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Synthesis of N-(dimethylamino)propyliminodialanes

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Stable new N-alkyliminodialanes $[(CH_3)_2N(CH_2)_3N(AlH_2)_2]_2 \cdot THF$ *and* $[(CH_3)_2NCH_2(CH_3)CHN(AlH_2)_2]_2 \cdot THF$ *have been prepared from* $AlH_3 \cdot THF$ *(or* $NaAlH_4$*) and the corresponding amine (or hydrochloride derivative). These products have been characterized principally by mass spectrometry.*

Introduction

N-alkyliminodialanes $RN(AlH_2)_2$ as complexes with Lewis bases are known to be rather difficult to synthesize due to their instability. We have previously reported [1] unsuccessful attempts to prepare this derivative from n.butylamine by reaction of the corresponding $n.C_4H_9N(AlCl_2)_2 \cdot Et_2O$ with LiH in diethylether; however, disproportionation gave $LiAlH_4$ and poly(N-alkyliminoalane), $(HAlN \cdot n.C_4H_9)_n$. Later [2] we found the reaction of Ehrlich and Young [3] for the synthesis of $C_2H_5N(AlH_2)_2 \cdot NR_3$ from $AlH_3 \cdot NR_3$ and CH_3CN in benzene to be not reproducible; in this case we obtained $(HAlNC_2H_5)_n$ together with $AlH_3 \cdot 2NR_3$. More recently [4] with the more basic solvent THF, we prepared the derivative from isopropylamine, complexed with THF or LiH, after having seen evidence of its formation in conductimetric measurements. However these compounds were identified on the basis of their chemical composition plus molecular weight measurements. No further physico-chemical characterization was possible.

The finding that dimethylamino-propylamines give stable open cage poly(N-alkyliminoalanes) [5] recently prompted us to use these substituted amines to prepare more stable N-alkyliminodialanes.

Results and Discussion

N-alkyliminodialanes from both 3-dimethylamino-n-propylamine and from 2-dimethylamino-isopropylamine were prepared according to reaction 1 by reaction of $NaAlH_4$ and amine bis(hydrochloride)

$$2NaAlH_4 + (CH_3)_2N\text{-}R\text{-}NH_2 \cdot 2HCl \xrightarrow{THF} \frac{1}{2}\,[(CH_3)_2N\text{-}R\text{-}N(AlH_2)_2]_2 \cdot THF + 4H_2 + 2NaCl \quad (1)$$

I, -R- = $-(CH_2)_3-$; II, -R- = $-CH_2(CH_3)CH-$

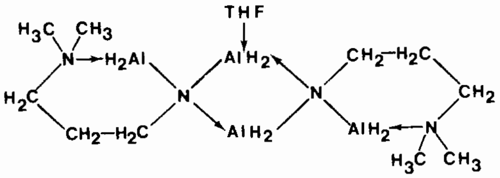
Derivative I was also prepared according to reaction 2

$$2AlH_3 + (CH_3)_2N\text{-}R\text{-}NH_2 \xrightarrow{THF} \frac{1}{2}\,[(CH_3)_2N\text{-}R\text{-}N(AlH_2)_2]_2 \cdot THF + 2H_2 \quad (2)$$

The results are reported in Table I. In every case crystalline products were obtained, whose chemical composition and physico-chemical characterization are consistent with complexes of N-alkyliminodialane dimer with one molecule of THF.

The mass spectra of I and II show ions $(M - H)^+ \cdot THF$ at m/e 387, $(M - AlH_4)^+ \cdot THF$ at m/e 357, and $(M - AlH_3 - AlH_2)^+ \cdot THF$ at m/e 329, in addition to dominating ions attributable to THF-free N-alkyliminodialane dimers (III) *i.e.* $(M - H)^+$ ions at m/e 315, $(M - 2H)^+$ at m/e 314, $(M - AlH_2)^+$ at m/e 287, $(M - AlH_4)^+$ at m/e 285, $(M - AlH_3 - AlH_2)^+$ at m/e 257, $(M - AlH_4 - AlH_3)^+$ at m/e 255. These assignments were confirmed by high resolution measurements and by metastable ions. The formation of III by dissociation of I or II in the mass spectrometer is quite reasonable.

Among the possible structures, IV seems to be the most probable, as supported also by the I.R. spectrum. In particular the I.R. spectrum in nujol shows νAl–H absorptions consistent [6] with tetra-coordinated aluminum atoms with different environment (1845 and 1790 cm^{-1}) as well as with possible penta-coordinated aluminum (1750 cm^{-1}).



(IV)

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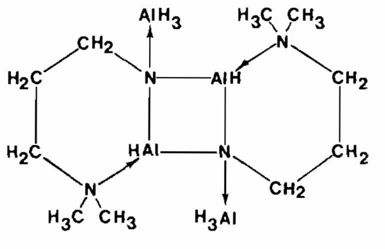
TABLE I. Results of the Synthesis of N-alkyliminodialanes from 3.Dimethylamino.n.propylamine or 2.Dimethylamino-iso-propylamine.

Run	Reagent		Reaction Conditions			Reaction Product[a]					
	Alane (mmol)	Amine (mmol)	THF ml	Temp. °C	Time h	g	Chemical Composition Al %	N %	H_{act}	νAl–H cm^{-1} [b]	X-ray Powder Analysis
1	$NaAlH_4$ (80)	$H_2N(CH_2)_3N(CH_3)_2 \cdot 2HCl$ (40)	150	25	7	6.3	28.3	15.3	20.1	1790 1845 (sh) 1750 (sh)	Crystalline
2	$NaAlH_4$ (80)	$H_2NCH(CH_3)CH_2N(CH_3)_2 \cdot 2HCl$ (40)	150	25	6	7.0	27	14.5	19.9	1760 1780	Crystalline
3	$AlH_3 \cdot THF$ (54)	$H_2N(CH_2)_3N(CH_3)_2$ (27)	120	25	10	4.4	28.5	13.9	21.7	1790 1845 (sh) 1750 (sh)	Crystalline

[a] Calcd. for $C_{14}H_{40}Al_4N_4O$: Al, 27.8; N, 14.4%; $H_{act.}$ 20.6 meq/g. [b] Infrared measurements in nujol mull.



(V)

The alternative structure V appears rather improbable. In fact such a compound could decompose under the measurement conditions by elimination of AlH_3 and probable rearrangement of the residue fragments to more complex structure. As a matter of fact mass spectrometry did not detect the complex (HAlN – iso.$C_3H_7)_6 \cdot AlH_3$ (VI), although it was fully characterized by X-ray molecular determination on a single crystal [7]. In that case the mass spectrum showed ions due to (HAl – N-iso.$C_3(H_7)_6$ derived from the dissociation of VI.

Experimental

Reagents and Solvents

$AlH_3 \cdot THF$ was obtained from the reaction of Finholt *et al.* [8] between $LiAlH_4$ and $AlCl_3$ in tetrahydrofuran. Commercial $NaAlH_4$ (Metalgesellschaft A.G.) was used without further treatment. Pure commercial amines were dried and purified by distillation from Na or from KOH. All solvents were purified and dried using known methods and all syntheses were carried out under a nitrogen atmosphere.

Chemical Analyses and Physico-chemical Measurements

Chemical analyses were as described in our previous papers using the same instruments with the exception of a Perkin-Elmer model 157 I.R. spectrometer.

Synthesis of $[(CH_3)_2N(CH_2)_3N(AlH_2)_2]_2 \cdot THF$

(*a*) 3-dimethylamino-n-propylamine bis(hydrochloride) (40 mmol) was added to a stirred suspension of $NaAlH_4$ (80 mmol) in THF (150 ml) at 25 °C. The reaction mixture was stirred 7 h at 25 °C. Then the solution was filtered to remove insoluble material and evaporated *in vacuo*. The white solid residue was dried *in vacuo* (4 h, 25 °C, 1×10^{-3} mmHg) and analyzed (Found: Al, 28.3; N, 15.3%; $H_{act.}$, 20.1 meq/g). Calcd. for $C_{14}H_{40}Al_4N_4O$: Al, 27.8; N, 14.4%; $H_{act.}$, 20.6 meq/g). The yield was 6.3 g. The analogous derivative from $(CH_3)_2NCH_2(CH_3)CHNH_2$ was prepared using the same procedure.

(*b*) A solution of 3-dimethylamino-n-propylamine (27 mmol) in tetrahydrofuran (40 ml) was added dropwise to a stirred solution of AlH_3 (54 mmol) in tetrahydrofuran (80 ml) at 25 °C. Hydrogen evolution occurred immediately. The reaction solution was stirred 10 h at 25 °C. Then it was filtered from traces of insoluble material and evaporated *in vacuo*. The white solid residue was dried *in vacuo* (4 h, 25 °C, 1×10^{-3} mmHg) and analyzed (Found: Al, 28.5; N, 13.9%; $H_{act.}$, 21.7 meq/g. Calcd. for $C_{14}H_{40}Al_4N_4O$: Al, 27.8; N, 14.4%; $H_{act.}$, 20.6 meq/g) The yield was 4.4 g.

Acknowledgment

The permission of ASSORENI management to publish these results is gratefully acknowledged.

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