Synthesis and Structures of Magnesium Tetrahydridoaluminates[☆]

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The molecular structures of $XMg(AlH_4) \cdot 4$ THF (**1a**, **2**, **3a**) ($X = AlH_4$, Cl, Br) have been determined by X-ray structural analysis. Each compound possesses a hexacoordinated Mg center and AlH_4^- groups bound to this center via a single hydride bridge bond. Attempts to prepare $ROMg(AlH_4)$ compounds were successful only for sterically demanding groups R (R = CMe_3, CPh_3, naph, mes, smes). The 2-naphthoxy derivative **7**, a compound with the composition (naphO)Mg(AlH_4) · 2.5 THF, is a dimer with a central Mg_2O_2 ring. One of its two AlH_4^- groups is terminally bound to one Mg atom, the other bridges the two Mg centers. This structure indicates how AlH_4^- transfer may occur from $ROMg(AlH_4)$ compounds to form $Mg(OR)_2$ and $Mg(AlH_4)_2$.

Amongst all hitherto known metal tetrahydridoaluminates, $LiAlH_4$ has been most extensively studied. Since its discovery by Schlesinger and his group[1], it has developed into an indispensable commercially produced reagent[2]. The potential of $NaAlH_4$ as a reducing agent is known to a lesser extent[3]; and our knowledge about the alkaline earth metal tetrahydridoaluminates has been reviewed recently[4] but is quite scarce. Among the known compounds, $Mg(AlH_4)_2$, and its solvates have attracted the most interest. This compound was first synthesized by Bauer and Wiberg[5] by the routes described in eq. (1)−(3).

$$4\,MgH_2 + 2\,AlCl_3 \Rightarrow Mg(AlH_4)_2 + 3\,MgCl_2 \quad (1)$$

$$MgH_2 + 2\,AlH_3 \Rightarrow Mg(AlH_4)_2 \quad (2)$$

$$2\,LiAlH_4 + MgBr_2 \Rightarrow Mg(AlH_4)_2 + 2\,LiBr \quad (3)$$

$Mg(AlH_4)_2 \cdot 4THF$	$Mg(AlH_4)_2 \cdot 2THF$	$Mg(AlD_4)_2 \cdot 4THF$
1a	**1b**	**1c**
$MgCl(AlH_4) \cdot 4THF$	$MgBr(AlH_4) \cdot 4THF$	
2	**3a**	

Hertwig[6] used the reaction between HMgX (X = Cl, Br) and $AlCl_3$ to produce $Mg(AlH_4)_2$; HMgX was generated by hydrogenolysis of RMgX. A better method for the synthesis of $Mg(AlH_4)_2$, the metathesis involving $NaAlH_4$ and $MgCl_2$ in diethyl ether, was described by Ashby et al.[7]. Ashby and coworkers also verified the formation of $Mg(AlH_4)_2$ in THF solution[8] as reported by Plešek and Hermànek[9]. Furthermore, the tetrahydridoaluminates $Mg(AlH_4)_2 \cdot 4$ THF (**1a**), $Mg(AlH_4) \cdot 2$ THF (**1b**), $MgCl(AlH_4) \cdot 4$ THF (**2**), and $MgBr(AlH_4) \cdot 4$ THF (**3a**) were characterized by IR spectroscopy and X-ray powder patterns. They not only determined that **1a** loses THF readily to form **1b**[7], but also[7] used IR spectroscopy extensively to follow reactions between $MAlH_4$ (M = Li, Na) and MgX_2 (X = Cl, Br, I) in diethyl ether or THF[8]. From the band shifts attributed to AlH_4 stretching vibrations it was concluded that the interaction between the Mg center and the AlH_4 group increases as fewer solvent molecules are coordinated to the Mg atom.

1a is considered to be ionic; that is, it should be described as $[Mg(THF)_4]$ $(AlH_4)_2$[8]. However, there is a significant difference in the AlH_4 stretching vibrations between **1a** and the compounds **2** and **3a**. If **2** and **3a** are also "ionic" like **1a**, than there should be no difference between the AlH_4^- stretching vibrations for all three compounds. This is not the case; therefore, it is more likely, that these compounds are not truly ionic, i.e. the anions are not solvent-separated from the cation. This was one of the reasons why we started to reinvestigate the chemistry of magnesium tetrahydridoaluminates with the aim of getting more information on their structures. We report on the structures of **1a**, **2**, and **3a** as well as on our results on (organyloxo)magnesium tetrahydridoaluminates, $ROMgAlH_4 \cdot n$ THF.

Synthesis, Spectra, and Molecular Structures of Magnesium Tetrahydridoaluminates

The tetrahydroaluminates **1a**, **2**, and **3a** were readily prepared by Ashby's method from MgX_2 (X = Cl, Br, I) and $M(AlH_4)$ (M = Li, Na)[8]. Single crystals were grown by allowing ether vapor to slowly diffuse into saturated THF solutions of these magnesium tetrahydridoaluminates. $Mg(AlD_4)_2 \cdot 4$ THF (**1c**) was obtained by analogy to **1a**. **1d** is obtained when 1,2-dimethoxyethane replaces THF from **1a** as described in eq. (4). The composition of **1d** suggests that this compound may indeed be ionic because six oxygen atoms are provided as ligand atoms for the Mg center.

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$$\mathrm{Mg(AlH_4)_2 \cdot 4THF} \xrightarrow[\text{- 4THF}]{\text{+ 3DME}} \mathrm{Mg(AlH_4)_2 \cdot 3DME} \quad (4)$$

1d

$$\mathrm{MgBr(AlH_4) \cdot 4THF} \xrightarrow[\text{- 4THF}]{\text{+ 18-crown-6}} \mathrm{MgBr(AlH_4) \cdot 18\text{-}crown\text{-}6} \quad (5)$$

3b

There was no problem to obtain compounds **2** and **3a** as single crystals. Furthermore, they lose THF either in a vacuum at 60°C or by crystallisation from hot toluene. However, these crystals of $\mathrm{MgX(AlH_4) \cdot 2\ THF}$ were of unsuitable quality for X-ray structural analysis. Replacement of THF from **3a** can be achieved in THF solutions by 18-crown-6 as shown in eq. (5) and the complex $\mathrm{MgBr(AlH_4) \cdot}$ 18-crown-6 (**3b**) separated from the solution as a powder.

^{27}Al-NMR spectroscopy, in most cases, distinguishes between various states of coordination at the Al center[10]. The ^{27}Al-NMR signals move upfield as the coordination number increases, and its line width depends strongly on the symmetry about the Al atom[10].

A signal at $\delta^{27}\mathrm{Al} = 98-104$ is typical for the $\mathrm{AlH_4^-}$ ion, and its quintuplet structure can be observed in the proton-coupled ^{27}Al-NMR spectra only if solvent-separated ion pairs are present[11]. However, only a broad signal results if contact ion pairs are present, or if an equilibrium is operating involving the $\mathrm{AlH_4^-}$ group in exchange processes, or if the $\mathrm{AlH_4^-}$ ion is involved in covalent bonding[12]. Thus the type of the ^{27}Al-NMR signal varies considerably, and the solvent, as well as the cation, has a significant influence on its shape[13].

Table 1. ^{27}Al-NMR data for magnesium tetrahydridoaluminates in THF and C_6D_6 solution. Half width fwhm given in Hz

	THF			C_6D_6
δ in ppm, fwhm (Hz)	δ^{27}Al	fwhm	δ^{27}Al	fwhm
$\mathrm{Mg(AlH_4)_2 \cdot 4\ THF}$ (**1a**)	110	1240	108	2260
$\mathrm{Mg(AlD_4)_2 \cdot 4\ THF}$ (**1c**)	1 01	1020		
$\mathrm{Mg(AlH_4)_2 \cdot 3\ DME}$ (**1d**)			100	2350
$\mathrm{MgCl(AlH_4) \cdot 4\ THF}$ **2**	109	1000		
$\mathrm{MgBr(AlH_4) \cdot 4\ THF}$ (**3a**)	109	1060	108	1920
$\mathrm{MgBr(AlH_4) \cdot}$18-crown-6 (**3b**)			100	860

Table 1 lists ^{27}Al-NMR data for various magnesium tetrahydridoaluminates in THF and C_6D_6 solutions. The data show the presence of the $\mathrm{AlH_4^-}$ species in all compounds. The shift difference of ≈8 ppm between **1a** and **1d**, or **3a** and **3b**, is an indication that we can assume in compounds **1d** and **3b** the presence of a hexacoordinated Mg atom. This results in a small but better shielding of the Al nucleus due to the DME and 18-crown-6 ligand. This indicates free $\mathrm{AlH_4^-}$ species. This conclusion is supported by the relatively small line width for **3b** in C_6D_6 solution; however, **1d** does not fit into this scheme.

Table 2. Temperature dependence of δ^{27}Al and fwhm of $\mathrm{Mg(AlH_4)_2}$ and $\mathrm{BrMgAlH_4}$ in DME solution

°C	+20[a]	+20[b]	+ 60[a]	+60[b]	-50c[a]	-50[b]
$\mathrm{Mg(AlH_4)_2}$ (**1a**): δ^{27}Al	106	104	105	104	105	105
fwhm in Hz	1300	740	820	570	1880	1300
$\mathrm{BrMgAlH_4}$ (**3a**): δ^{27}Al	106	105	106	106	102	102
fwhm in Hz	1030	920	680	690	900	610

[a] Proton-coupled spectra. – [b] Proton-decoupled spectra.

In THF solution, the ^{27}Al-NMR signal of **3a** is found at $\delta = 109-110$, and this suggests a bonding situation comparable with **1a**. This is also emphasized by the line width. In contrast, the Al nucleus of the $\mathrm{AlD_4^-}$ species **1c** is deshielded by 9 ppm compared with the resonance for $\mathrm{AlH_4^-}$. This is an isotopic effect which is well documented for the pair $\mathrm{LiAlH_4/LiAlD_4}$[12].

The influence of temperature on δ^{27}Al and the line width was studied for **1a** and **3a** in DME because it was expected that resolution of the ^{27}Al-NMR signal into a quintuplet might be achieved in this solvent analogously to $\mathrm{LiAlH_4}$[12] or $\mathrm{NaAlH_4}$[13].

Inspection of Table 1 shows that no quintuplet signal can be observed in spite of the sharper lines compared to the THF solution. The line width increases considerably as the temperature is decreased. Furthermore, the line width is larger in the coupled spectra as compared to the decoupled. It is also noteworthy that this difference is remarkably smaller for **3a** as compared with **1a**. These data suggest that there is a considerable interaction between the $\mathrm{(AlH_4)^-}$ group and the solvated $\mathrm{Mg^{2+}}$ ion in **1a**. This influence seems to be reduced for **3b**, probably due to the formation of a $\mathrm{[BrMg \cdot 18\text{-}crown\text{-}6]^+}$ cation which forms a contact ion pair with its $\mathrm{AlH_4^-}$ anion. To summarize: the ^{27}Al-NMR spectra suggest the absence of undisturbed $\mathrm{AlH_4^-}$ ions in any of the solutions investigated.

^{1}H- and ^{13}C-NMR spectra were not informative. In C_6D_6 solutions only signals for the donor molecules were recorded, and these were found to be deshielded with respect to the free solvent. In particular, the ^{1}H-NMR signal for **1a** and **3a** was comparatively broad. This is to be expected if an exchange process between free and bonded solvent molecules is occuring.

The interaction of the Mg center with the $\mathrm{AlH_4^-}$ ion should lead to a distortion of the $\mathrm{AlH_4}$ tetrahedron and, consequently, this will result in a change of symmetry as well as a change in the appearance of the vibrational spectrum. The IR spectrum for the free and undisturbed $\mathrm{AlH_4^-}$ in $\mathrm{[Et_4N]AlH_4}$ shows two bands at 1680 and 765 cm^{-1} assigned to the stretching vibration of class T and the asymmetric bending[15]. For solid $\mathrm{NaAlH_4}$, the stretchng vibration $\nu_{as}(\mathrm{AlH_4})$ is observed at 1678 cm^{-1}. Furthermore, two deformation vibrations at 752 and 688 cm^{-1}[16] are found. Solid $LiAlH_4$ exhibits two stretching vibrations, one at 1780 and the other at 1645 cm^{-1}[17]. This is an indication either of the presence of a distorted tetrahedron or an AlH_4^- tetrahedron in an asymmetric environment. The latter explanation is consistent with the crystal structure of $LiAlH_4$[18].

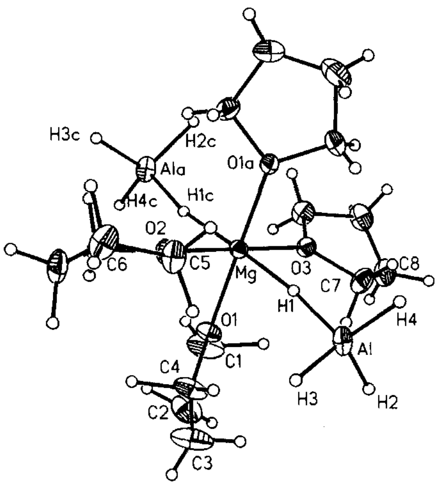
The IR spectrum of $Mg(AlH_4)_2 \cdot 4$ THF (**1a**) shows a strong band at 1728 cm^{-1} for the AlH_4 stretching vibrations together with two weak bands at 1875 and 1808 cm^{-1}. $Mg(AlD_4)_2 \cdot 4$ THF (**1c**) exhibits a band for $\nu_{as}(AlD_4)$ at 1262 cm^{-1} in agreement with the expected isotope shift. Comparison of the two spectra reveals three additional bands at 787, 765, and 745 cm^{-1} (all strong) for **1a**, and 574 and 555 cm^{-1} (very strong for **1c**). These must be associated with IR-active AlH_4 deformation frequencies. Group theory predicts only a single IR active stretching vibration for the AlH_4 unit with T_d symmetry. Therefore, the $(AlH_4)^-$ and $(AlD_4)^-$ groups in **1a** and **1c** must have a lower symmetry. The same is true for **2** [1712 (vs, br), 1584 (w), 793 (s), 764 (s), 749 (s)] and **3a** [1714 (vs, br) 1588 (w) 791 (s) 761 (s), 749 (s)]. Ashby et al.[7] noted that the AlH_4-stretching vibration of $Mg(AlH_4)_2 \cdot 2$ THF (**1b**) not only shows a pronounced splitting, but also is observed at higher wave numbers in comparison with $BrMg(AlH_4) \cdot 2$ THF [our data for **1b**: 1994 (s), 1928 (sh), 1862 (vs), 1834 (vs) cm^{-1}; for $BrMg(AlH_4) \cdot 2$ THF: 1815 (vs), 1790 (vs)]. This is attributed to the presence of Mg–H–Al bridge bonds, which makes the terminal Al–H bonds stronger. A band which can be definitely assigned to an Al–H–Mg or $Al-\mu H_2-Mg$ stretching vibration unambiguously has not yet been found. The observed pattern for the AlH_4^- group in these bistetrahydrofuran adducts does not fit a simple model for a mononuclear species. Since we were unable to grow single crystals of these compound, their true structure remains uninvestigated.

Ashby et al.[8] have speculated that **1a**, **2**, and **3a** might be ionic compounds built from $[Mg(THF)_4]^{2+}$ cations and AlH_4^- and Cl^- or Br^- anions, respectively. As indicated, neither IR nor NMR data fit this interpretation. However, the results of an X-ray structural analysis of these three compounds clarifies the situation at least for the solid state.

Figure 1 shows the molecular structure of **1a**. The molecule has a crystallographically imposed C_2 symmetry with a twofold axis passing through the center of the Mg atom. This atom is coordinated by four oxygen and two hydrogen atoms, and the oxygen atoms form an almost perfect plane with the Mg^{2+} ion in its center. The coordination sphere is completed by two hydrogen atoms in a *trans* orientation because the AlH_4^- groups form only single hydride bridges with the Mg^{2+} center. This is actually the most remarkable structural feature of this compound.

Although the position of the Al-bonded hydrogen atoms could be clearly located, refinement lead to different Al–H bond lengths, and only two are in the expected range while the other two are too short. Consequently, the Al–H–Mg bond angle cannot be determined accuratly, but appears to be bent (≈165°).

Figure 1. ORTEP plot of the molecular structure of **1a** in the crystal. Thermal ellipsoids are represented on a 25% probability scale. Esd's are quoted in parenthesis. Selected bond lengths [Å]: Mg–O1 2.054(3), Mg–O2 2.084(4), Mg–O3 2.083(4), Mg–O4 2.054(3), Mg–H1 2.28(1), Al–H1 1.21, Al–H2 1.53, Al–H3 1.57, Al–H4 1.24; Atom distance: Al–Mg 3.47. – Selected bond angles [°]: O1–Mg–O4 179.72(8), O1–Mg–O2 89.83(8), O1–Mg–O3 90.17(8), O2–Mg–O3 180.0(2), H1–Mg–H1a 179.9, H2–Al–H3 109



The structural parameters of the THF molecules in compound **1a** reveal no disorder. The oxygen atoms can be considered as sp^2-hydridized beause the sum of bond angles at the O atoms are 360°. We assume, however, that the bonding between the Mg^{2+} center and the THF molecules is predominantly governed by a dipole-ion interaction.

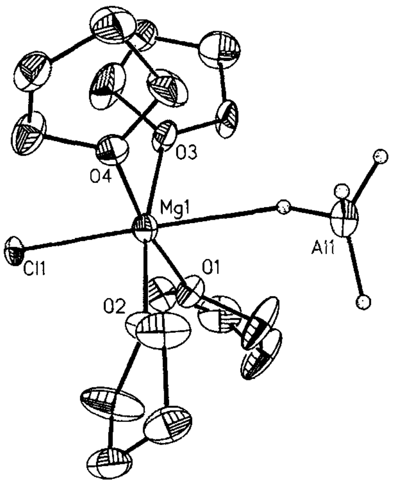
Figure 2 depicts the molecular structure of **2** which displays also a hexacoordinated Mg^{2+} center surrounded by four oxygen atoms, arranged in a plane, and a hydride and halide ion in *trans* orientation. Compound **3a** is isomorphous with compound **2**. Both compounds can be derived from the molecular structure of **1a** by replacing one AlH_4^- group for a halide ligand. The asymmetry introduced by this ligand pushes the oxygen atoms towards the AlH_4^- group making the MgO_4 unit slightly tetragonal-pyramidal, and, as a consequence, we find longer Mg···Al atom distances (for **2** 3.63 and for **3a** 3.62 Å, respectively) as compared to compound **1a** (3.47 Å). It appears that the AlH_4 tetrahedra in all three magnesium tetrahydroaluminates are distorted. However, the hydrogen positions are too inaccurate to allow a more detailed discussion.

The oxygen atoms of the THF molecules in compound **2** and **3** are in a planar environment as observed for **1a**. However, the position of the carbon atom C12 in **2** seems to be disordered, and the same is the case for atom C4 in **3a**. All other C atoms show no anomalous thermal parameters. Irrespective of the group X in the $XMg(AlH_4) \cdot 4$ THF compounds, all Mg–O atom distances lie in a very narrow range and correspond to other THF coordination compounds of MgX_2, e.g. $MgBr_2 \cdot 2$ THF or $MgBr_2 \cdot 4$ THF[19]. In this respect it should be noted that the two bromine atoms of $MgBr_2 \cdot 4$ THF are also in a *trans* orientation in analogy to **3a**.

Synthesis and Structures of (Organyloxo)magnesium Tetrahydridoaluminates

Replacement of the halogen atom in compounds **2** and **3a** by an RO ligand leads to (organyloxo)magnesium tetrahydridoaluminates $ROMg(AlH_4)$. Since the RO^- group is a stronger base than either Cl^- or Br^-, it was expected that these might be able to replace THF molecules from $ROMg(AlH_4) \cdot 4$ THF compounds and allow, therefore, the formation of magnesium tetrahydridoaluminates with higher nuclearity.

Figure 2. ORTEP Plot of the molecular structure of **2** in the solid state. Thermal ellipsoids are represented at the 25% probability level. Esd's in parenthesis. Selected bond lengths [A]: Mg−Cl 2.478(3), Mg−O1 2.092(9), Mg−O2 2.073(9), Mg−O3 2.085(10), Mg−O4 2.108(9), Mg−H1 2.51(3), atom distance: Mg−Al 3.627(5). − Selected bond angles [°]: Cl−Mg−O1 94.3(3), Cl−Mg−O2 93.0(3), Cl−Mg−O3 97.7(3), Cl−Mg−O4 94.4(3), O1−Mg−O2 90.5(4), O1−Mg−O3 88.1(4), O1−Mg−O4 170.8(4), O2−Mg−O3 169.3(4), O2−Mg−O4 92.1(4), O3−Mg−O4 87.7(4), Al−H1−Mg 153(1), Cl−Mg−H1 178.5(2), H1−Al−H2 113, H1−Al−H3 101.5



Bonding parameters of **3a**: Mg−Br 2.576(2), Mg−O1 2.069(4), Mg−O2 2.102(4), Mg−O3 2.086(5), Mg−O4 2.096(4), Mg−H1 2.41, Al−H1 1.27, Al−H2 1.62, Al−H3 1.69, Al−H4 1.45, Mg···Al 3.618. − Selected bond angles [°]: Al−H1−Mg 156.9(7), Br−Mg−H1 177.9(10), O1−Mg−O2, O1−Mg−O3 170.2(2), O1−Mg−O4 88.3(2), O2−Mg−O3 92.1(2), O2−Mg−O4 170.7(2), O3−Mg−O4 91.1(2), Br−Mg−O1 97.3(2), Br−Mg−O2 94.8(1), Br−Mg−O3 92.5(1), Br−Mg−O4 93.8(1), H1−Mg−O(x): 84.8−86.1

The investigation of compounds $ROMg(AlH_4)$ was first addressed by Ashby et al.[20]. The compounds proved to be unstable, and it was demonstrated that ligand exchange leads to $HMg(AlH_3OR)$. As a consequence, compounds of type $ROMg[AlH_{3-n}(OR)_{1+n}]$ and/or $Mg[AlH_{3-n}(OR)_{1+n}]_2^+$[21,22] could be formed by allowing alkoxyalanes $AlH_{3-n}(OR)_n$ to react with MgH_2[23].

Although several routes to $ROMg(AlH_4) \cdot n$THF compounds are feasible we concentrated on the metathesis described in eq. (6).

$$ROMgCl + NaAlH_4 \xrightarrow{THF} NaCl + ROMgAlH_4 \quad (6)$$

$NaAlH_4$ instead of $LiAlH_4$ must be employed to drive rection (6) to the side of the products because NaCl is insoluble in THF whereas LiCl is not. Moreover, Na^+ proved to catalyse RO^-/H^- exchange less readily than Li^+. $ROMg(AlH_4)$ adheres strongly to NaCl (complex formation?), but the $ROMg(AlH)_4$ compounds can be removed from NaCl by extraction of the precipitated "NaCl" with THF. Compounds **4**−**9** were isolated.

$Me_3COMg(AlH_4) \cdot 0.5$ THF **4**

$Ph_3COMg(AlH_4)$ **5**

$PhOMg(AlH_4) \cdot 1.5$ THF **6**

$naphOMg(AlH_4) \cdot 2.5$ THF **7**

$mesOMg(AlH_4) \cdot 2.5$ THF **8**

$smesOMg(AlH_4) \cdot 3$ THF **9**

All these complexes show a tendency to form $Mg(OR)_2$ in THF and $Mg(AlH_4)_2 \cdot 4$ THF when their THF solutions are diluted with diethyl ether.

NMR Spectra

$ROMg(AlH_4)$ and $HMg(AlH_3OR)$ may not be distinguished from one another by chemical analysis because both contain the same amount of hydridic hydrogen. ^{27}Al-NMR spectroscopy would be an ideal method for characterization if Al-H coupling can be resolved. However, no coupling was observed, and in view of the results obtained with compounds **1**−**3** this was not expected. However, Gavrilenko et al. demonstrated in elegant ^{27}Al-NMR studies that the compounds of the series $AlH_{4-n}(OR)_n^-$ can be readily characterized due to their different chemical shifts[24]. These are compiled in Table 3 together with the data for compounds **4**−**9**.

Table 3. ^{27}Al resonance of $AlH_{4-n}(OR)_n^-$ species and $\delta^{27}Al$ data for $ROMgAlH_4$ compounds [a] in THF or [b] C_6D_6 solution. Half widths of the signals are given in Hz

	AlH_4^-	AlH_3OR^-	$AlH_2(OR)_2^-$	$AlH(OR)_3^-$	$Al(OR)_4^-$	
$\delta^{27}Al$	110	118-124	115-120	74-96	60 - 77	
$ROMgAlH_4$						
R	Me_3C (**4**)	Ph_3C (**5**)	Ph (**6**)	Napht (**7**)	mes (**8**)	smes **9**
$\delta^{27}Al$	105 [a]	106[a]	108[a]	113[a]	97[a]	106[a]
fwhm	2230	1920	1800	2700	255	2750
$\delta^{27}Al$	114 [b]	108[b]	113[b]	127[b]	101[b]	85b]
fwhm	2050	2550	3580		7780	4000

[a] THF. − [b] C_6D_6.

The data for the latter compounds span a small range that is centered around the δ value of AlH_4^-. However, the line widths are rather large, and both $\delta^{27}Al$ and the line width fwhm (see Table 1) for **7** are exceptional as are the data for **9** in C_6D_6 solution. Another point worth noting is that the difference in line width in THF and C_6D_6 solution for a particular compound are larger than for compounds **1a**, **2**, and **3a** under similar conditions. We take this as evidence that the molecular structures of the $ROMg(AlH_4)$ compounds differ from those of $MgX(AlH_4) \cdot 4\ THF$ (X = Cl, Br, AlH_4). But the data provide clear evidence that they are true $ROMg(AlH_4)$ compounds, and that RO^-/H^- exchange has not occurred.

The *tert*-butoxo species **4** exhibits a broad signal at δ = 1.40 in its ^1H-NMR spectrum which is, in part, superimposed by a CH_2 signal from THF. The chemical composition of this compound makes it unlikely that it is monomeric. Thus, if the compound is di- or trinuclear, its Me_3CO units must be arranged in a symmetrical manner. The Ph_3C group of **5** is also represented by a single set of signals, indicating that all Ph groups are equivalent. Although the ^1H-NMR spectrum of the phenoxo derivative **6** shows a large number of signals in the aromatic region, a doublet at δ = 7.65 [$J(^1H^1H)$ = 9 Hz] can be assigned to the 2,6-protons. Whereas none of the ^1H-NMR signals for the naphthoxo group in **7** can be definitely assigned, there are two readily recognizable ^1H resonances in a 2:1 ratio at δ = 2.23 and 2.39 for the methyl groups of **8**, while the CH protons of the mesityl group are depicted by a single resonance at δ = 6.81. Finally, the CMe_3 and CH groups of the supermesityl group of **9** are not equivalent.

The ^{13}C-NMR spectra complement the ^1H-NMR spectra. In most cases they are rather similar to the corresponding $ROMgCl \cdot nTHF$ compounds which are dimers for R = *t*Bu, Ph, and naph[25]. However, the ^{13}C-NMR data of the mesityl compound **8** shows only a single set of signals while two sets are observed for $mesOMgCl \cdot 2\ THF$. The signals for the mes group in **8** can be readily explained if the compound is of the same structural type as **7**.

The ^{13}C-NMR signals for carbon atoms bound to the oxygen atom of the RO group provides a criterion for distinguishing a terminal (doubly-coordinated O atom) from a bridging RO group (triply-coordinated O atom). Thus, the signal at $\delta^{13}C$ = 83.2 of **5** gives evidence of its monomeric state because the same resonance is found for monomeric $Mg(OCPh_3)_2 \cdot 2$ dioxane[25]. Other $ROMg(AlH_4)$ compounds (R = Ph, naph) show a resonance for the CO atom in the range of δ = 161 ($\pm$ 1.5). This is typical for bridging RO groups while C atoms of aryloxo groups in terminal positions exhibit a ^{13}C resonance in the range of δ = 154–157. This holds also for compounds **8** and **9**.

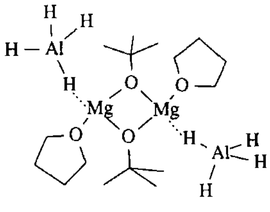
Although the NMR data allow some conclusions about possible structures for the (organyloxo)magnesium tetrahydroaluminates they give no information on the bonding of the $(AlH_4)^-$ group. However, IR data were helpful to some extent.

Table 4 presents data for $\nu(AlH_4)$ and $\delta(AlH_4)$, and tentative assignments are given. It seems that $Me_3COMg(AlH_4) \cdot 0.5\ THF$ (**4**) contains bidentate AlH_4 groups: IR bands can be assigned to terminal and bridging AlH_2 units of the AlH_4 group. The pattern for **5** and **6** would fit with a monodentate AlH_4 group, because it corresponds closely to IR bands found for **1a**, **2**, and **3a**. There are two strong bands in the IR spectrum of **7**: the band at 1717 cm^{-1} matches with those found for **2** and **3a**, and this indicates the presence of a monodentate AlH_4 group. The second band at 1750 cm^{-1} represents stronger Al–H bonding as expected for a bidentate or tridentate AlH_4 group. Finally, the AlH_4 stretching frequencies in **8** and **9** are difficult to assign. While the strongest band in the IR spectrum of **8** would indicate an ionic AlH_4^- group, five bands for **9** point to a more complex situation.

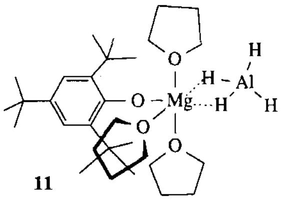
Table 4. IR bands [cm^{-1}] in the AlH stretching and deformation region for $ROMgAlH_4 \cdot n\ THF$ compounds

	4	**5**	**6**	**7**	**8**	**9**
νAlH_4	1816 m	1806 sh			1802 sh	1799 m
	1784 s		1731 vs	1750 vs		1774 s
	1729 vs	1732 vs		1717 vs	1685 vs,b	1753 s
	1649 sh	1645 sh			1613 sh	1725 m
						1676 m
δAlH_4	795 vs	790 vs				789 vs
	774 vs	764 vs	769 vs	769 vs	768 vs	781 s
	745 s	744 s	749 s	758 s		762 s
				737 s		749 s

Tentative structural assignments are represented in formulae **10** and **11** for compounds **4** and **9**.



10



11

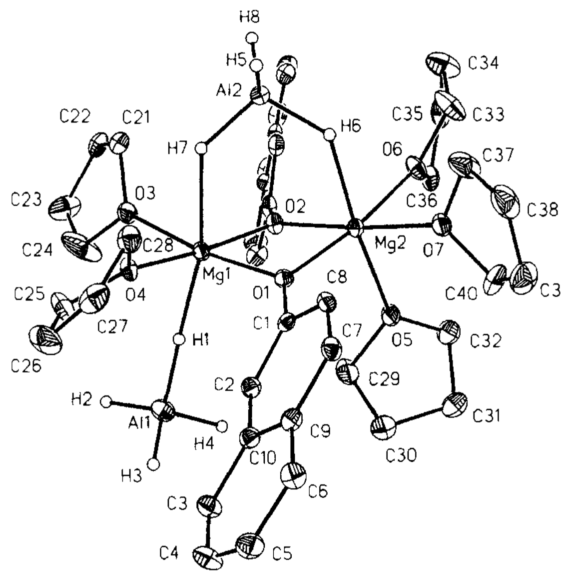
More light was shed on the structures of this class of compounds by the molecular structure of **7** which was determined by X-ray methods (Figure 3).

Compound **7** is dinuclear with a central Mg_2O_2 unit carrying 2-naphthyl groups. One of the two AlH_4 groups bridges *both* Mg centers by two single hydride bridge bonds while the second AlH_4 units is μ_1-bonded to one of the two magnesium atoms. In contrast to the molecular structures of **1a**, **2**, and **3** all Al–H bond lengths lie in the expected range, and the H–Al–H bond angles are close to tetrahedral. The THF molecules complete the coordination shell of the hexacoordinated Mg ions. The molecular structure of **7** is unexpectedly asymmetric.

This is further demonstrated by the Mg_2O_2 ring which is bent by 13.2°, with endocyclic angles at the Mg atoms of about 80° while those at the oxygen atoms are about 100°. This results in a Mg···Mg distance of 3.108(2) Å. The Mg–O bond length for the ring atoms range from 2.006(4) to 2.053(4) Å, and Mg–O atom distances to the THF molecules are of the same order [2.073(4)–2.173(4) Å].

The Mg–Al atom distances to the doubly bridging AlH_4 group is 3.350(2) and 3.309(2) Å, respectively, and the Al1···Mg1 distance is 3.627(2) Å, compared to distances of 3.627(5) and 3.618(3) Å in **2** and **3a**. The shorter distance

Figure 3. ORTEP representation of the molecular structure of compound **7**. Thermal ellipsoids are drawn on a 25% probability scale. Selected bond lengths [Å]: Mg1−O1 2.031(4), Mg1−O2 2.006(4), Mg1−O1 2.053(4), Mg2−O2 2.037(4), Mg1−O3 2.108(4), Mg1−O4 2.73(4), Mg2−O5 2.086(4), Mg2−O6 2.134(4), Mg2−O7 2.173(4), O1−C1 1.344.5(5), O2−C11 1.348(6); Mg1−H1 2.01(4), Mg1−H7 2.11(4), Mg2−H6 2.02(4); Al(1)−H1 1.62(5), Al(1)−H2 1.49(2), Al(1)−H3 1.52(5), Al(1)−H4 1.51(5), Al(2)−H5 1.57(4), Al(2)−H6 1.55(5), Al(2)−H7 1.54(4), Al(2)−H8 1.58(4). − Selected bond angles [°]: O2−Mg1−O1 79.4(1), Mg1−O1−Mg2 99.1(2), Mg1−O2−Mg2 100.5(2), O3−Mg1−O4 92.0(2), O5−Mg2−O7 78.1(1), O5−Mg2−O6 91.6(2), H−Al(1)−H 106−114(3), H−Al(2)−H 107−114(2). Folding angle at O2−Mg1−O1/O2−Mg2−O1 13.2°



in the doubly bridging AlH_4 group results from acute Mg−H−Al2 bond angles of 135 and 133°, respectively, as compared to 178° for Mg1−H1−Al1.

Discussion

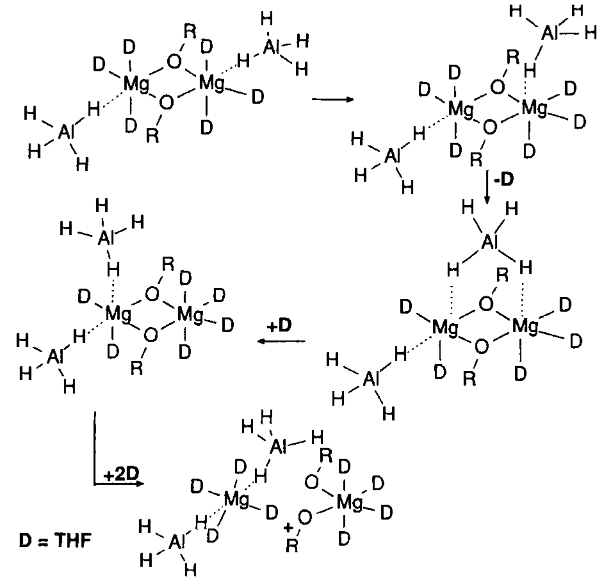
This study shows that NMR data (^1H, ^{13}C, ^{27}Al) provide only limited information on structure and bonding in various kinds of magnesium tetrahydroaluminates.

No resolution of the ^{27}Al-NMR signals due to $^1J(^{27}Al^1H)$ coupling was possible, and this is most likely due to rapid relaxation in an asymmetric environment[10]. IR spectra demonstrate that no free AlH_4^- ions are present in the compounds under investigation, except for $BrMg(AlH_4) \cdot$ 18-crown-6 (**3b**) [$\nu_{as}(AlH_4)$ 1653 cm^{-1}].

The splitting of the $\nu_{as}(AlH_4^-)$ vibration, which is to be expected if the symmetry of this anion is reduced from T_d to C_{3v} (μ_1-AlH_4) or C_{2v} (μ_2-AlH_4), is usually not pronounced. Thus, only X-ray structural analysis allows an unambiguous structure determination, at least for the solid state. The examples studied demonstrate that μ_1-AlH_4 bonding seems to be a characteristic element for magnesium tetrahydridoaluminates in contrast to magnesium tetrahydridoborates which are characterized by μ_2-BH_4^- and μ_3-BH_4^- groups[26]. The structural data for the AlH_4^- units in **7** indicate that this ligand is less strongly bound to Mg centers than BH_4^- ligands, but this must be further demonstrated by additional examples. This requires a more accurate determination of the hydrogen positions than can be obtained from X-ray methods.

In addition, it has been demonstrated that RO^-/H^- exchange in $ROMg(AlH_4)$ compounds can be prevented in THF by bulky RO groups. However, when diethyl ether dilutes the THF solutions of $ROMg(AlH_4)$, a ligand exchange into soluble $Mg(OR)_2$ and insoluble $Mg(AlH_4)_2 \cdot 4$ THF occurs, making it extremely difficult to grow single crystals of $ROMg(AlH_4)$ species. Single crystals only for **7** were obtained. The structure of this compound reveals how this exchange may occur. It represents an intermediate stage of the ligand exchange, which is depicted in Scheme 1.

Scheme 1



Our results indicate that the structural chemistry of metal tetrahydridoaluminates of main group metals is at least as rich in variations as found for transition metal tetrahydroaluminates, where μ_2-AlH_4[28], μ_2-$H_2Al[H$-μ_2-$H_2Al(H)$-$\mu_1H]$[29] and μ_3-AlH_4 units[30] were observed.

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Experimental

All experiments were conducted under dry nitrogen using Schlenk-tube techniques. Flame-dried glassware was used throughout as well as dry solvents, stored under N_2. Hydride contents were determined gasvolumetrically, Al^{3+} and Mg^{2+} by complexometric titration. $NaAlH_4$ was a gift from Chemetall mbH, Frankfurt. − NMR: Jeol EX 400 (^1H, ^{13}C), Jeol GSX 270 (^1H, ^{13}C, ^{27}Al), standards: iTMS, aqueous 1 M solutions of $AlCl_3$ and $MgCl_2$. IR: Nicolet 520 FTIR. − X-ray structural analyses: Siemens P4 diffractometer.

Magnesium Bis(tetrahydridoaluminate)−4 Tetrahydrofuran (**1a**): A 0.157 M solution of $LiAlH_4$ (180 ml, 103 mmol) was added to a well-stirred suspension of MgI_2 (12.9 g, 46.5 mmol) in 100 ml of

THF. Stirring was continued overnight, the solid material removed by filtration (G3 frit), washed with a small amount of THF (5 ml) and dried for 30 min in a vacuum of 0.1 Torr. Yield: 10.3 g of **1a** (57%), dec. >186°C.

$Mg(AlH_4)_2 \cdot 2$ THF (**1b**) is obtained by desolvating **1a** at 60°C and 0.1 Torr for 4 h. Single crystals of **1a** suitable for an X-ray structural analysis were obtained by allowing ether vapor to diffuse into a saturated solution of **1a** in THF. – **1a**: $C_{16}H_{40}Al_2MgO_4$ (374.8): calcd. Al 14.40, Mg 6.49, H^- 2.15; found Al 13.26, Mg 6.44, H^- 2.03. – **1b**: $C_8H_{24}Al_2MgO_2$ (230.5): calcd. Al 23.41, Mg 10.54, H^- 3.50; found Al 22.12, Mg 10.22, H^- 3.47.

Magnesium Bis(tetradeuterioaluminate)–4 Tetrahydrofuran (**1c**): Prepared analogously to **1a** from MgI_2 (2.296 g, 8.26 mmol) and $LiAlD_4$ (25.8 mmol, 25 ml of a 1.03 M solution in THF, diluted with 75 ml of THF). Yield: 0.88 g of **1c** (28%); dec. >300°C.

Magnesium Bis(tetrahydridoaluminate)–3 1,2-Dimethoxyethane (**1d**): Compound **1a** (1.0 g) was dissolved in 40 ml of DME with stirring overnight. Insoluble material was removed by centrifugation, and ether vapor was then allowed to diffuse into the saturated solution of $Mg(AlH_4)_2$ in DME. Clear crystals, m.p. 160°C, suitable for X-ray structural analysis formed within 2 d. The yield was not determined. – $C_{12}H_{38}Al_2MgO_6$ (356.7): calcd. Al 15.12, Mg 6.81, H^- 2.26; found Al 14.99, Mg 6.85, H^- 2.18.

MgCl(AlH₄) · 4 THF (**2**) *and MgBrAlH₄ · 4 THF* (**3a**) were prepared according to literature procedures[7].

Preparation of (Organooxo)magnesium Tetrahydridoaluminates. – General Procedure: ROMgCl was dissolved in THF, and a $NaAlH_4$ solution in THF was added with stirring. The precipitate which formed was removed by filtration. THF was evaporated from the soluton in vacuo and the residue analyzed. The precipitate was extracted with THF, insoluble material was removed by filtration and solvent was removed under vacuum from the clear filtrate. The solid residue, which was obtained, was analyzed and gave, in most cases, better analytical data than for the first crop.

tert-Butoxomagnesium Tetrahydridoaluminate (**4**): 2.02 g (15.2 mmol) of $Me_3COMgCl$; $NaAlH_4$: 11.5 ml of a 1.33 M solution (15.3 mmol) in THF; 20 ml of THF. Yield: 1.13 g of **4** (45%), dec. >360°C. – IR (Nujol, Hostaflon): $\tilde{\nu}$ = 1816 cm^{-1} (m), 1784 (s), 1729 (vs, b.), 873 [$\nu(OC_2)$], 795 (vs), 774 (vs), 428 [ν(MgO)]. – ^1H NMR (C_6D_6): δ = 3.59 (OCH_2, 2H), 1.4 (b. m, CH_2, CH_3, 11H). – ^{13}C NMR (C_6D_6): δ = 67.9 (OCH_2), 26.5 (Me), 25.8 (CH_2), CMe_3 not found. – $C_6H_{17}AlMgO_{1.5} = C_4H_{13}AlMgO \cdot 0.5$ THF (164.5): calcd. Mg 14.77, Al 16.40, Mg 14.77, H^- 2.45; found Al 16.75, Mg 14.63, H^- 2.13.

(Trityloxo)magnesium Tetrahydridoaluminate (**5**): 4.00 g of $Ph_3COMgCl$ (10.2 mmol); $NaAlH_4$: 7.7 ml of a 1.33 M solution (10.2 mmol), 40 ml of THF. Pure **5** was extracted from the precipitate. Yield: 1.73 g (54%), m.p. 154°C. – IR (Nujol/Hostaflon): $\tilde{\nu}$ = 1806 cm^{-1} (sh), 1732 (vs), 1654 (sh), 879 (s), 790 (s), 764 (vs), 744 (vs). – ^1H NMR (C_6D_6): δ = 7.63 [d, ^3J(H,H) = 7.33 Hz, *p*-H, 3H], 7.17 (m, *m*-H, 6H), 7.06 [t, ^3J(H,H) = 7.33 Hz, *o*-H, 6H], 3.59 (b. 16H). – ^{13}C NMR (C_6D_6): δ = 151.1 (*i*-C); 129.2 (*m*-C), 128.9 (*p*-C), 126.6 (*o*-C), 83.2 (*C*O). – $C_{19}H_{19}AlMgO$ (314.6): calcd. Al 8.58, Mg 7.72, H^- 1.28; found Al 9.27, Mg 7.61, H^- 1.24.

Phenoxomagnesium Tetrahydridoaluminate (**6**): 1.08 g of $PhOMgCl \cdot 2$ THF (3.6 mmol); $NaAlH_4$: 5.8 ml of a 0.62 M THF solution (3.6 mmol); 20 ml of THF. Precipitate removed after stirring for 15 h. Yield: 0.73 g of **6** (78%), m.p. >202° (dec.). If ether vapor was allowed to diffuse into the solution of **6**, a precipitate of **1a** formed. – IR (Nujol, Hostaflon): $\tilde{\nu}$ = 1732 cm^{-1} (vs), 769 (vs), 879 (s), 749 [(s), $\delta(AlH_4)$], 421 [ν(MgO)]. – ^1H NMR (C_6D_6): δ = 7.70 [d, ^3J(H,H) = 7.32 Hz), *o*-H, 2H], 6.74 (m, *p*-H, 1H), 3.57 (THF, 6H), 1.25 (THF, 6H). – ^{13}C NMR (C_6D_6): δ = 162.5 (*i*-C), 129.2 (*m*-C), 121.8 (*p*-C), 119.1 (*o*-C), 69.0 (THF), 24.7 (THF). – $C_6H_9AlMgO \cdot 1.5\ C_4H_8O$ (256.6): calcd. Al 10.52, Mg 9.47, H^- 1.57; found Al 10.28, Mg 9.57, H^- 1.77.

2-Naphthoxomagnesium Tetrahydridoaluminate (**7**): 3.564 g of $naphOMgCl \cdot 2$ THF (10.3 mmol); $NaAlH_4$: 7.7 ml of a 1.33 M solution in THF (10.2 mmol); 10 ml of THF. Precipitate removed after 1 h. Single crystals were obtained by letting ether vapor dissolve in the THF solution of **7**. Yield: 1.65 g of **7** (52%), m.p. 162°C, dec. 192°C. – IR (Nujol, Hostaflon): $\tilde{\nu}$ = 1750 cm^{-1} (vs), 1717 (vs), 796 (vs, b.), 737 (s, b.), 421 [ν(MgO)]; in THF: 1734 (b.), 750 (vs). – ^1H NMR (C_6D_6): δ = 7.67, 7.17 (m), 4.0 (AlH), 3.57 (THF, 6H), (THF, 6H). – ^{13}C NMR (C_6D_6): δ = 160.2, 135.9, 129.2, 128.6, 127.4, 126.5, 125.3, 124.5, 116.2, 69.0, 25.3. – $C_{10}H_{11}AlMgO \cdot 1.5\ OC_4H_8$ (306.6): calcd. Al 8.79, Mg 7.93, H^- 1.31; found Al 8.77, Mg 7.80, H^- 1.21.

(Mesityloxo)magnesium Tetrahydridoaluminate (**8**): 3.07 g of $mesOMgCl \cdot 2$ THF (9.1 mmol); $NaAlH_4$: 14.6 ml of a 0.62 M solution in THF (9.05 mmol); 30 ml of THF. The solution became free from Cl^- only after cooling to −78°C for 14 h. The supernatant solution gave a low yield of **8** after removal of the solvent. Therefore, the precipitate was extracted several times with THF. Yield: 2.17 g of **8** (65%), m.p. >220°C (dec.). – IR (Nujol, Hostaflon): $\tilde{\nu}$ = 1802 cm^{-1} (sh), 1685 (vs, b.), 1613 (sh), 768 (b.). – ^1H NMR (C_6D_6): δ = 6.81 (s, *m*-H, 2H), 3.44 (THF), 2.39 (s, *o*-CH_3, 6H), 2.23 (s, *p*-CH_3, 3H), 1.30 (THF). – ^{13}C NMR (C_6D_6): δ = 154.5 (*i*-C), 129.2 (*o*-C), 128.8 (*m*-C), 126.4 (*p*-C), 67.2 (THF), 20.9 (*p*-CH_3), 18.3 (*o*-CH_3). – $C_9H_{15}AlMgO \cdot 2.5\ C_4H_8O$ (370.8): calcd. Al 7.28, Mg 6.55, H^- 1.08; found Al 7.80, Mg 6.40, H^- 1.04.

(2,4,6-Tri-tert-butylphenoxo)magnesium Tetrahydridoaluminate (**9**): 640 mg of smesOMgCl (2 mmol); $NaAlH_4$: 3.3 ml of a 0.62 M solution (2 mmol) in THF; 20 ml THF. The "NaCl" precipitate was extracted with THF to give a total yield of 3.82 g of **9** (69%). If ether vapor was allowed to diffuse into the THF solution of **9** the compound $Mg(AlH_4)_2 \cdot 4$ THF (**1a**) separated. – **9**: IR (Nujol, Hostaflon): $\tilde{\nu}$ = 1799 cm^{-1} (m), 1774 (s), 1753 (s), 1725 (m), 1676 (m), 789 (vs), 762 (vs), 749 [vs, $\delta(AlH_4)$], 885 (sh), 876 (vs), 863 (vs), 842 (vs), 433 [ν(MgO)?]. – ^1H NMR (C_6D_6): δ = 7.56, 7.50 (*m*-H, 2H), 3.62 (THF, 12H), 1.80 (THF, 12H), 1.46, 1.40 (s, *o*-CH_3, 18H), 1.38 (s, *p*-CH_3, 9H). – ^{13}C NMR (C_6D_6): δ = 156.3, 139.1, 138.1, 137.4, 136.6, 121.9, 68.9, 35.9, 35.6, 34.6, 34.5, 32.2, 32.1, 31.6, 25.4. – $C_{18}H_{33}AlMgO \cdot 3\ OC_4H_8$ (533.1): calcd. Al 5.06, Mg 4.56, H^- 0.76; found Al 5.40, Mg 4.12, H^- 0.76.

X-ray Structure Determinations[31]. **1a**: $C_{16}H_{40}Al_2MgO_4$ (374.75), colorless rhombus, crystal size = 0.6 × 0.5 × 0.45 mm^3; a = 10.158(3), b = 16.459(3), c = 14.025(5) Å, V = 2345(1) $Å^3$, Z = 4, orthorhombic, space group *Pbcn*, μ = 1.64 cm^{-1}, d = 1.062 g/cm^3, $F(000)$ = 824. – 2Θ range = 4.7–47° in $-9 \leqslant h \leqslant 9$, $-18 \leqslant k \leqslant 1$, $0 \leqslant l \leqslant 15$, 3013 reflections collected, 1726 unique and observed reflections (R_{int} = 0.0338), data:parameter = 15.4:1, R = 0.0647, $wR2$ = 0.173, GOF = 1.034, largest difference peak/hole = 0.834/−0.311 e/$Å^3$.

2: $C_{16}H_{36}AlClMgO_4$ (379.19), crystal size = 0.4 × 0.4 × 0.3 mm^3, colorless rhombus, T = 173 K, a = 18.95(1), b = 14.590(6), c = 7.978(3) Å, V = 2206(3) $Å^3$, orthorhombic, space group $Pna2_1$, Z = 4, $d_{calc.}$ 1.142 Mg/m^3, μ = 0.255 mm^{-1}, $F(000)$ = 824. – 2Θ range = 3.5–47° in h, $-k$, l, 1990 refl. collected, 1869 indepent and 1397 observed. – Parameters refined: 207; R = 0.088, GOF = 1.070, lagest peak/hole = 0.997/−0.316 $eÅ^{-3}$.

3a: $C_{16}H_{36}AlBrMgO_4$ (323.65), colorless cube, crystal size: 0.6 × 0.6 × 0.4 mm^3; a = 19.094(8), b = 14.620(7), c = 7.943(3) Å,

$V = 2217(2)$ Å^3, $Z = 4$, orthorhombic, space group $Pna2_1$, $F(000) = 986$. – 2Θ range: 3.5–48° in $-21 \leq h \leq 21$, $-16 \leq k \leq 0$, $-9 \leq l \leq 9$, 5350 data collected, 3444 independent reflections ($R_{\mathrm{int}} = 0.0566$), semiempirical absorption correction, max/min transmission: 1.000/0.441, $R = 0.048$, $wR2 = 0.1083$, GOF = 1.026, largest diff. peak/hole = 0.407/–0.397 e/Å^3.

7: $C_{40}H_{62}Al_2Mg_2O_7$ (613.28), colorless cube, crystal size = 0.48 × 0.3 × 0.25 mm^3; $a = 11.139(4)$, $b = 11.667(5)$, $c = 18.996(5)$ Å, $\alpha = 90.08(3)$, $\beta = 104.21(2)$, $\gamma = 115.94(3)°$, $V = 2135(2)$ Å^3, $Z = 2$, $d = 1.178$ g/cm^3, $\mu = 1.42$ cm^{-1}, triclinic, space group $P1$bar, $F(000) = 816$. – 2Θ range = 2–46° in $0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$. 5972 data collected, 5664 unique reflections [$F > 4\sigma(F)$], 484 parameters refined, $R = 0.0599$, $wR2 = 0.1242$, GOF = 1.029, largest diff. peak/hole = 0.351/–0.271 e/Å^3. Positions of AlH_4 hydrogen atoms were freely refined.

☆ Dedicated to Dr. *R. Bauer*, who first synthesized magnesium tetrahydridoaluminate, on the occasion of his 70th birthday.

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