originate from (II) by opening of an Al←N bond and addition of one diethyl ether molecule to the Al atom:



(III)

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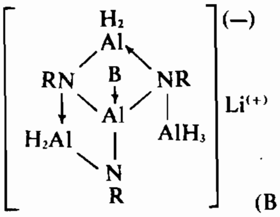
(8) E. Wiberg and M. Schmidt, *Z. Naturforsch.*, *6b*, 333 (1951).
(9) K. Mödritzer, Dissertation, Univ. München 1955, through H. Nöth and E. Wiberg, *Fortschr. Chem. Forsch.*, *8*, 380 (1967).
(*) Name proposed by authors, according to the referee's suggestion.

Alternatively, a structure as (II) with a central pentacoordinated aluminum is not improbable at all. Furthermore, dissolving the complex (II) in tetrahydrofuran, a new complex, $Al(NC_4H_9{-}AlCl_2)_3 . 2THF$ was obtained. This complex, rather surprisingly, was found dimeric by ebulliometry in tetrahydrofuran.

The reduction reaction of the complex (II) with LiH (excess) carried out in diethyl ether (or tetrahydrofuran) gives the corresponding reduced derivatives with ether (or tetrahydrofuran) as ligands instead of the original NR_3. Some LiH is complexed too. Working in tetrahydrofuran, we have obtained $Al(NC_4H_9{-}AlH_2)_3 . THF . LiH$ for which, in analogy with (III), the following structure is suggested: *



(IV)

(B=THF)

Molecular weight measurements in diethyl ether confirm a monomeric form. Infrared spectrum of (IV) in THF shows a well resolved absorption band νAl–H with maximum at 5.61 μ, corresponding to the tetracoordinated aluminum.

Because of the absence of bands νAl–H at higher wave length the structure with pentacoordinated central aluminum bonded to H^- of LiH is, in our opinion, less probable than (IV).

Carring out the reduction reaction in diethyl ether, complexes are obtained with non-stoichiometric amount of LiH, such as $Al(NC_4H_9{-}AlH_2)_3 . O(C_2H_5)_2 . x(LiH)$ with x ranging from 0.1 to 0.7.

The complex $Al(NC_4H_9{-}AlH_2)_3 . O(C_2H_5)_2 . 0.7LiH$ shows an association degree of 1.6÷1.7 in diethyl ether. Its infrared spectrum in nujol shows a large absorption band νAl–H between 5.3 μ and 5.86 μ with two maxima at 5.50 μ and 5.74 μ probably due to associations through Al–H bonds. By addition of tetrahydrofuran the infrared spectrum is similar to that of (IV): a well definite band at 5.55 μ was observed to indicate a similar structure for both compounds, except for a slight difference in the association degree. Also $Al(NC_4H_9{-}AlH_2)_3 . O(C_2H_5)_2 . 0.1LiH$ shows a definite band at 5.55 μ in tetrahydrofuran.

Experimental Section

All reactions were carried out in a nitrogen atmosphere. Solvents and reagents were purified according to usual techniques for alanes chemistry. Analysis methods were the same as reported in our preceeding paper;[2c,10] in particular for nitrogen determination Dumas method was followed (the standard deviation was ±0,3). Generally molecular weight measurements were carried out by ebullioscopy in diethyl ether. Infrared spectra were obtained using a Perkin Elmer 125 instrument.

Synthesis of $Cl_2Al{-}N\,C_4H_9{-}AlCl_2 . O(C_2H_5)_2$. Anhydrous n-butylamine (31.5 mmole) in 50 ml of anhydrous toluene was added dropwise to a solution of $AlHCl_2 . O(C_2H_5)_2$ (63 mmole) in 150 ml of toluene.

Hydrogen is evolved during 20 hrs at room temp. and 6 hrs at 80°C. The solvent was removed in vacuo at room temp. and the oily residue was analysed.

Anal. Calcd. for $C_8H_{19}Cl_4NOAl_2$ (341) C, 28.17; H, 5.61; Cl, 41.58; N, 4.11; Al, 15.82. Found: C, 27.56; H, 5.47; Cl, 41.16; N, 4.80; Al, 16.26.

The cryoscopic molecular weight in benzene resulted 363. Molecular weight determinations by ebullioscopy in diethyl ether at different concentrations gave 326 (0.56 weight %), 335 (1.68), 338 (2.47).

Attempts to Synthesize $H_2Al{-}N\,C_4H_9{-}AlH_2$. To a toluene solution of $Cl_2Al{-}N\,C_4H_9{-}AlCl_2$ (60 mmole in 200 ml of solvent) 25% by volume of diethyl ether and an excess of LiH were added. The mixture was allowed to react at 50°C until disappearance of chlorine in the solution. LiCl was filtered and the solvent removed in vacuo. The dried residue was analysed. Yield 85%.

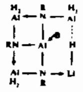
Anal. Calcd. for $C_4H_{14}N\,Al_2Li$ (137,06) C, 35.05; H, 10.29; N, 10.22; Al, 39.36; Li, 5.06. Found: C, 34.12; H, 10.14; N, 9.19; Al, 36.83; Li, 4.78.

A similar reduction reaction carried out exclusively in diethyl ether gave a solid product for which infrared analysis in diethyl ether showed two absorption νAl–H bands at 5.55 μ and 5.80 μ, corresponding to the typical bands for a mechanical mixture of $LiAlH_4$ and $(HAl\,NC_4H_9)_n$ in 1:1 molar ratio.

Decomposition products were also obtained either when the stoichiometric amount of LiH was added or the reduction was carried out in the presence of $N(C_2H_5)_3$.

Synthesis of $Al(NC_4H_9{-}AlCl_2)_3 . N(CH_3)_3$. (a) To a stirred solution of 210 mmole of $n{-}C_4H_9NH_2$ in 150 ml of toluene an equimolar amount of $AlHCl_2 . O(C_2H_5)_2$ in 50 ml of toluene was added dropwise, keeping the mixture at room temperature. The stirring was continued at room temperature for 60 hrs until chemical analyses showed disappearance of active hydrogen. To the intermediately obtained $AlCl_2NHC_4H_9$ (200 mmole), not separated from the reaction solution, 29 ml of a 0.23 *M* toluenic solution of $AlH_3 . N(CH_3)_3$ were added slowly at room temperature. The reaction was completed by heating at 70°C (~24 hrs) until active hydrogen disappeared. Finally the solvent was removed in vacuo; the solid residue was dried (7 hrs at 40°C and 5×10^{-3} mm Hg) and analysed.

(*) In the referee's opinion, by admitting a structure with a central tetra-coordinated aluminum, lithium ion could add to the lone electrons pair on the nitrogen in the following way:



in order to explain why only one molecule of tetrahydrofuran adds to the aforesaid compound, whereas lithium ion in $LiAlH_4$ retains tetrahydrofuran very tenaciously.

[10] W. Marconi, A. Mazzei, S. Cucinella, and M. Greco, *Ann. Chim.* (Rome), 55, 897 (1965).

Anal. Calcd. for $C_{15}H_{36}Cl_6N_4Al_4$ (593,10) C, 30.37; H, 6.12; Cl, 35.86; N, 9.45; Al, 18.19. Found: C, 30.08; H, 6.45; Cl, 33.96; N, 9.26; Al, 17.38.

Molecular weight measurements by ebulliometry in benzene gave 603 (0.73), 600 (1.02), 617 (1.25); ebullioscopic molecular weight in diethyl ether resulted 579 (1.02), 553.9 (1.75).

(b) To a stirred suspension of 20.7 mmole of $Al(NHC_4H_9)_3$ in 100 ml of toluene a solution of 62.1 mmole of $AlHCl_2 . N(CH_3)_3$ in 60 ml of toluene was added dropwise at room temperature. Then the stirring was continued at 80°C until hydrogen active was disappeared ($\sim$80 hrs). On cooling at –78°C a crystalline precipitate was separated by filtration. This solid was dried in vacuo (8 hrs, 30°C, 5×10^{-3} mm Hg) and analysed.

Anal. Calcd. for $C_{15}H_{36}Cl_6N_4Al_4$ (593.10) C, 30.37; H, 6.12; Cl, 35.86; N, 9.45; Al, 18.19. Found: C, 31.16; H, 6.28; Cl, 34.96; N, 9.45; Al, 18.21.

Molecular weight measurements gave 664.3 (1.20); 627.9 (1.50); 647 (1.58). The yield in the final product was 60%.

When the crystalline product is dried under milder conditions (*e.g.* 1 hr at room temperature and 0.1 mm Hg), chemical analyses show Al:Cl:N = 1:1.56:1.25, corresponding to the complex with two $N(CH_3)_3$ molecules.

Attempts to prepare the complex with two molecules of $N(CH_3)_3$ by adding an excess of amine to the diethyl-ether solution of $Al(NC_4H_9–AlCl_2)_3 . N(CH_3)_3$ gave $Al(NC_4H_9–AlCl_2)_3 . N(CH_3)_3 . O(C_2H_5)_2$, instead of the bis trialkylaminate.

The solid product was separated removing the solvent in vacuo and dried at room temperature (2 hrs 10^{-2} mm Hg).

Anal. Calcd. for $C_{19}H_{46}Cl_6N_4OAl_4$ (667.22) C, 34.20; H, 6.94; Cl, 31.87; N, 8.40; Al, 16.17. Found: C, 34.20; H, 6.59; Cl, 31.64; N, 8.28; Al, 16.45.

Molecular weight measurements: 647.2 (0.75); 753.8 (1.14); 630.1 (1.93).

$Al(NC_4H_9–AlCl_2)_3 . 20(CH_2–CH_2)_2$ was obtained by dissolving 7 g of $Al(NC_4H_9–AlCl_2)_3 . N(CH_3)_3$ in 100 ml of tetrahydrofuran, allowing the solution to stay at room temperature overnight, and removing the excess of solvent in vacuo.

The solid residue was dried 7 hrs at 30-35°C and 5×10^{-3} mm Hg.

Anal. Calcd. for $C_{20}H_{43}Cl_6N_3O_2Al_4$ (678.19) C, 35.41; H, 6.39; Cl, 31.36; N, 6.20; Al, 15.91. Found: C, 35.25; H, 6.71; Cl, 30.41; N, 6.30; Al, 15.41.

Ebullioscopic molecular weight in tetrahydrofuran resulted 1441.8 (0.65); 1244.4 (1.21); 1318.8 (1.3).

Synthesis of $Al(NC_4H_9–AlH_2)_3 . xLiH . O(C_2H_5)_2$. (a) To a solution of 14 g of $Al(NC_4H_9–AlCl_2)_3 . NMe_3$ in 450 ml of diethyl ether, 5.5 g of LiH were added. The mixture was stirred overnight at rom temperature and then refluxed 7 hrs. An analysed sample showed atomic ratio Cl/Al = 0.5. The mixture was filtered and 5.5 g of LiH were added again to the solution. After stirring overnight at room temperature the reduction was complete. The mixture was filtered and the solvent was removed in vacuo. The solid residue was dried 8 hrs at room temperature and 10^{-2} mm Hg. Yield about 90%.

Anal. Calcd. for $C_{16}H_{44}N_3OAl_4Li$ (409.4) C, 46.94; H, 10.83; N, 10.26; Al, 26.36; Li, 1.69; H_{active} 38.3 ml/100 mg. Found: C, 46.35; H, 9.98; N, 10.60; Al, 26.70; Li, 1.20; H_{active} 36.6 ml/100 mg.

Molecular weight measurements gave 696.1 (0.74); 676.7 (0.78).

(b) Starting with stoichiometric amounts of LiH in diethyl-ether and adding an excess of LiH after 73 hrs, a complex retaining only small amounts of LiH was obtained.

Anal. Calcd. for $C_{16}H_{43}N_3OAl_4$ (401.45) N, 10.47; Al, 26.88; H_{active} 33.47 ml/100 mg. Found: N, 10.18; Al, 26.31; H_{active} 32.7 ml/100 mg.

Experimental atomic ratio Li/Al resulted 0.031.

Synthesis of $Al(NC_4H_9–AlH_2)_3 . LiH . O(CH_2–CH_2)_2$. To a solution of 14 g of $Al(NC_4H_9–AlCl_2)_3 . N(CH_3)_3$ in 450 ml of diethylether, 5.5 g of LiH were added. The mixture was stirred overnight at room temperature, then refluxed for 7 hrs. The mixture was filtered and the solvent removed in vacuo. The residue was dissolved again in 300 ml of tetrahydrofuran and 5.5 g of LiH were added. This procedure was followed in order to prevent the cleavage of tetrahydrofuran.[11] After stirring overnight at room temperature the reduction was complete. The mixture was filtered, to separate LiCl and the excess of LiH. The solvent was removed in vacuo and the solid residue was dried 6 hrs at 10^{-2} mm Hg. The yield was 90%.

Anal. Calcd. for $C_{16}H_{42}N_3OAl_4Li$ (407.38) C, 47.17; H, 10.39; N, 10.32; Al, 26.49; Li, 1.70; H_{active} 38.4 ml/100 mg. Found: C, 47.11; H, 9.90; N, 10.34; Al, 24.89; Li, 1.52; H_{active} 32.50 ml/100 mg.

The low active hydrogen content is probably due to a partial cleavage of tetrahydrofuran.

Molecular weight measurements gave 425 (0.47); 397.8 (1.01); 419.8 (1.42).

(11) W. J. Bailey and F. Marktscheffel, *J. Org. Chem.*, 25, 1797 (1960).