ALUMINUM CONTAINING SPECIES FORMED IN REDUCTION PROCESSES OF SEC.AMINO(DIHALOGENO)BORANES WITH LiAlH$_4$[**]

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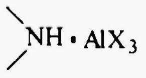
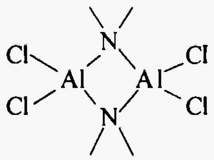
ABSTRACT

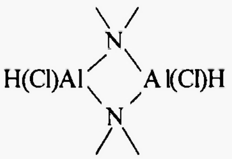
Aluminum containing species (**xa** - **xe**) formed in the reduction process of sec.amino(dihalogeno)boranes with LiAlH$_4$ (as described in [1,2]) generally have a lower fugacity as the boron compounds and remain in the residues of the distillation processes. The individual compounds were identified in the high boiling fractions by their ^{27}Al- (and ^{11}B-)NMR signals and by mass spectrometry (Table 1, Table 3). In those cases where aluminum containing species were separated from the mixtures, they were characterized also by elemental analyses or high resolution MS.

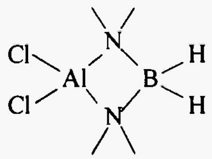
INTRODUCTION

In two preceding papers "Sterically Encumbered Monomeric Sec.Amino(halogeno)hydroboranes and the Corresponding Dihalogeno- and Dihydroborane Precursors" [1] and "Reduction of Piperidino- and Related Sec.Amino(dihalogeno)boranes with LiAlH$_4$ in Toluene and Related Reactions"[2] we described the boron containing products obtained in a variety of reduction reactions of the title compounds and the influence of the steric demand of their substituents. The Al-containing species observed as byproducts in the process P VI[2], the reduction of sec.amino(halogeno)boranes with LiAlH$_4$ in toluene belong to the following moieties:


xa


xb


xc


xd

The reduction of amino(halogeno)boranes with LiAlH$_4$ is a quite complex reaction. Aluminum-nitrogen compounds have high boiling points and therefore they were not identified for the compounds carrying extremely bulky substituents as reported in [1], where they remained in the residue. However, if the substituents are not as big as in the case of the piperidino group [2], amino(halogeno)boranes may be used for the synthesis of mixed aluminum-boron-nitrogen moieties as **xd**, a class of compound, which is scarcely documented till now [3-8]. Regarding the chemistry and structure of (AlN) compounds there exist good reviews [9, 10], however, with the exception of the simple adducts, **xa**, only a few papers deal with moieties substituted by halogen atoms of the types **xb** or **xc** [11-16]. For **xe** see p. 214.

This paper supplements [1,2] and can only be utilized by making use of the data given there. For the identification of the substituents on the nitrogen atoms use Tables 1 of [1] (MGMC **1999**, 717-719) and of [2] (MGMC **2000**, 746-748).

The compounds identified and their ^{27}Al- [17, 18] and ^{11}B-NMR [19] data are compiled in Table 1. The preparative data and the results of high resolution mass spectroscopy and (for **16xc**) elemental analyses are summarized in Table 2 and the generalized NMR and MS results for moieties **xa** – **xe** in Table 3.

[**] All compounds are labeled in accordance with [1, 2].

Table 1. Al-Containing Byproducts from the Reduction Process of R_2NBCl_2 with $LiAlH_4$ in Toluene

Comp.	Fraction b.p. °C/Torr	m.p. °C	Method	^{27}Al-NMR	Products by ^{27}Al-NMR (* ^{11}B-NMR)
9	135/0.0001	132-5	P VI/2	106.0	**9xa**
16	144/0.0001	173-5	P VI/2	127.44	**16xc**
23	160/0.0001		P VI/1	104.75	**23xa + 23h**
	156/0.0001		P VI/2	104.57	**23xa + 23h**
25	131/0.001		P VI/1	112.23 I	**25xb** +
				108.82 II (–0.8*)	**25xd** +
				115.04 III	**25xe**
				Int. I:II:III = 3:1:1	
	200/0.001			112.23 I	**25xb** +
				116.25 II	**25xe**
				Int. I:II = 6:1	
26	131/0.001		P VI/1	112.29 I	**26xb** +
				108.92 II (–0.8*)	**26xd**
	195/0.0001			112.10 I	**26xb** +
				115.00 II	**26xe**
				Int. I:II = 8:1	
27	95/0.0001		P VI/1	107.98 I	**27xb** +
				115.66 II	**27xe**
				Int. I:II = 6:1	
	156/0.0001			107.89 I	
				114.68 II	**27xe**
				Int. I:II = 8:1	
28	155/0.001		P VI/1	113.31 I	**28b + 28xb**
				109.61 II (–0.7*)	**+ 28xd**
				116.47 III	**+ 28xe**
				Int. I:II:III = 1:4:4	
	95/0.0001	157-62		113.34 I	**28xb** +
				116.78 II	**28xe**
				Int. I:II = 1:2	
29	112/0.001	149-55	P VI/1	112.56 I	**29xb** +
				116.26 II	**29xe**
				Int. I:II = 1:8	
30	95/0.0001		P VI/1	106.50	**30xa**
	130/0.0001	150 (dec.)		116.46	**30xe**
	127/0.001		P VI/2	108.36 I (–0.7*)	**30xd** +
				116.83 II	**30xe**
				Int. I:II = 4:1	
31	123/0.001		P VI/1		**31b** +
				109.72 I	**31xd** +
				115.09 II	**31xe**
				Int. I:II = 8:1	
33	115/0.001		P VI/1		**33b** +
				116.68	**33xe**
	130/0.0001				**33b** +
				112.78	**33xb**

Table 2. Preparative Data of the Compounds Containing Al

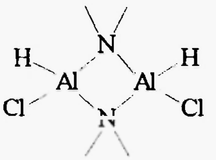
Comp.	Stoichiometric Formula	Molar Weight (g/mol)	High Resolution or Anal. [element] Calcd.	Found
9xa	$C_{13}H_{21}AlCl_3N$	324.66	4.31	4.26 [N]
16xc	$C_{14}H_{30}Al_2Cl_2N_2$	351.27	335.11821 [M^+–CH_3, ^{35}Cl]	335.11899
23xa	$C_9H_{13}AlCl_3N$	268.55		
25xe	$C_6H_{13}AlCl_3N$	232.52	195.01622 [M^+–HCl, ^{35}Cl]	195.02041
25xd	$C_{12}H_{26}AlBCl_2N_2$	306.99	306.13815 [^{11}B, ^{35}Cl]	306.13610
27xb	$C_7H_{14}AlCl_2N$	209.06	208.02405	208.02681
28xb	$C_6H_{12}AlCl_2N$ (monomer)	196.05	195.01622 [^{11}B, ^{35}Cl]	195.02020
28xe	$C_{12}H_{26}Al_2Cl_6N_2$	465.03	392.03312 [M^+–2 HCl, $^{35}Cl_3{}^{37}Cl$]	392.03115
28xd	$C_{12}H_{26}AlBCl_2N_2$	306.99	306.13815 [^{11}B, ^{35}Cl]	306.13784
29xd	$C_{10}H_{22}AlBCl_2N_2$	277.96	277.09903 [^{11}B, ^{35}Cl]	277.10223
30xb	$C_7H_{14}AlCl_2N$	209.06	208.02405 [^{35}Cl]	208.02702
31xd	$C_{14}H_{30}AlBCl_2N_2$	335.03	334.16945 [^{35}Cl]	334.16823
33xe	$C_8H_{11}AlCl_3N$	254.52	218.00840 [M^+–HCl, ^{11}B, ^{35}Cl]	218.00873

Table 3. ^{27}Al-NMR-, ^{11}B-NMR (**xd** only) and MS-Data of Al-Compounds

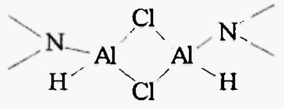
Type	^{27}Al-NMR δ (ppm) ($h_{1/2}$ Hz)	^{11}B-NMR δ (ppm) ($^1J_{BH}$ (Hz))	MS-Data (E.I.*1) (F.I. *2)
xa	104-7 (250-750)		*1: No M^+ of **xa**; M^+ of sec.amine (high intensity) and $AlCl_3$ (low intensity)
xb	107-13 (80-500)		*1: [M^+] may be overlapped by [M^++H] (= **xe**) (M^+ monomer, dimer)
xc	127 (1500)		*1: [M^+–CH_3] (**16**) (M^+ monomer, dimer) *2: [M^+] (**16**)
xd	108-10 (100-200)	–0.7 to –0.8 (100)	*1: [M^+] fragments R_2N–$AlCl_2$, R_2N–BH_2 *2: [M^+]
xe	114-17 (80-250)		*1: [M^++H] (M^+ monomer, dimer) *2: [M^+]

Molecules of the type **xb** can be detected in the MS spectra sometimes only by FI measurements. Compounds, which appear to be type **xb** compounds in the EI-MS, actually are fragments of **xe** type moieties. FI-MS spectra in these cases show a molecular ion with a mass of [$\mathbf{xb}^+$+H] (monomer) or [$\mathbf{xb}^+$+2H] (dimer). Since for **xd** in EI-MS spectra the fragments R_2NAlCl_2 and R_2NBH_2 are observed, the four-membered ring system **xd** results:

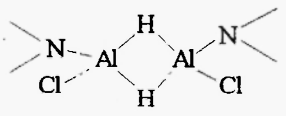
For **xc** the following types of structure (and isomers of each of them) appear possible:



xc

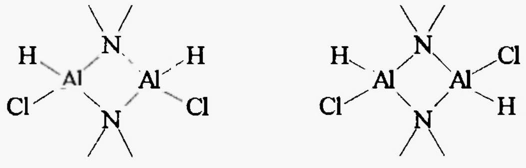


I



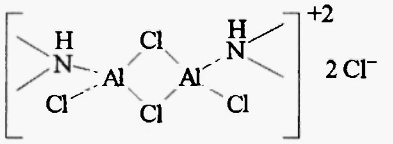
II

Species **I** and **II** have both a highly improbable arrangement. So the only compound of this type, **16xc**, was obtained by method P VI/2 (excess of $LiAlH_4$). The EI-MS spectrum of **16xc** shows signals for $[M^+{-}CH_3]$ (335/30), 237/100 and 140/80. The signal 140/80 is assigned to $[M^+/2{-}Cl]$, the basic-peak at m/z 237 corresponds to $[R_2N{-}Al(H){-}NR_2\ {-}CH_3]$. Such a sequence is found only for **xe**. Asymmetric structures can also be excluded as the ^{27}Al-NMR spectra show only one signal. For **xc** two isomers (cis/trans) are possible and accordingly in the ^{13}C-NMR spectrum two sets of signals occur. Otherwise the ^{13}C-spectra piperidino substituents are very similar to those in the boron compounds [1,2]. The proton signals of the H-atoms bonded to Al in **xc** and **xd** are not helpful to determine the structures as they extend over 1.5 ppm (3.8 - 5.3 ppm).

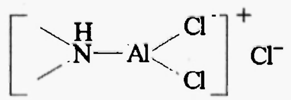


Isomers of **16xc**

In the EI-MS spectra of compounds of the type **xe** usually an isotopic pattern for $[M^+{-}HCl]$ (monomer) and for $[M^+{-}2\ HCl]$ (dimer) is found. As has been noted already, FI-MS spectra show the mass of the cation (monomeric or dimeric) of **xe**. Since the N-atom in monomeric **xe** has the coordination number four, a four-membered Al_2N_2 ring system of the dimer (containing bridging NH-groups with pentacoordinated N-atoms) must be excluded and a dimeric, ionic structure with bridging chlorine atoms is proposed:



xe (dimer)



xe (monomer)

^{27}Al-NMR measurements indicate that most of the fractions obtained of the Al-compounds (with the exception **16xc**) are mixtures of the substances **xb**, **xd** and **xe**, with one of these compounds of the types **b** (dimer, as in **28b**, **31b**) or even $(R_2NAlH_2)_n$ (**23**) may be contained. Therefore elemental analyses are only a tool to determine the main constituent of a fraction, e.g. **xb** or **xe**. Signals in ^{27}Al-NMR spectra were assigned in accordance to the analytical results, as the analytical data of **xb** and **xe** are rather different. For example, the elemental analyses of **29** (fraction 112°C/0.0001 Torr) show that it contains more **xe** than **xb**:

29xb. Calcd. C, 32.96; H, 5.49; N, 7.69
29xe: Calcd. C, 27.45; H, 5.03; N, 6.41.

For the fraction mentioned:

Found C, 28.35; H. 5.19; N, 6.71.

Therefore the intense signal at 116.26 ppm in ^{27}Al-NMR must correspond to **29xe**, the other to **29xb**. This is in agreement with the analytical results and ^{27}Al-NMR measurements of **27** (fraction 95°C/0.0001 Torr), which is a mixture of **27xb** + **27xe**.

27xb: Calcd. N, 6.66
27xe: Calcd. N, 5.69.
Found: N, 6.35

In this case the signal at $\delta^{27}Al$ = 107.98 is more intense and can be attributed to **27xb**.

For **31xd** δ^{11}B doesn't appear as the signal is overlapped by that of **31b** (~1.8 ppm). For **25xd**, **26xd** and **28xd** it is found to be at –0.7 to –0.8 ppm.

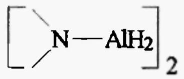
The yields of the aluminum compounds are not given, as these compounds were only byproducts in side reactions and were not obtained in an analytically pure state. To unambiguously identify the compounds described, however, high resolution MS measurements of the molecular peaks or of characteristic fragments were performed (Table 2). Usually about 5 – 10 g of the fractions (Table 1) remain in the residue of distillation of compounds of the type **b** (made by P VI), if the vacuum is not very good in the distillation procedure (carried out in a rotating three-bulb tube). The lowest boiling compounds in this case are those of type **xd**, which distill usually together with residual amounts of dimeric **b** (**28**, **31**). Difficulties in the separation procedure arise from the fact that compounds of type **xe** may split off hydrogen chloride at high temperatures and partially give compounds of type **xb**. Furtheron it cannot be excluded, that compounds of type **xb** and **xc** are formed from the adducts of type **xa** during the distillation process.

The formation of **xd** can be explained by addition of monomeric b, (RBH_2) [1] formed from the dimeric form at elevated temperatures, to monomeric **xb**. This appears to be the only path for the formation of compounds of the type **xd**, as all aluminum compounds of the types **xb** and **xe** are dimeric at room temperature. Therefore the structure of the molecule **xd** combines the H_2B- and the Cl_2Al-units.

In reactions according performed following procedure P VI/2, in which bis(piperidino)chloroboranes were reacted with $LiAlH_4$ in the molar ratio of 1:1, additional side-reactions give rise to the formation of several byproducts. For example in case of **27**, the FI-MS spectrum of a fraction (93°C/0.00001 Torr) exhibits in addition to **27b** the molecular peaks of

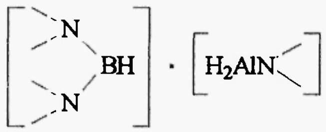
m/z:

282/10

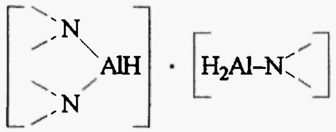


347/55

377/80



393/100



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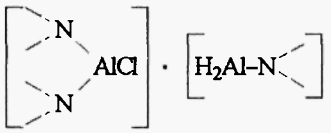
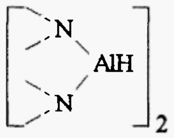


504/30



The molecular peaks with *m/z* 282, 347, 377, 393, 427 and 504 correspond to four-membered ring systems, which contain chlorine-, hydrogen- and nitrogen atoms as ring members. The most probable structures are four-membered $AlBN_2$ or Al_2N_2 units. Exact structure determinations were not possible as attempts for the purification of this fraction failed. However, among all of the components, there is only one which contains chlorine. This is attributed to the excess of $LiAlH_4$, used in all reactions of the procedure P VI/2.

The yields of these reduction reactions are lowered by side reactions (probably equilibrium reactions). Products of amino group transfer between boron atoms (e.g. trisaminoboranes) or to aluminum atoms (e. g. **xb** to **xe**) are frequently observed. This is the result of the competition between the Lewis acidic boron and aluminum centers. The Lewis acidity of these atoms at the same time gives rise to the formation of homoatomic dimers and furtheron is controlled by the substituents (H, Cl, N). Also ionic intermediates (see also [20]) have to be considered. This makes the overall process difficult to survey.

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