Lithium and Sodium Alkoxy- and Aryloxyhydridoaluminates in Solution and in the Solid State

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Dedicated to Professor Hans Bock on the occasion of his 70th birthday

Abstract: The reactions of lithium and sodium aluminium hydride with alcohols and phenols in ether solvents were studied as a route to mono-, di- and triorganyloxyhydridoaluminates $MAlH_{4-n}(OR)_n$. However, the stability of these compounds towards disproportionation is strongly dependent on the steric demand of the organic group and the solvent. This process leads to the formation of $MAlH_4$ and more highly substituted organyloxyalumohydrides, as shown by ^{27}Al NMR spectroscopy. The crystal structures of nine organyloxyhydridoaluminates were determined by X-ray structure analysis. Both Al-H-M and Al-O-M bridges were found for the coordination of the cation M (Li or Na). The species $LiAlH_3(OR)$ was stable only for $R = 2,6\text{-}t\mathrm{Bu}_2C_6H_3$; it is dimeric in the solid state. Four stable solvated compounds $MAlH_2(OR)_2$ were obtained for M = Li, $R = t\mathrm{Bu}_2\mathrm{MeC}$ (M = Li, Na), $2,6\text{-}t\mathrm{Bu}_2C_6H_3$ and M = Na, $R = CPh_3$, all of which are molecular complexes in the solid state. Reductive ring opening of THF occurs for $MAlH_2(OC_6H_3t\mathrm{Bu}_2\text{-}2,6)_2$ (M = Li, Na). Triorganyloxyhydridoaluminates are the most stable compounds in this series. For M = Li, $R = t\mathrm{Bu}_2\mathrm{MeC}$, CPh_3, $2,6\text{-}i\mathrm{Pr}_2C_6H_3$ and M = Na, $R = CPh_3$, crystal structures were determined. Depending on the bulk of the group R, both M-H-Al and M-O-Al bridges (smaller R groups) are observed.

Keywords: alkali metals · aluminum · hydrido complexes · NMR spectroscopy · structure elucidation

Introduction

Since the discovery of $LiAlH_4$ by Schlesinger in the 1940s,[1] substituted complex metal aluminium hydrides have found many applications as reducing agents in organic synthesis.[2] The introduction of appropriate substituents in $MAlH_4$ (M = Li, Na) lowers the reactivity and increases the chemo- and/or stereoselectivity. Among the modified aluminium hydrides, the alkoxy-substituted hydridoaluminates play an important role.[2b] For example, lithium tri-*tert*-butoxyhydridoaluminate (LTTBA) is a commonly used and versatile reducing agent which reduces sterically demanding cyclohexanones such as 3,3,5-trimethylcyclohexanone (dihydroisophorone, DHI) to the axial *trans*-3,3,5-trimethylcyclohexanol with 98 % selectivity because the bulky *tert*-butoxyl substituents inhibit approach of the hydride from the sterically more hindered side of the ring. With lithium trimethoxyhydridoaluminate, however, even higher yields of axial alcohols are reported,[3] although the methoxyl substituents are far less bulky than the *tert*-butyl groups in LTTBA. The reason for this apparent contradiction is that the association of $LiAlH(OMe)_3$ in solution makes it more bulky than $LiAlH(Ot\mathrm{Bu})_3$. Therefore, understanding how hydride reagents function requires knowledge of their structures in solution and in the solid state. Moreover, details of the kinetics and of the reaction mechanisms would be helpful. Studies on the composition of lithium aluminium hydride and its alkoxy derivatives in ether solvents have been the subject of several papers. Conclusions were derived from molecular association and conductance studies.[4] Much information in the literature on the preparation of well-defined alkali metal alkoxy- and aryloxyhydridoaluminates is contradictory and irregular.

Here we report on the behaviour of alcohols and phenols towards lithium and sodium tetrahydridoaluminate in ether solvents (Et_2O and THF) with an emphasis on sterically demanding RO substituents. X-ray structure determination allowed the degree of association in the solid state to be determined, and this was helpful for judging the behaviour in solution. To our knowledge, the mixed lithium neopentyloxyhydridoaluminate $[Li(Et_2O)(t\mathrm{Bu}CH_2O)_5Al_3H_5]$[5] is the only structurally characterized alkoxy-substituted alkali metal hydridoaluminate so far. In addition, ^{27}Al NMR spectroscopy provided reliable information on the number and the nature of $[AlH_{4-n}(OR)_n]^-$ species in solution.

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[+] X-ray structure determinations.

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Results and Discussion

The lithium and sodium (M) alkoxy- and aryloxy- (RO) substituted hydridoaluminates ($MAlH_{4-n}(OR)_n$) were prepared by adding *n* equivalents of ROH to a standardized ethereal solution (S = Et_2O, THF) of $LiAlH_4$ or $NaAlH_4$. The reactions [Eqs. (1)–(3)] were carried out with the following alcohols and phenols ROH: MeOH, EtOH, *t*BuOH, tBu$_2$(Me)COH, (−)-menthol, Ph_3COH, PhOH, 2,6-$Me_2C_6H_3OH$, 2,6-iPr$_2C_6H_3OH$, 2,6-tBu$_2C_6H_3OH$ and 2,6-tBu$_2$,4-MeC_6H_2OH. Although the amount of hydrogen liberated during the reaction was equivalent to the molar quantity of the alcohol [with the exception of Eq. (3) with 2,6-tBu$_2C_6H_3OH$ and 2,6-tBu$_2$,4-MeC_6H_2OH; see below], the composition of the reaction mixture depends on the size and the branching of the alkyl or aryl group R.

$$MAlH_4 + ROH \xrightarrow{S} MAlH_3(OR) + H_2 \qquad (1)$$

[{Li(Et_2O)$_2$(μ-H)$_2$Al(H)(OC_6H_3tBu$_2$-2,6)}$_2$] (**1**)

$$MAlH_4 + 2\,ROH \xrightarrow{S} MAlH_2(OR)_2 + 2\,H_2 \qquad (2)$$

[Li(thf)$_2$(μ-O-(−)-Ment)$_2$Al(H)$_2$] · THF (**2**)
[Na(thf)$_2$(μ-$OCPh_3$)$_2$Al(H)$_2$] (**3**)
[Li(Et_2O)$_2$Al(H)$_2$(OCMetBu$_2$)$_2$] (**4**)
[Li(Et_2O)$_2$(μ-H)$_2$Al(OC_6H_3tBu$_2$-2,6)$_2$] · 1/3 Et_2O (**5**)
[Li(thf)$_3$(μ-H)Al(H)(OC_6H_3tBu$_2$-2,6)$_2$] (**6b**)
[Na(thf)$_3$Al(H)$_2$(OC_6H_3tBu$_2$-2,6)$_2$] (**7**)

$$MAlH_4 + 3\,ROH \xrightarrow{S} MAlH(OR)_3 + 3\,H_2 \qquad (3)$$

[LiAl(H)(O-(−)-Ment)$_3$] (**10**)
[Li(thf)$_3$(μ-H)Al($OCPh_3$)$_3$] · 0.5 THF (**11**)
[Na(thf)$_3$(μ-H)Al($OCPh_3$)$_3$] (**12**)
[Li(Et_2O)(μ-OCMetBu$_2$)$_2$Al(H)(OCMetBu$_2$)] (**13**)
[Li(Et_2O)(μ-OC_6H_3iPr$_2$-2,6)$_2$Al(H)(OC_6H_3iPr$_2$-2,6)] (**14**)
[Li(Et_2O)Al(H)($OC_6H_3Me_2$-2,6)$_3$] (**15**)

Alkali metal alkoxy- and aryloxytrihydridoaluminates: Alcohols with sterically less demanding groups R do not lead to well-defined alkoxy- or aryloxytrihydridoaluminates; instead, in accordance with previous observations,[4, 6–9] the monosubstituted alkoxyaluminates disproportionate [Eq. (4)]. Because

$$MAlH_3OR \rightleftharpoons a\,MAlH_4 + b\,MAlH_2(OR)_2 + c\,MAlH(OR)_3 + d\,MAl(OR)_4 \qquad (4)$$
$$a + b + c + d = 1$$

of this disproportionation, the solutions contain a large proportion of $LiAlH_4$, which is therefore the dominant reducing agent.[10] A similar disproportionation was proposed by Gavrilenko et al. for R = alkyl,[11] alkynyl,[12] and amino.[13]

The equilibrium [Eq. (4)] depends 1) on the size and the branching of the alcohol, 2) on the solubility of the complexes, and 3) on the nature of the cation. However, the reactions are not strongly affected by temperature provided point 2 is not dominant.

We have observed this behaviour for all RO groups tested in organyloxytrihydridoaluminates, with the exception of 2,6-tBu$_2C_6H_3OH$, both in THF and diethyl ether. In THF, the solution remained clear over a long period of time. In diethyl ether, however, species such as $LiAlH_n(OMe)_{4-n}$, $LiAlH_n(OEt)_{4-n}$ and $LiAlH_n(OtBu)_{4-n}$ ($n = 0-3$) are insoluble.[14] Therefore, the precipitate may contain a mixture of disproportionation products of Equation (4), which is shifted to the right due to the insolubility of these products. The insolubility of $NaAlH_4$ prevents homogeneous reactions being performed in diethyl ether.

However, in THF clear solutions were obtained, and only three ^{27}Al NMR signals were detected for R = Me, Et, *t*Bu, CPh_3, CMetBu$_2$, and M = Li, Na [Eq. (5)]. This

$$2\,MAlH_3(OR) \overset{THF}{\rightleftharpoons} MAlH_4 + MAlH_2(OR)_2 \qquad (5)$$

contrasts with the findings of Gavrilenko et al., who observed all possible ligand redistribution products according to Equation (4).[6] For R = CPh_3 and M = Na, the disubstituted product **3** crystallized (see below). Nevertheless, the THF solution showed a signal for $NaAlH_4$; this indicates that Equation (5) was shifted to the right.

Only for the phenols 2,6-tBu$_2C_6H_3OH$ and 2,6-tBu$_2$-4-MeC_6H_2OH did the ^{27}Al NMR spectrum show only the signal of $LiAlH_3(OR)$. Crystallization at 2 °C yielded colourless crystals of **1**, which were soluble in toluene and in THF without decomposition. Clearly, ligand exchange according to Equation (5) is inhibited by the steric influence of the two *t*Bu groups in the *ortho* positions of the phenyl ring. This is in contrast to reports by Barron and Power that no gas evolution was observed in the reaction of $LiAlH_4$ with one equivalent of 2,6-tBu$_2$-4-MeC_6H_2OH.[15, 16]

We assume that ligand exchange in solution is induced by interaction of the (solvated) cation (M = Li, Na), rather than proceeding by RO^-/H^- exchange between aluminium centres via a transition state with five-coordinate Al, which would be required for the addition of another ligand in an associative mechanism. The X-ray structure of **1** shows that the cation is coordinated to the hydrogen atoms but not to the oxygen atoms, a situation that is realized in structures with sterically less demanding alcohols (see below). The stability of **1** thus results from the presence of bulky substituents.

The aryloxytrihydridoaluminate **1** crystallizes as a dimer (Figure 1) with Li-H-Al bridges and an eight-membered ring which can be regarded as a distorted chair. Each Li atom is coordinated to two hydrido groups and additionally to two diethyl ether molecules (see also Table 1). The two Li–H

Table 1. Selected interatomic distances [Å] and angles [°] for **1**.

Al1–H1	1.55(2)	H1-Al1-H2	106(1)
Al1–H2	1.59(2)	H1-Al1-H3	110(1)
Al1–H3	1.51(2)	H1-Al1-O1	109.9(8)
Li1–H1A	1.87(2)	H2-Al1-H3	111(1)
Li1–H2	1.90(2)	H2-Al1-O1	107.6(8)
Al1–O1	1.739(2)	H3-Al1-O1	111.9(9)
Li1–O2	1.933(4)	Al1-H1-Li1A	130(1)
Li1–O3	1.949(4)	Al1-H2-Li1	126(1)
Al1–Li1	3.116(4)	H2-Li1-H1A	97(1)
Al1–Li1A	3.099(4)	H2-Li1-O2	109.4(7)
		H2-Li1-O3	107.7(7)
		H1A-Li1-O2	127.2(7)
		H1A-Li1-O3	103.4(7)
		O2-Li1-O3	110.2(2)

distances in **1** are equal within standard deviations (av 1.89 Å) and are shorter than those of $LiAlH_4$ (av 1.96 Å).[17] The deviation from tetrahedral coordination geometry is small at the aluminium centres but large at the lithium centres: The H-Li-H angle is rather small (97(1)°), and the H1A-Li1-O2 angle quite obtuse (127.2(7)°). A structure comparable to that of **1** is found for $[Li(thf)_2(\mu\text{-}H)_2AlH[C(SiMe_2Ph)_3]]_2]$.[18] Shorter Li–H bonds (1.78 Å) are reported for the amidohydridoaluminate $[\{Li(Et_2O)_2(\mu\text{-}H)_2Al(H)N(SiMe_3)_2\}_2]$, which has a planar eight-membered ring due to the lower steric requirements of the $(Me_3Si)_2N$ group.[19]

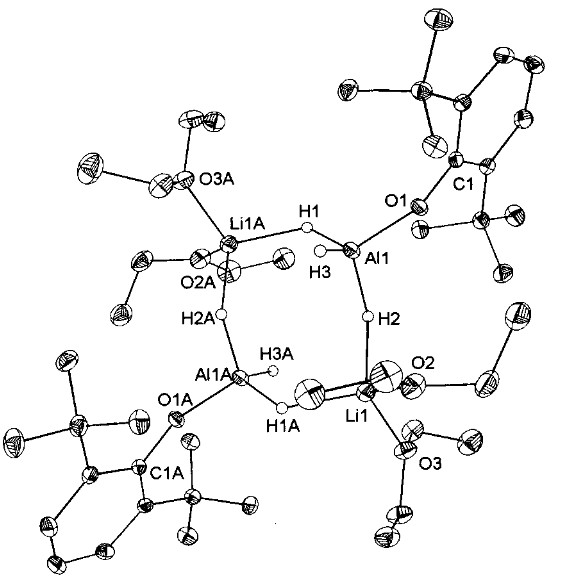


Figure 1. Crystal structure of **1**.

Alkali metal dialkoxy- and diaryloxydihydridoaluminates: Reactions of ROH with $MAlH_4$ in the ratio 2:1 [Eq. (2)] in THF (M = Li, Na; ROH = *t*BuOH, (−)-menthol, Ph_3COH, $2,6\text{-}Me_2C_6H_3OH$, and $2,6\text{-}i\text{Pr}_2C_6H_3OH$) should produce lithium and sodium diorganyloxydihydridoaluminates. The ^{27}Al NMR data reveal the presence of an equilibrium [Eq. (6)]

$$3\,MAlH_2(OR)_2 \overset{THF}{\rightleftharpoons} MAlH_4 + 2\,MAlH(OR)_3 \qquad (6)$$

involving the disproportionation products tetrahydridoaluminate and the trialkoxy- or triaryloxy-substituted hydridoaluminate species. The ^{27}Al NMR spectrum in Figure 2 is an example for the disproportionation of $LiAlH_2(OtBu)_2$.

Monosubstituted products $[AlH_3(OR)]^-$ do not seem to be stable enough to be present in the equilibrium mixture in THF in a detectable proportion. However, for alcohols with small R groups (R = Me, Et), $MAlH_3(OR)$ could also be detected by ^{27}Al NMR spectroscopy. The white amorphous powders that precipitate from their THF solutions at lower temperatures (+2 °C, −20 °C, −78 °C) consisted of a mixture of three compounds [Eq. (6)]. Only two reactions led to single crystals suitable for X-ray structure determinations (R = (−)-Ment, CPh_3).

Although the ^{27}Al NMR spectrum of the hydridoaluminate $MAlH_2(OR)_2$ with R = (−)-Ment and M = Li showed the existence of three products, single crystals of $[Li(thf)_2(\mu\text{-}O\text{-}(-)\text{-}Ment)_2Al(H)_2]$ (**2**) separated from the colourless reaction mixture. The ^1H, ^{13}C and ^{27}Al NMR spectra of the crystalline fraction, as well as the IR spectrum, revealed the presence of $LiAlH_4$ and $LiAlH(O\text{-}(-)\text{-}Ment)_3$ (**10**) [Eq. (6)]. The structure of **2** (Figure 3) reveals a monomeric dihydride $[Li(thf)_2(\mu\text{-}O\text{-}(-)\text{-}Ment)_2Al(H)_2]$. There is one additional THF molecule within the unit cell. The lithium cation is coordinated by the oxygen atoms of the two alkoxy groups. This leads to a four-membered planar $LiAlO_2$ ring (Table 2).

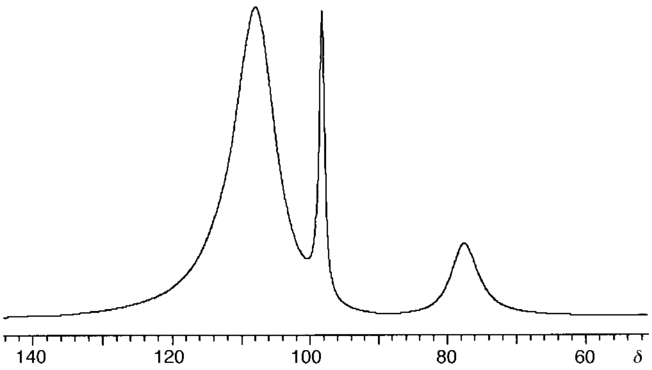


Figure 2. ^{27}Al NMR spectrum of $LiAlH_4 + 2\,t$BuOH. Signals (from left to right): $LiAlH_2(OtBu)_2$, $LiAlH_4$, $LiAlH(OtBu)_3$ (proton-decoupled).

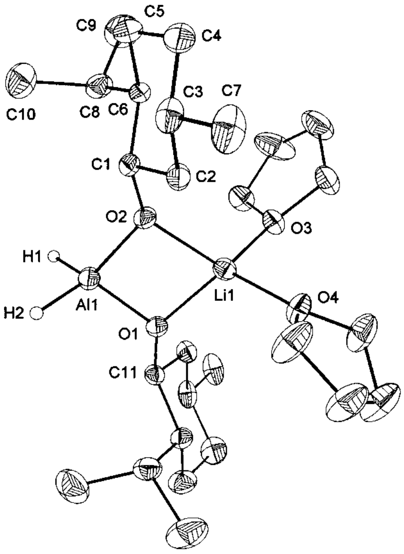


Figure 3. Crystal structure of **2**.

Table 2. Selected interatomic distances [Å] and angles [°] for **2**.

Al1–H1	1.50(5)	H1-Al1-H2	111(3)
Al1–H2	1.58(5)	H1-Al1-O1	110(2)
Al1–O1	1.775(3)	H1-Al1-O2	116(2)
Al1–O2	1.772(3)	H2-Al1-O2	113(2)
Li1–O1	1.934(7)	H2-Al1-O1	115(2)
Li1–O2	1.955(7)	O1-Al1-O2	91.2(1)
Li1–O3	1.960(7)	O1-Li1-O2	81.3(3)
Li1–O4	1.969(7)	Al1-O1-Li1	94.1(2)
		Al1-O2-Li1	93.5(2)
		O3-Li1-O4	102.2(3)
		O3-Li1-O1	119.3(3)
		O3-Li1-O2	112.3(3)
		O4-Li1-O1	117.0(3)
		O4-Li1-O2	125.3(3)

The Al–O bond lengths (av 1.773 Å) are much shorter than the Al–O distances usually observed in dimeric alkoxyaluminium dihydrides with Al_2O_2 rings (av 1.84 Å).[5, 20] The aluminium and lithium centres have slightly distorted tetrahedral coordination geometries.

The attempted preparation of $LiAlH_2(OCPh_3)_2$ in THF failed because of disproportionation [Eq. (6)] at all temperatures and concentrations. This is inconsistent with previous reports that $LiAlH_2(OCPh_3)_2$ is stable in THF.[6] We observed that at room temperature, shortly after hydrogen evolution has ceased, colourless crystals formed. These crystals were isolated and immediately analyzed by X-ray diffraction. The molecular structure showed the trisubstituted compound **11** (see Figure 8). The clear THF solution turned yellow and slowly to dark red on standing. Within days, **11** crystallized in quantitative yield. The dark red THF solution contained mainly $LiAlH_4$. We take the red colour as an indication that a small amount of lithiated triphenylmethoxide is present in solution.

The reaction of $NaAlH_4$ with two equivalents of $HOCPh_3$ in THF, in contrast to that of the lithium salt, results in the formation of $NaAlH_2(OCPh_3)_2$ (**3**) without side products. Crystallization at 2 °C gave colourless prisms of **3**. The molecular structure of this compound (Figure 4, Table 3) is quite similar to that of **2**.

Most of the disproportionation products were insoluble in diethyl ether. Reactions with R = Me, Et, *t*Bu were therefore not examined further. In the case of R = $t\text{Bu}_2\text{MeCOH}$, the ^{27}Al NMR spectrum of the reaction solution showed only one signal at $\delta = 109$, in accordance with a dialkoxydihydridoaluminate. Although colourless prisms of **4** separated from a diethyl ether/pentane solution at −20 °C, they were strongly intergrown, and the crystal structure could therefore not be determined. It is likely that **4** has a structure similar to $[LiAl(H)\{OC(Me)t\text{Bu}_2\}_3]$ (**13**) (see Figure 10), with a central four-membered LiO_2Al ring and a tetracoordinate lithium centre. The IR spectrum shows two strong bands at 1781 and 1739 cm^{-1} for the symmetric and antisymmetric AlH_2 stretching vibrations, as expected for terminal Al–H bonds.

The reaction of $LiAlH_4$ with two equivalents of 2,6-$t\text{Bu}_2C_6H_3OH$ also gave an analytically pure lithium diaryloxydihydridoaluminate, as shown by ^{27}Al, ^1H, and ^{13}C NMR spectroscopy. This contrasts with the reported observation of several aluminium aryloxide compounds.[16] Crystallization at 2 °C yielded colourless prisms of **5**. There are two independent monomeric molecules in the unit cell, one of which has a crystallographic C_2 axis. As Figure 5 shows, the lithium cation is no longer coordinated by oxygen atoms, as in the structures of **2** and **3**, but to two hydrogen atoms to form two Li-H-Al three-centre, two-electron bonds in a planar four-membered LiH_2Al ring (Table 4). The reason for this coordination mode is the large steric demand of the two 2,6-$t\text{Bu}_2C_6H_3O$ sub-

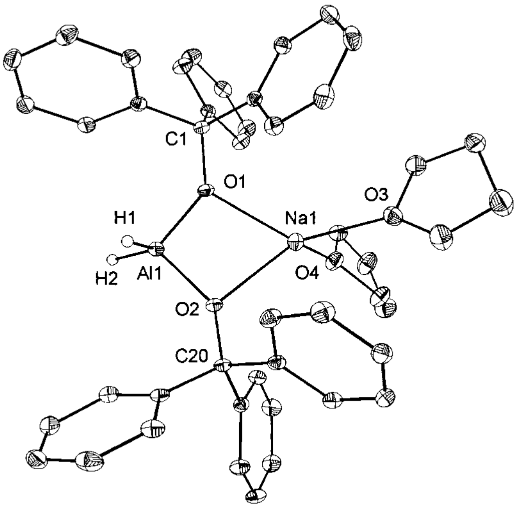


Figure 4. Crystal structure of **3**.

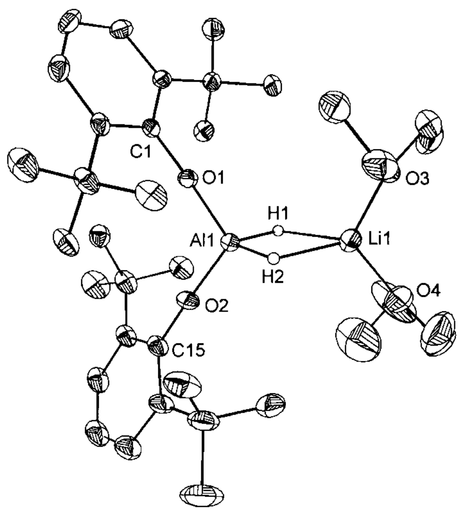


Figure 5. Crystal structure of **5**.

Table 3. Selected interatomic distances [Å] and angles [°] for **3**.

Al1–H1	1.49(3)	H1-Al1-H2	115(1)
Al1–H2	1.52(3)	H1-Al1-O1	110(1)
Al1–O1	1.784(2)	H1-Al1-O2	111(1)
Al1–O2	1.783(2)	H2-Al1-O1	112(1)
Na1–O1	2.350(2)	H2-Al1-O2	111(1)
Na1–O2	2.339(2)	O1-Al1-O2	95.44(7)
Na1–O3	2.289(2)	Al1-O1-Na1	97.54(7)
Na1–O4	2.395(2)	Al1-O2-Na1	97.97(7)
		O1-Na1-O2	68.50(6)
		O1-Na1-O3	131.45(7)
		O1-Na1-O4	119.35(7)
		O2-Na1-O3	143.89(7)
		O2-Na1-O4	112.14(7)
		O3-Na1-O4	85.29(7)

Table 4. Selected interatomic distances [Å] and angles [°] for **5**.

Al1–H1	1.53(3)	H1-Al1-O1	114(1)
Al1–H2	1.55(3)	H1-Al1-O2	110(1)
Li1–H1	2.03(3)	H2-Al1-O1	108(1)
Li1–H2	1.97(3)	H2-Al1-O2	113(1)
Al1–O1	1.713(2)	O1-Al1-O2	113.5(1)
Al1–O2	1.705(2)	H1-Al1-H2	98(2)
Li1–O3	1.910(7)	Al1-H1-Li1	97(1)
Li1–O4	1.880(7)	Al1-H2-Li1	94(2)
Al1–Li1	2.638(6)	H1-Li1-H2	71(1)
		O3-Li1-O4	121.3(3)
		H1-Li1-O3	121.4(9)
		H1-Li1-O4	110.3(9)
		H2-Li1-O3	99(1)
		H2-Li1-O4	124(1)

stituents at the aluminium centre. A similar structure is realized in $[Li(Et_2O)_2(\mu\text{-}H)_2Al\{N(SiMe_3)_2\}_2]$,[19] which also contains a four-membered LiH_2Al ring. Again, the coordination geometry around the lithium and aluminium centres is distorted tetrahedral. The H1-Al1-H2 angle in **5** of 98(2)° is quite obtuse and similar to the corresponding value in the amido alanate (94.3°),[19] and only 8° smaller than that of **1** (106(1)°). The H1-Li1-H2 angle of 71(1)° is 26° smaller than the corresponding value for compound **1**. The Li–H distances of 2.00(3) Å are similar to those in $LiAlH_4$ (1.98(2) Å).[17]

When two equivalents of 2,6-tBu$_2$C$_6$H$_3$OH were treated with $LiAlH_4$ in THF at −20 °C, the reaction mixture remained clear and the ^{27}Al NMR spectrum showed only one signal at $\delta = 89$; hence the disubstituted product $LiAlH_2(OR)_2$ is stable in THF. Colourless needles of **6a** formed on storing the reaction mixture at −78 °C but melted above −25 °C. Since the crystals were strongly intergrown, the structure could not be fully refined, and the presence of several disordered THF molecules in the unit cell prevents meaningful discussion of bond lengths and angles. The most important feature of the gross structure is that the lithium cation is coordinated to four THF molecules and therefore has no contact to the hydride or aryloxyl ligands of the aluminium centre. We assume that **6a** is the dominant species in THF solution.

When the solvent was removed, a colourless solid with a lower THF content separated (**6b**). Recrystallization of the product at 2 °C gave needles suitable for X-ray structure determination (Figure 6). In **6b** the lithium cation is bound to three THF molecules and to one hydrido group of the $[AlH_2(RO)_2]^-$ ion. The Li–H distance (2.01(5) Å; see Table 5) is the same as observed for **5** (av. 2.00(3) Å). The large Al-H2-Li1 angle (140(3)°) compared to the corresponding angle of 128(1)° for **1** is notable. Compared to the diethyl etherate **5**, the stronger Lewis base THF makes Li-μ^1 coordination to one hydride feasible, similar to that in $Mg(AlH_4)_2\cdot 4THF$.[21] Both aluminium and lithium centres are coordinated in a slightly distorted tetrahedral fashion. The Al–H bond lengths (av 1.54(3) Å) lie in the range observed for other aryloxyhydridoaluminates.

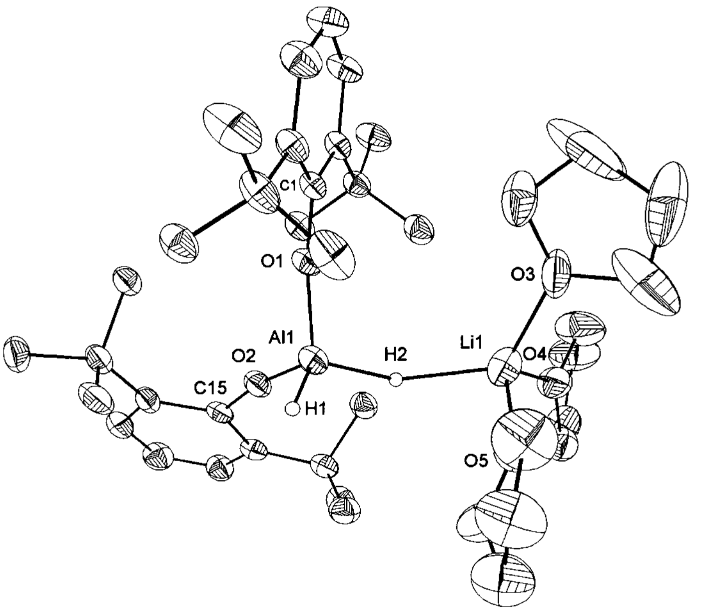


Figure 6. Crystal structure of **6b**.

Table 5. Selected interatomic distances [Å] and angles [°] for **6b**.

Al1–H1	1.52(6)	H1-Al1-H2	106(3)
Al1–H2	1.57(5)	H1-Al1-O1	115(2)
Li1–H2	2.01(5)	H1-Al1-O2	109(2)
Al1–O1	1.730(5)	H2-Al1-O1	108(2)
Al1–O2	1.729(5)	H2-Al1-O2	111(2)
Li1–O3	1.93(2)	O1-Al1-O2	107.7(2)
Li1–O4	1.92(2)	Al1-H2-Li1	140(3)
Li1–O5	1.85(2)	H2-Li1-O3	128(2)
		H2-Li1-O4	105(2)
		H2-Li1-O5	100(2)

The reaction of two equivalents of 2,6-tBu$_2$C$_6$H$_3$OH with $NaAlH_4$ in THF at −20 °C also leads to one signal in the ^{27}Al NMR spectrum ($\delta = 88$), consistent with the disubstituted sodium salt **7**. Two strong $\nu(AlH_2)$ IR bands at 1793 and 1709 cm^{-1} suggest that its structure is similar to that of **6b**. The three THF molecules which were found analytically are most likely attached to the cation.

When a THF solution of **6b** was heated to reflux for two days, the clear solution turned light yellow, and the ^{27}Al NMR signal shifted to high field ($\delta = 51$). The IR spectrum showed the absence of AlH bands. Colourless crystals of **8** were obtained from THF/hexane at −20 °C. An X-ray structure analysis of the crystals showed that the two hydrido groups of **6b** were replaced by two butoxyl groups, which bridge the aluminium and the lithium centres (Figure 7). The central four-membered LiO_2Al ring is planar (see Table 6). In addition, the lithium cation bears two THF molecules. Hence, **8** results from THF cleavage. There are two possible mechanisms for this ring-opening reaction.[22] First, an equilibrium could exist in THF between **6b** and the lithium aryloxide **16** and result in the formation of a Lewis acidic aryloxyaluminium dihydride, coordinated by THF [Eq. (7);

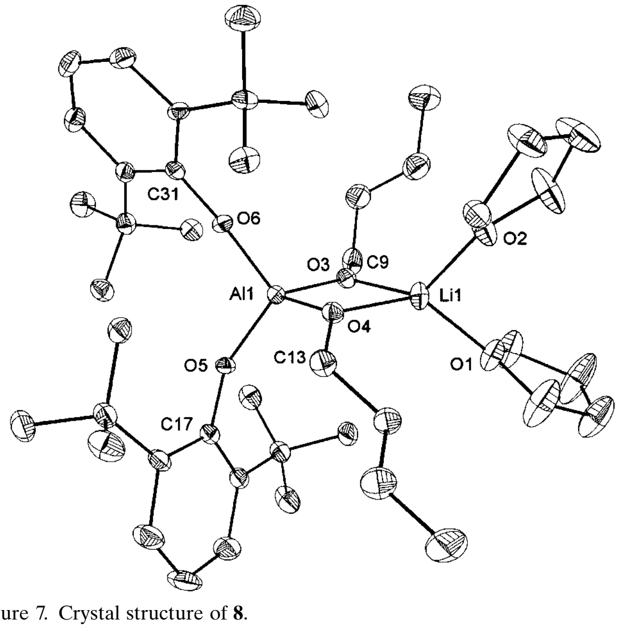


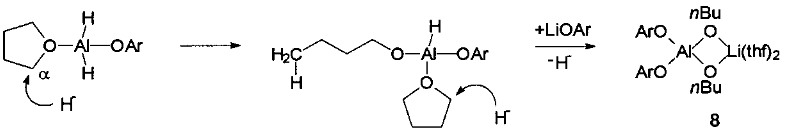
Figure 7. Crystal structure of **8**.

Table 6. Selected interatomic distances [Å] and angles [°] for **8**.

Al1–O5	1.724(3)	O5-Al1-O6	107.0(1)
Al1–O6	1.714(3)	O3-Al1-O6	107.3(1)
Al1–O3	1.762(3)	O4-Al1-O5	108.4(1)
Al1–O4	1.759(3)	O3-Al1-O5	120.8(1)
Li1–O3	1.960(7)	O4-Al1-O6	122.9(1)
Li1–O4	1.959(7)	O3-Al1-O4	90.9(1)
Li1–O1	1.976(8)	O3-Li1-O4	79.7(3)
Li1–O2	1.972(8)	O1-Li1-O2	98.7(3)
Li1–Al1	2.740(7)	O1-Li1-O3	113.1(4)
		O1-Li1-O4	134.5(4)
		O2-Li1-O3	131.7(5)
		O2-Li1-O4	103.5(4)
		Al1-O3-Li1	94.6(2)
		Al1-O4-Li1	94.8(2)

$$\underset{\mathbf{6b}}{LiAlH_2(OAr)_2} \xrightleftharpoons{THF} \underset{\mathbf{16}}{LiOAr} \cdot THF + AlH_2(OAr) \cdot THF \qquad (7)$$

Ar = 2,6-tBu$_2$C$_6$H$_3$O]. The function of AlH$_2$(OAr) · THF apparently is to weaken the carbon–oxygen bond so that a rearrangement or attack by hydride can occur (Scheme 1). Ring opening of lithium-coordinated THF could occur by hydride attack of **6b** at the α-carbon atom.



Scheme 1. Proposed mechanism of THF cleavage by AlH$_2$(OAr) · THF.

In the case of **7**, only one THF molecule is reduced by one hydride equivalent. Refluxing a solution of **7** in THF for 2 d results only in the formation of **9**, which has a single Al–H stretching band in the IR spectrum at 1787 cm^{-1}. Although we isolated colourless crystals from the THF solution, from which the size of the unit cell could be determined, strong disorder of the n-butoxyl group prevented a satisfactory solution of its structure. Considering the position of the infrared AlH band, it is more likely that the sodium cation is coordinated by the n-butoxyl group rather than by the hydrido group.

Alkali metal trialkoxy- and triaryloxyhydridoaluminates: The stability of alkali metal triorganyloxyhydridoaluminates MAlH(OR)$_3$ depends strongly on the solvent (S = THF or Et$_2$O), the branching of the alcohol ROH, and the cation M. Reactions of LiAlH$_4$ in Et$_2$O [Eq. (3)] with methanol, ethanol, isopropyl alcohol and phenol show that the expected MAlH(OR)$_3$ complexes exist in equilibrium with their disproportionation products [Eq. (8); $n = a + b + c + d$].[14] In

$$n\,MAlH(OR)_3 \rightleftharpoons a\,MAlH_4 + b\,MAlH_3OR + c\,MAlH_2(OR)_2 + d\,MAl(OR)_4 \quad (8)$$

these cases, a white precipitate formed, which was completely soluble in THF. For R = Me and tBu, ^{27}Al NMR and IR spectra revealed that MAlH(OR)$_3$ was the main product.

Although there is good evidence that the stability of most trisubstituted complexes [AlH(OR)$_3$]$^-$ is higher in THF, some are unstable even in this solvent (e.g., M = Li, Na; R = Me, Et). For M = Li, Na, R = Me, the dominant ^{27}Al NMR signal is a satisfactorily resolved doublet at δ = 98. However, the presence of further signals of lower intensity (δ = 129, 62, 44 and 12) shows that ligand redistribution takes place to a certain extent. This observation contrasts with previous experience that LiAlH(OMe)$_3$ is stable in THF.[14]

Organyloxyhydridoaluminates with bulky R groups (R = tBu, tBu$_2$MeC, (−)-Ment, Ph$_3$C, 2,6-Me$_2$C$_6$H$_3$, 2,6-iPr$_2$C$_6$H$_3$) are stable in THF and show no tendency to disproportionate. The ^{27}Al NMR spectra of these compounds contain one broad singlet for which the ^{27}Al–^{1}H coupling could not be resolved. In the case of (−)-menthol for example, the NMR data show that only the trisubstituted product **10** is present in solution. Although we failed to obtain single crystals, it is most likely that the lithium cation is coordinated to two oxygen atoms of the menthoxyl ligands in a similar manner as in **2**. We base our proposition on the observation of a single sharp Al–H stretching band at 1752 cm^{-1}, which is characteristic of a terminal Al–H bond. The reaction of three equivalents of Ph$_3$COH with lithium tetrahydridoaluminate gave [Li(thf)$_3$(μ-H)Al(OCPh$_3$)$_3$] · 0.5 THF (**11**). However, most of the material was sparingly soluble in THF. Compound **11** was obtained as single crystals in nearly quantitative yield by the reaction of LiAlH$_4$ with two equivalents of Ph$_3$COH according to Equation (6). As its molecular structure (Figure 8) shows, the Li cation is attached to the hydride but not to oxygen atoms of the Ph$_3$CO ligands because of severe steric crowding. The aluminium and lithium centres are tetrahedral and are linked by a linear hydride bridge (180°). The bridge has a C_3 symmetry axis (space group $R3$). The Li–H distance of 1.83(7) Å (Table 7) is much shorter than that of LiAlH$_4$ (1.98(2) Å).[17]

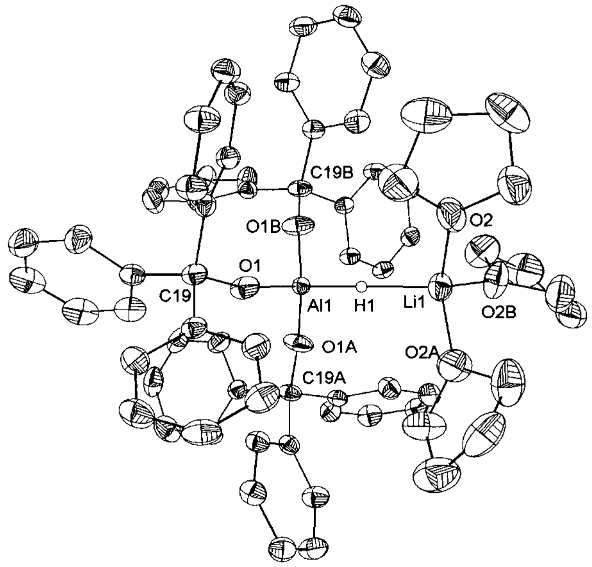


Figure 8. Crystal structure of **11**.

Table 7. Selected interatomic distances [Å] and angles [°] for **11**.

Al1–H1	1.50(7)	Al1-H1-Li1	180(4)
Li1–H1	1.83(7)	H1-Al1-O1, O1A, O1B	107.7(1)
Al1–O1, O1A, O1B	1.688(2)	O1-Al1-O1A, O1B	111.2(1)
Li1–O2, O2A, O2B	1.897(4)	O1A-Al1-O1B	111.2(1)
		H1-Li1-O2, O2A, O2B	109.2(3)
		O2-Li1-O2A, O2B	109.7(3)
		O2A-Li1-O2B	109.7(3)

The reaction of three equivalents of Ph_3COH with sodium tetrahydridoaluminate gave $[Na(thf)_3(\mu\text{-}H)Al(OCPh_3)_3]$ (**12**). Again, the steric demand of the Ph_3CO ligands is the reason for the formation of a hydride bridge between the tetracoordinate aluminium and sodium centres (Figure 9). Compared to the lithium tricarbinoyloxyhydridoaluminate **11** (see above), the sodium species **12** reveals a new structural pattern for the interaction of the hydride and the cation. The Al-H-Na bridge forms an angle of 123(2)°, as opposed to the linear Al-H-Li arrangement in **11** (see Table 8). This angle about the hydrogen atom is even smaller than the Al-H-Li angle in **5** (140(3)°), but much larger than the Al-H-Li angles in **6b** (av 96(2)°). Whereas the Al–H bond length is not significantly longer than those of the other alkoxyhydridoaluminates (1.50 Å), the Na–H distance (2.18(4) Å) is much shorter than those of $NaAlH_4$ (av 2.497(7) Å).[23] The coordination sphere around the aluminium atom is best described as a tetrahedron. This also holds for the Na centre, but with noticeable distortion. Due to severe disorder, the THF ligands could only be refined with isotropic displacement parameters. Therefore, the final R value is rather high, and bonding parameters are not accurate enough to allow a detailed discussion.

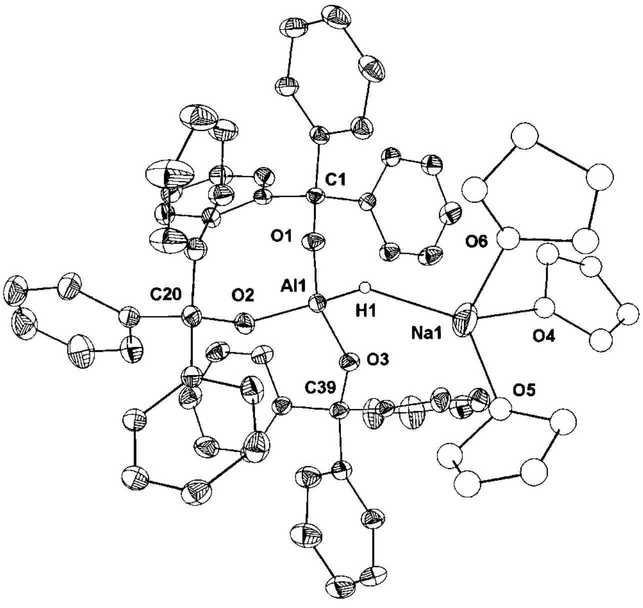


Figure 9. Crystal structure of **12**.

Table 8. Selected interatomic distances [Å] and angles [°] for **12**.

Al1–H1	1.50(4)	Al1-H1-Na1	123(2)
Na1–H1	2.18(4)	H1-Al1-O1	107(1)
Al1–O1	1.705(3)	H1-Al1-O2	112(1)
Al1–O2	1.717(3)	H1-Al1-O3	104(1)
Al1–O3	1.737(3)	O1-Al1-O2	112.3(2)
Na1–O4	2.266(5)	O1-Al1-O3	110.0(2)
Na1–O5	2.223(6)	O2-Al1-O3	112.1(1)
Na1–O6	2.316(8)	H1-Na1-O4	141(1)
		H1-Na1-O5	117.6(9)
		H1-Na1-O6	93(1)
		O4-Na1-O5	99.9(2)
		O4-Na1-O6	91.8(2)
		O5-Na1-O6	96.7(3)

$LiAlH(OR)_3$ compounds with $R = t\text{Bu}_2\text{MeC}$, $2,6\text{-}Me_2C_6H_3$, and $2,6\text{-}i\text{Pr}_2C_6H_3$ are also stable when prepared in diethyl ether. Compound **13** was obtained by reaction of three equivalents of $t\text{Bu}_2\text{MeCOH}$ with $LiAlH_4$. Colourless plates, suitable for X-ray structure determination crystallized from ethereal solution. The lithium atom is coordinated by the oxygen atoms of two alkoxyl ligands to give a planar four-membered AlO_2Li ring (Figure 10, Table 9). In addition, one diethyl ether molecule is coordinated to the lithium centre. Thus, the lithium atom is tricoordinate and lies almost in the plane of the O atoms. A planar environment is found for the two bridging oxygen atoms.

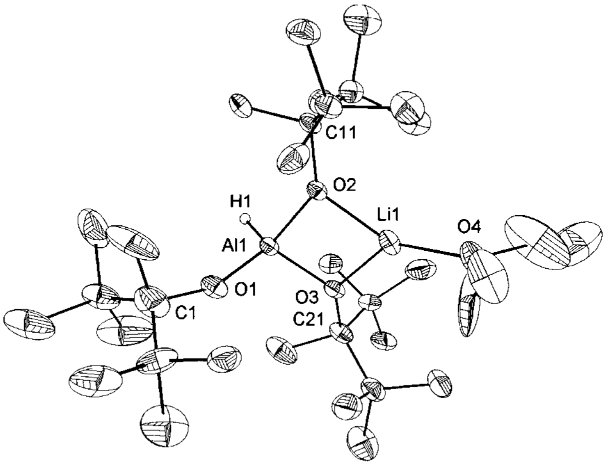


Figure 10. Crystal structure of **13**.

Table 9. Selected interatomic distances [Å] and angles [°] for **13**.

Al1–H1	1.41(5)	O2-Al1-O3	90.9(1)
Al1–O1	1.701(4)	O1-Al1-O2	116.1(2)
Al1–O2	1.796(3)	O1-Al1-O3	113.5(2)
Al1–O3	1.797(3)	H1-Al1-O1	113(2)
Li1–O2	1.910(8)	H1-Al1-O2	109(2)
Li1–O3	1.917(9)	H1-Al1-O3	112(2)
Li1–O4	1.976(9)	O2-Li1-O3	83.9(3)
Al1–Li1	2.670(8)	O2-Li1-O4	135.2(5)
		O3-Li1-O4	135.8(4)
		Al1-O2-Li1	92.1(3)
		Al1-O3-Li1	91.9(3)

The same structural pattern is observed for the lithium triaryloxyhydridoaluminate **14**, in which two 2,6-di-isopropylphenoxyl ligands bridge the aluminium and lithium centres (Figure 11). The structural data of **14** (Table 10) are similar to those of **13**. Clearly, the two *ortho* isopropyl groups on the phenyl ring are not sufficiently bulky to prevent a coordination of the O atoms and promote coordination of the Li cation towards the hydride ligand.

The reaction of $LiAlH_4$ with three equivalents of $2,6\text{-}Me_2C_6H_3OH$ also resulted in the formation of the expected triaryloxyhydridoaluminate **15** as colourless prisms. Although the molecular structure could not be solved by X-ray structure analysis, it is reasonable to assume a structure analogous to **14**, in which lithium is coordinated by oxygen atoms rather than by hydrido groups. This argument is based on the single sharp IR band at 1825 cm^{-1}, which is characteristic of a terminal AlH stretching vibration.

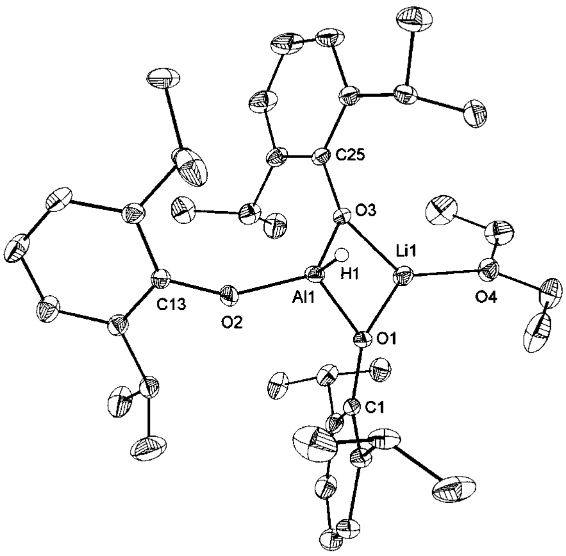


Figure 11. Crystal structure of **14**.

Table 10. Selected interatomic distances [Å] and angles [°] for **14**.

Al1 - H1	1.47(2)	O1-Al1-O3	90.29(6)
Al1 - O2	1.701(2)	O1-Al1-O2	108.54(7)
Al1 - O1	1.787(1)	O2-Al1-O3	114.64(8)
Al1 - O3	1.786(1)	H1-Al1-O2	115.5(8)
Li1 - O1	1.912(3)	H1-Al1-O1	113.3(8)
Li1 - O3	1.912(3)	H1-Al1-O3	111.8(8)
Li1 - O4	1.892(4)	O1-Li1-O3	82.9(1)
Al1 - Li1	2.672(3)	O1-Li1-O4	128.6(2)
		O3-Li1-O4	134.1(2)
		Al1-O1-Li1	92.4(1)
		Al1-O3-Li1	92.5(1)

We were interested in the question whether the reaction of $LiAlH_4$ with three equivalents of 2,6-di-*tert*-butylphenol, which is more bulky than 2,6-diisopropylphenol, would lead to a tris(2,6-di-*tert*-butylphenoxy)hydridoaluminate. However, in accordance with the results described in the literature,[7, 15, 16, 24, 25] we observed the evolution of at most two equivalents of hydrogen gas in THF at room temperature. We attribute this to steric hindrance in the formation of $[LiAlH(OC_6H_3t Bu_2\text{-}2,6)_3]$. Heteronuclear NMR and IR spectroscopy on the solution showed that **6b** and residual 2,6-di-*tert*-butylphenol in a molar ratio of 1:1 were present after gas evolution had ceased. Stirring the reaction mixture for two days at room temperature resulted in the formation of the lithium aryloxide $[Li(THF)(OC_6H_3t Bu_2\text{-}2,6)]_2$ (**16**) and the THF-cleavage product **8** besides the phenol and other side products. Colourless crystals of **16**, which is dimeric,[26] were obtained in low yields at 0 °C by adding pentane to a sample of the reaction mixture. The isolation of the lithium aryloxide **16** proves that the lithium diaryloxyhydridoaluminate **6b** decomposes according to Equation (7) to a certain extent. Heating the reaction mixture induces cleavage of THF by the tricoordinate aluminium species.

In contrast to the reaction in THF, alcoholysis in diethyl ether liberates three equivalents of hydrogen when the reaction mixture is stirred for three hours at room temperature. In the course of this reaction a precipitate formed and turned out to consist of a mixture of the aryloxide $[Li(Et_2O)(OC_6H_2t Bu_2\text{-}2,6)]$ and some neutral aryloxyalane **17** [Eqs. (9) and (10); Ar = 2,6-$t Bu_2C_6H_3O$]. Solely the aryloxy

$$LiAlH_2(OAr)_2 \overset{Et_2O}{\rightleftharpoons} LiOAr + H_2Al(OAr) \quad (9)$$

$$H_2Al(OAr) + ArOH \xrightarrow{Et_2O} \underset{17}{HAl(OAr)_2} \cdot Et_2O + H_2 \quad (10)$$

alane **17** remains in solution. Crystallization at 0 °C gave **17** as colourless prisms in 70% yield. The IR spectrum of **17** shows one sharp band at 1893 cm^{-1}, consistent with a monomeric structure. As Figure 12 shows, tetracoordination of the aluminium centre is realized by the coordination of one diethyl ether molecule, and the deviation from tetrahedral geometry is large, whereby the smallest angles are associated with the oxygen atom of the Lewis base (Table 11). An analogous structure was found for $[AlH(OEt_2)(OC_6H_2t Bu_2\text{-}2,6\text{-}Me\text{-}4)_2]$ by Barron et al.; however they also found evidence for a dimeric associate.[15]

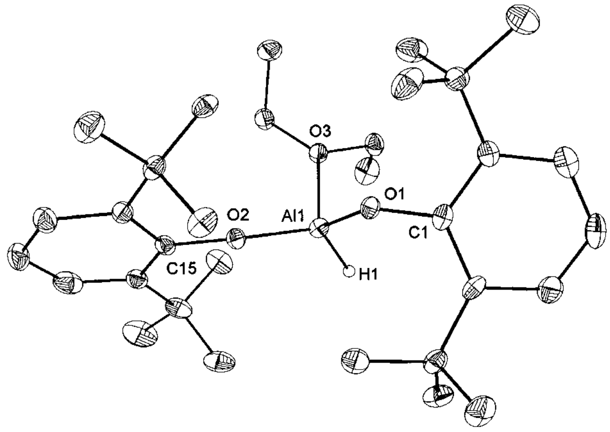


Figure 12. Crystal structure of **16**.

Table 11. Selected interatomic distances [Å] and angles [°] for **17**.

Al1 - H1	1.48(6)	H1-Al1-O1	116(2)
Al1 - O1	1.734(5)	H1-Al1-O2	118(2)
Al1 - O2	1.684(5)	H1-Al1-O3	98(2)
Al1 - O3	1.900(5)	O1-Al1-O2	113.2(2)
		O1-Al1-O3	106.3(2)
		O2-Al1-O3	102.2(2)

^{27}Al and ^{7}Li NMR spectroscopy: The equilibrium position of Equation (4) can be determined qualitatively by ^{27}Al NMR spectroscopy, because in most cases there is a correlation between the chemical shift and the degree of association and substitution.[27] The shielding of the Al nucleus increases with increasing number of RO groups attached to the Al centre, a trend found for $R'_nAl(OR)_{3-n} \cdot L$.[27c] An assignment of the ^{27}Al NMR signals to the organyloxyhydridoaluminates was reported by Gavrilenko et al. (Figure 13).[6, 7]

With a few exceptions (see below), the ^{27}Al NMR shifts of hydridoaluminates having less bulky organyloxy groups fit into this scheme. $LiAlH_4$ itself is clearly characterized by its

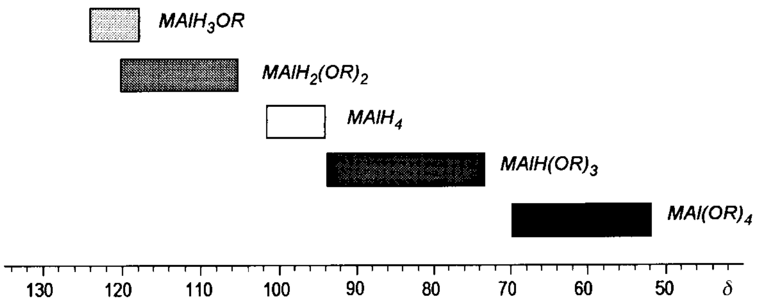


Figure 13. Chemical shift ranges for ^{27}Al NMR in metal alkoxy/aryloxy aluminium hydrides ($M = Li$, Na).

quintet in the ^{1}H-coupled ^{27}Al spectrum ($^1J_{Al,H} = 174$ Hz).[28] However, the signals assigned to the other species are broad, and coupling to the H atoms could not be resolved due to the high asymmetry around the Al atom, which allows rapid relaxation due to the quadrupole moment of the ^{27}Al nucleus. However, Hermánek et al. observed coupling to ^{1}H in $[N(C_4H_9)_4][AlH_{4-n}(OR)_n]$ by replacing Li^+ or Na^+ with the $(C_4H_9)_4N^+$ ion.[29] The signals were substantially narrower due to the expected weak interaction of the R_4N^+ ion with the anion. Secondly, the asymmetry of the alkyl- and aryloxy-substituted hydridoaluminates may also be due to the interaction of the cations Li^+ or Na^+ with oxygen atoms or hydrido groups in solution. In this context, it is important to know the extent to which the cation interactions in the solid state are retained in solution. The ^{27}Al NMR signals of the compounds **1**, **5**, **6a**, **6b**, **7**, **11** and **12** fit less well to Figure 13; their chemical shifts lie approximately 20 ppm to higher field than expected. These are the compounds in which the alkali metal cation is coordinated to a hydridic hydrogen but not to an oxygen atom of the $[AlH_{4-n}(OR)_n]^-$ unit in the solid state. All the other cases involve coordination of M to OR. If the M–H interaction is maintained in ether and benzene or toluene solutions, then the two-coordinate oxygen atoms provide a better shielding of the aluminium centre and lead to a high-field shift. If electron density at the aluminium centre is lowered by coordination of Li or Na to the oxygen ligands, then the aluminium signals lie at comparatively low field. This effect has proven to be even more pronounced in benzene solution (see Experimental Section). Hence, the aluminium chemical shift is a useful tool for predicting the cation–ligand coordination in solution.

The ^{7}Li NMR spectra are also helpful in obtaining information on the state of solvation of the $LiAlH_{4-n}(OR)_n$ species. Reaction mixtures in THF or Et_2O containing several aluminium species show only one ^{7}Li signal at a given temperature, and in each case it lies in the range of $\Delta\delta = \pm 1$. We take this as an evidence for the presence of separated ion pairs or rapid exchange among the various species.

Unlike Stalke et al., who succeeded in resolving Li–H coupling in the amidolithium compound $[Li(Et_2O)_2(\mu\text{-}H)_2AlN(SiMe_3)_2]_2$,[19] we were unable to detect Li–H coupling for **1**, **5**, **6b**, **11** and **12** at any temperature in THF, Et_2O or toluene. As the X-ray structure of the solvent-separated structure **6a** shows, coordination of THF competes favourably with Li-H-Al interactions.

Conclusions

The reaction of lithium and sodium aluminium hydrides with alcohols and phenols in ether solvents (Et_2O, THF) provides a convenient route to mono-, di- and triorganyloxyhydridoaluminates. The tendency of these species to undergo disproportionation [Eqs. (4), (6) and (8)] is mainly dependent on the size and the branching of the organic moiety R. The degree of disproportionation can easily be monitored by ^{27}Al NMR spectroscopy. The stability of some of these species depends on the solubility in the given solvent. Of thirteen characterized lithium or sodium organyloxyhydridoaluminates, nine crystal structures were determined. Coordination of the cation (lithium or sodium) to the anion occurs through O or H atoms, depending on the steric requirements of the organic ligand.[30] These results on the stability and the structure of these complexes are of fundamental importance in understanding their function as reducing agents towards organic functional groups.

Experimental Section

All experiments were performed by Schlenk techniques under an atmosphere of dry nitrogen as all compounds are oxygen- and especially moisture-sensitive. Solvents were dried over $LiAlH_4$ and freshly distilled prior to use. Lithium and sodium tetrahydridoaluminate were dissolved in diethyl ether or THF, then filtered and the concentration of the solution determined by titration of aluminium with EDTA/$ZnSO_4$.[31] Alcohols were recrystallized from ethereal solutions or distilled and dried according to literature methods.[32]

Elemental analyses were performed by the analytical laboratory of the Institut für Anorganische Chemie der Universität München. Incorrect H and C values may result from loss of coordinated solvent or from formation of aluminium carbide. Aluminium was determined by titration with EDTA/$ZnSO_4$,[31] hydridic hydrogen was collected as hydrogen gas after acidic hydrolysis of the compound by using a Toeppler pump. NMR spectra were recorded at 25 °C on Jeol-270 and Jeol-400 spectrometers. FT-IR spectra were measured on a Nicolet 520 spectrometer as Hostaflon (4000–1400 cm^{-1}) and Nujol mulls (1400–400 cm^{-1}). Melting points were measured in sealed glass tubes and are uncorrected.

General procedure for the preparation of the organyloxyhydridoaluminates: The stoichiometric amount of alcohol or phenol was dissolved in ether and slowly added to a stirred standardized solution of the tetrahydridoaluminate in the ether at the quoted temperature. The volume of hydrogen evolved was measured.

1: 2,6-$tBu_2C_6H_3OH$ (3.85 g, 18.64 mmol) in Et_2O (30 mL); $LiAlH_4$ (18.64 mmol) in Et_2O (20 mL) at 24 °C. Hydrogen gas was immediately liberated (465 mL, 100 %). The reaction mixture was stirred at ambient temperature for 3 h and insoluble material was removed by means of a G4 frit. The clear solution was then stored at 4 °C. After 1 h crystals of **1** had formed.[33] Fractional crystallization at −20 °C gave 5.74 g (78.9 %) of **1**. M.p. 69 °C (decomp); ^{27}Al NMR (70 MHz, C_6D_6): $\delta = 97$ ($h_{1/2} = 1091$ Hz), (Et_2O): $\delta = 101$ ($h_{1/2} = 687$ Hz); ^{7}Li NMR (105 MHz, C_6D_6): $\delta = -0.3$ ($h_{1/2} = 5.3$ Hz); (Et_2O): $\delta = -0.9$ ($h_{1/2} = 2.7$ Hz); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.96$ (t, 24 H; $CH_3(Et_2O)$), 1.68 (s, 36 H, $CH_3(tBu)$), 3.20 (q, 16 H, $CH_2(Et_2O)$), ca. 3.8 (br s, 6 H, AlH_3), 6.90 (dd, $^3J(H,H) = 7.7$ Hz, 2 H, p-H(Ar)), 7.39 (d, $^3J(H,H) = 7.7$ Hz, 4 H, m-H(Ar)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.8$ ($CH_3(Et_2O)$), 31.5 (CH_3(Ar)), 35.3 ($C_q(tBu)$), 65.8 ($CH_2(Et_2O)$), 117.6 (p-C(Ar)), 125.3 (m-C(Ar)), 139.3 (o-C(Ar)), 158.0 (i-C(Ar)); IR: $\tilde{\nu} = 3085$ (w), 3066 (w), 2954 (vs, br), 2912 (s), 2871 (s), 1797-1704 (vs, vbr), 1654 (m, sh, $\nu(AlH_3)$), 1583 (m), 1482 (s), 1459 (s), 1446 (s), 1420 (vs), 1387 (vs), 1356 (s), 1286 (vs, br), 1261 (s), 1186 (m), 1154 (m), 1130 (m), 1095 (vs), 1065 (vs), 1023 (s), 911 (s), 882 (vs), 882 (vs), 857 (s), 832 (s), 814 (vs), 795 (vs), 698 (m), 689 (s), 676 cm^{-1} (s); $C_{22}H_{44}O_3AlLi$ (390.49): calcd: C 67.67, H 11.36, Al 6.91; found: C 66.98, H 11.18, Al 6.14.

2: (−)-MentOH (2.85 g, 18.3 mmol) in THF (10 mL); $LiAlH_4$ (9.13 mmol) in THF (10 mL) at −20 °C, was stirred for 1 h at room temperature. Pentane (5 mL) was added to the solution and colourless crystals of **2** formed at −20 °C within four months.[33] Yield: 1.04 g (20.3 %). M.p. 217–219 °C (decomp); ^{27}Al NMR (70 MHz, [D$_8$]THF): $\delta = 116$ (br); ^{7}Li NMR (105 MHz, [D$_8$]THF): $\delta = -0.2$ ($h_{1/2} = 4.0$ Hz); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 0.73-0.94$ (m), 1.28–1.44 (m), 1.51–1.63 (m), 1.72 (m), 1.77 (m, 12 H, β-C*H*$_2$(THF)), 1.91–2.06 (m), 2.41–2.55 (m), 3.30–3.44 (m), 3.61 (m, 12 H, α-C*H*$_2$(THF)); ^{13}C NMR (100 MHz, [D$_8$]THF): $\delta = 16.2$ (C_8), 21.9 (C_9), 22.9 (C_{10}), 23.5 (C_7), 25.6 (β-*C*H$_2$(THF)), 26.2 (C_5), 32.7 (C_3), 36.0 (C_4), 48.9 (C_2), 52.8 (C_6), 68.0 (α-*C*H$_2$(THF)), 70.8 (C_1); IR: $\tilde{\nu} = 2951$ (vs), 2918 (vs), 2895 (vs), 2884 (vs), 2868 (vs), 2860 (vs), 2849 (vs), 1817 (m, $\nu_{as,s}$(AlH$_2$)), 1754 (s, $\nu_{as,s}$(AlH$_2$)), 1464 (m), 1475 (m), 1444 (m), 1383 (m), 1368 (s), 1346 (m), 1286 (w, br), 1267 (m), 1234 (m), 1180 (s), 1159 (s), 1150 (m, sh), 1110 (vs), 1098 (vs), 1082 (vs), 1065 (vs), 1050 (vs), 1033 (vs), 997 (s), 977 (s), 922 (s), 897 (vs), 877 (vs), 849 (vs), 782 (vs), 769 (vs, sh), 744 (vs, br), 717 (vs, sh), 707 (vs), 673 cm^{-1} (m, sh); $C_{32}H_{64}AlLiO_5$ (562.75): calcd: C 68.54, H 11.50, Al 4.79; found: C 66.69, H 11.23, Al 4.32.

3: Ph_3COH (10.38g, 39.86 mmol) in THF (30 mL); $NaAlH_4$ (19.93 mmol) in THF (20 mL) at ambient temperature. The reaction mixture immediately turned reddish. The solution became dark red when stored at 4 °C. Colourless crystals of **3** formed after 12 h.[33] Crystallization at −20 °C yielded 8.25 g (91.0 %) **3**. M.p. >120 °C (decomp); ^{27}Al NMR (70 MHz, [D$_8$]THF): $\delta = 95$ ($h_{1/2} = 1986$ Hz); ^{23}Na NMR (71 MHz, [D$_8$]THF): $\delta = -4.1$ (br); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 1.76$ (m, 8 H, β-C*H*$_2$(THF)), 3.61 (m, 8 H, α-C*H*$_2$(THF)), 7.08–7.11, 7.34–7.37 (m, 30 H, C*H*(Ar)); ^{13}C NMR (100 MHz, [D$_8$]THF): $\delta = 26.1$ (β-*C*H$_2$(THF)), 68.0 (α-*C*H$_2$(THF)), 84.1 (Ph$_3$*C*O), 126.0 (*o*-*C*(Ar)), 127.4 (*p*-*C*(Ar)), 129.4 (*m*-*C*(Ar)), 152.1 (*i*-*C*(Ar)); IR: $\tilde{\nu} = 3086$ (w), 3066 (m), 3055 (s), 3033 (m), 3020 (s), 2978 (vs), 2952 (s), 2882 (vs), 1773 (s, $\nu_{as,s}$(AlH$_2$)), 1717 (vs, $\nu_{as,s}$(AlH$_2$)), 1596 (s), 1491 (vs), 1443 (vs), 1318 (m), 1295 (m), 1205 (s), 1195(s), 1186 (s), 1176 (s), 1163 (vs), 1101 (s), 1098 (s), 1090 (vs), 1083 (s), 1057 (vs), 1032 (vs), 1001 (s), 947 (s), 937 (m), 918 (vs), 897 (vs), 790 (vs), 772 (vs), 760 (vs), 750 (vs), 727 (vs), 698 (vs), 667 (vs), 640 cm^{-1} (vs); $C_{46}H_{48}AlNaO_4$ (714.86): calcd: C 77.29, H 6.77, Al 3.77; found: C 77.03, H 6.47, Al 3.56.

4: *t*Bu$_2$MeCOH (1.97 g, 12.5 mmol) in Et$_2$O (25 mL); $LiAlH_4$ (6.25 mmol) in Et$_2$O (15 mL) at 0 °C. Stirring was continued for 1 h at ambient temperature. Crystallization at −20 °C yielded **4** as colourless plates:[33] 1.78 g (67.4 %). M.p. 113 °C (decomp); ^{27}Al NMR (70 MHz, Et$_2$O): $\delta = 109$ ($h_{1/2} = 969$ Hz); (C$_6$D$_6$): $\delta = 111$ ($h_{1/2} = 1658$ Hz); ^{7}Li NMR (105 MHz, Et$_2$O): $\delta = -0.25$ ($h_{1/2} = 2.8$ Hz), (C$_6$D$_6$): $\delta = -0.20$ ($h_{1/2} = 6.6$ Hz); ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 1.01$ (t, ^3J(H,H) = 7.2 Hz, 12 H, C*H*$_3$(Et$_2$O)), 1.19 (s, 36 H, C*H*$_3$(*t*Bu)), 1.60 (s, 6 H, C*Me*), 3.21 (q, ^3J(H,H) = 7.2 Hz, 8 H, C*H*$_2$(Et$_2$O)); ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 14.7$ (C*H*$_3$(Et$_2$O)), 22.0 (C*Me*), 29.7 (*C*H$_3$(*t*Bu)), 42.0 (*C*Me$_3$), 65.6 (C*H*$_2$(Et$_2$O)), 81.5 (*i*-C); IR: $\tilde{\nu} =$ 2983 (vs), 2960 (vs), 2915 (vs), 2875 (vs, $\nu_{as,s}$(CH$_3$), 1822 (s), 1781 (s), 1739 (s) ($\nu_{as,s}$(AlH$_2$)), 1482 (s), 1451 (w), 1389 (vs), 1371 (vs), 1368 (vs, $\nu_{as,s}$(CH$_3$)), 1117 (vs), 1103 (vs), 1095 (vs, ν(CO)), 1059 (m), 1024 (m, sh), 1004 (s) 938 (s), 913 (s), 873 (m), 835 (s) 808 (s), 789 (vs), 774 (vs) 766 (vs), 693 (s), 665 (s), 620 cm^{-1} (s, δ(AlH$_2$), δ(AlO$_2$)); $C_{24}H_{54}AlLiO_3$ (424.61): calcd: C 67.89, H 12.82, Al 6.35; found: C 66.82, H 12.72, Al 6.25.

5: 2,6-*t*Bu$_2$C$_6$H$_3$OH (7.69 g, 37.28 mmol) in Et$_2$O (40 mL); $LiAlH_4$ (18.64 mmol) in Et$_2$O (20 mL) at 20 °C. The reaction mixture was stirred at ambient temperature for 1 h and insoluble material was removed by means of a G4 frit. The clear solution was stored at 4 °C. After 3 h crystals of **5** had formed.[33] Fractional crystallization at −20 °C gave 10.26 g (88.8 %) of **5**. M.p. 89–90 °C; ^{27}Al NMR (70 MHz, C$_6$D$_6$): $\delta = 79$ ($h_{1/2} =$ 1452 Hz), (Et$_2$O): $\delta = 76$ ($h_{1/2} = 292$ Hz); ^{7}Li NMR (105 MHz, Et$_2$O): $\delta = -0.7$ ($h_{1/2} = 16.5$ Hz); (C$_6$D$_6$): $\delta = -0.9$ ($h_{1/2} = 91.6$ Hz); ^{1}H NMR (400 MHz, C$_6$D$_6$): 0.81 (t, 13 H, C*H*$_3$(Et$_2$O)), 1.69 (s, 36 H, C*H*$_3$(*t*Bu)), 3.04 (q, 9 H, C*H*$_2$(Et$_2$O)), 6.86 (dd, ^3J(H,H) = 7.8 Hz, 2 H, *p*-*H*(Ar)), 7.39 (d, ^3J(H,H) = 7.8 Hz, 4 H, *m*-*H*(Ar); ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 14.2$ (*C*H$_3$(Et$_2$O)), 31.7 (*C*H$_3$(Ar)), 35.4 (*C*$_q$(*t*Bu)), 65.6 (*C*H$_2$(Et$_2$O)), 117.7 (*p*-*C*(Ar)), 125.5 (*m*-*C*(Ar)), 139.3 (*o*-*C*(Ar)), 157.3 (*i*-*C*(Ar)); IR: $\tilde{\nu} = 3077$ (w), 3011 (w), 2951 (vs), 2911 (vs), 2870 (vs), 1723 (s)/ 1646 (w, sh)/ 1601 (s, br, ν(AlH$_2$)), 1597 (s), 1482 (w), 1467 (s), 1452 (s), 1415 (vs), 1389 (vs), 1359 (s), 1296 (vs), 1283 (vs), 1275 (vs), 1264 (vs), 1240 (s), 1213 (m), 1202 (s), 1191 (s), 1152 (m), 1131 (m), 1121 (m), 1104 (s), 1093 (s), 1064 (s), 1022 (m), 999 (m), 913 (vs), 883 (s), 858 (m), 830 (s), 809 (vs), 750 (vs), 705 (m), 692 (m), 649 cm^{-1} (m); $C_{37.3}H_{67.3}O_{4.3}AlLi$ (619.50): calcd: C 72.38, H 10.95, Al 4.36; found: C 72.49, H 10.31, Al 4.25.

6a, 6b: 2,6-*t*Bu$_2$C$_6$H$_3$OH (7.53 g, 36.50 mmol) in THF (30 mL); $LiAlH_4$ (18.25 mmol) in THF (10 mL) at −20 °C; stirred for 1 h at room temperature. The colourless solution was stored at −78 °C, and colourless crystals of **6a** with a melting point of about −26 to −24 °C were obtained. The single crystals of **6a** were removed from the solution at −78 °C under vapours of liquid nitrogen, prepared in perfluorated polyether oil at −100 °C and mounted on the goniometer head at that temperature. Removing THF at 10^{-3} bar and 20 °C gave 10.07 g (83.2 %) of **6b** as a colourless solid. Colourless crystals of **6b** were isolated from a solution of the solid in Et$_2$O/THF (2/1) at 4 °C.[33] M.p. 68–71 °C; ^{27}Al NMR (70 MHz, C$_6$D$_6$): $\delta = 79$ ($h_{1/2} = 1903$ Hz), (THF) $\delta = 89$ ($h_{1/2} = 2807$ Hz); ^{7}Li NMR (105 MHz, C$_6$D$_6$): $\delta = -0.8$ ($h_{1/2} = 3.5$ Hz); (THF): −0.4 ($h_{1/2} = 4.3$ Hz); ^{1}H NMR (400 MHz, C$_6$D$_6$): 1.33 (m, 12 H, β-C*H*$_2$(THF)), 1.81 (s, 36 H, C*H*$_3$(*t*Bu)), 3.38 (m, 12 H, α-C*H*$_2$(THF)), 6.88 (dd, ^3J(H,H) = 7.8 Hz, 2 H, *p*-*H*(Ar)), 7.47 (d, ^3J(H,H) = 7.8 Hz, 4 H, *m*-*H*(Ar)); ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 25.3$ (β-*C*H$_2$(THF)), 31.9 (*C*H$_3$(*t*Bu)), 35.4 (C$_q$(*t*Bu)), 68.1 (α-*C*H$_2$(THF)), 116.5 (*p*-*C*(Ar)), 125.3 (*m*-*C*(Ar)) 139.5 (*o*-*C*(Ar)) 158.6 (*i*-*C*(Ar)); IR: $\tilde{\nu} = 2948$ (vs), 2908 (vs), 2891 (vs), 1812 [Hostaflon/Nujol] (m, br), 1785 [Nujol] (m, br), 1717 [Hostaflon/Nujol] (s, br,ν(AlH$_2$)), 1583 (m), 1476 (m, sh), 1464 (s), 1457 (s), 1416 (vs), 1387 (vs), 1358 (s), 1282 (vs), 1260 (vs), 1131 (s), 1104 (s), 1045 (vs), 901 (vs), 885 (vs), 829 (vs), 793 (vs, br), 746 (vs), 695 (s), 686 cm^{-1} (s); IR (THF): $\tilde{\nu} = 1781$ (s), 1723 cm^{-1} (vs, ν(AlH$_2$)); $C_{40}H_{68}O_5AlLi$ (662.90): calcd: C 72.48, H 10.34, Al 4.07, H$^-$ 0.30; found: C 71.62, H 10.34, Al 3.77, H$^-$ 0.21.

7: 2,6-*t*Bu$_2$C$_6$H$_3$OH (8.22 g, 39.86 mmol) in THF (20 mL); $NaAlH_4$ (19.93 mmol) in THF (15 mL) at −20 °C; stirred for 2 h at room temperature. The solvent was removed in a vacuum at 0 °C, and the colourless solid dried in vacuum to give 12.35 g (91.3 %) of **7**. M.p. 154–157 °C; ^{27}Al NMR (70 MHz, [D$_8$]THF): $\delta = 88$ ($h_{1/2} = 2464$ Hz); ^{23}Na NMR (70 MHz, [D$_8$]THF): $\delta = -8.5$ ($h_{1/2} = 92.0$ Hz); ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta =$ 1.45 (s, 36 H, C*H*$_3$(*t*Bu)), 1.77 (m, 12 H, β-C*H*$_2$(THF)), 3.61 (m, 12 H, α-C*H*$_2$(THF)), 6.31 (dd,^3J(H,H) = 7.8 Hz, 2 H, *p*-*H*(Ar)), 6.96 (d, ^3J(H,H) = 7.8 Hz, 4 H, *m*-*H*(Ar)); ^{13}C NMR (100 MHz, [D$_8$]THF): $\delta = 26.0$ (β-CH$_2$(THF)), 31.7 (*C*H$_3$(*t*Bu)), 35.3 (C$_q$(*t*Bu)), 68.1 (α-*C*H$_2$(THF)), 114.6 (*p*-*C*(Ar)), 124.3 (*m*-*C*(Ar)), 139.4 (*o*-*C*(Ar)), 159.7 (*i*-*C*(Ar)); IR: $\tilde{\nu} = 2948$ (vs), 2911 (vs), 2870 (vs), 1793 (s, br, ν(AlH$_2$)), 1709 (s, br, ν(AlH$_2$)), 1585 (m), 1480 (m), 1459 (s), 1413 (vs), 1387 (vs), 1359 (s), 1356 (s), 1271 (vs), 1203 (m), 1193 (m), 1131 (s), 1102 (m), 1049 (vs), 1042 (vs), 902 (vs), 883 (vs), 847 (vs), 830 (vs), 797 (vs), 748 (vs), 741 (vs), 702 (m), 689 (m), 654 cm^{-1} (m). $C_{40}H_{68}O_5AlNa$ (678.95): calcd: C 70.76, H 10.10, Al 3.97; found: C 70.61, H 9.98, Al 3.75.

8: 2,6-*t*Bu$_2$C$_6$H$_3$OH (7.70 g, 37.30 mmol) in THF (20 mL); $LiAlH_4$ (18.65 mmol) in THF (15 mL) at room temperature; then kept at reflux for 2 d. The clear solution became yellow. The reaction mixture was cooled to room temperature, 60 % of the solvent removed in vacuum, and pentane (10 mL) added. At −20 °C colourless crystals formed.[33] Fractional cristallization yielded 12.33 g (90.0 %) of **8**. M.p. 97–101 °C; ^{27}Al NMR (70 MHz, C$_6$D$_6$): $\delta = 51$ ($h_{1/2} = 1869$ Hz); (THF): $\delta = 48$ ($h_{1/2} = 2357$ Hz); ^{7}Li NMR (105 MHz, C$_6$D$_6$): $\delta = -0.1$ ($h_{1/2} = 9.5$ Hz), (THF): −0.1 ($h_{1/2} =$ 6.4 Hz); ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 0.75$ (t, ^3J(H,H) = 6.8 Hz, 6 H, C*H*$_3$(*n*Bu)), 1.03–1.08 (m, 8 H, MeC*H*$_2$C*H*$_2$(*n*Bu)), 1.31 (m, 8 H, β-C*H*$_2$(THF)), 1.76 (s, 36 H, C*H*$_3$(*t*Bu)), 3.37 (m, 8 H), α-C*H*$_2$(THF)), 3.55 (t, ^3J(H,H) = 7.2 Hz, 4 H, α-C*H*$_2$(*n*Bu)), 6.92 (dd, ^3J(H,H) = 7.7 Hz, 2 H, *p*-*H*(Ar)), 7.41 (d, ^3J(H,H) = 7.7 Hz, 4 H, *m*-*H*(Ar)); ^{13}C NMR (100 MHz, C$_6$D$_6$): $\delta = 14.3$ (*C*H$_3$(*n*Bu)), 19.3 (γ-*C*H$_2$(*n*Bu)), 25.3 (β-*C*H$_2$(THF)), 32.2 (C*H*$_3$(*t*Bu)), 35.8 (*C*$_q$(*t*Bu)), 36.9 (β-*C*H$_2$(*n*Bu)), 63.0 (α-*C*H$_2$(*n*Bu)), 68.3 (α-*C*H$_2$(THF)), 117.4 (*p*-*C*(Ar)), 125.4 (*m*-*C*(Ar)), 139.4 (*o*-*C*(Ar)), 159.3 (*i*-*C*(Ar)); IR: $\tilde{\nu} = 2956$ (vs), 2930 (vs), 2871 (vs), 2861 (vs, sh), 1586 (m), 1482 (m), 1464 (m), 1458 (m), 1415 (vs), 1389 (s), 1360 (m), 1296 (vs), 1274 (vs), 1210 (m), 1193 (m), 1193 (m), 1166 (m), 1152 (m), 1129 (s), 1093 (vs), 1052 (vs), 1044 (vs), 900 (vs, br), 831 (m), 827 (m), 795 (m), 749 (vs), 709 (vs), 657 (vs), 608 cm^{-1} (m); $C_{44}H_{76}O_6AlLi$ (734.97): calcd: C 71.91, H 10.42, Al 3.67; found: C 71.25, H 10.03, Al 3.29.

9: 2,6-*t*Bu$_2$C$_6$H$_3$OH (8.22 g, 39.86 mmol) in THF (20 mL), $NaAlH_4$ (19.93 mmol) in THF (10 mL) at room temperature, then kept under reflux for 2 d. The clear solution became yellow. When cooled to room temperature, colourless crystals were obtained, from which the cell could be determined, but disorder of the *n*-butyl group impeded solution of the structure. Crystallization at $-20\,^{\circ}$C yielded 13.19 g of **9** (84.1 %). M. p. 86–97 °C (softening range); ^{27}Al NMR (70 MHz, C_6D_6): $\delta = 64$ ($h_{1/2} =$ 1454 Hz); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.87$ (t, ^3J(H,H) = 7.4 Hz, 3 H, CH_3(*n*Bu)), 1.24 (tq, ^3J(H,H) = 7.4 Hz, 2 H, γ-CH_2(*n*Bu)), 1.37 (m, 14 H, β-CH_2(THF)), 1.46 (tt, ^3J(H,H) = 7.4 Hz, 2 H, β-CH_2(*n*Bu)), 1.72 (s, 36 H, CH_3(*t*Bu)), 3.38 (m, 14 H, α-CH_2(THF)), 3.96 (t, ^3J(H,H) = 7.4 Hz, 2 H, α-CH_2(*n*Bu)), 6.80 (dd, ^3J(H,H) = 7.7 Hz, 2 H, *p-H*(Ar)), 7.37 (d, ^3J(H,H) = 7.7 Hz, 4 H, *m-H*(Ar)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.5$ (CH_3(*n*Bu)), 19.4 (γ-CH_2(*n*Bu)), 25.6 (β-CH_2(THF)), 32.0 (CH_3(*t*Bu)), 35.6 (C_q(*t*Bu)), 37.7 (β-CH_2(*n*Bu)), 63.2 (α-CH_2(*n*Bu)), 68.1 (α-CH_2(THF)), 116.7 (*p-C*(Ar)), 125.4 (*m-C*(Ar)), 139.3 (*o-C*(Ar)), 158.5 (*i-C*(Ar)); IR: $\tilde{\nu} = 2955$ (vs), 2911 (vs), 2870 (vs), 1787 (m, br, ν(AlH), 1586 (m), 1478 (m, sh), 1466 (s), 1456 (s, sh), 1417 (vs), 1387 (vs), 1359 (s), 1303 (s, sh), 1283 (vs), 1271 (s, sh), 1261 (s), 1249 (s, sh), 1217 (m), 1201 (s), 1194 (s), 1166 (m), 1153 (m), 1132 (s), 1120 (vs), 1105 (vs), 1069 (m), 1051 (vs), 945 (m), 904 (vs), 883 (s), 828 (s), 796 (s), 746 (vs), 726 (vs), 697 cm^{-1} (s). $C_{46}H_{80}O_{6.5}AlNa$ (787.11): calcd: C 70.19, H 10.24, Al 3.43; found: C 70.05, H 10.12, Al 3.38.

10: (–)-MentOH (4.28g, 27.39 mmol) in THF (30 mL); $LiAlH_4$ (9.13 mmol) in THF (10 mL) at ambient temperature; stirred for 2 h. THF was removed in vacuo, and the colourless oily product washed several times with pentane to give a colourless solid, which was dried in vacuo. Yield: 2.86 g (62.6 %). Decomp. 206–210 °C; ^{27}Al NMR (70 MHz, [D_8]THF): $\delta = 88$ ($h_{1/2} = 1536$ Hz); ^{7}Li NMR (105 MHz, [D_8]THF): $\delta = -0.2$ ($h_{1/2} = 5.7$ Hz); ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 0.69$–0.81 (br m), 1.30–1.67 (br m), 1.98 (br m), 2.44 (br m), 3.35 (br m), 3.56 (br m); ^{13}C NMR (100 MHz, [D_8]THF): $\delta = 16.2$ (C_8), 21.9 (C_9), 22.8 (C_{10}), 23.5 (C_7), 25.3 (C_5), 32.6 (C_3), 35.9 (C_4), 48.9 (C_2), 52.7 (C_6), 70.7 (C_1); IR: $\tilde{\nu} =$ 2954 (vs), 2927 (vs), 2869 (vs), 2849 (vs, sh), 1752 (s, ν(AlH)), 1465 (s, sh), 1455 (s), 1445 (s, sh), 1385 (s), 1368 (s), 1345 (m), 1284 (m), 1268 (m), 1236 (m), 1180 (s), 1158 (s), 1109 (vs), 1098 (vs), 1081 (vs), 1064 (vs), 1050 (vs), 1032 (vs), 998 (s), 976 (s), 924 (s), 851 (vs), 769 (s, sh), 729 (vs, br), 712 (vs), 695 (s, sh), 672 cm^{-1} (s). $C_{30}H_{58}AlLiO_3$ (500.71): calcd: C 71.96, H 11.68, Al 5.39; found: C 71.01, H 11.60, Al 5.25.

11: Ph_3COH (9.27g, 35.60 mmol) in THF (50 mL); $LiAlH_4$ (17.80 mmol) in THF (10 mL) at ambient temperature. Stirring was continued for 2 h. The reaction mixture remained colourless and was stored at 4 °C. After 1 d the solution turned yellow. After 4 d it had become dark red, and colourless crystals of **11** formed.[33] Repeated crystallization at $-20\,^{\circ}$C gave **11** in quantitative yield: 12.34 g (97.6 %). M.p. 259–263 °C, >275 °C (decomp); ^{27}Al NMR (70 MHz, C_6D_6): $\delta = 61$ (br); ^{7}Li NMR (105 MHz, THF): $\delta = -2.9$ ($h_{1/2} = 76.0$ Hz), (C_6D_6): $\delta = -2.9$ ($h_{1/2} = 15.1$ Hz); ^{1}H NMR (400 MHz, C_6D_6): 1.27 (m, 12 H, β-CH_2(THF)), 3.32 (m, 12 H, α-CH_2(THF)), 6.98–7.00, 7.42–7.45 (m, 45 H, CH(Ar)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.5$ (β-CH_2(THF)), 67.8 (α-CH_2(THF)), 84.6 (Ph_3CO), 126.5 (*o-C*(Ar)), 127.8 (*p-C*(Ar)), 129.3 (*m-C*(Ar)), 150.3 (*i-C*(Ar)); IR: $\tilde{\nu} = 3081$ (m), 3059 (vs), 3028 (m), 3017 (m), 2978 (vs), 2957 (s), 2942 (s, sh), 2875 (vs), 1967-1730 (m, br, ν(AlH)), 1593 (s), 1488 (vs), 1443 (vs), 1188 (vs, br), 1153 (m), 1129 (vs), 1074 (vs), 1043 (vs), 1034 (sh, br), 1000 (m), 939 (m), 919 (s), 894 (vs), 825 (vs), 758 (vs), 737 (m), 701 (vs), 684 (vs), 667 (s), 638 cm^{-1} (m); $C_{72}H_{70}AlLiO_{6.5}$ (1073.20): calcd: C 80.58, H 6.57, Al 2.51; found: C 80.24, H 7.47, Al 2.05.

12: Ph_3COH (14.16g, 54.39 mmol) in THF (50 mL); $NaAlH_4$ (18.13 mmol) in THF (30 mL) at ambient temperature. The turbid reaction mixture was filtered, and the colourless filtrate stored at $-20\,^{\circ}$C. Overnight, the solution became yellow, and colourless crystals of **12** formed:[33] 12.36 g (65.0 %). M.p. 273–280 °C (decomp); ^{27}Al NMR (70 MHz, [D_8]THF): $\delta = 61$ ($h_{1/2} =$ 939 Hz); ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 1.77$ (m, 12 H, β-CH_2(THF)), 3.61 (m, 12 H, α-CH_2(THF)), 6.86-6.98, 7.01–7.15 (m, 45 H, CH(Ar)); ^{13}C NMR (100 MHz, [D_8]THF): $\delta = 26.2$ (β-CH_2(THF)), 68.1 (α-CH_2(THF)), 84.5 (Ph_3CO), 125.7 (*o-C*(Ar)), 127.3 (*p-C*(Ar)), 129.9 (*m-C*(Ar)), 152.5 (*i-C*(Ar)); IR: $\tilde{\nu} = 3086$ (m), 3061 (s), 3030 (m), 3019 (m), 2980 (m), 2959 (s), 2935 (m, sh), 2877 (s), 1782–1622 (m, br, ν(AlH)), 1595 (m), 1490 (vs), 1444 (vs), 1378 (s), 1319 (m), 1316 (m), 1284 (s), 1208 (vs), 1188 (vs), 1175 (vs), 1161 (vs), 1134 (m), 1124 (s), 1096 (s), 1075 (vs), 1066 (vs), 1044 (vs), 1031 (vs), 1000 (m), 938 (m), 920 (s), 901 (vs), 894 (vs), 849 (s), 834 (vs), 813 (s), 791 (vs), 763 (vs), 760 (vs), 742 (m), 728 (m), 706 (vs), 703 (vs), 673 (s), 663 (m), 639 cm^{-1} (vs); $C_{69}H_{73}AlNaO_6$ (1048.31): calcd: 79.06, H 7.02, Al 2.57; found: C 79.73, H 6.49, Al 2.09.

13: *t*Bu_2MeCOH (1.56 g, 9.9 mmol) in Et_2O (20 mL); $LiAlH_4$ (3.3 mmol) in Et_2O (15 mL) at ambient temperature. Stirring was continued for 1 h. Crystallization at $-20\,^{\circ}$C yielded **13** as colourless plates:[33] 1.34 g (70.1 %). M.p. 194 °C; ^{27}Al NMR (70 MHz, Et_2O): $\delta = 74$ ($h_{1/2} = 605$ Hz); (C_6D_6): $\delta =$ 73 ($h_{1/2} = 1384$ Hz); ^{7}Li NMR (105 MHz, Et_2O): $\delta = 0.68$ ($h_{1/2} = 4.5$ Hz), (C_6D_6): $\delta = 0.40$ ($h_{1/2} = 3.9$ Hz); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.00$ (t, ^3J(H,H) = 7.2 Hz, 6 H, CH_3(Et_2O)), 1.17 (s, 54 H, CH_3(*t*Bu)), 1.49 (s, 9 H, C*Me*), 3.21 (q, ^3J(H,H) = 7.2 Hz, 4 H, CH_2(Et_2O)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.5$ (CH_3(Et_2O)), 23.8 (C*Me*), 30.0 (CH_3(*t*Bu)), 42.0 (CMe_3), 65.4 (CH_2(Et_2O)), 81.4 (*i*-C); IR: $\tilde{\nu} = 3009$ (s, sh), 2974 (vs), 2961 (vs), 2918 (vs), 2874 (s, $\nu_{as,s}$(CH_3)), 1798 (vs, ν(AlH)), 1480 (s), 1460 (s), 1389 (vs), 1373 (s), 1366 (vs, $\nu_{as,s}$(CH_3)), 1140 (s), 1117 (vs), 1104 (vs, ν(CO)), 1055 (s), 1027 (s), 1002 (s), 960 (s), 939 (s), 926 (s, sh), 906 (vs), 873 (m), 835 (m), 764 (vs), 727 (vs), 670 (s), 625 (s), 609 cm^{-1} (s, ν(AlO_2)); $C_{34}H_{74}AlLiO_4$ (580.85): calcd: C 70.31, H 12.84, Al 4.65, H^- 0.17; found: C 69.71, H 12.30, Al 4.28, H^- 0.16.

14: (2,6-*i*Pr)$_2C_6H_3OH$ (9.51 g, 9.89 mL, 35.34 mmol) in Et_2O (15 mL); $LiAlH_4$ (17.8 mmol) in Et_2O (20 mL) at ambient temperature. Stirring was continued for 1 h. Crystallization at $-20\,^{\circ}$C yielded **14** as colourless prisms [33]: 10.05 g (88.2 %). M.p. 144 °C; ^{27}Al NMR (70 MHz, Et_2O): $\delta = 79$ ($h_{1/2} =$ 4274 Hz), (C_6D_6): $\delta = 78$ ($h_{1/2} = 3695$ Hz); ^{7}Li NMR (155 MHz, C_6D_6): $\delta =$ 0.96 ($h_{1/2} = 7.0$ Hz); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.62$ (t, 6 H, CH_3(Et_2O)), 1.20 (d, ^3J(H,H) = 6.5 Hz, 36 H, CH_3(*i*Pr)), 2.77 (q, 4 H, CH_2(Et_2O)), 3.59 (qq, ^3J(H,H) = 6.5 Hz, 6 H, CH(*i*Pr)), 6.96 (dd, ^3J(H,H) = 8.0 Hz, 3 H, *p-H*(Ar)), 7.11 (d, ^3J(H,H) = 8.0 Hz, 6 H, *m-H*(Ar)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.1$ (CH_3(Et_2O)), 24.2 (CH_3(*i*Pr)), 27.1 (CH(*i*Pr)), 66.3 (CH_2(Et_2O)), 120.9 (*p-C*(Ar)), 123.7 (*m-C*(Ar)), 138.2 (*o-C*(Ar)), 151.7 (*i-C*(Ar)); IR: $\tilde{\nu} = 3074$ (w), 3063 (w), 3026 (w), 2961 (vs), 2927 (vs), 2902 (s), 2868 (s), 1843 (vs, ν(AlH)), 1592 (m), 1460 (vs), 1439 (vs), 1383 (s), 1361 (s), 1348 (s), 1329 (s), 1313 (m), 1284 (s), 1257 (vs), 1249 (s), 1217 (m), 1196 (vs), 1156 (m), 1108 (m), 1099 (m), 1083 (m), 1062 (s), 1042 (s), 921 (vs), 887 (vs), 855 (vs), 805 (m), 794 (m), 756 (vs), 751 (vs), 730 (s), 700 (vs), 688 (vs), 609 cm^{-1} (m); IR (Et_2O): $\tilde{\nu} = 1850$ (vs, ν(AlH)); $C_{40}H_{62}O_4AlLi$ (640.82): calcd: C 74.97, H 9.75, Al 4.21; found: C 74.63, 10.07, Al 3.89.

15: 2,6-$Me_2C_6H_3OH$ (7.15 g, 58.50 mmol) in Et_2O (35 mL); $LiAlH_4$ (19.50 mmol) in Et_2O (20 mL) at $-20\,^{\circ}$C. The colourless solution was stirred at ambient temperature for 1 h and was stored at $-20\,^{\circ}$C. After 1 d crystals of **15** formed. The unit cell was determined, but no reasonable solution was found: for the structure. Fractional crystallization at $-20\,^{\circ}$C gave 10.66 g (90.9 %) of **15**. M.p. 90–91 °C (decomp); ^{27}Al NMR (70 MHz, C_6D_6): $\delta = 77$ ($h_{1/2} = 2958$ Hz), (Et_2O): $\delta = 77$ ($h_{1/2} = 2112$ Hz); ^{7}Li NMR (105 MHz, C_6D_6): $\delta = -0.1$ ($h_{1/2} = 14.9$ Hz), (Et_2O): $\delta = -0.2$ ($h_{1/2} =$ 6.3 Hz); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.77$ (t, 12 H, CH_3(Et_2O)), 2.26 (s, 18 H, CH_3(Ar)), 2.97 (q, 8 H, CH_2(Et_2O), 6.74 (dd, ^3J(H,H) = 7.5 Hz, 3 H, *p-H*(Ar)), 6.95 (d, ^3J(H,H) = 7.5 Hz, 6 H, *m-H*(Ar)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 14.5$ (CH_3(Et_2O)), 18.0 (CH_3(Ar)), 65.9 (CH_2(Et_2O)), 120.0 (*p-C*(Ar)), 127.8 (*m-C*(Ar)), 128.9 (*o-C*(Ar)), 155.1 (*i-C*(Ar)); IR: $\tilde{\nu} = 3073$ (w), 3036 (m), 3013 (m), 2977 (vs), 2943 (vs), 2918 (vs), 2856 (s), 1896 (w), 1825 (vs, $\tilde{\nu}$(AlH)), 1781 (w), 1592 (vs), 1477 (vs), 1471 (vs), 1428 (vs), 1386 (m), 1295 (m, sh), 1289 (vs), 1270 (vs), 1155 (w), 1093 (vs), 1063 (s), 982 (m), 949 (m), 916 (s), 896 (s), 865 (vs), 758 (vs), 739 (m, sh), 719 (vs), 690 (m), 650 (m), 613 (m), 593 (m, sh); $C_{32}H_{48}O_5AlLi$ (546.65): calcd: C 70.31, H 8.85, Al 4.94; found: C 69.75, H 8.40, Al 4.64.

16: A stirred solution of 2,6-*t*$Bu_2C_6H_3OH$ (3.17 g, 15.4 mmol) in hexane was treated with a standardized solution of *n*BuLi in hexane (10 mL, 15.4 mmol). Butane gas was allowed to escape through a bubbler. The reaction mixture was stirred overnight, then the colourless precipitate was isolated by means of a G4 glass frit and washed twice with hexane (10 mL). The precipitate was dissolved in THF (40 mL). The light yellow solution was stored at $-78\,^{\circ}$C to give colourless crystals of **16**. M.p. 301–303 °C; ^{7}Li NMR (105 MHz, C_6D_6): $\delta = -1.0$ ($h_{1/2} = 7.1$ Hz), (THF): $\delta = 0.8$ ($h_{1/2} =$ 43.5 Hz); ^{1}H NMR (400 MHz, C_6D_6): 1.06 (m, 8 H, β-CH_2(THF)), 1.68 (s, 36 H, CH_3(*t*Bu)), 3.19 (m, 8 H, α-CH_2(THF)), 6.82 (dd, ^3J(H,H) = 7.7 Hz, 2 H, *p-H*(Ar)), 7.47 (d, ^3J(H,H) = 7.7 Hz, 4 H, *m-H*(Ar)); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.0$ (β-CH_2(THF)), 31.7 (CH_3(*t*Bu)), 35.6 (C_q(*t*Bu)), 68.4 (α-CH_2(THF)), 113.9 (*p-C*(Ar)), 125.2 (*m-C*(Ar)), 138.0 (*o-C*(Ar)), 165.7 (*i-C*(Ar)); IR: $\tilde{\nu} = 3015$ (s), 3003 (s), 2952 (vs), 2909 (vs), 2890 (vs), 1581 (m), 1484 (m), 1464 (m), 1454 (m, sh), 1446 (m, sh), 1412 (vs), 1381 (vs), 1350 (vs), 1275 (vs), 1260 (vs), 1200 (s), 1188 (s), 1149 (m), 1104 (vs), 1040 (vs), 916 (vs), 890 (vs), 883 (vs), 859 (vs), 817 (vs), 756 (vs), 678 (w), 650 cm^{-1} (vs); $C_{36}H_{58}O_4Li_2$ (568.70): calcd: C 76.03, H 10.28; found: C 75.45, H 10.27.

17: A solution of $AlCl_3$ (0.85 g, 6.38 mmol) in Et_2O (25 mL) was added to a stirred solution of $LiAlH_4$ (0.73 g, 19.12 mmol) in Et_2O (11 mL) at 0 °C.[34]

Table 12. Crystal data and data-collection parameters.

Compound	**1**	**2**[a]	**3**	**5**	**6b**	**8**	**11**	**12**	**13**	**14**	**17**
formula	$C_{44}H_{88}Al_2Li_2O_6$	$C_{32}H_{64}AlLiO_5$	$C_{46}H_{47}AlNaO_4$	$C_{37.33}H_{67.33}AlLiO_{4.33}$	$C_{40}H_{68}AlLiO_5$	$C_{44}H_{76}AlLiO_6$	$C_{72}H_{70}AlLiO_{6.5}$	$C_{72}H_{73}AlNaO_6$	$C_{34}H_{74}AlLiO_4$	$C_{40}H_{62}AlLiO_4$	$C_{32}H_{53}AlO_6$
M_r	780.98	562.75	713.81	619.50	662.86	734.97	1073.20	1084.27	580.85	640.82	512.73
crystal dimensions [mm³]	0.4 × 0.3 × 0.3	0.25 × 0.3 × 0.35	0.4 × 0.4 × 0.3	0.3 × 0.3 × 0.2	0.3 × 0.1 × 0.1	0.1 × 0.2 × 0.4	0.2 × 0.25 × 0.3	0.3 × 0.3 × 0.2	0.15 × 0.3 × 0.3	0.3 × 0.3 × 0.4	0.4 × 0.3 × 0.3
crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	rhombohedral	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)2(1)2(1)	*P*2(1)/*n*	*Pccn*	*P*2(1)/*n*	*P*2(1)/c	*R*3	*P*2(1)/*n*	*Pna*2(1)	*P*2(1)/*n*	*P*2(1)/c
a [Å]	10.868(4)	9.465(3)	9.048(2)	39.398(1)	10.8807(7)	11.243(1)	12.0635(2)	12.603(3)	18.54(2)	12.8614(3)	12.5712(3)
b [Å]	16.879(6)	17.191(6)	23.018(3)	13.9490(3)	18.316(1)	19.862(2)	12.0635(2)	21.579(4)	17.04(2)	20.9681(5)	24.7891(3)
c [Å]	14.071(5)	22.635(9)	18.647(4)	22.0837(7)	20.802(2)	20.5009(1)	12.0635(2)	22.394(5)	12.074(7)	14.9870(4)	20.3444(2)
α [°]	90	90	90	90	90	90	71.47(1)	90	90	90	90
β [°]	95.09(1)	90	91.361(5)	90	91.33	100.761(1)	71.47(1)	100.403(6)	90	97.806(1)	90.264(1)
γ [°]	90	90	90	90	90	90	71.47(1)	90	90	90	90
V [Å³]	2571(2)	3683(2)	3882.5(13)	12136.3(6)	4144.4(5)	4497.47(2)	1531.62(4)	5990(2)	3815(5)	4004.2(2)	6339.8(2)
Z	4	4	4	12	4	4	1	4	4	4	4
ρ_{calcd} [Mg m⁻³]	1.009	1.015	1.221	1.017	1.062	1.085	1.164	1.202	1.011	1.063	1.074
μ [mm⁻¹]	0.095	0.087	0.106	0.083	0.086	0.087	0.086	0.094	0.084	0.086	0.092
F (000)	864	1248	1516	4104	1456	1616	570	2308	1304	1400	2256
T [K]	173(2)	193(3)	193(2)	173(2)	173(2)	173(2)	183(3)	183(3)	163(2)	193(3)	193(2)
2θ [°]	3.78–55.22	2.98–58.42	13.60–50.68	13.62–45.98	2.96–54.96	2.88–58.28	58.72	2.64–58.48	3.24–58.08	3.36–58.76	13.62–43.94
no. refl. recorded	11181	21178	19451	47255	17960	24269	8905	33973	21070	23091	23753
no. refl. unique	4976	7581	5742	8069	7458	7141	3482	11874	7520	7012	7170
no. refl. obs. $F4\sigma(F)$	3950	4379	4732	6160	2642	3954	2570	7192	3949	5412	5868
R(int)	0.0486	0.0515	0.0335	0.0795	0.1060	0.1128	0.0304	0.0436	0.0544	0.0288	0.0476
refined parameters	256	341	477	629	444	483	272	648	397	433	685
GOF	1.153	1.144	1.066	1.115	1.135	1.146	1.139	1.034	1.115	1.078	1.210
$R(4\sigma)$	0.0556	0.0711	0.0479	0.0784	0.1071	0.0755	0.0441	0.1026	0.0653	0.0511	0.1081
$wR2$	0.1172	0.1664	0.1028	0.1585	0.2117	0.1631	0.0993	0.2632	0.1529	0.1130	0.2542
$\Delta\rho$ [e Å⁻³]	0.272	0.337	0.401	0.385	0.463	0.786	0.146	0.890	0.341	0.254	0.426

[a] Absolute structure: −0.22(33): H. D. Flack, *Acta Cryst. A* **1983**, *39*, 876–881.

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The resulting suspension was treated with a solution of 2,6-$t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$ (10.52 g, 51.0 mmol) in $\mathrm{Et_2O}$ (30 mL) at room temperature. Hydrogen gas was liberated. The suspension was stirred for 3 h, and the insoluble material removed by filtration (G4 glass frit). Colourless crystals of **17** formed at 4 °C.[33] $\mathrm{Et_2O}$ was removed from the filtrate and the residue dried in vacuo. Yield: 12.14 g (92.8 %). M.p. 145 – 147 °C (softening range: 137 – 145 °C); ^{27}Al NMR (70 MHz, $\mathrm{C_6D_6}$): $\delta = 62$ ($h_{1/2} = 6473$ Hz); ($\mathrm{Et_2O}$): 65 ($h_{1/2} = 4000$ Hz); (THF): $\delta = 66$ ($h_{1/2} = 4722$ Hz); ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$): $\delta = 0.64$ (br s, 6 H, $\mathrm{C}H_3(\mathrm{Et_2O})$), 1.55 (s, 36 H, $\mathrm{C}H_3(t\mathrm{Bu})$), 3.68 (br s, 4 H, $\mathrm{C}H_2(\mathrm{Et_2O})$), 4.5 (br s, 1 H, $\mathrm{Al}H$), 6.87 (dd, $^3J(\mathrm{H,H}) = 7.6$ Hz, 2 H, p-H(Ar)), 7.34 (d, $^3J(\mathrm{H,H}) = 7.6$ Hz, 4 H, m-H(Ar)); ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$): $\delta = 11.6$ (br, $C\mathrm{H_3}(\mathrm{Et_2O})$), 31.8 ($C\mathrm{H_3}(t\mathrm{Bu})$), 35.5 ($\mathrm{C_q}(t\mathrm{Bu})$), 66.2 ($C\mathrm{H_2}(\mathrm{Et_2O})$), 118.6 ($p$-$C$(Ar)), 125.9 ($m$-$C$(Ar)), 139.1 ($o$-$C$(Ar)), 156.4 ($i$-$C$(Ar)); IR: $\tilde{\nu} = 3058$ (w), 3013 (m), 2959 (vs), 2909 (vs), 2869 (vs), 1893 (vs, ν(AlH)), 1584 (m), 1469 (s), 1449 (s), 1415 (vs), 1390 (vs), 1360 (s), 1288 (vs), 1269 (vs), 1260 (vs), 1241 (vs), 1211 (m), 1202 (m), 1193 (s), 1150 (m), 1131 (m), 1122 (m), 1095 (s), 1014 (vs), 995 (m, sh), 925 (vs), 886 (vs), 828 (s), 796 (s), 749 (vs), 737 (vs), 737 (vs), 726 (vs), 697 (s), 681 $\mathrm{cm^{-1}}$ (vs); $\mathrm{C_{32}H_{53}O_3Al}$ (512.75): calcd: C 74.96, H 10.42, Al 5.26; found: C 74.13, H 9.95, Al 5.11.

X-ray crystallography: Data for X-ray structure determinations were collected with a Siemens P4 diffractometer equipped with a CCD area detector ($\mathrm{Mo_{K\alpha}}$, $\lambda = 0.71073$ Å). The reflections were recorded in a total of 1200 frames with $\Delta\varphi = 0.3°$ at two different χ settings. The structures were solved by direct methods with the programme XS (Siemens). The structure was refined with least-squares methods (SHELXL97, G. M. Sheldrick, Göttingen, Germany, **1997**). Carbon-bound hydrogen atoms were included in the refinement with a riding model with fixed isotropic temperature parameter U, and the positions of the Al- and Li-bound hydrogen atoms were freely refined. The thermal ellipsoids in the figures are depicted at a probability level of 25 %. Carbon-bound hydrogen atoms are omitted for clarity. Crystal data for the compounds are listed in Table 12.

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