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The Solvent-free Lithium Alanate $\{Li[t\text{-}Bu_2AlH_2]\}_n$: A New Product Obtained from a Long-Known Reaction

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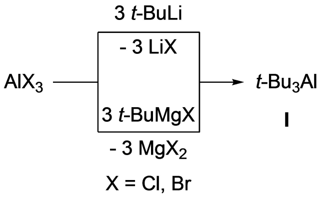
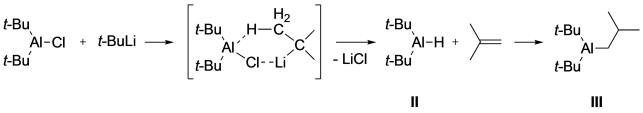
We report the isolation and characterization of an unknown reaction product from the reaction of $AlBr_3$ with three equivalents of *t*-BuLi. The polymeric and solvent-free lithium alanate $\{Li[t\text{-}Bu_2AlH_2]\}_n$ was characterized by X-ray structure analysis, NMR and IR spectroscopy. The title compound was found to be a suitable starting material for the synthesis of $[t\text{-}Bu_2AlH]_3$ by reacting it with readily available $[t\text{-}Bu_2AlBr]_2$.

Introduction

The first report on the synthesis, stability, and reactivity of *t*-Bu_3Al (**I**) was published in 1968, in which Lehmkuhl reported that **I** and the adducts **I**·D (D = OEt_2, thf) are stable at room temperature and resistant to isomerization to *iso*-butylaluminum compounds.[1] In general, **I** can be obtained by the reaction of AlX_3 with *tert*-butyllithium or *t*-BuMgX (X = Cl, Br) (Scheme 1). Lehmkuhl et al. also found that the reaction of *t*-Bu_2AlF and *t*-BuLi leads to **I** without isomers as side products.[2]



Scheme 1. Possibilities to synthesize *t*-Bu_3Al.



Scheme 2. Postulated mechanism for the formation of $[t\text{-}Bu_2AlH]_3$ and *t*-Bu_2Ali-Bu.

In contrast, analysis of the composition of the products from the reaction of $AlBr_3$ with three equivalents of *t*-butyllithium revealed that, in addition to the desired *t*-Bu_3Al, the reaction mixture contained three by-products including $[t\text{-}Bu_2AlH]_3$ (**II**), *t*-Bu_2Al*i*-Bu (**III**), and $\{Li[t\text{-}Bu_3AlH]\}_2$ (**IV**). They described "[…] that this reaction is often not reproducible; we obtained even from identical fractions of the starting compounds once the desired product, another time, the mixed *t*-Bu_2Al*i*-Bu (**III**) derivative formed via isomerization" (Scheme 2).

The authors showed that the formation of $[t\text{-}Bu_2AlH]_3$ (**II**) is favored at low temperatures and the subsequent hydroalumination reaction of **II** with isobutene to furnish *t*-Bu_2Al*i*-Bu (**III**) is unfavorable. Thus, when the solvent is removed at low temperatures (0 °C), **II** can be isolated in yields of 22 %. All products were isolated and fully characterized.

The same group described that the formation of the different reaction products strongly depends on the temperature. All species formed in the reaction exhibited very good solubility in non-polar solvents such as pentane or hexane.[3] Ziemkowska and co-workers obtained similar results. The reaction of $AlCl_3$ with *t*-BuMgCl in diethyl ether solution gives not only **I**·OEt_2 but often **II**·OEt_2. The percentage of **II**·OEt_2 depends on both the temperature of the process and the molar ratio of $AlCl_3$ and *t*-BuMgCl and increases with increasing temperature.[4]

The hydride $[t\text{-}Bu_2AlH]_3$ (**II**), identified as a trimer by X-ray structural analysis by Uhl and co-workers, has found wide application over the last three decades in synthetic inorganic chemistry for the preparation of a variety of aluminum compounds.[4–5] Aluminum hydrides show diverse reactivity towards a broad range of substrates. The β-diketiminate-ligated aluminum hydrides of the type $[(^{R}Nacnac)AlH_2]$ ($^{R}Nacnac$ = $\{HC(MeCNR)_2\}^-$ with R = Dipp, Mes or Xylyl) are particularly well studied.[6] They readily react with a variety of OH acidic compounds like alcohols, silanoles, peroxides and phosphorus(V) acids.[7] Even with less acidic amines they undergo a dehydrocoupling reaction to afford the mono-aminated aluminum hydride.[8] Furthermore, they are capable of reducing CO_2 by forming the formate-bridged aluminum hydride dimer. The reduction of the phosphorus ylide $Ph_3P{=}CH_2$ to Ph_2PMe under formation of the phenyl substituted hydride $(^{Dipp}Nacnac)Al(H)Ph$ was also reported.[9] Furthermore, aluminum hydrides where applied as catalyst in the reduction of carbonyl

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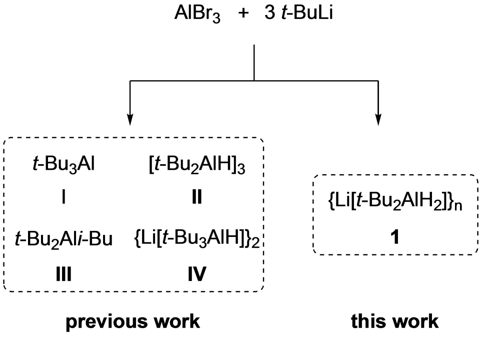
compounds, nitriles and alkynes.[10] As shown by the group of Mulvey, the mixed alkali metal aluminum hydrides show divers applications in synthetic chemistry.[11] A recently published review about main group hydrides underline their importance in synthetic chemistry.[12]

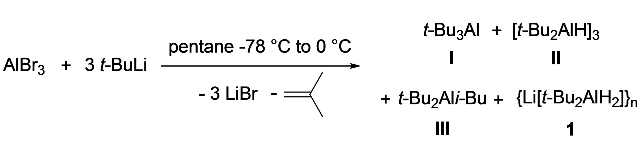
We herein report the isolation and characterization of a previously unknown reaction product from the reaction of $AlBr_3$ with three equivalents of *t*-BuLi (Scheme 3). We were able to isolate the polymeric solvent-free $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**) by distillation of the reaction mixture from the residue and characterize it completely by X-ray structure analysis, NMR and IR spectroscopy. In addition, we found a new synthetic strategy to the often used $[t\text{-}Bu_2AlH]_3$ (**II**).

Results and Discussion

In the course of our work, we were able to confirm Uhl's statement about the fact that the reaction of $AlBr_3$ with three equivalents of *t*-BuLi sometimes yields non-reproducible reaction product mixtures. First, as described, we were able to isolate the desired hydride $[t\text{-}Bu_2AlH]_3$ (**II**, 1.5 g, 18.6 %, based on the amount of $AlBr_3$ used) present as a trimer by crystallization from pentane by following literature procedure. To this end, $AlBr_3$ was dissolved in pentane and cooled to −78 °C. Three equivalents of *t*-BuLi (1.7 M in pentane) where slowly added whereupon the solution became cloudy. After complete addition, the reaction mixture was warmed to 0 °C and the solvent was removed under reduced pressure. The residue was extracted with pentane and filtered to remove the LiBr. Concentration of the filtrate and cooling to −30 °C furnished **II** as colorless crystals, as described previously (Scheme 4).[3] Further syntheses attempts following this route showed in cases that sometimes only very small amounts of **II** can be isolated (*ca.* 90 mg, *ca.* 1 %). As seen in the ^1H NMR spectrum of the isolated crystalline batch after the first crystallization (Figure 1), a mixture of $[t\text{-}Bu_2AlH]_3$ (**II**), $t\text{-}Bu_3Al$ (**I**) and another product, later identified as the polymeric $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**), was observed.



Scheme 3. Known reaction products from the reaction of $AlBr_3$ with three equivalents of *t*-BuLi and the polymeric $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**) reported in this work.



Scheme 4. Reaction of $AlBr_3$ with three equivalents of *t*-BuLi.

Based on these results, we modified the workup procedure. Instead of crystallizing the product from pentane after extraction, the solvent was removed under reduced pressure at room temperature. Following this, all volatile components, *i.e.* $t\text{-}Bu_3Al$ (**I**) and $t\text{-}Bu_2Al\textit{i}\text{-}Bu$ (**III**), which is only present in traces under these conditions, are distilled off at 110 °C into a flask cooled with liquid nitrogen. The remaining colorless solid can be sublimed at 110 °C. Instead of sublimation, the residue can also be suspended in pentane, isolated by filtration, and dried in high vacuum. In this way, $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**) was obtained in pure form (840 mg, 10 %). The ^1H NMR spectrum of the colorless solid (Figure 2) in C_6D_6 shows a signal for *t*-butyl groups (δ_{1H} = 1.26 ppm) and a broad signal characteristic of hydridic Al-H species (δ_{1H} = 2.16 ppm). These signals integrate in a ratio of 18 : 2, indicating the formation of a compound containing two *t*-butyl and two hydride entities. The chemical shifts differ significantly from those reported for the trimer $[t\text{-}Bu_2AlH]_3$ (**II**) in the literature (δ_{1H} = 2.96 (bs, Al-H) and 1.22 (s, *t*-Bu) ppm).[3] The acquisition of a ^7Li NMR spectrum, which revealed a signal at δ_{7Li} = −3.71 ppm, indicated the formation of $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**).

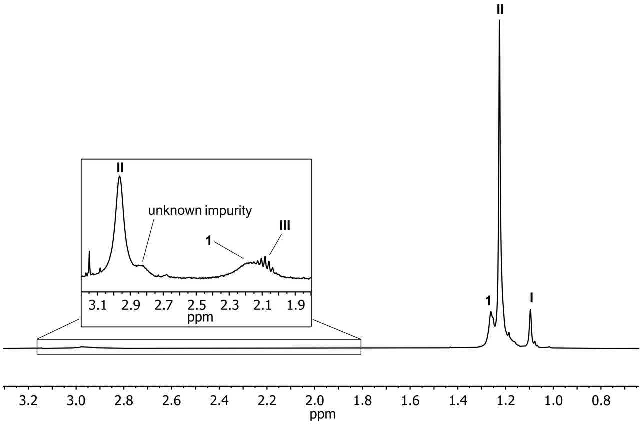


Figure 1. ^1H NMR spectrum of the isolated crystalline batch after the first crystallization in C_6D_6.

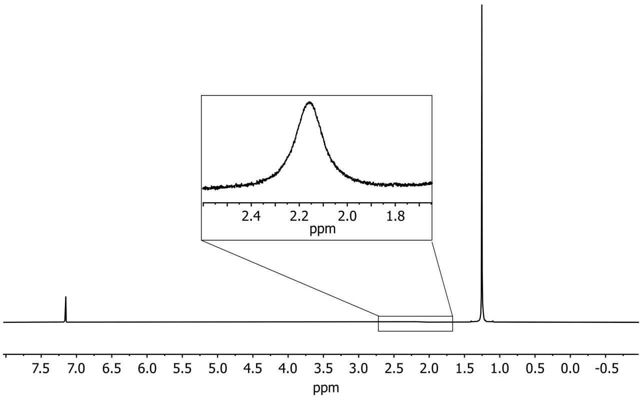


Figure 2. ^1H NMR spectrum of the isolated $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**) in C_6D_6.

To our surprise, the solid was found to be almost insoluble in hydrocarbons such as pentane or hexane, and only poorly soluble in benzene. We note in passing that the product dissolves exceptionally well in pentane even at −30 °C when it contains small amounts of $t\text{-Bu}_3\text{Al}$ (**I**) (in cases it was not completely removed during distillation). Crystals suitable for X-ray structural analysis were obtained by sublimation (Figure 3, space group *C*2/*c*).

As can be seen from Figure 3, the product was identified as the solvent-free hydride-bridged polymer $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**). Note that the THF adduct $\text{Li(thf)}_2[t\text{-Bu}_2\text{AlH}_2]$ was prepared by Smith and co-workers from $\text{Li[AlH}_4]$ and two equivalents of t-BuLi, but was not studied by X-ray crystallography.[13] Compared with other hydride-containing lithium alanates studied by X-ray crystallography, the average Al-H bond length of 1.62 Å is about as long as in $\{\text{Li(thf}_2)[(\text{Me}_2\text{PhSi})_3\text{CAlH}_3]\}_2$ (1.61 Å),[13] but significantly shorter than in $\{\text{Li}[t\text{-Bu}_3\text{AlH}]\}_2$ (1.75 Å).[3] The Li-H distances of 1.91(2) Å in the Li_2H_2 four-membered core structure are very similar to those reported in the literature (1.93 and 1.94 Å). The bond angles around Al1 clearly show a distorted tetrahedral coordination environment.

The naturally arising question was how the title compound **1** was formed. Initially, we speculated that **1** is a product from the reaction of $[t\text{-Bu}_2\text{AlH}]_3$ (**II**) with LiH (a conceivable impurity in t-BuLi).[14] To this end, we performed several control reactions. It quickly turned out that **II** and equimolar amounts of LiH showed no reaction in pentane and benzene. We also checked if **1** is formed by thermal decomposition of $\{\text{Li}[t\text{-Bu}_3\text{AlH}]\}_2$ (**IV**) at the distillation step. However, at 130 °C, no formation of **1** could be observed as verified by ^{1}H NMR spectroscopy. However, when $[t\text{-Bu}_2\text{AlH}]_3$ (**II**) was reacted with $\{\text{Li}[t\text{-Bu}_3\text{AlH}]\}_2$ (**IV**), $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**) and $t\text{-Bu}_3\text{Al}$ (**I**) are readily obtained (Scheme 5). Since both compounds, *i.e.* **II** and **IV**, are present in the original reaction mixture, it appears reasonable to assume that they react with each other at higher temperatures to provide **1** and **I**. The latter is subsequently removed by distillation to provide pure **1**.

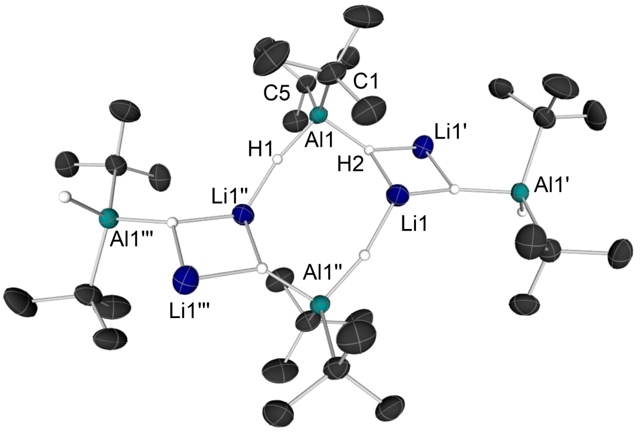
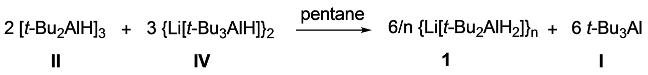


Figure 3. Section of the polymeric solid state structure of $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**). Four formula units are shown. All hydrogen atoms, except for the hydridic ones, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-H1 = 1.65(2); Al1-H2 = 1.59(2); Al1-C1 = 1.979(2); Al1-C5 = 1.989(3); Al1-Li1 = 3.064(4); Li1-H1 = 1.91(2); Li-H2 = 1.85(2); H1-Al1-H2 = 99.7(11); C1-Al1-H1 = 107.3(7); C1-Al1-H2 = 111.1(9); C1-Al1-C5 = 124.46(11); Li1-Al1-H1 = 33.2(7). Operators for generating equivalent atoms: −x + 1, y, −z + 3/2 and −x + 1, −y + 1, −z + 1.



$$\underset{\textbf{II}}{2\,[t\text{-Bu}_2\text{AlH}]_3} + \underset{\textbf{IV}}{3\,\{\text{Li}[t\text{-Bu}_3\text{AlH}]\}_2} \xrightarrow{\text{pentane}} \underset{\textbf{1}}{6/n\,\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n} + \underset{\textbf{I}}{6\,t\text{-Bu}_3\text{Al}}$$

Scheme 5. Formation of $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**).

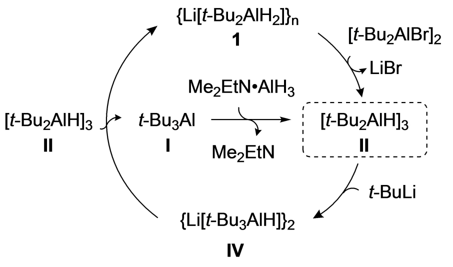
Interestingly, **1** was found to be a very suitable starting material for the synthesis of $[t\text{-Bu}_2\text{AlH}]_3$ (**II**). Reaction of **1** with the readily available bromide $[t\text{-Bu}_2\text{AlBr}]_2$[15] in the stochiometric ration 1:1 (based on the monomeric formula unit) quantitatively forms two equivalents of the desired product **II**. This in turn can be reacted with t-BuLi to provide $\{\text{Li}[t\text{-Bu}_3\text{AlH}]\}_2$ (**IV**), which can subsequently be reacted again with **II** (Scheme 5) to provide $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**). In the correct sequential ordering, a cyclic reaction cascade is obtained (Scheme 6) by which $[t\text{-Bu}_2\text{AlH}]_3$ (**II**) and $t\text{-Bu}_3\text{Al}$ (**I**) can be generated. By reacting the latter with $\text{Me}_2\text{EtN·AlH}_3$, **II** can be produced.[16] Scheme 6 gives an overview of the possible products from the reaction of three equivalents t-BuLi and AlBr_3 and how they can be converted into each other.

Conclusions

We report on the isolation and full characterization including X-ray structure analysis, NMR and IR spectroscopy, of the previously unknown polymer solvent-free lithium alanate $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**). The title compound was isolated in pure form from the long-known reaction of AlBr_3 with three equivalents of t-BuLi as a colorless solid in isolated yields of 10%. The synthetic key was found to be a distillation step at 110 °C in high vacuum, by which all other products of the reaction were removed. Supported by control reactions, it is assumed that under these conditions **1** is a product of the reaction of $[t\text{-Bu}_2\text{AlH}]_3$ (**II**) with $\{\text{Li}[t\text{-Bu}_3\text{AlH}]\}_2$ (**IV**). Furthermore, we report a new synthetic route to $[t\text{-Bu}_2\text{AlH}]_3$ (**II**) starting from **1** with $[t\text{-Bu}_2\text{AlBr}]_2$.

Experimental Section

General Methods: All operations were carried out under dry argon using standard Schlenk and glovebox techniques. *Tert*-BuLi (1.7 M in pentane) was used as purchased from Sigma-Aldrich. AlBr_3 was purchased from Sigma-Aldrich or abcr and sublimed prior to use.



Scheme 6. New synthetic route to $[t\text{-Bu}_2\text{AlH}]_3$ (**II**) from $\{\text{Li}[t\text{-Bu}_2\text{AlH}_2]\}_n$ (**1**) and $[t\text{-Bu}_2\text{AlBr}]_2$. Stoichiometric factors are omitted for clarity.

t-Bu$_2$AlBr and {Li[t-Bu$_3$AlH]} were synthesized according to literature procedures.[15],[3] Solvents were dried over Na/K and rigorously degassed before use. NMR spectra were recorded on Bruker Avance Neo 400 or an Avance 300 spectrometer operating at ^{1}H Larmor frequencies of 400 or 300 MHz in dry degassed deuterated solvents. ^{1}H, ^{13}C{^{1}H} chemical shifts were reported against TMS. Coupling constants (J) are given in Hertz as positive values, regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, q, sept, or m for singlet, doublet, quartet, septet, or multiplet, respectively. The assignments were confirmed, as necessary, with the use of 2D NMR correlation experiments. IR spectra were measured on a Bruker Alpha spectrometer using the attenuated reflection technique (ATR), and the data are reported in wavenumbers (cm^{-1}). The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong), and br (broad). Melting points were measured with a Thermo Fischer melting point apparatus and are not corrected. Elemental analyses were carried out in the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

Synthesis of {Li[t-Bu$_2$AlH$_2$]}$_n$ (1): AlBr$_3$ (15.11 g, 56.7 mmol) was dissolved in pentane and cooled to −78 °C. Three equivalents t-BuLi (1.7 M in hexane, 100 ml, 170 mmol) were added over a period of 1.5 h. Warming the reaction mixture to 0 °C over 2 h and removing all volatiles *in vacuo* at this temperature gave a pale grey sticky solid. Extracting with pentane (100 ml), filtration and washing the residue with pentane (2 x 20 ml) resulted in a colourless solution. The solvent was again removed *in vacuo* at ambient temperature to give a colourless sticky solid. Afterwards all volatile side products (mainly t-Bu$_3$Al) where distilled of to a flask cooled with liquid N$_2$ at 110 °C. The remaining colourless residue was suspended in pentane (40 ml), filtrated and washed with pentane (20 ml) to remove the last traces of t-Bu$_3$Al. Drying in high vacuum yielded pure {Li[t-Bu$_2$AlH$_2$]}$_n$ (840 mg, 5.6 mmol, 10 %) as colourless solid which can be sublimed at 110 °C at $1\cdot10^{-3}$ bar. mp: 128 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$, ppm): $\delta = 2.21$ (bs, H$_{\mathrm{Al}}$, 2H), 1.25 (s, H$_{t\text{-Bu}}$, 18H). ^{13}C{^{1}H} NMR (75 MHz, 298 K, C$_6$D$_6$, ppm): 31.5 (s, C$_{\mathrm{Me}}$) 16.0 (bs, C$_{\mathrm{Me3}}$). ^{7}Li NMR (116 MHz, 298 K, C$_6$D$_6$, ppm): $\delta = -3.71$ (s). IR (ATR, cm^{-1}): $\tilde{\upsilon} =$ 3285 (vw), 2831 (vw), 2557 (vw), 2481 (vw), 2433 (vw), 2273 (vw), 2261 (vw), 2253 (vw), 2239 (vw), 2232 (vw), 2220 (m), 2210 (w), 2197 (w), 2181 (s), 2165 (s), 2158 (s), 2150 (m), 2133 (vw), 2120 (vw), 2106 (vw), 2084 (vw), 2066 (vw), 2048 (w), 2043 (w), 2025 (m), 2006 (m), 1994 (vw), 1982 (w), 1967 (w), 1893 (vw), 1460 (vw), 1072 (vw), 1002 (w), 988 (vw), 927 (vw), 910 (vw), 897 (vw), 875 (vw), 809 (w), 788 (w), 771 (m), 760 (w), 744 (w), 737 (vw), 719 (vw), 698 (vw), 684 (vw), 644 (vw), 638 (vw), 621 (w), 602 (w), 592 (vw), 581 (vw), 562 (w), 551 (w), 536 (w), 522 (vw), 505 (m), 490 (m), 482 (m), 475 (s), 465 (s), 455 (s), 447 (s), 441 (s), 427 (s), 419 (vs), 403 (vs), 396 (vs), 383 (s). Elemental analysis: Due to high sensitivity towards air and moisture no satisfactory EA could be obtained.

Reaction of {Li[t-Bu$_2$AlH$_2$]}$_n$ with [t-Bu$_2$AlBr]$_2$: To a suspension of {Li[t-Bu$_2$AlH$_2$]}$_n$ (100 mg, 0.67 mmol) in pentane (3 ml) a solution of [t-Bu$_2$AlBr]$_2$ (147 mg, 0.35 mmol) in pentane (5 ml) was added at ambient temperature. Stirring overnight resulted in a colourless suspension. Filtration *via* syringe filter and storing the resulting colourless solution at −30 °C overnight yielded [t-Bu$_2$AlH]$_3$ as colourless crystals (100 mg, 0.35 mmol, 53 %). The NMR spectra of the product agrees well with the literature.[3]

Reaction of [t-Bu$_2$AlH]$_3$ with {Li[t-Bu$_3$AlH]}$_2$: In an NMR tube scale reaction, {Li[t-Bu$_3$AlH]}$_2$ was in situ generated from [t-Bu$_2$AlH]$_3$ (20 mg, 46.9 μmol) and three equivalents of t-BuLi (9 mg, 140 μmol) in hexane (3 ml). Stirring for 3 h and removal of the solvent in vacuo furnished a colourless solid, which was identified as {Li[t-Bu$_3$AlH]}$_2$ by ^{1}H NMR spectroscopy. To the solution of {Li[t-Bu$_3$AlH]}$_2$ in d$_6$-benzene, one equivalent of [t-Bu$_2$AlH]$_3$ (20 mg, 46.9 μmol) was added. As can clearly be seen from the ^{1}H NMR spectrum (Figure S2), the formation of {Li[t-Bu$_2$AlH$_2$]}$_n$ ($\delta_{1H} = 1.26$ ppm) and t-Bu$_3$Al ($\delta_{1H} = 1.10$ ppm) is observed. The starting compounds [t-Bu$_2$AlH]$_3$ ($\delta_{1H} = 1.22$ ppm) and {Li[t-Bu$_3$AlH]}$_2$ ($\delta_{1H} = 1.31$ ppm) can also be observed. The signal at ($\delta_{1H} = 1.20$ ppm) could not be clearly assigned.

Crystallographic details

The structure of {Li[t-Bu$_2$AlH$_2$]}$_n$ (**1**) has been deposited at the Cambridge Crystallographic Data Centre: 2293500. For further crystallographic details, see the Supporting Information, Section 4.

Deposition Number 2293500 (for {Li[t-Bu$_2$AlH$_2$]}$_n$ (**1**)) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supporting Information

For experimental details and analytical data see Supporting Information. The authors have cited additional references within the Supporting Information (Ref. [17]).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. Methods, synthesis and characterization, NMR spectra, IR spectra, and XRD details are provided in the Supporting Information.

Keywords: aluminum · group 13 elements · hydrides · main group chemistry · polymers

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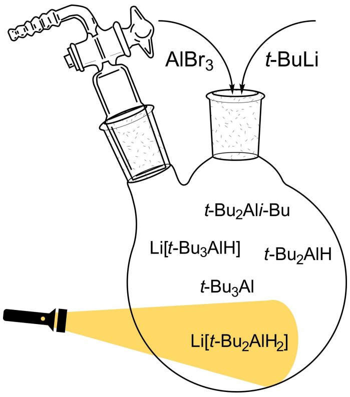
RESEARCH ARTICLE

Complex reaction, one new product! We herein report the isolation and full characterization of the previously unknown polymer solvent-free lithium alanate $\{Li[t\text{-}Bu_2AlH_2]\}_n$ (**1**), which was isolated in pure form from the long-known reaction of $AlBr_3$ with three equivalents of *t*-BuLi.



*Dr. F. Krämer, M. Leskov, Prof. Dr. F. Breher**

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The Solvent-free Lithium Alanate $\{Li[t\text{-}Bu_2AlH_2]\}_n$: A New Product Obtained from a Long-Known Reaction