Metal Tetrahydroborates and Tetrahydroborato Metalates. 30 [1] Solvates of Alcoholato-, Phenolato-, and Bis(trimethylsilyl)amido-Magnesium Tetrahydroborates $XMgBH_4(L_n)$

Metall Tetrahydroborate und Tetrahydroborato Metallate, 30 [1]. Solvate der Alkoholato-, Phenolato- und Bis(trimethylsilyl)amino-magnesiumtetrahydroborate $XMgBH_4(L_n)$

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Dedicated to Professor Martin Jansen on the Occasion of his 60th Birthday

Abstract. A series of alcoholato and phenolato magnesium tetrahydroborates have been prepared as solvates (RO)Mg(BH₄)(OEt₂) by 1:1 reactions of ROH (R = Me, Et, *i*Pr, *t*Bu, CH₂CMe₃, Et₂(*t*Bu)C, Ph₃C, Ph, 2,4,6-Me₃C₆H₂, (2,6-iPr)₂C₆H₃, (2,6-tBu₂)C₆H₃, 2-(iPrO)C₆H₄, 2,6-(MeO)₂C₆H₃) with diethyl ether solutions of EtMg(BH₄). Displacement of diethyl ether by thf, dme, and diglyme produced various solvates $(RO)Mg(BH_4)(L)_n$ (L = thf, dme, diglyme, n = 1, 2, 3). Most of these compounds are centrosymmetric dimers with a central Mg₂O₂ four membered ring. Irrespective of the composition, the ¹¹B NMR signals are 1:4:6:4:1 quintets showing that the hydrogen atoms of the BH4 groups are magnetically equivalent. The molecular structure of eight compounds $[(RO)Mg(BH_4)(OEt_2)]_2$ (R = *i*Pr, *t*Bu, *t*BuCH₂, Et₃C, Me₃Si), [(PhO)Mg(BH₄)(thf)₂]₂, (2,6-tBu₂C₆H₃O)Mg(BH₄)(thf)₂, (2,6-tBu₂-C₆H₃O)-Mg(BH₄)(thf)(dme)) have been determined. Typical for all compounds are hexacoordinated Mg atoms. The mononuclear complexes feature bidentate BH4 groups while dinuclear species show di- or tridentate BH4 groups depending on the number of coordinated O atoms.

Mononuclear species are obtained only for compounds with bulky R groups, e. g. $2,6-(tBu_2)(C_6H_3O)Mg(BH_4)(thf)_2$ with tridentate BH₄ groups. This compound has a linear O-C-Mg unit. In Me₂SO the compound [(2-iPrO)C₆H₄O]Mg(BH₄)(OEt₂) underwent ligand exchange to produce [(2-*i*PrO)C₆H₄O]₂Mg(OSMe₂)]₂.

Reaction of EtMgBH₄ with a stoichiometric amount (1:1) of $(Me_{3-}Si)_2NH$ gives [($(Me_3Si)_2N$)-Mg(BH₄)(OEt₂)]₂, **46** with a tridentate BH₄ group. Its diethyl ether molecule can be replaced by thf, dme and diglyme. Amongst these solvates the compound [(Me₃₋Si)₂N]Mg(BH₄)(diglyme) is mononuclear and its structure shows a bidentate BH₄ group. Compound **46** on repeated crystallization from diethyl ether is transformed into [(Me₃SiO)Mg(BH₄)(OEt₂)]₂. No compound with a BH₄ group bonded to two Mg atoms has so far been found.

Keywords: Boron; Magnesium; Tetrahydroborates; Alkoxo compounds; BH_4 bonding

Introduction

Beryllium and magnesium tetrahydroborate bridge the gap between the ionic metal tetrahydroborates such as NaBH₄ or KBH₄ and the covalent metal tetrahydroborates exemplified by Al(BH₄)₃ and Zr(BH₄)₄. While the structure of Be(BH₄)₂ is well established for the solid state [2] showing hexacoordinated Be atoms in a helical chain, the analyses of its vibrational spectra allows no firm conclusion as to the structure in solution, even using isotopic labeling [3, 4]. Calculations for the monomeric molecule shows [5] that the most stable species has D_{3d} symmetry. In contrast, the

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structure of non solvated $Mg(BH_4)_2$ is still unknown but it can be expected that the BH_4 groups will bridge to at least two Mg atoms forming either a chain like $Be(BH_4)_2$, or, more likely, a layer or even an extended three dimensional array in the solid state because the Mg atom prefers higher co-ordination numbers than Be.

Solvates of magnesium tetrahydroborate, $Mg(BH_4)_2(L)_n$, are, in general, mononuclear with bidentate BH_4 units. Typical examples are $Mg(BH_4)_2(thf)_3$ [6, 7], $Mg(BH_4)_2(di$ glyme) [8] or $Mg(BH_4)_2(py)_4$ [1]. Although a number of "mixed" magnesium tetrahydroborates $XMg(BH_4)$ are known (X = H [9], Cl [10, 11], Et [12–14]) there is no information about their molecular state in solution nor on their structures in the solid state. However, it is to be expected that the bonding mode for the BH_4 group may change within the series of magnesium tetrahydroborates $XMgBH_4(L)_n$ (X = RO, R₂N; L = various ethers, n = 1, 2, 3), and that the substituents X will bridge Mg atoms more readily than BH_4 , generating di-, tri- or even polynu-

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clear species, and the degree of association will also depend on the type and number of coordinated solvent molecules L. These aspects initiated the present study.

Solvates of Organyloxomagnesium Tetrahydroborates

Synthesis

Mixed magnesium tetrahydroborates have been prepared by several routes. These are summarized by equations (1) to (5) ignoring formation of solvates:

 $MgH_2 + BH_3 \cdot thf \rightarrow HMg(BH_4) + thf$ (1)

$$ClMgH + BH_3 \cdot thf \rightarrow ClMg(BH_4) + thf$$
 (2)

$$\begin{split} XMgR + 2 & BH_3 \cdot thf \rightarrow XMg(BH_4) + RBH_2 + thf \eqno(3) \\ (X = Cl, Br; R = Et, Pr, Ph) \end{split}$$

 $RMgCl + M(BH_4) \rightarrow RMg(BH_4) + MCl$ (4) (R = Me, Et; M = Li, Na)

 $EtMg(BH_4) + HX \rightarrow XMg(BH_4) + EtH$ (5) (X = Cl, RO)

 $(RO)Mg(BH_4)(L_n) + m L' \rightarrow (RO)Mg(BH_4)(L')_m + n L$ (6)

 $EtMgBH_4 + tBu_2C = O \rightarrow (tBu_2EtCO)Mg(BH_4)$ (7)

EtMgBH₄ was the first in the series of mixed magnesium tetrahydroborates obtained by reaction (4), and both, LiBH₄ and NaBH₄ were used for the metathesis [12, 13]. HMg(BH₄) resulted by allowing a large excess of solid MgH₂ to react with BH₃·thf in thf solution [9]. ClMg(BH₄) was synthesized from HMgCl or EtMgCl and BH₃·thf in thf [10, 11]. For the preparation of organyloxo and amido magnesium tetrahydroborates we chose reactions according to equation (5) because other starting materials such as RMgX and XMgCl (X = RO, R₂N) are in most cases not well defined. Several reactions according to equation (5) were followed by ¹¹B NMR spectroscopy. These studies showed that the B–H bond of the BH₄ group of EtMg(BH₄) is not attacked by the protic reagents ROH and R₂NH in contrast to the Mg–C bond.

Diethyl ether solvates (RO)Mg(BH₄)(OEt₂)_n (n = 1, compounds 1 to 11, 14; n = 2, compounds 12, 13) were readily obtained in 1: 1 reactions and in good yield from diethyl ether solutions of EtMg(BH₄) and ROH. These diethyl ether solvates on treatment with thf, dme or diglyme provided the thf solvates 16 to 25, the dme solvates 26 to 34, and the diglyme solvates 35 to 44 as shown in equation (6). Ether displacement is achieved according to the series $Et_2O < thf < dme < diglyme < Me_2SO$. Usually, the ether displacement is quantitative, but in case of thf displacement by dme a mixed solvate was obtained in case of (2,6-*t*Bu₂. C_6H_3O)Mg(BH₄) which was isolated as (2,6-*t*Bu₂. C_6H_3O)Mg(BH₄)(thf)(dme), 33. An alternative route to alcoholato magnesium tetrahydroborates was found in the re-

Table 1 Solubilities of various (RO)MgBH_4 compounds in ethers (mol/l) at 20 $^{\circ}\mathrm{C}$

RO	Et ₂ O	thf	dme	diglyme	
MeO	0.48	0.11 ^{a,b)}	_		
EtO	0.11	0.14 ^{a)}	0.04	0.18	
iPrO	0.04	0.37 ^{a)}	0.43	_	
tBuO	0.11	0.12 ^{a)}	0.02 ^{e)}	0.27	
Et ₃ CO	0.09	0.12 ^{a)}	0.87	0.08	
Me ₃ CCH ₂ O	0.56	-	-	_	
Ph ₃ CO	0.03	-	-	_	
PhO	0.07	0.02	0.63 ^{f)}	0.17	
2,4,6-Me ₃ C ₆ H ₂ O	0.35	0.7 ^{c)}	-	0.31	
2,6-iPr ₂ C ₆ H ₃ O	0.32	d)	0.14 ^{g)}	0.77	
$2,6-tBu_2C_6H_3O$	0.14	>0.32	-	0.36	
2-(iPrO)C ₆ H ₄ O	0.12	0.06	-	_	
$2,6-(MeO)_2C_6H_3O$	0.01	0.05	0.08	0.13	

^{a)} at 5 – 8 °C; ^{b)} 1:1 mixture of Et₂O and thf; ^{c)} at –20 °C; ^{d)} crystals separated from a 1M solution at –20 °C; ^{c)} 2:1 diethyl ether diglyme solution; ^{f)} solubility after heating to reflux and cooling to 20 °C; ^{g)} a 3.5 : 1 diethyl ether/dme solution was used.

action of diethylketone with $(tBu)Mg(BH_4)$, which leads to $(tBuEt_2CO)Mg(BH_4)(OEt_2)$, **15**, as shown in equation (7). This demonstrates that the Mg-C bond is more reactive than the BH bonds of the MgBH₄ group. The alkoholato and phenolato magnesium tetrahydroborates are much less soluble in diethyl ether than EtMg(BH₄) but most of them are sufficiently soluble in benzene for NMR studies. The solubility has been determined for 13 compounds in four different ethers (see Table 1).

It is surprising that $(MeO)Mg(BH_4)$ is much better soluble in diethyl ether than $(iPrO)Mg(BH_4)$ or $(tBuO)Mg(BH_4)$ in contrast to the solubility in thf and dme. Several of the dme and diglyme solvates are only sparingly soluble in their own ether, but all dissolve readily in Me₂SO. ¹¹B NMR studies in acetonitrile show that at ambient temperature acetonitrile is not reduced rapidly by these magnesium tetrahydridoborates as the quintet for the BH₄ group can be observed for several hours.

Table 2 lists the isolated ether solvates of the (RO)Mg(BH₄) compounds, their ¹H and ¹¹B chemical shifts (in ppm) and the ¹J(¹¹B¹H) coupling constants in Hz. Also ¹J(¹⁰B¹H) values are quoted when observed.

Most (RO)Mg(BH₄) compounds bind one diethyl ether molecule, exceptions being the compounds **12** and **13** which coordinate two diethyl ether molecules. This suggests, that the structures of the latter two differ from the 1 : 1 solvates. Most likely **12** and **13** are mononuclear species while the others are dinuclear (v. i.).

The base thf coordinates more strongly than Et_2O to the Mg centers of (RO)Mg(BH₄). Most compounds contain two thf solvate molecules (16, 28, 23, and 24) but even three thf molecules may act as ligands as shown for compound 22 which most likely is mononuclear. A 2 : 3 ratio of Mg : thf was observed for 17. Solvates of (RO)Mg(BH₄) with one dme molecule (26, 27, 33) may be mononuclear, while those of formula (RO)Mg(BH₄)(dme)_{0.5} (28, 29) are probably di-

Table 2 Composition of the isolated solid (RO)Mg(BH₄)(L)_n compounds, numbering of the compounds in bold letters, ¹¹B (upper line) chemical shifts (in ppm), and the corresponding coupling constants ${}^{1}J({}^{11}B^{1}H)$ (Hz, in parenthesis) of the ${}^{11}BH_{4}$ unit. (in addition for **8**, **24**, **25**, **34**, 44: ${}^{1}J({}^{10}B^{1}H)$

	Et ₂ O	thf,n	dme,n	diglyme,n
MeO	1, n = 1 -44.2 (78.6) ^a	16, n = 2, -2.0 (81.1) ^{a)} 0.42 (81.6)	-	35 , n =1, -3.4 (80.2) ^{a)}
EtO	- 2, n = 1 $-42.6 (81.0)^{a}$ $-0.33 (81.5)^{b}$	0.42 (81.0) 17, n = 1.5, -38.5 (79.1) a) 0.42 (80.1) a)	26 , n = 1, -41.2 (79.6) ^{c)}	-36, n = 1, -42.3 (br) ^{a)}
iPrO	3 , n = 1, -43.7 (82.6) ^{a)} 0.40 (84.4) ^{a)}	$18, n = 1, -42.1 (81.6)^{a}$	27 , n = 1, -41.3.(82.3) ^{a)}	37 , n = 2, -41.4 (82.3) ^{a)}
tBuO	$\begin{array}{c} \textbf{4, n = 1,} \\ -43.0 \ (82.1) \ ^{a) \ d)} \\ 0 \ 55 \ (82.4) \end{array}$	19 , n = 1, -42.7 (81.4) ^{a)} 0.61 (83.4)	28 , n = 0.5, -40.3 (79.1) ^{a)}	38 , n = 0.33, -42.9 (82.3) ^{a)}
Et ₃ CO	5. $n = 1$, -42.5 (80.9) ^{a)} 0.75 (81.0)	20 , $n = 1$, -43.0 (82.8) ^{a)} 0.55 (82.3)	29 , n = 0.5, -42.9 (82.0) ^{a)} 0.55 (81.9)	39 , n = 0.5, -43.7 (82.4) ^{a)}
Me ₃ CCH ₂ O	6, n = 1, $-44.4 (82.8)^{a}$ 0.48 (82.8)	_	_	40 , n = 1.33, $-35.7 (80.9)^{\circ}$ -0.29 (81.5)
Ph ₃ CO	7, n = 1, -40.9 (81.2) ^{a)} -0.16 (82.8)	-	-	$41, n = 1, -42.8 (83.4)^{a}$
MeOCH ₂ CH ₂ O	8 , n = 1, -35.9 (81.6) ^{c)} 0.42 (81.5, 27.4)	-	30 , n = 0.66, -41.5 (80.3)	_
PhO	9 , $n = 1$, -40.9 (81.2) ^{a)}	21 , n = 2 -41.4 (79.5) ^{a)} 0.72 (83.1)	31 , n = 1.5, $-39.4 (84)^{a}$ -0.80 (79.1)	_ <e< td=""></e<>
2,4,6-Me ₃ C ₆ H ₂ O	10 , n = 1, -42.4 (81.3) ° ^o -0.29 (81.5, 27.3) ^b)	_	-	-
2,6-iPr ₂ C ₆ H ₃ O	$11, n = 1, -40.8 (97.5)^{c) e}$	22 , n = 3 $-41.8(82.6)^{a}$ 0 36 (83 3)	32 , n = 1, -40.4 (80.8) ^{b)} -0.27 (81.5)	42 , n =1, -43.3 (80.7) ^{a)} 0.37 (81.9)
2,6- <i>t</i> Bu ₂ C ₆ H ₃ O	12 , n =2, -41.0 (79.1) ^{a)}	23 , n = 2, -42.6 (79.6)	33 , $n = 1, 1$ thf, -41.5 (82.2) ^{a)}	$43, n = 1, -42.6 (82.2)^{a} 0.45 (82.0)$
2-(iPrO)C ₆ H ₄ O	13, n = 2, -41.7 (br) ^{a) f)} -0.09 (81.5), -0.12 (81.5) ^{b)}	24 , n = 2, -38.5 and -42.6 °) broad, nresolv. - 32 (81 6 27 3)	_	
(2,6-MeO) ₂ C ₆ H ₃ O	$ \begin{array}{l} \mathbf{14, n = 1} \\ -45.2 (81.4)^{(a) (g)} \\ 0 31 (81.5)^{(b)} \end{array} $	25, n = 1 -36.0 (81.5) b -0.31 (82.1, 27.4)	34 , n = 1.5 -34.5 (81.0) ^{b)} -0.31 (81.6, 27.1)	44, n = 0.33 -34.6 (br) ^{b)} -0.31 (81.5, 27.3) ^{b)}
Et ₂ (<i>t</i> Bu)CO	$\begin{array}{l} \textbf{15, n = 1} \\ -43.0 \ (82.1)^{\text{ a)}} \\ -0.4 \ (82.2) \end{array}$	-	_	-

^{a)} in C₆D₆, ^{b)} in d₆-Me₂SO, ^{c)} in thf, ^{d)} in Et₂O, ^{e)} in Me₂SO: -35.5 ppm (81.6), ^{f)} in Me₂SO -36.0 ppm (80.9), ^{g)} in Me₂SO: -35.9 (81.4)

nuclear with a bridging dme ligand between two Mg atoms. Compound $[(PhO)Mg(BH_4)]_2(dme)_3$, **32**, must surely be dinuclear. Provided that the Mg atoms are equivalent, one can speculate that one dme molecule bridges the Mg atoms, while the other two are bonded as monodentate dme ligands. This would require bidentate BH₄ groups (v. i.). On the other hand, we assume that compounds of type (RO)Mg(BH₄)(diglyme) (**36** and **41**) are mononuclear with hexacoordinated Mg atoms and bidentate BH₄ groups, while that of composition (RO)Mg(BH₄)(diglyme)_{0.33}, **38**, most likely binds one Mg atom per solvent oxygen atom. If we assume that all compounds contain a hexacoordinated Mg atom then the structures A to E shown in scheme 1 are feasible. Only one isomer is shown.

While no ligand exchange to produce $Mg(BH_4)_2$ and Mg(OR) has been observed during the ether displacement reactions this happened during the crystallization of [(2-iPrO)C₆H₄O]-Mg(BH₄)(OEt₂) from Me₂SO as shown in Eq. (8).

 $2 [(2-iPrO)C_{6}H_{4}O]Mg(BH_{4})(OEt_{2}) + 7 Me_{2}SO \rightarrow [(2-iPrO)C_{6}H_{4}O]_{2}Mg(OSMe_{2}) + [Mg(OSMe_{2})_{6}](BH_{4})_{2}$ (8)



Scheme 1



Figure 1 Molecular structure of dimeric (*i*PrO)Mg(BH₄)(OEt₂), (**3**). Selected bond lengths/Å: Mg-O1 1.945(2), Mg-O1A 1-950(2), Mg-O2 2.022(2), Mg··B 2.251(3), Mg-H10 2.08(3), Mg-H11 2.06(3), B-H10 1.11(3), B-H11 1.16(3), B-H12 1.11(3). B-H13 1.06(3). – Selected bond angles/°: O1-Mg-O1A 84.0(1), Mg-O1-Mg1A 96.0(1), Mg-H10-B 84(2), Mg-H11-B 83.(2), Mg-B-H13 177(2), H10-B-H11 107(2), H10-B-H12 102(2), H10-B-H13 115(2), H11-B-H12 108(2), H11-B-H13 111(2), H12-B-H13 113(2).

Molecular Structures

Knowledge of the structure of the $(RO)Mg(BH_4)(L)_n$ compounds could be helpful for the interpretation of NMR and IR spectroscopic data. For this reason we determined the structures of several of the organyloxo magnesium tetrahydroborates.

Compounds (RO)Mg(BH₄)(OEt₂) (R = Me₂CH, **3**; Me₃C, **4**; Me₃CCH₂, **6**, and Me₃Si, **50**) crystallize in the monoclinic system, space group P2₁/n. They all are dinuclear with the RO oxygen atom bridging the two Mg atoms. The molecules feature planar four-membered Mg₂O₂ rings with a crystallographic inversion centre in the middle of this ring. A consequence of the inversion centre is that the ligands and substituents are *trans* oriented. Their structures including the triclinic **5** are shown in Figures 1 to 5.

Typical for these compounds are tridentate BH_4 groups. The Mg···B distances vary from 2.168(5) to 2.244(6) Å. The shortest distance is observed for the neopentyl derivative **6**. Moreover, also the B-Mg-O angle of this compound is quite different compared with those of the other four com-



Figure 2 Molecular structure of dimeric $(tBuO)Mg(BH_4)(OEt_2)$, (4).

Selected bond lengths/Å: Mg-O1 1.947(2), Mg-O2 2.045(2), Mg-O1A 1.949(2), O1-C1 1.436(4), O2-C7 1.455(4), O2-C5 1.453(4), Mg-H1 2.05(4), Mg-H2 2.02(4), Mg-H3 2.11(4), B-H1 1.19(4), B-H2 1.20(4), B-H3 1.10(4), B-H4 1.10(4), Mg \cdots B 2.268(5). – Selected bond angles/°: O1-Mg-O2 107.5(1), B-Mg-O1 122.5(1), B-Mg-O2 108.6(1), B-Mg-O1A 123.4(1), O2-Mg-O1A 108.0(1), O1-Mg-O1A 84.0(1), Mg-O1-C1 132.7(2), Mg-O1-MgA 96.0(1), MgA-O1-C1 131.3(2), Mg-O2-C5 19.7(2), Mg-O2-C7 124.8(2), C5-O2-C7 114.3(3), H1-Mg-H2 53(1), H1-Mg-H3 51(1), H2-Mg-H3 53(1), H1-B-H2 99(2), H1-B-H3 103(2), H1-B-H4 122(3), H2-B-H3 107(3), H2-B-H4 123(3), H3-B-H4 111(3).

pounds. While the lengths of the Mg-O bonds are practically the same for $(iPrO)Mg(BH_4)(OEt_2)$, **3**, $(tBuO)Mg(B-H_4)(OEt_2)$, **4**, and $(tBuCH_2O)Mg(BH_4)(OEt_2)$, **6**, those of $(Et_3CO)Mg(BH_4)(thf)$, **20**, are significantly longer. This is obviously a consequence of the high steric demand of the Et_3C group. The diethyl ether molecule is most firmly attached to the Mg centre in the neopentyloxy derivative **6**. The difference in the Mg–OR and Mg–OEt₂ bond lengths is largest in **4**. Moreover, the B–Mg–O1 bond angle is sharper by 6° in compound **6** than in the other three compounds. The smaller the B–Mg–O1 bond angle the larger the B–Mg–O2 bond angle.

If we consider the BH_4 anion as a "pseudohalide" (BH_4^- has the same number of valence electrons as fluoride, but its effective ions radius corresponds with that of the bromide ion), then the Mg atoms in [(RO)Mg(BH_4)(OEt₂)]₂ are tetracoordinated. But the bond angles around the Mg atom are strongly distorted from a tetrahedral geometry, considering only the MgO₃B core, due to the sharp O1-Mg1-O1A bond angle of the Mg₂O₂ ring. However, the Mg atoms in these compounds can also be looked at as being hexacoordinated, if we take the Mg-H interactions into account. Then the coordination polyhedron around the Mg atom is a strongly distorted octahedron. This is, in particular, due to the very sharp H-Mg-H bite angles which are close to 70°.

In this context we include here also the molecular structure of [(Me₃SiO)Mg(BH₄)(OEt₂)]₂, **50** (v. i., see Figure 5).



Figure 3 Molecular structure of dimeric $(Et_3CO)Mg(BH_4)(thf)$, (20).

Selected bond lengths/Å: Mg-O1 1.963(2), Mg-O2 2.034(2), Mg-O1A 1.960(2), Mg···B 2.290(5), O1-C1 1.437(3), O2-C8 1.441(5). O2-C11 1.44(5), Mg-H1 2.12(4), Mg-H2 2.18(4), Mg-H3 2.09(4), B-H1 1.13(4), B-H2 1.10(3), B-H3 1.14(4), B-H4 0.97(4). – Selected bond angles/°: O1-Mg-O2 108.5(1), O1-Mg-O1A 84.8(1), O1-Mg-B 123.4(1), O2-Mg-B 104.8(1), B-Mg-O1A 125.2(1), Mg-O1-C1 132.5(2), Mg-O1-MgA 95.2(1), MgA-O1-C1 132.3(2), Mg-O2-C11 127.0(2), Mg-O2-C8 123.7(2), C8-O2-C11 109.1(3), H1-Mg-H2 49(1), H1-Mg-H2 51(1), H2-Mg-H3 50(1), Mg-H1-B 84(1), Mg-H2-B 82(2), H3-Mg-B 85(2), H1-B-H2 95.2(2), H1-B-H3 106.5(26), H1-B-H4113(3), H2-B-3 107(2), H2-B-H4 108(3), H3-B-H4 116(3).

Its Si-O bond is comparatively short (1.612(2) Å), and the oxygen atom is located in a planar environment. The short Mg-B distance fits to a tridentate BH₄ group as found for compounds **3** to **6**.

The phenolate (PhO)Mg(BH₄)(thf)₂, **21**, may be mononuclear with a tridentate BH₄ anion and hexacoordinated Mg or dinuclear with a bidentate BH₄ group. The latter alternative is realized as shown by its molecular structure (Figure 6).

This molecule has also a crystallographic centre of symmetry. The Mg-O bonds are somewhat longer than in the previous examples (by 0.02 Å) but the Mg-O bond to one of the thf molecules is shorter (1.984(3) Å) than the Mg–O bond to the second thf molecule (2.074(3) Å). Because the Mg-O-Mg bond angle is larger than in the diethyl ether complexes 3 to 6, the Mg...Mg distance across the four membered ring has enlarged to 3.095 Å, corresponding to a difference of 0.2 Å. The BH_4 group is present as a bidentate ligand, and, as a consequence, the Mg-B distance is longer than in the diethyl ether complexes with tridentate BH₄ groups. It is well known that the M…B distances decrease in the order monodentate > bidentate > tridentate simply for geometric reasons. Thus, as *Edelstein* [15] has pointed out, the M-B distance is a good criterion for the type of bonding of the BH₄ group in mononuclear metal tetrahydroborates.



Figure 4 Molecular structure of dimeric (Me₃CCH₂O)Mg(BH₄)-(OEt₂), (6), in the solid state. Selected bond lengths/A: Mg-O1 1.942(3), Mg-O2 2.028(3), Mg-O1A 1.949(3), Mg-B 2.244(6). Mg-Ha 2.24, Mg-Hb 2.15, Mg-Hc 2.15, B-Ha 1.11, B-Hb 0.91, B-Hc 1.11, B-Hd 1.15. - Selected bond angles/º: O1-Mg-O2 112.0(1), O1-Mg-O1a 84.4(1), B-Mg-O1 117.5(2), B-Mg-O2 110.5(2), B-Mg-Ola 126.8(2), O1-Mg-Ha 98.0(2), O2-Mg-Hb 101.5(2), O1-Mg-Hc 146.0(2), Ha-Mg-Hb 40.4(1), H-Mg-Hc 49.3(1), Hb-Mg-Hc 49.1(1), Ha-B-Hb 97.1(7), Ha-B-Hc 111.7(6), Hb-B-Hc 124.5(8), Ha-B-Hd 99.1(6), Hb-B-Hd 104.1(7), Hc-B-Hd 116.0(7).



Figure 5 Molecular structure of dimeric (Me₃SiO)Mg(BH₄)-(OEt₂), (**50**).

Selected bond lengths/Å: Mg-O1 2.015(3), Mg-O2 1.960(2), Mg-O2A 1.964(2), Mg-H1 2.07(4), Mg-H2 2.00(4). Mg-H3 2.22(4), O2-Si2 1.621(2), Mg···B1 2.254(5), B-H1 1.06(4), B-H2 1.12(4), B-H3 1.09(4), B-H4 1.09(4). Selected bond angles/°: O2-Mg-O2A 86.5(1), Mg-O2-MgA 93.5(1), O2-Mg-O1 108.4(1), Mg-B-H4 177(2), H1-B-H4 114(3), H4-B-H2 115(3), H4-B-H3 108(3), H1-B-H2 110(3), H1-B-H3 100(3), H2- B-H3 108(3).

In contrast to the dinuclear structure of **21** the compound $(2,6-tBu_2C_6H_3O)Mg(BH_4)(dme)(thf)$, **33**, is mononuclear. Its molecular structure is shown in Fig. 7. The Mg atom is hexacoordinated. As expected, the coordination sphere is a



Figure 6 Molecular structure of dimeric $(PhO)Mg(BH_4)(thf)_2$, (21), in the solid state.

Selected bond lengths/Å: Mg-O1 1.984(3), Mg-O2 2.094(3). Mg-O3 2.074(3), Mg-O1A 2.037(3), Mg···B 2.454(5), O1-C1 1.360(4). Selected bond angles/in °: B-Mg-O1 122.2(2), B-MgO2 93.6(1), B-Mg-O3 121.7(2), O1-Mg-O2 93.3(1), O1-Mg-O3 116.1(3), O2-Mg-O3 83.4(1), O1-Mg-O1A 79.4(1), O2-Mg-O1A 165.0(1), Mg-O1-MgA 100.6(1), Mg-O1-C1 131.7(2), O3-Mg-O1A 88. (1), C7-O2-C10 109.0(3), C11-O3-C14 108.5(3).

highly distorted octahedron due to the sharp O-Mg-O and H-Mg-H bond angles. The sum of bond angles about the "trigonal plane" (pentacoordinated Mg with B and 4 O atoms) is 359.2°, the angle B-Mg-O1 being most open with 126.8°, while the angle B-Mg-O2 is smallest (110.5°). All other angles are close to 90° with maximal deviations of 6.5 and 15°.

A striking feature of the structure of **33** is the almost linear C1–O1–Mg1 unit of the phenolate ligand $(177.0(2)^\circ)$. This is in accord with a very short C1–O1 (1.335(4) Å) and Mg–O1 bond (1.883(3) Å). The C–O bond lengths suggests a bond order of 1.5. Its Mg–O bond is 0.2 Å shorter than all other Mg–O bonds observed in this study. This suggests multiple bond contributions (the shrinking of the Mg–O distance is due only to the dicoordinated O atom because the Mg atom remains hexacoordinated). In accord with a bidentate BH₄ group is the comparatively long Mg···B distance (2.446 Å).

It follows from the structural data now available that all $(RO)Mg(BH_4)(L)_n$ molecules have a hexacoordinated Mg atom. Except for compounds with sterically demanding phenolate groups the RO group form bridges between the Mg atoms. The remaining coordination sites are either occupied by O atoms of the ether ligands or H atoms of the BH₄ anions which may be either bidentate or tridentate.

¹¹B NMR Spectra

¹¹B chemical shift data and ¹J(¹¹B¹H) coupling constants of the (RO)Mg(BH₄) compounds were recorded in C₆D₆ or



Figure 7 Molecular structure of $(2,6-tBu_2C_6H_3O)Mg(BH_4)(thf)-(dme)$, (33).

Selected bond lengths/Å: Mg–O1 1.883(3), Mg–O2 2.094(4), Mg–O3 2.112(4), Mg–O4 2.107(4), Mg···B 2.446(6), O1–C1 1.335(4), O2–C15 1.453(4), O2–C18 1.451(6), O3–C20 1.435(5), O3–C21 1.429(6), O4–C19 1.443(5), O4–C22 1.429(6). – Selected bond angles/°: O1–Mg–O2 95.3(1), O1–Mg–O3 96.5(1), O1–Mg–O4 121.9(1), O2–Mg–O3 163.2(1), O2–Mg–O4 88.5(1), O3–Mg–O4 75.1(1), B–Mg–O1 126.8(1), B–Mg–O2 94.1(2), B–Mg–O3 96.5(1), B–Mg–O4 110.5(1), Mg–O1–C1 177.0(2), Mg–O2–C18 125–4(3), Mg–O2–C15 127.9(2), C15–O2–C18 106.3(3), Mg–O3–C20 112.0(3), Mg–O3–C21 123.5(3), C20–O3–C21 113.4(3), Mg–O4–C19 117.4(3), Mg–O4–C22 131.0(3), C19–O4–C22 110.7(3).

d₆-Me₂SO or the coresponding ether solution. Data recorded in C₆D₆ solution do not deviate much from those obtained in the ether solutions, and this holds also for the coupling constant ${}^{1}J({}^{11}B^{1}H)$. We take this as evidence that the molecular state of the compounds studied is the same in nonpolar and polar solvents. Usually well resolved 1:4:6 : 4 : 1 quintets were observed in the ¹¹B NMR spectra as expected for the presence of BH₄ groups. Even at low temperature $(-60 \,^{\circ}\text{C})$, no change in the coupling pattern was observed. Therefore, the NMR method gives no indication how the BH₄ groups binds to the Mg atom, i. e. via one, two, or three of its hydrogen atoms because all four hydrogen atoms of the BH₄ groups are magnetically equivalent. This is typical for most metal tetrahydridoborates [16, 17, 18]. The shielding of the boron nuclei as well as the coupling constant change only little by changing the ether solvent. For the diethyl ether solvates of the whole range of RO groups, δ^{11} B varies only between -40.8 and -44.2 ppm, for thf solutions from -38.5 to -42.7 ppm, for dme solutions from -40.3 to -42.9 ppm and for diglyme solutions from -41.6 to -43.7 ppm. This suggests that the boron atoms in all of these compounds carry more or less the same charge. The δ^{11} B values are close to those of the alkali metal tetrahydroborates [19] and amine solvates of $Mg(BH_4)_2$ [1]. In contrast to the ether solvates the ¹¹B nuclei are less well shielded in d₆-Me₂SO as a solvent. As was shown for $Mg(BH_4)_2$ ether complexes these are present in d₆-Me₂SO solution as the ionic compound [Mg(OS-Me₂)₆](BH₄)₂(OSMe₂)₂, whose structure has been determi-



ned in the solid state [1]. $\delta^{11}B$ in d₆-Me₂SO solution for all compounds (RO)Mg(BH₄) is found in a narrow range (-35(±1) ppm. We rationalize this by the formation of free BH₄ anions as indicated in equation (9). Thus, ¹¹B NMR data for the (RO)Mg(BH₄) compounds in deutero benzene solutions not only point to an interaction of the BH₄ units with the Mg atoms as determined for the solid state but also to a dependence from the coordinated ether.

$$(\text{RO})\text{Mg}(\text{BH}_4)(\text{L})_n + 5 \text{ Me}_2\text{SO} \rightarrow \\ [(\text{RO})\text{Mg}(\text{OSMe}_2)_5]^+ + \text{BH}_4^- \text{ n L}$$
(9)

For several (RO)Mg(BH₄) compounds in ether solutions the proton signals for the BH₄ group was found in the range from 0.61 to -0.16 ppm. There is, therefore, some influence both by the solvent and the RO group. In d₆-Me₂SO solutions δ^1 H for BH₄⁻ is always found at -0.30 ppm, and the 1:1:1:1 quartet is often accompanied by a septet due to ${}^1J({}^{10}B^1$ H) coupling of about 27.3 Hz. The uniformity of the ¹H chemical shifts for the Me₂SO solutions clearly demonstrate the presence of free BH₄ ions. Moreover, the NMR data exclude any RO⁻/H⁻ exchange within the (RO)Mg(BH₄) molecule but allows no conclusion as to the bonding mode of the BH₄ group.

While all (RO)Mg(BH₄) compounds showed only a single ¹¹B NMR resonance, $[(2-iPrO)-C_6H_4O]Mg(BH_4)(thf)_2$, **24**, in C₆D₆ solution exhibited two signals at -38.5 and -42.6 ppm. There are, obviously, two species present. The simplest explanation would be the assumption of an equilibrium between a dinuclear and a mononuclear species without rapid scrambling between the two. There could also be two isomers (F and G, see scheme 2) in solution as shown for mononuclear **24** in scheme 2. On the other hand, $[(2-iPrO)C_6H_4O]Mg(BH_4)(OEt_2)$, **13**, crystallized from Me₂SO as $[(2-iPrO)C_6H_4O]_2Mg-(OSMe_2)]_2$, **45**, showing that a ligand exchange between the two BH₄⁻ species is indicated.

IR Spectra

As the ¹¹B NMR spectra are inconclusive regarding the bonding mode of the BH_4 group to the Mg centre, we hoped that IR. spectra might provide the data necessary to





distinguish between bidentate- and tridentate-bonded BH₄ groups for mononuclear and dinuclear (RO)Mg(BH₄)(L_n) compounds. The IR spectra, however, often did not show a good enough resolution for the BH stretching vibrations in nujol mulls. Although the number of resolved bands differ for the series of compounds $(RO)Mg(BH_4)(OEt_2)$ the observed pattern corresponds best with tridentate BH₄ groups (local C_{3v} -symmetry). There is a band at high wave numbers (2472 to 2426 cm⁻¹, v (BH_{terminal}) in addition to two bands at lower frequencies (range 2200 to 2180 cm⁻¹, v_{as} and $v_{sym}BH_3$). The IR spectra of the thf solvates show also very different resolutions of the bands in the BH stretching region. With the exception of $(tBuO)Mg(BH_4)(thf)$, 19, which shows an IR spectrum typical for a tridentate BH₄ group, all others exhibit intense bands at about 2380, 2290 to 2250 and 2200 to 2240 cm⁻¹. Two sets of two bands (v_{as} and v_{symm}) are expected for bridging and terminal ¹¹BH₂ units. The observed patterns correspond closely to those for a bidentate BH_4 group. Compound $[(2-iPrO)C_6H_4O]$ - $Mg(BH_4)(thf)_2$ may have the structure of either F or G. $[(2,6-MeO)_2C_6H_3O]Mg(BH_4)(thf), 25$, should have structure H because the methoxy groups are not equivalent (by NMR) which points to the presence of a coordinated and a non-coordinated MeO group.

No IR bands higher than 2400 cm^{-1} have been observed for the dme and diglyme solvates. This shows that tridentate BH₄ groups are not present. Thus, the models of type I and K may represent [20] the structures of the dme and diglyme 1 : 1 solvates of (RO)Mg(BH₄), respectively. The numerical values of the IR spectra are reported in [20].

Solvates of Bis(trimethylsilylamino)magnesium Tetrahydroborates

Aminomagnesium tetrahydroborates have almost not been investigated, and only bis(2,6-diisopropyl- β -diketoiminate magnesium tetrahydroborate carrying a tridentate BH₄ group is known [21]. Although primary and secondary amines may react in different ways with EtMg(BH₄) as shown in equations (11) to (13) we observed only the reaction according to (11) on treatment of EtMg(BH₄) with (Me₃-Si)₂NH.

 $EtMgBH_4 + (Me_3Si)_2NH \rightarrow (Me_3Si)_2NMgBH_4 + EtH$ (11) $EtMgBH_4 + (Me_3Si)_2NH \rightarrow EtMg[(BH_3N(SiMe_3)_2] + H_2$ (12)

 $EtMgBH_4 + (Me_3Si)_2NH \rightarrow Me_3SiNHMgBH_4 + Me_3SiH$ (13)

Table 3 ¹¹B and ¹H chemical shifts (ppm), ${}^{1}J({}^{11}B{}^{1}H)$ coupling constants (Hz) in deuterobenzene of the bis(trimethylsilylamino)magnesium tetrahydroborates

RX	L	$\delta^{11} \textbf{B}$	${}^{1}J({}^{11}B^{1}H)$	$\delta^1 H$	${}^{1}J({}^{11}B^{1}H)$
(Me ₃ Si) ₂ N	OEt ₂ , 46	-37.8	br	-0.37	82.3
Me ₃ SiO	OEt ₂ , 50	-43.8	82.5	-0.39	82.4
(Me ₃ Si) ₂ N	thf, 47	-39.9	81.4	-0.39	82.2
(Me ₃ Si) ₂ N	dme, 48	-39.1	81.8	-0.39	82.2
(Me ₃ Si) ₂ N	diglyme, 49	-41.9	81.4	-0.41	81.4

Hexamethyldisilazane has been chosen as an appropriate secondary amine because the $(Me_3Si)_2N$ group generally provides good solubility of its derivatives. $[(Me_3Si)_2N]$ -Mg(BH₄), results also by reacting NaBH₄ with $[(Me_3Si)_2N]$ -MgCl (only checked by NMR). $[(Me_3Si)_2N]Mg(BH_4)$ -(OEt₂), **46**, crystallizes from diethyl ether. The coordinated diethyl ether can be replaced by thf, dme, and diglyme, giving compounds **47** to **49**.

$$[(Me_{3}Si)_{2}N]Mg(BH_{4})(OEt_{2})_{2} \qquad [(Me_{3}Si)_{2}N]Mg(BH_{4})(thf)_{2} \\ 46 & 47 \\ [(Me_{3}Si)_{2}N]Mg(BH_{4})(dme) \\ 48 \\ [(Me_{3}Si)_{2}N]Mg(BH_{4})(diglyme) \qquad [(Me_{3}SiO)Mg(BH_{4})(OEt_{2})_{2}], \\ 49 & 50 \\ [(Me_{3}SiO)Mg(BH_{4})(OEt_{2})_{2}], \\ [(Me_{3}SiO)Mg(BH_{4})(OEt_{2})], \\$$

Although all these compounds were crystalline, they diffracted only very weakly. So their structures could not be reliably determined. Repeated crystallisation of **46** from diethyl ether gave crystals that proved to be dimeric **50** (see Fig. 5).

Spectroscopy

Table 3 lists relevant ¹H and ¹¹B chemicals shifts as well as ¹J(¹¹B¹H) coupling constants. ²⁵Mg chemical shifts have already been reported [22]. The strong BH band at 2438 cm⁻¹ and two strong bands at 2288 and 2244 cm⁻¹ for **46** indicate the presence of a tridentate BH₄ group. This would be in accord with a dimeric molecule having a hexa-coordinated Mg atom.

Thus, it is most likely that compound **46** is dinuclear in the crystal, too, in analogy to $[(Me_3SiO)Mg(BH_4)(OEt_2)]_2$, **50**. Since 4 BH stretching bands in the region $2350-2180 \text{ cm}^{-1}$ have been observed for **48** and **49**, these compounds should have bidentate BH₄ units in order to achieve hexacoordination at the Mg centers. This has been ascertained by the X-ray structure of mononuclear **49** (Mg coordinated to three O, one N and two H atoms). Therefore, one can expect that **48** is dimeric with bridging (Me₃. Si)₂N groups between the Mg atoms. Possible structures are shown in scheme 4.



Scheme 4

We favor the first of these three structures because only one type of $(Me_3Si)_2N$ and dme groups are observed in its ¹H NMR spectrum.

Hexacoordination at Mg is achieved for **49** by a tridentate diglyme ligand. Wheras only one set of signals for the MeOCH₂CH₂O units of the diglyme molecule is observed in the ¹H and ¹³C NMR spectra there were two signals for the (Me₃Si)₂N group. This indicates hindered rotation about the Mg-N bond.

Compounds **46** to **50** show 1:4:6:4:1 quintets in their ¹¹B NMR spectra, and 1:1:1:1 quartets in the ¹H NMR spectra, typical for the tetrahydroborate group. The ¹¹B chemical shifts depend on the ether ligand while the ¹J(¹¹B¹H) coupling constant is independent. The increase in the shielding of the ¹¹B nucleus is in accord with an increase of charge separation along the series **46** to **49** as suggested by *Gutmann* [23], because the increasing donor strength of the solvent molecule will weaken the MgH₂B interaction.

Molecular Structure of 49

As can be seen in Figure 9 the BH_4 group binds as a bidentate ligand to the Mg atom. The bridging hydrogen atoms form longer bonds to the B atom than the terminal ones. Hexacoordination at Mg is achieved by the diglyme molecule which occupies, in a distorted fashion, the meridional sites of the complex. As expected the H-Mg-H bond angle is quite sharp (71.3°). This is also true for the O1-Mg1-O2 bond angle which is 72.4(3)°, wheras the O1-Mg1-O1A bond angle is quite wide (140.0(3)°). Thus the octahedral geometry around the hexacoordinated Mg atom is distorted.

Although all compounds **46** to **50** are crystalline, their diffracting power as mentioned above was quite weak and no reflections were observed at 2θ angles higher than 30° except for compound **49** and **50**.

Not unexpected is the planar geometry around its N atom. Its Mg–O bond lengths are different. Thus, the central Mg–O2 bond is much shorter (2.141 Å) than the bonds to the MeO groups (2.175(5) Å). Although the standard deviation of the Mg–O2 bond is twice that of the Mg1–O1 bond, no disorder could be detected. The molecular data correspond nicely with those found for Mg[N(SiMe₃)₂](thf)₂ (Si–N 1.702, 1-709 Å, Si–N–Si 120.2, 121.7°) [24] but deviate strongly compared with those of K[N(SiMe₃)₂](dioxane)₂ (N–Si 1.64 Å, N–Si–N 136.2°) [25].

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Figure 8 Molecular structure of $[(Me_3Si)_2N]Mg(BH_4)(diglyme)$, (49).

Selected bond lengths/Å: Mg–N 2.013(7), N–Si1 1.698(5), N–Si2 1.711(7), Mg–O1 2.175(5), Mg–O2 2.14(1), Mg–O1A 2.175(5), B–H10 1.07(5), Mg–H10 2.09(4), B–H11 1.06(6), B–H12 0.93(6). – Selected bond angles/°: O1–Mg–O2 72.4(2), O1–Mg–O1A 140.0(3), Si1–N–Si2 122.6(4), Mg–N–Si1 117.0(4), Mg–N–Si2 120.4(3), N–Mg–B 120(4), H10–B–H12 103(3), H11–B–H12 120(5), H10–B–H11 109(3).

Discussion

The structure of solvent-free $Mg(BH_4)_2$ is still unknown. However, several solvates of this compound have been prepared and structurally characterized. Apart from $Mg(BH_2)_4(thf)_3$ [6-8] with a heptacoordinated Mg atom, almost all of its coordination compounds with amines are mononuclear with a hexacoordinated Mg atom [1]. An exception is $Mg(BH_4)_2)(py)_4$ with an octacoordinated Mg centre. Another compound, Mg(BH₄)₂(OSMe₂)₆, is also exceptional in so far as it has an ionic structure [Mg(OS- $Me_{2}_{6}(BH_{4})_{2}$ [1]. In the present study a number of ether solvates of alcoholato- and phenolato magnesium tetrahydroborates have been prepared, and characterized by NMR and IR spectroscopy, and eight of them by X-ray diffraction methods. All compounds of type $(RO)Mg(BH_4)(OEt_2)$ are dimeric with a centrosymmetric Mg₂O₂ core, making the Mg atoms hexacoordinated. Those of type (RO)Mg(B- H_4)(OEt₂)₂ (RO = 2-isopropoxyphenolato, 13, or 2,6-di*tert*-buytlphenolato, **12**) are monomeric. In case of **12**, the phenolato group is almost linearly bound to the Mg centre, and its BH₄ group is tridentate. Again hexacoordination for the Mg atom is achieved. Although the structure of 14 has not been determined by X-ray crystallography, it is most likely, that the complex is dimeric with Mg atoms coordinated to four O and two H atoms.

The base thf adds to (RO)Mg(BH₄) compounds in ratios 1 : 1 (18, 19, 20, 25), 1 : 1.5 (17), 1 : 2 (16, 21, 23, 24) or even 1 : 3 (22). For the 1:1 complexes, one can assume that the Mg atoms are coordinated by three O atoms and a tridentate BH₄ group. As shown for (PhO)Mg(BH₄)(thf)₂, 21, this compound is centrosymmetric with hexacoordinated Mg atoms and bidentate BH₄ groups. On the other hand, it seems logical that the compound (2,6-*i*Pr₂C₆H₃O)-Mg(BH₄)(thf)₃, 22, is monomeric, having a bidentate BH₄ group to complete hexaco-ordination. This would be in line

with the determined structures of compound **35**. It is the only example of a compound with two different ether molecules as ligands. Its (2,6-di(tert-butyl))phenolato group is almost linearly bonded to the Mg centre, and the BH₄ group is bidentate. Compounds of type (RO)Mg(BH₄)(dme) may contain a dme molecule that bridges two Mg atoms. Thus each Mg atom would coordinate with three O atoms, two from two dme molecules and one from the bridging OR group. Consequently, the BH₄ group should be of a tridentate type. However, the IR data do not comply with this assumption. In case of a bidentate BH₄ group, the Mg atom would be pentacoordinated.

For the diglyme solvates of (RO)Mg(BH₄(diglyme)_n the 1:1 ratio dominates. Provided that all O atoms of diglyme coordinate to the Mg atom, then all compounds of this type should be monomeric with bidentate BH₄ groups. This fits with the IR data. Moreover, this assumption is also supported by the structure of the mononuclear compound [(Me₃. Si)₂N]Mg(BH₄)(diglyme), **49**.

In general, all compounds reported here show no tendency in their respective ether solution to exchange their substituents according to

$$2 (\text{RO})\text{Mg}(\text{BH}_4) \rightleftharpoons (\text{RO})_2\text{Mg} + \text{Mg}(\text{BH}_4)_2$$
(13)

This has been observed only for $[(2-iPrO)C_6H_4O]-Mg(BH_4)(thf)$ **24**, in Me₂SO solution (see Eq.(9)). And this may be due to the fact that Me₂SO replaces the BH₄ group, thus inducing the ligand exchange. But there remains the question why this is observed only for this compound. The resulting {[2-iPrO)C₆H₄O]]₂Mg(OSMe₂)}₂ is one of the few characterized magnesium phenolates. Other examples are [Mg(OC₆H₃(*t*Bu₂)]₂ [26], (Mg(O-Tol)(thf)₂ [27], [(2,6-*i*Pr₂C₆H₃O)₂Mg]₃ [28] or Mg(OC₆H₃-(2,6-Me₂)(py)₃ [28]. Coordination numbers 3, 4, and 5 are realized in these compounds.

In contrast to many of the (RO)Mg(BH₄) compounds the silyl amide $[(Me_3Si)_2N]Mg(BH_4)$ is much better soluble in ethers. In this case, like the RO groups, the silylamido group occupies the bridging position in the dimeric molecules **46** and the BH₄ is bidentate. In case of mononuclear **49** the tridentate diglyme prevents the formation of a bridging amino group. In no case was it possible to observe the BH₄ group in a bridging position between Mg atoms. This, however, can be expected for compounds of type Mg(BH₄)₂(L) (L = Et₂O, thf), and of course also for MgH(BH₄)(L), and particularly for solvent-free Mg(BH₄)₂.

Experimental

All experiments were conducted under anhydrous conditions and under a blanket of dinitrogen gas using Schlenk techniques. Ether solvents were dried by conventional methods, distilled and stored under N₂. Usually, LiAlH₄ was employed as the drying agent. NMR: Bruker WP 200 and/or 400 using tms, BF₃·OEt₂ as standards for ¹H, ¹¹B and ¹³C NMR spectra. Coupling constants are given in Hz, chemical shifts in ppm. IR: Perkin Elmer 325 instrument, nujol mulls, KBr plates. X-ray structure determinations: Siemens P4 diffractometer operated with MoK α radiation, graphite monochromator. LT2 low temperature device, scintillation detector, $\omega/2\theta$ -scans. Abbreviation used: s = singlet, d = doublet, t = triplet, quart = quartet, quint = quintet, sept = septet.

Preparation of a stock solution of $EtMg(BH_4)$ in diethyl ether: A Grignard solution of EtMgBr in diethyl ether was prepared by standard procedures, and 500 mL of the solution containing 500 mmol of the Grignard reagent was transferred into a Schlenk vessel containing a stirring bar. 40 g of finely powdered NaBH₄ were added and the suspension stirred for 3 h at ambient temperature until a test showed that the solution was free of bromide. Then the insoluble material was removed by centrifugation. The solid material was treated twice with 100 mL of diethyl ether. About 250 mL of the solvent were removed in vacuo and the concentration of $EtMg(BH_4)$ solution determined after hydrolysis by analysis of Mg^{2+} , $B(OH)_3$ and H^- . The stock solutions used showed concentrations between 1 and 1.5 mol/L.

Elemental analysis: Mg^{2+} by titration with EDTA. B(OH)₃ after solvolysis with MeOH and distillation of B(OMe)₃ followed by hydrolysis and addition of mannitol and acidimetric titration. H⁻ by collecting the hydrogen gas evolved after acid hydrolysis of EtMgBH₄ in a high vacuum apparatus using a Toepler pump. The ethane generated was absorbed on active carbon at -196 C.

Diethyl Ether Solvates of (RO)Mg(BH₄)

To a stirred diethyl ether solution of $EtMg(BH_4)$ was added an diethyl ether solution of the alcohol or phenol. After gas evolution has subsided, the solid that has been formed was isolated by filtration, washed with some diethyl ether and dried shortly in vacuo. If a clear solution resulted, then diethyl ether was partially stripped off, the solution cooled to -20 °C and the solid which formed was isolated.

Methylato-magnesium tetrahydroborate diethyl ether, (1): To a stirred diethyl ether solution of EtMg(BH₄) (105 ml, 1.08 M, 113 mmol) was dropwise added methanol (4.64 mL, 113 mmol). Ethane was rapidly generated . A precipitate formed that was isolated by filtration and dried in vacuo. Yield: 8.83 g (54.1 %), m. p. dec. >400 °C. The compound is slightly soluble in diethyl ether, benzene, and toluene, but freely soluble in thf (with ether displacement). NMR (in C₆D₆): δ^{1} H = 3.27 (quart, ${}^{3}J({}^{1}$ H¹H) = 7.0, OCH₂), 1.07 (t, ${}^{3}J({}^{1}$ H, 1 H) = 7.0, CH₃); 1.35 (s, OCH₃); ratio = 4 : 6 : 3. $-\delta^{13}$ C = 15.6 (CH₂CH₃), 30.4 (OCH₃), 65.9 (OCH₂), and weak additional signals at 20.3, 22.7, 27.4, 37.3. $-C_{5}$ H₁₇O₂BMg (144.30): calc. Mg 16.84, B 7.49, H⁻ 2.80; found Mg 16.64, B 7.43, H⁻ 2.80 %.

Ethylato-magnesium tetrahydroborate diethyl ether, (2) : Prepared in analogy to 1 from a diethyl ether solution of EtMg(BH₄) (93 mL, 1.08 M, 100 mmol) and a solution of ethanol (5.80 mL, 100 mmol) in diethyl ether (100 mL). Yield: 12.5 g (78 %), m. p. 245 – 250 °C. The compound is slightly soluble in diethyl ether, benzene and toluene but excellently in thf and Me₂SO. NMR (in d₆-Me₂SO): δ^{1} H= 1.03 (br, CH₃CH₂O⁻, 9 H)), 3.40 (m, br, 2 H), 3.60 (m, br, 4 H). – δ^{13} C = 15.2, 64.9 (OEt₂), 18.7 (H₃CCH₂O⁻), 56.1 (br, H₃CCH₂O⁻). – C₆H₁₉O₂BMg (158.33): calc. Mg 15.35, B 6.83, H⁻ 2.55; found Mg 15.50, B 6.83, H⁻ 2.36 %.

Isopropylato-magnesium tetrahydroborate diethyl ether, (3): Prepared in analogy to 1 from EtMgBH₄ (13.0 mL, 1.54 M, 20.0 mmol) and a solution of isopropanol (1.53 mL, 20.0 mmol) in diethyl ether (150 mL). Yield 1.94 g (56.3 %), m. p. 72 - 74 °C. NMR (in C₆D₆):

 δ^{1} H = 0.94 (t, ${}^{3}J({}^{1}$ H 1 H) = 7.0, CH₂CH₃), 1.23 (d, ${}^{3}J({}^{1}$ H 1 H) = 7.0), 4.10 (sept, ${}^{3}J({}^{1}$ H 1 H) = 6.2, CH). - C₇H₂₁O₂BMg (172.36): calc. Mg 14.10, B 6.72, H⁻ 2.34; found Mg 14.52, B 6.34, H⁻ 2.30 %.

Tert-butylato-magnesium tetrahydroborate diethyl ether, (4): Prepared from a diethyl ether solution of EtMgBH₄ (17.3 mL, 1.54 M, 26.6 mmol) and *tert*-butyl alcohol (2.50 mL, 26.6 mmol), dissolved in diethyl ether (150 mL). Yield: 1.55 g (31.3 %). NMR (in C₆D₆): δ^{1} H = 0.92 (t, ${}^{3}J({}^{1}$ H¹H) = 7.0, H_{3} C-CH₂, 4 H), 1.37 (s, 9H), 3.52 (quart, ${}^{3}J({}^{1}$ H¹H) = 7.0, 4 H). $- \delta^{13}$ C = 14.0, 65.2 (Et₂O), 34.2 (H₃CC), 68.9 ppm (H₃CC). $- C_{8}H_{23}BO_{2}Mg$ (186.39): calc. Mg 13.04, B 5.80, H⁻ 2.16; found Mg 14.30, B 5.74, H⁻ 2.35 %.

Triethylmethylato-magnesium tetrahydroborate diethyl ether, (5): Prepared from EtMg(BH₄) (77.0 mL, 1.30 M, 100 mmol) and Et₃. COH (11.62 g, 100 mmol) dissolved in diethyl ether (200 mL). Yield: 17.3 g (75.3 %), m. p. >400 °C (dec.). NMR (in C₆D₆): δ^{1} H = 0.81 (t, ${}^{3}J({}^{1}$ H¹H) = 7.6, 6H, CH₂), 1.11 (t, ${}^{3}J({}^{1}$ H¹H) = 7.6 Hz, 9H, CH₃), 1.30 and 1.59 (quart, ${}^{3}J({}^{1}$ H¹H) = 7.5, 6H), 3.27 (quart, ${}^{3}J({}^{1}$ H¹H) = 7.6, 4H, CH₂ of Et₂O). $-\delta^{13}$ C = 15.5, 65.8 (Et₂O), 29.9, 30.0, 30.8 (OC(CH₂), 7.9 (CH₃CH₂)₃C). -C₁₇H₂₉O₂BMg (229.45): calc. Mg 10.64, B 4.73, H⁻ 1.75; found Mg 11.21, B 4.77, H⁻ 1.72 %.

Neopentylato-magnesium tetrahydroborate diethyl ether, (6): Prepared from EtMg(BH₄) (20 mL, 1.05 M, 73.4 mmol) and neopentyl alcohol (6.47 g, 73.4 mmol) dissolved in diethyl ether (40 mL). Yield: 2.34 g (16.5 %). The mother liquor has not been worked up to increase the yield. m. p. 108 – 109 °C. NMR (in C₆D₆): δ^{1} H = 0.95 (br, 6 H, Et₂O), 1.01 (br, 9H, *Me*₃CH₂), 4.40 (br, 6H, (MeC*H*₂)₃), Et₂O and Me₃CC*H*₂O), – δ^{13} C = 4.0 (br, 65.6 (CH₃CH₂O), 26.9 (H₃C), 33.6 (Me₃CH₂), 74.7 (CH₂O). – C₉H₂₅O₂BMg (200.40): calc. Mg 12.13, B 5.39, H⁻ 2.01; found Mg 12.48, B 5.16, H⁻ 1.95 %.

Triphenylmethylato-magnesium tetrahydroborate diethyl ether, (7): Prepared from EtMg(BH₄) (38.4 mL, 1.30 M, 50 mmol) and Ph₃COH (13.0 g, 50 mmol) dissolved in diethyl ether (150 mL). Yield: 13.2 g (70.6 %), m. p. 120 – 125 °C. NMR (in C₆D₆): δ^1 H = 0.96 (t, 6H, Et₂O), 3.26 (quart, 4H, Et₂O), 7.00 – 7.13, 7.29 – 7.36, 7.49 – 7.59 (mult, 15 H). – δ^{13} C = 15.5, 65.9 (OEt₂), 82.1, 87.2 (*C*Ph₃), 126.5, 127.83, 127.87, 128.9, 129.9, 146.6, 147.6 (arom C). – C₂₀H₂₉O₂BMg (372.60): calc. Mg 6.52, B 2.90, H⁻ 1.08; found Mg 6.68, B 2.87, H⁻ 0.97 %.

2-Methoxyethylato-magnesium tetrahydroborate diethyl ether, (8): To a stirred solution of EtMg(BH₄) in diethyl ether (105 M, 19.3 mL) was added MeOCH₂CH₂OH (1.54 g, 1.60 mL, 20.3 mol). After gas evolution ceased the precipitate was isolated. Yield: 1.08 g (46.6 %), m. p. 195 – 198 °C. NMR (in d₆-Me₂SO): δ^{1} H = 3.80 – 4.60 ppm (m, 7 H, CH₂, CH₃). – δ^{13} C = 58.1, 58.7, 60.6, 61.3 (MeO(CH₂)₂), 15.0, 65.1 (Et₂O). – C₇H₂₁O₃BMg (114.24): calc. Mg 21.28, B 9.46, H⁻ 3.53; found Mg 20.41, B 8.86, H⁻ 3.08 %.

Phenolato-magnesium tetrahydroborate diethyl ether, (9): EtMg(BH₄) (13.1 mL, 1.54 M, 21.7 mmol) was allowed to react with phenol (2.05 g, 21.7 mmol) dissolved in diethyl ether (100 mL). Yield: 2.40 g (53.6 %), m. p. 185 – 187 °C. NMR (in C₆D₆): δ^{1} H = 0.68 (t, ${}^{3}J({}^{1}$ H¹H) = 7.1, 6 H, Et₂O), 3.23 (t, ${}^{3}J({}^{1}$ H¹H) = 7.1, 4H, Et₂O), 6.72 – 7.42 (m, 5H). – δ^{13} C = 13.9, 66.3 (OEt₂), 119.5, 130.3, 159.4 ppm (ipso C not detected). – C₁₀H₁₉O₂Mg (206.38): calc. Mg 11.78, B 5.24, H⁻ 1.95; found Mg 11.79, B 4.84, H⁻ 1.76 %.

2,4,6-Trimethylphenolato-magnesium tetrahydroborate diethyl ether (1/1.5), (10): Prepared in analogy to 1 from EtMg(BH₄)

(78.7 mL, 1.27 M, 100 mmol) and 2,4,6-trimethylphenol (13.6 g, 100 mmol) dissolved in diethyl ether (100 mL). A clear solution resulted. All volatile material was removed in vacuo and the residue crystallized from a small amount of diethyl ether. Yield: 9.0 g (36.2 %), m.p. 151 – 153 °C. NMR (in d₆-Me₂SO): δ^{1} H = 1.09 (t, ${}^{3}J({}^{1}$ H¹H) = 7.1, H_{3} C-CH₂, 6 H), 3.38 (quart, ${}^{3}J({}^{1}$ H¹H) = 7.1, H_{3} C-CH₂, 6 H), 2.12 (s, 3 H, 4-Me), 6.67 (s, 2H), 7.86 (s, 1 H). – δ^{13} C = 15.1, 64.8 (Et₂O), 20.0, 16.5, *Me*), 123.9, 127.0, 128.5 (*C*_{qrom}). – C₃₀H₅₀O₅B₂Mg₂ (571.02): calc. Mg 8.51, B 3.79, H⁻ 1.41; found Mg 9.73, B 3.65, H⁻ 1.37 %.

2,6-Diisopropylphenolato–magnesium tetrahydroborate diethyl ether, (11): Prepared from a diethyl ether solution of EtMg(BH₄) (70.0 mL, 1.05 M, 73.4 mmol) and (2,6-iPr₂C₆H₃OH (13.6 g, 73.4 mmol) dissolved in diethyl ether (50 ml). Yield: 13.3 g (65.2 %), m. p. 140 °C, dec. NMR (in C₆D₆): δ^{1} H = 0.99 and 1.07 (d, ³J(¹H¹H), 6.8 and 6.6 Hz, each 6 H), 1.09 (t, ³J(¹H¹H) = 7.1, 6 H, CH₃CH₂), 3.37 (quart, ³J(¹H¹H) = 7.1, CH₂O, 4 H), 3.60 (sept, ³J(¹H¹H) = 6.5, 2 H), 6.15 (t, ³J(¹H¹H) = 7.2, 1 H), 6.65 (d, ³J(¹H¹H) = 7.3, 2 H). – δ^{13} C = 15.3, 65.1 (Et₂O), 23.6 and 23.8 (H₃C)₂CH,), 25.6, 25.8 (CH₃)₂CH), 110.6, 121.3, 135.6, 135.8, 161.4 (arom C). – C₁₆H₃O₂BMg (290.52): calc. Mg 8.37, B 3.72, H⁻ 1.39; found Mg 8.39, B 3.32, H⁻ 1.28.

2,6-Di(*tert*-butyl)phenolato-magnesium tetrahydroborate diethyl ether, (12): Prepared from EtMg(BH₄) (54.8 mL, 0.73 M, 40.0 mmol) in diethyl ether and (2,6-*t*Bu₂)C₆H₃OH (8.25 g, 40.0 mmol) dissolved in diethyl ether (30 mL). Yield 10.6 g (69.9 %); m. p. 154 – 156 °C. NMR (in C₆D₆): δ^{1} H = 1.02 (t, ³*J*(¹H¹H) = 6.8, 8 H, *H*₃CCH₂), 1.35 (s, 18 H, *Me*₃C), 1.64 (s, 6 H), 3.31 (quart, ³*J*(¹H¹H) = 6.9, 8 H, *CH*₂O), 6.85 (t, ³*J*(¹H¹H) = 7.8), 7.17 (d, ³*J*(¹H¹H) = 7.8) (3 arom H). – δ^{13} C = 30.3, 31.4, 34.3, 35.4 (H₃C)₃C, 14.5, 65.5 (OEt₂), 68.9 (CO), 114.5, 125.3, 136.0, 138.0 (arom C). – C₁₈H₃₅O₂BMg (382.70): calc. Mg 5.35, B 2.82, H⁻ 1.05; found Mg 5.98, B 2.87, H⁻ 1.07 %.

2-Isopropoxyphenolato-magnesium tetrahydroborate diethyl ether (1/2), (13): Compound 13 was obtained by reacting a diethyl ether solution of EtMg(BH₄) (70.0 mL, 1.05 M, 73.4 mmol) with an ether solution of 2-isopropoxyphenol (11.12 g, 73.4 mmol) dissolved in diethyl ether (30 mL). Yield: 20.8 g (83.5 %), m. p. 280 °C. NMR (in d₆-Me₂SO): δ^{1} H = -1.09 (t, ${}^{3}J({}^{1}$ H¹H) = 7.0), 12 H, CH₃CH₂O), 1.24 (d, ${}^{3}J({}^{1}$ H¹H) = 4.4, 6 H, (CH₃)₂CH), 3:36 (quart, ${}^{3}J({}^{1}$ H¹H) = 7.1, 8 H, MeCH₂O), 4.59 (br; 1 H, Me₂CH), 6.75 (m, 4 H_{arom}). - δ^{13} C = 15.4, 65.2 (Et₂O), 22.0 (H₃C)₂CH, 70.5 (Me₂CH), 121.7, 127.8, 127.9, 128.1, 128.2 (arom C). - C₁₇H₃₅O₄BMg (318.7): calc. Mg 7.18, B 2.19, H⁻ 1.19; found Mg 7.38, B 2.26, H⁻ 1.25 %.

2,6-Dimethoxyphenolato–magnesium tetrahydroborate diethyl ether, (14): Prepared from a diethyl ether solution of EtMg(BH₄) (89.0 mL, 0.95 M, 84.3 mmol) and a diethyl ether solution (110 mL) of 2,6-dimethoxyphenol (13.0 g, 84. 3 mmol). Yield: 20.9 g (93.2 %), m. p. 300 °C, dec.. NMR (in d₆-Me₂SO): δ^{1} H = 1.09 (m, 6 H, H₃CCH₂), 3.38 (m, 4 H, CH₂O), 3.64 and 3.73 (two s, each 3 H, OCH₃), 6.09 (dd, 1 H, 6.41 (dd, not resolved, 1 H), 6.41 (d, ³J(¹H¹H) = 8.3), 6.49 (d, ³J(¹H¹H) = 7.8, 1 H). – δ^{13} C = 15.2, 64.9 (Et₂O), 55.64, 56.08 (OMe), 106.7, 107.3, 108.1, 148.5, 149.3 (arom C). – C₁₂H₂₃O₃BMg (266.38): calc. Mg 9.12, B 4.06, H⁻ 1.51; found Mg 9.19, B 4.45, H⁻ 1.67 %.

2,6-Dimethoxyphenolato-magnesium tetrahydroborate, (14a): To compound **14** (2.90 g, 10.9 mmol) was added toluene (100 mL). From the suspension the toluene was distilled off at normal pressure. This produced solvent free 14 = 14a. Yield 2.10 g (100 %), m. p. 350 °C (dec.). The compound dissolved readily in thf or Me₂SO

but was only slightly soluble in benzene and almost insoluble in hexane. NMR (in d_6 -Me₂SO): δ^1 H = 3.63 (s, 3 H, OCH₃), 3.72 (s, 3 H, OCH₃), 6.09 (m, 1 H), 6.42 (d, ${}^3J({}^1$ H¹H) = 8.3 Hz, 1 H), 6.49 (d, ${}^3J({}^1$ H¹H) = 8.3, 1 H). $-\delta^{13}$ C = 55.9, 56.0 (OCH₃), 106.6, 107.2, 128.1, 128.7, 149.2 (arom. C). $-C_8H_{13}O_3BMg$ (192.31): calc. Mg 12.64, B 5.63, H⁻2.10 – found Mg 12.15, B 4.67, H⁻ 2.22 %.

(2,2-Diethyl-3,3-dimethylpropylato-magnesium tetrahydroborate diethyl ether, (15): A solution of diethylketone (1.84 mL, 20.0 mmol) in diethyl ether (20 mL) was dropped into a stirred solution of *t*BuMg(BH₄) 1.33 OEt₂ [29] (3.35 g, 20.0 mmol, 100 mL Et₂O). Stirring was continued for 1 h. Then all volatile material was removed in an oil pump vacuo. Yield: 4.67 g, (92.0 %), m. p. >350 °C. NMR (in C₆D₆): δ^{1} H = 1.37 (s, (CH₃)₃C), 1.45 (m, CH₃ and CH₂ groups), 3.59 (m, broad, CH₂ of Et₂O). $- \delta^{13}$ C = 14.3, 64.6 (OEt₂), 10.2 (s, H₃C-CH₂), 29.4 (Me-CH₂), 34.2 (H₃C)₃C), 84.21, H⁻ 1.57; found Mg 9.14, B 3.89, H⁻ 1.63 %.

Tetrahydrofuran Solvates of ROMgBH₄ Compounds

General procedure: Diethyl ether solvates of $\text{ROMg}(BH_4)$ were dissolved in thf. Usually a clear solution formed. Depending on concentration crystals of $\text{ROMg}(BH_4)(\text{thf})_n$ separated. These were isolated by filtration. Otherwise the volatile material was removed from the solutions after some hours, and the solid white residue analyzed.

Methylato-magnesium tetrahydroborate tetrahydrofuran (1/2), (16): To 20 mL of a diethyl ether solution of (MeO)Mg(BH₄)(OEt₂) (1.47 g, 10.2 mmol) was added thf (20 mL). Crystals separated from the solution at -20 °C. Yield: 1.04 g (57.4 %), m. p. 70 - 72 °C. NMR (in C₆D₆): δ^{1} H = 0.94 (s, 3 H, H₃CO), 1.33 and 2.64 (m, each 4 H, thf). $-\delta^{13}$ C = 25.4, 59.9 (THF), 30.1 (H₃C). -C₉H₂₀O₃MgB (214.99): calc. Mg 11.34, B 5.04, H⁻ 1.88; found Mg 12.74, B 5.64, H⁻ 2.06 %.

Ethylato-magnesium tetrahydroborate tetrahydrofuran (1/1.5), (17): EtMg(BH₄)(OEt₂) (1.86 g, 11.7 mmol) was dissolved in thf (100 mL). About 70 % of the solvent was removed in vacuo. From the remaining solution crystals separated on cooling in a refrigerator. Yield: 1.43 g (63.5 %), m. p. ~20 °C. NMR (in C₆D₆): δ^1 H = 1.27 (m, broad, ~ 8 H, thf and MeCH₂O), 3.64 (m, 5.3 H, thf), 3.86-3.71 (m, 2H). - δ^{13} C = 25.3, 69.4 (thf), 21.6 (H₃CCH₂), 58.4 (MeCH₂). - C₁₄H₃₃O₅B₂Mg₂ (384.72): calc. Mg 12.64, B 5.62, H⁻ 2.10; found Mg 11.56, B 5.63, H⁻ 2.12 %.

Isopropylato-magnesium tetrahydroborate tetrahydrofuran, (18): iPrOMg(BH₄)(OEt₂) (2.54 g, 14.7 mmol) was dissolved in 20 mL of thf. A precipitate formed on storing the solution at -20 °C. Yield: 1.24 g, (49.5 %), m. p. 79 - 80 °C. NMR (in C₆D₆): δ^{1} H = 1.22 (d, ${}^{3}J({}^{1}$ H¹H) = 6.1, 6 H, (H_{3} C)₂C), 1.34 (m, 4 H), thf), 3.68 (m, 4 H), 4.12 (sept, 1 H, ${}^{3}J({}^{1}$ H¹H) = 6.1). $-\delta^{13}$ C = 25.3, 69.4 (thf), 28.4 ((H_{3} C)₂C), 63.8 (CH). - C₇H₁₉O₂BMg (170.34): calc. Mg 14.23, B 6.35, H⁻ 2.37; found Mg 12.91, B 7.02, H⁻ 2.61 %.

Tert-butylato-magnesium tetrahydroborate tetrahydrofuran, (19): Crystals separated from a solution of $(tBuO)Mg(BH_4)(OEt_2)$ (1.67 g, 5.74 mmol) in thf (50 mL) on storing in a refrigerator. Yield: 1.67 g (74.2 %, m. p. 214 – 216 °C. NMR (in C₆D₆): δ^1 H = 1.15 (m, 4H, THF), 1.35 (s, 8 H, (H₃C)₃C), 3.67 (m, 4 H, thf). – $\delta^{13}C = 25.0, 69.6$ (thf), 34.1 (H₃C)₃C), 69.6 (*C*-O). – C₈H₂₁O₂BMg (187.37): calc. Mg 13.18, B 5.86, H⁻ 2.19; found Mg 11.30, B 5.30, H⁻ 2.21 %. (Triethyl)methylato-magnesium tetrahydroborate tetrahydrofuran, (20): (Et₃CO)Mg(BH₄)(OEt₂) (2.90 g, 12.6 mmol) was dissolved in thf (150 mL). After 1 h 70 - 75 % of the solvent was removed in vacuo. Crystal separated from the remaining solution on standing in a refrigerator. Yield: 1.91 g (66.6 %), m. p. 145 - 147 °C. NMR (in C₆D₆): δ^{1} H = 0.96 (t, ${}^{3}J$ (1 H¹H) = 7.5, 9 H), 1.21 (br, 4 H, thf), 1.35 (s.3H), 1.76 (s, 3 H), 3.76 (br, 4 H, thf). - δ^{13} C = 25.0, 69.5 (thf), 9.2 (H₃CCH₂), 34.1 (H₃C), 75.1 (CO). - C₁₁H₂₇O₂BMg (226,44): calc. Mg 10.73, B 4.77, H⁻ 1.77; found Mg 10.87, B 4.77, H⁻ 1.80 %.

Phenolato–magnesium tetrahydroborate tetrahydrofuran (1/2), (21): **9** (0.78 g, 3.8 mmol) was dissolved in thf (75 mL). After stirring for several hours the insoluble part was isolated by filtration and analyzed. Yield: 0.63 g (60 %), m. p. 270 °C dec.. NMR (in C₆D₆): $\delta^{1}H = 1.14$ (m, 8 H), 3.63 (m, 8 H), 6.14 – 6.89 (m, 1 H), 7.16 – 7.64 (m, 4 H). – $\delta^{13}C = 25.4$, 68.7 (thf), 119.1, 120.3, 129.8, 161.2 (arom C). – $C_{14}H_{25}O_{3}BMg$ (276.45): calc. Mg 8.79, B 3.91, H⁻ 1.46; found Mg 9.44, B 4.09, H⁻ 1.40 %.

2,6-(Diisopropyl)phenolato-magnesium tetrahydroborate tetrahydrofuran (1/3)), (22): Prepared form ((2,6-iPr₂)C₆H₃O)-Mg(BH₄)(OEt₂) (2.91 g, 10.0 mmol) and thf (20 mL). Yield: 3.98 g (92.0 %), m. p. 58 - 62 °C. NMR (in C₆D₆): δ^{1} H = 1.33 (d, ³*J*(¹H¹H) = 7.3, 12 H, *Me*₂C), 1.36 (m, 12 H, thf), 3.75 (m, 12 H, thf), 3.78 (m, 2H Me₂CH), 6.98 (m, 1 H, p-H), 7.16 (m, 2 H, m-H). - C₂₄H₄₅O₄BMg (432.73): calc. Mg 5.62, B 2.50, H⁻ 0.93; found Mg 6.08, B 2.52, H⁻ 0.94 %.

(2,6-Di-*tert*-butyl)phenolato-magnesium tetrahydroborate tetrahydrofuran (1/2), (23): $(2,6-tBu_2C_6H_3O)Mg(BH_4)(OEt_2)$ (3.02 g, 7.89 mmol) was dissolved in thf (50 ml). Crystals separated from the concentrated solution on standing in a refrigerator. Yield: 2.10 g, (68.7 %), m. p. 114 – 118 °C. NMR (in C₆D₆): $\delta^{1}H = 1.13$ (m, 8 H), 1.40 (s, 18 H, Me_3C), 3.37 (m, 8 H), 6.60 (t, ${}^{3}J({}^{1}H^{1}H) =$ 7.7, 2 H), 6.94 (s), 7.22 (d, ${}^{3}J({}^{1}H^{1}H) =$ 7.7), intensity of the last three signals 3 H). – $\delta^{13}C = 25.2$, 69.4 (THF), 30.4, 31.0, 31.9, 35.3 (H₃C-C), 114.0, 120.3, 125.0, 137.8, 162.9 (arom C). – C₂₂H₄₁O₃BMg (387.64): calc. Mg 6.27, B 2.79, H⁻ 1.04; found Mg 5.84, B 2.60, H⁻ 0.89 %.

2-Isopropoxyphenolato–magnesium tetrahydroborate tetrahydrofuran (1/2), (24): Prepared from **13**, (3.96 g, 11.7 mmol) and thf (70 mL). Yield: 2.62 g (67.0 %), m. p. 230 – 235 °C dec.. NMR (in d₆-Me₂SO) : δ^{1} H = 1.22 (d, ${}^{3}J({}^{1}$ H^{1}H) = 5.6, 6 H, *Me*₂CH), 1.75 (br, 4 H, thf), 3.59 (br, 4 H, thf), 4.50 (sept, ${}^{3}J({}^{1}$ H^{1}H) = 5.6, 1 H, *CHM*e₂), 6.6 – 6.8 (arom. H). – δ^{13} C = 25.3, 68.6 (thf), 20.9 (*Me*₂CH), 72.8 (*CO*), 111.9, 117.0, 120.0, 122.9, 152.0, 154.0 (arom C). – C₁₇H₃₁O₄BMg (334.55): calc. Mg 7.27, B 3.23, H⁻ 1.21; found Mg 9.09, B 2.99, H⁻ 1.15 %.

2,6-Dimethoxyphenolato–magnesium tetrahydroborate tetrahydrofuran, (25): Obtained from **14** (2.22 g, 8.33 mmol) and thf (50 mL).Yield: 1.60 g (72.7 %), m. p. 320 °C, dec.. NMR (in d_6 -Me₂SO): δ^1 H = 1.76 (m, 4 H, thf) 3.61 (m, 4 H, thf), 3.74 (s, 3 H, MeO), 3.78 (s, 3 H, MeO), 6.09 (m, 1 H), 6.41 (d, ${}^{3}J({}^{1}\text{H}{}^{1}\text{H})$, 7.8, 1 H), 6.49 (d, ${}^{3}J({}^{1}\text{H}{}^{1}\text{H})$ = 7.8, 1 H). $-\delta^{13}$ C = 25.0, 66.9 (thf), 55.6 and 56.0 (MeO), 106.7, 107.2, 108.0, 148.5, 149.4 (arom. C). $-C_{12}H_{21}O_4$ BMg (264.38): calc. Mg 9.19, B 4.09, H⁻ 1.52; found Mg 9.29, B 3.97, H⁻ 1.31 %.

Dimethoxyethane Solvates of ROMgBH₄

These compounds were prepared from $ROMgBH_4$ ·OEt₂ by ether displacement. Most of the compounds are only slightly soluble in dme and benzene.

Ethylato-magnesium tetrahydroborate dimethoxyethane, (26): EtOMg(BH₄)(OEt₂) (2.18 g, 13.8 mmol) was added to dme (100 mL) with stirring, After 3 h the insoluble material was isolated by filtration, washed with some dme and dried in vacuo. Yield: 1.8 g (74.9 %), m. p. 185 – 188 °C. NMR (in C₆D₆): δ^1 H = 0.92 (m, br, 2 H, MeCH₂O), 1.34 (br, 3 H, H₃CCH₂), 3.11 (s, 6 H, H₃CO), 3.22 (s, 4 H, H₂CO). – C₆H₁₉O₃BMg (174.33): calc. Mg 13.94, B 6.20, H⁻ 2.31; found Mg 13.00, B 5.62, H⁻ 2.11 %.

Isopropylato–magnesium tetrahydroborate dimethoxyethane, (27): Obtained as a white powder from (iPrO)Mg(BH₄)(OEt₂) (2.49 g, 14.4 mmol) and dme (15 mL). Yield: 1.50 g (55.3 %), m. p. 300 – 305 °C. NMR (in C₆D₆): δ^{1} H = 1.08, 1.17, 1.36 (all d, ${}^{3}J({}^{1}$ H¹H) = 6.1 (H_{3} C)₂CH), 3.14, 3.26 (both s, H_{3} COCH₂), 4.27, 4.54 (both m., Me₂CH). – δ^{13} C = 58.9, 71.9 (H₃COCH₂). The iPrO group was not clearly observed). – C₉H₂₁O₃BMg (188.51): calc. Mg 12.89, B 5.73, H⁻ 2.14; found Mg 13.16, B 5.13, H⁻ 2.27 %.

Tert-butylato-magnesium tetrahydroborate dimethoxyethane (2/1), (28): To a stirred solution of $(tBuO)Mg(BH_4)(OEt_2)$ (0.85 g, 4.56 mmol) in diethyl ether (50 mL) was added dme (25 mL). A white precipitate formed immediately. It dissolved in thf but is only sparingly soluble in benzene. Yield: 0.46 g (64.1 %), m. p. 146 – 148 °C. NMR (in C₆D₆): $\delta^1H = 1.04$ (s., 9 H, (H_3C)₃C), 3.11 (s., 3 H, H_3CO), 3.32 (s, 2 H, H_2CO). – $\delta^{13}C = 30.9$ (H₃C), 59.7, 72.1 (dme), signal for Me₃C not observed). – C₆H₁₈O₂BMg (157.31): calc. Mg 15.35, B 6.87, H⁻ 2.56; found Mg 13.24, B 7.54, H⁻ 2.80 %.

Triethylmethylato-magnesium tetrahydroborate dimethoxyethane (2/1), (29): A suspension made from $(Et_3CO)Mg(BH_4)(OEt_2)$ (1.85 g, 8.06 mmol) in dme (10 mL) was heated to reflux. From the clear solution 29 separated on cooling as a colorless precipitate. Yield: 0.80 g (45.9 %), m. p. 300 – 305 °C, dec.. NMR (in C₆D₆): $\delta^1H = 0.76$, 0.82, 0.90 (three t, all with ${}^3J({}^1H^1H) = 7.5$ Hz, 9 H, H_3CH_2), 1.32, 1.59, 1.63 (three quart, ${}^1J({}^1H^1H) = 7.5$, 6 H, MeC H_2), 3.09 (s, 3 H, H_3CO), 3.25 (s, 2 H, H_2CO). – $\delta^{13}C = 7.9$, 8.9, 10.5 (H₃CCH₂), 30.7, 32.8, 34.5 (H₃CCH₂), 59.6, 72.1 (H₃COCH₂), 75.5 (Et₃C). – C₉H₂₄O₂BMg (216.45): calc. Mg 12.18, B 5.42, H⁻ 2.02; found Mg 11.52, B 4.96, H⁻ 2.24 %.

2-Methoxyethylato-magnesium tetrahydroborate dimethoxyethane (2/1), (30): Prepared from (MeOCH₂CH₂O)Mg(BH₄)(OEt₂) (2.6 g, 22.8 mmol) and dme (20 mL). The colorless powder is slightly soluble in dme and highly soluble in Me₂SO. Yield: 2.84 g (71.5 %), m. p. 110 °C. NMR (in d₆-Me₂SO): δ^{1} H = 0.57 (m, 2 H), 3.15 to 3.80 (several m, 11 H). $-\delta^{13}$ C = 16.3 16.7, 17.2, 17.6 (all weak), 58.1, 71.1 (dme). $-C_{17}H_{53}O_{10}B_{3}Mg_{3}$ (522.93): calc. Mg 13.94, B 6.20, H⁻ 2.31; found Mg 14.04, B 6.06, H⁻ 2.26 %.

Phenolato-magnesium tetrahydroborate dimethoxyethane (2/3), (31): On heating a suspension of (PhO)Mg(BH₄)(OEt₂) (1.72 g, 8.33 mmol) in dme (10 mL) a clear solution resulted. On storing it in a refrigerator at -4 °C a white microcrystalline precipitate formed within 3 d. Yield: 0.53 g (23.9 %), m. p. 180 °C. NMR (in C₆D₆): δ^{1} H = 2.90, 3.04 (two s, 15 H, H_{3} COC H_{2}), 6.85 (t), 7.27 (t), 7.39 (d, together 5 H). $-C_{24}H_{48}O_8B_2Mg_2$ (535.16): calc. Mg 9.10, B 4.05, H⁻ 1.51; found Mg 10.77, B 3.96, H⁻ 1.55 %.

(2,6-Diisopropyl)phenolato-magnesium tetrahydroborate dimethoxyethane, (32): To a 1 M ether solution of (iPr₂C₆H₃O)Mg-(BH₄)(OEt₂) (15 mL) was added with stirring dme (10 mL). The resulting precipitate was isolated. Yield: 2.46 g (53.6 %), m. p. 206 – 209 °C. NMR (in d₆-Me₂SO): δ^{1} H = 0.99 (d, ³J(¹H¹H) = 6.3, 4 H) and 1.13 (d, ³J(¹H¹H) = 5.4, 8 H, (H₃C)₂CH), 3.24 (s, 6 H, H₃CO), 3.42 (s, 4 H, H₂CO), 3.60 (m, 2 H, Me₂CH), 6.66 (d, ${}^{3}J({}^{1}H^{1}H) = 6.8, 1 H, p-H), 6.92$ (br, 2 H, m-H). $-\delta^{13}C = 16.3, 1.70, 17.1, 17.5$ (CH₃)₂C), 23.3, 23.6, 25.4, 25.9 (Me₂C), 58.0, 71.1 (dme), 110.4, 121.3, 135.3, 161.2 (arom. C). $-C_{16}H_{31}O_{3}BMg$ (306.53): calc. Mg 7.93, B 3.53, H⁻ 1.23; found Mg 8.33, B 3.40, H⁻ 1.20 %.

2,5-Di(*tert*-butyl)phenolato-magnesium tetrahydroborate tetrahydrofuran dimethoxy-ethane, (33): 2,6-*t*BuC₆H₃OMgBH₄·2OEt₂ (2.75 g, 7.20 mmol) was dissolved in thf (14 mL). Then dme (3.7 mL) was added with stirring. No precipitate formed, also not on cooling. Therefore, about 70 % of the solvents were distilled off in vacuo. Yellow crystals separated on standing for some days at -20 °C. Yield: 1.07 g (38.0 %), m. p. 114 - 120 °C. NMR (in C₆D₆): δ^{1} H = 1.35 (s, br, 9 H, (*H*₃C)₃C), 1.40 (m, 4 H, thf), 3.11 (s, 6 H, *H*₃CO), 3.33 (s, 4 H, *H*₂CO), 3.56 m, 4 H, thf), 6.86 (t, ³*J*(¹H¹H) = 7.8, 1 H, p-H), 7.18 (³*J*(¹H¹H) = 7.8, 2 H, m-H). $-\delta^{13}$ C = 30.4, 31.9, 34.3, 35.3 (H₃C)₃C), 25.8, 67.8 (thf), 58.7, 72.1 (dme), 120.3, 125.3, 128.1, 136.1 (arom C). $-C_{22}H_{43}O_4$ BMg (406.7): calc. Mg 5.74, B 2.65, H⁻ 0.99; found Mg 6.53, B 2.75, H⁻ 1.03 %.

(2,6-Dimethoxy)phenolato-magnesium tetrahydroborate dimethoxyethane (2/3), (34): Obtained from $[(MeO)_2C_6H_3O]Mg(BH_4)(OEt_2)$ (2.3 g, 8.37 mmol) and dme (50 mL). Yield: 1.36 g (51 %), m. p. >250 °C. NMR (in d₆-Me₂SO): $\delta^1H = 3.24$ (s, H_3CO), 3.42 (s, H_2CO), 3.64, 3.73 (H_3CO), 6.17 (m, 1 H). 6.41 (d., $^3J(^1H^1H) = 7.8$, 1 H), 6.49 (d, $^3J(^1H^1H) = 7.8$, 1 H). $-\delta^{13}C = 55.6$, 56.0 (CH₃O), 58.0, 71.0 (dme), 106.7, 107.3, 108.0, 148.6, 149.3 (arom C). - $C_{28}H_{56}O_{12}B_2Mg_2$ (654.98): calc. B 3.31, H⁻ 1.23; found B 3.42, H⁻ 1.29 %.

Diglyme Solvates of ROMgBH₄

Prepared in analogy to the dme solvates.

Methylato-magnesium tetrahydroborate diglyme (2/3), (35): (MeO)Mg(BH₄)(OEt₂) (1.52 g, 10.5 mmol) was dissolved in thf (80 mL). To the stirred solution was added drop wise diglyme (30 mL). About 70 % of the solvents were then removed at 60 °C in an oil pump vacuo. The white solid that formed was isolated. Yield 1.02 g (35.8 %)., m. p. 350 °C dec.. NMR (in C₆D₆): δ^1 H = 0.28, 0.93, 1.35 (all br, 40 H, diglyme,), 3.11 ppm (9 H, H₃COMg). – δ^{13} C = 30.3 (H₃CO) and other signals in the range of 55 to 73 ppm. – C₂₀H₅₂O₁₁B₂Mg₂ (542.92): calc. Mg 8.95, B 3.98, H⁻ 1.49; found Mg 13.86, B 4.27, H⁻ 1.33 %.

Ethylato-magnesium tetrahydroborate diglyme, (36): To a suspension of (EtO)Mg(BH₄)(OEt₂) in thf (1.65 g, 10.4 mmol, 20 mL) was added diglyme (5 mL). Heating to reflux for 24 h did not dissolve the Mg compound. The solid was isolated and proved to be compound **36**. Yield 1.63 g (56.6 %), m. p. 143 – 147 °C. NMR (in d₆-Me₂SO): δ^{1} H = 1.04 (t, ${}^{1}J({}^{1}$ H¹H) = 7.0, H_{3} CCH₂O), 1.75 (m, 1 H), 3.31–3.59 (m, 7 H). 4.29 (s, 1 H). – δ^{13} C = 18.5 (H₃CCH₂), 56.0 (MeCH₂O, 56.3, 69.5, 71.2 (diglyme C).). – C₈H₂₄Og (218.39): calc. Mg 11.13, B 4.95, H⁻ 1.85; found Mg 10.76, B 4.65, H⁻ 1.73 %.

Isopropylato–magnesium tetrahydroborate diglyme (1/2), (37): To (iPrO)Mg(BH₄)(OEt₂) (3.30 g, 19.1 mmol) was added diglyme (30 mL) and the mixture refluxed for 3 h while stirring. After cooling the solid was isolated. Yield 1.11 g (15.8 %), m. p. > 350 °C, dec.. NMR (in C₆D₆): (only main signals) δ^1 H = 3.44 (m), 3.35 (m), 3.11(s) (diglyme), 1.10 (d, (CH₃)₂C), 1.17 (d, (H₃C)₂C), 1.27 (m, br), 4.43 (sept). 4.45 (sept). $-\delta^{13}$ C = 58.7, 70.9, 72.3 (diglyme), signals of iPrO were weak.). $- C_{15}H_{39}O_7BMg$ (366.59): calc. Mg 6.63, B 2.95, H⁻ 1.10; found Mg 8.94, B 3.15, H⁻ 1.09 %.

Tert-butylato-magnesium tetrahydroborate diglyme (3/1), (38): tBuO)Mg(BH₄)(OEt₂) (2.77 g, 14.0 mmol) was suspended in diglyme (20 mL) and the mixture kept at reflux for 1 h. After cooling the solid was isolated by filtration. Yield: 1.70 g (63.8 %), m. p. >350 °C, dec.. NMR (in C₆D₆): δ^{1} H = 1.04 (s, 25 H, (H₃C)₃CO), 3.11 (s, 6 H), 3.35 (m, 4 H), 3.45 (m, 4 H) diglyme. – δ^{13} C = 58.6, 70.9, 72.3 (diglyme), *t*BuO not detected. C₁₈H₅₂O₆B₃Mg₃ (469.35): calc. Mg 15.51, B 6.01, H⁻ 2.57; found Mg 17.30, B 5.91, H⁻ 2.20 %.

Triethylmethylato-magnesium tetrahydroborate diglyme (2/1), (39): To a solution of $(Et_3CO)Mg(BH_4)(OEt_2)$ (1.46 g, 6.36 mmol) in thf (100 mL) was added diglyme (10 mL). The precipitate that formed was isolated and washed with 10 mL of diethyl ether. Yield: 1.23 g (86.9 %), m. p. 350 °C dec.. NMR (in C₆D₆): $\delta^1H = 0.75$ (t, ${}^3J({}^{1}H^{1}H) = 7.5$, 18 H, H_3CCH_2), 1.28 (quart, ${}^3J({}^{1}H^{1}H) = 7.5$, 12 H, MeC H_2), 3.11 (s, 6 H), 3.29 (s, 4 H), 3.40 (s, 4 H). $-\delta^{13}C =$ 60.2, 73.9 (diglyme), 15.5 (H₃CCH₂), 30.0 (MeC H_2), 60.4 (CH₂CO). $- C_{29}H_{52}O_{5-}B_2Mg_2$ (442.86); calc. Mg 10.98, B 4.88, H⁻ 1.82; found Mg 11.14, B 4.76, H⁻ 1.78 %.

Neopentylato–magnesium tetrahydroborate diglyme (3/4), (40): (NpO)Mg(BH₄)(OEt₂) (4.00 g, 20.0 mmol) was dissolved in diethyl ether (20 mL), and diglyme (15 mL) was added to the solution while stirring. The precipitate that formed was isolated. Yield: 3.77 g (46.4 %), m. p. > 300 °C. NMR (in d₆-Me₂SO): δ^{1} H = 0.92 (s, 1 H), 3.24 (s, 8 H), 3.44 (m, 4 H), 3.51 (m, 6 H). – δ^{13} C = 26.2, 58.0, 69.5, 71.2. – C₃₉H₁₀₁O₁₅B₃Mg₃ (1219.00): calc. Mg 7.98, B 3.55, H⁻ 1.32; found Mg 8.21, B 3.40, H⁻ 1.20 %.

Triphenylmethylato-magnesium tetrahydroborate diglyme, (41): (Ph₃CO)Mg(BH₄)(OEt₂) (3.10 g, 8.32 mmol) was dissolved in thf (25 mL) and diglyme was then added (10 mL) while stirring. After 3 h the precipitate was isolated. Yield: 1.53 g (43.2 %), m. p. 147 -155 °C. NMR (in C₆D₆): δ^1 H = 2.83 (m, 14 H) diglyme), 6.75 – 7.10 (m, 9 H), 7.12 (m, 2 H), 7.53 (d, 2 H), 7.61 (d, 2 H) arom H. - C₂₅H₃₃O₄BMg (432.66). calc. Mg 5.62, B 2.50, H⁻ 0.93; found Mg 5.77, B 2.39, H⁻ 0.95 %.

(2,6-Diisopropyl)phenolato-magnesium tetrahydroborate diglyme (3/1), (42): To a stirred diethyl ether solution of (2,6iPr₂C₆H₃O)Mg(BH₄)(OEt₂) (45 mL, 0.3 M, 13.5 mmol) was added diglyme (10 mL). A precipitate formed which was isolated. Yield: 1.53 g (43.2 %), m. p. 146 – 149 °C. NMR (in C₆D₆): δ^{1} H = 1.14 (d, ³J(¹H¹H) = 6.8, 12 H, (H₃C)CH), 3.32 (m, 2 H, Me₂CH), 3.24 (s, 8 H), 3.43 (m, 5H), 3.50 (m, 5 H), 6,88 (s, br, 1 H), 6.96 (m, 2 H). – δ^{13} C = 23.1 (H₃C)₂CH), 26.1 (Me₂CH), 58.1, 69.1, 71.3 (diglyme), 120.0, 122.8, 135.5 (arom C). – C₄₂H₅₆O₆B₃Mg₃ (762.25): calc. Mg 9.32, B 4.25, H⁻ 1.55; found Mg 9.30, B 4.70, H⁻ 1.53 %.

2,6-Di(*tert*-butyl)phenolato-magnesium tetrahydroborate diglyme, (43): Prepared from a solution of $(2,6-tBu_2C_6H_3O)Mg(BH_4)(OEt_2)$ (2.75 g, 7.20 mmol) in thf (140 mL) by adding diglyme (5 mL). Yield of the precipitate: 2.01 g (76.4 %), m. p. 213 – 215 °C. NMR (in C₆D₆): $\delta^1H = 1.34$ (s, 18 H, (*H*₃C)₃C), 3.10 (s. 6 H, Me), 3.30 (m, 4 H), 3.40 (m, 4 H), 6.85 (m, 1 H), 7.17 (d, ${}^{3}J({}^{1}H{}^{1}H) = 8.1$, 1 H), 7.49 (d, ${}^{3}J({}^{1}H{}^{1}H) = 7.8$, 1 H) (arom H). – C₂₀H₃₉O₄BMg (378.62): calc. Mg 6.41, B 2.85, H⁻ 1.06; found Mg 7.40, B 3.14, H⁻ 1.15 %.

2,6-Dimethoxyphenolato-magnesium tetrahydroborate diglyme (3/ 1), (44): 2,6-[(MeO)₂C₆H₃O]Mg(BH₄)(OEt₂) (2.70 g, 10.1 mmol) was suspended in diglyme (20 mL). After stirring for 3 h the insoluble material was isolated. Yield 2.08 g (86.7 %), m. p. 290 °C dec.. NMR (in d₆-Me₂SO): δ^1 H = 3.24 (6 H). 3.43 (m, 4 H), 3.49 (m.

Compound	3	4	20	6	21	33	49	50
Chem. formula Form. wght.	C ₇ H ₂₁ O ₂ BMg 172.4	C ₈ H ₂₃ O ₂ BMg 186.4	C ₁₁ H ₂₇ O ₂ BMg 226.4	C ₉ H ₂₅ O ₂ BMg 200.4	C ₁₄ H ₂₅ O ₃ BMg 276.5	C ₂₂ H ₄₃ O ₄ BMg 406.7	C ₁₂ H ₃₆ O ₃ NBMgSi ₂ 333.7	C ₇ H ₂₃ O ₂ BMgSi 202.5
Cryst. Size, mm Cryst. system	0.3x0.5x0.55 monoclinic	0.6x0.3x0.3 monoclinic	0.55x0.45x0.32 triclinic	0.48x0.3x0.25 monoclinic	0.6x0.6x0.45 monoclinic	0.5x0.5x1.3 monoclinic	0.4x0.28x0.31 monoclinic	0.4x0.4x0.45 monoclinic
a, Å b, Å c, Å	$\begin{array}{c} F_{2_1/11} \\ 9.379(2) \\ 10.531(2) \\ 11.668(3) \end{array}$	9.754(2) 10.960(2) 11.720(2)	8.622(1) 9.281(1) 9.486(1)	$P_{2_1/11}$ 9.365(7) 13.192(8) 11.528(9)	7.987(3) 10.087(2) 19.817(4)	12.198(1) 14.090(1) 14.882(1)	$\begin{array}{c} P2_{1}/11\\ 9.143(4)\\ 12.681(5)\\ 10.231(5) \end{array}$	9.412(2) 13,888(3) 10.517(2)
α, ° β, ° γ, °	95.87(1)	91.23(1)	81.89(1) 80.71(1) 81.65(1)	94.47(6)	92.04(3)	105.56(6)	115.72(1)	93.89(7)
V, Å ³ Z	1146.4(4) 4	1252.5(4) 4	735.8(1) 2	1422(1) 4	1595.5(8) 4	2464(1) 4	1067(1) 2	1371.6(7) 4
ρ (calcd.), Mg/m ³ μ , mm ⁻¹ F(000) Index range	0.999 0.115 384 $-1 \le h \le 10$ $0 \le k \le 12$	0.988 0.105 416 $0 \le h \le 11$ $0 \le k \le 13$	1.022 0.098 252 $0 \le h \le 10$ $-11 \le k \le 11$	0.936 0.095 448 $-4 \le h \le 10$ $-1 \le k \le 14$	1.151 0.106 600 $-2 \le h \le 8$ $-9 \le k \le 11$	1.096 0.089 896 $0 \le h \le 13$ $0 \le k \le 15$	1.037 0.200 368 $0 \le h \le 10$ $0 \le k \le 14$	0.980 0.187 448 $0 \le h \le 11$ $0 \le k \le 17$
2 θ, ° Temp, K Pofl. collected	$-13 \le 1 \le 13$ 50.0 203 2160	$-13 \le 1 \le 13$ 50 193 2347	$-11 \le 1 \le 11$ 52 293 2235	$-12 \le 1 \le 12$ 45.0 293 2001	$-22 \le 1 \le 22$ 47.0 193(3) 2843	$-16 \le 1 \le 16$ 47.0 193	$-12 \le 1 \le 10$ 50.0 253	$-12 \le j \le 12$ 52.0 273 2716
Refl. unique Refl. observed (4σ) R (int.)	1779 1443 0.0463	2094 1712 (3σ) 0.0202	2897 2420 (4σ) 0.0221	1864 1383 0.0017	2345 2309 1674 (3σ) 0.0885	3554 2781 (3σ) 0.0471	1893 1193 (4σ) 0.0248	2619 1805 2.95
No. variables Weight. scheme	112 σ²/0.0017	$155 \sigma^2/0.0003$	148 σ ² /0.0003	$\frac{118}{\sigma^2/0.00012}$	199 σ ² /0.0018	358 σ ² /0.0001	$110 \sigma^2/0.0003$	109 σ ² /0.0017
GOOF Final R (4σ) Final wR2 Larg. res. peak e/Å ³	1.25 0.0473 0.0659 0.35	2.40 0.0625 0.0742 0.49	3.72 0.0679 0.079c2 0.47	2.01 0.0697 0.0948 0.39	1.37 0.0638 0.1497 0.492	2.20 0.065 0.0635(wR) 0.30	2.29 0.0721 0.913 0.036	1.39 0.0569 0.0799 0.32

Table 4 Crystallographic data of compounds 3 to and 46 and data related to data collection and structure solution

^{a)} $w^{-1} = \delta^2(F) + x(F^2)$

4 H) diglyme; 3.63, 3.73 (each s, 18 H, OCH₃), 6.41 (d, 6 H), 6.49 (t, ${}^{3}J({}^{1}H{}^{1}H) = 7.8, 3$ H). $-C_{30}H_{50}O_{12}B_{3}Mg_{3}$ (711.57): calc. B 4.56, H⁻ 1.70; found B 4.56, H⁻ 1.73 %.

Bis(2-isopropoxyphenolato)-magnesium-dimethylsulfoxide, (45): Compound 13 (0.7 g, 2.2 mmol) was crystallized from Me₂SO (10 mL) . This produced crystals of compound 45. Yield was not determined. m. p. > 300 °C. NMR (in d₆-Me₂SO): δ^{1} H = 1.35 (d, ³*J*(¹H¹H) = 5.7, 6 H, CH(C*H*)₃), 2,71 (s, 6 H, Me₂SO). 4.70 (m, 1 H, OC*H*Me₂), 6-84 - 6.86 (br, m, 4 H). δ^{13} C = 21.2 (CH(*C*H₃)₂, 69.7 (*C*HMe₂), 117.0, 117.7, 121.3, 122.0, 147.1 (arom. C). C₂₀H₂₈O₅MgS (404.81): calc. C 59.34, H 6.97, O 19.76; found C 56.18, H 6.79, O 19.59 %.

Bis(trimethylsilyl)amino magnesium tetrahydroborate diethyl ether, (46): A solution of $(Me_3Si)_2NH$ (2.13 mL, 18.6 mmol) in diethyl ether (20 mL) was dropped into a stirred solution of EtMg(BH₄) in diethyl ether (0.93 M, 20 mL). After gas evolution had subsided the ether was stripped off from the solution in vacuo. No crystals separated on cooling the solution after various steps of ether removal. Finally a very viscous oil remained which hydrolysed rapidly in air. However, it turned solid after standing for 3 days. Yield: 4.5 g (89 %); m. p. 53 – 55 °C. NMR (in C₆D₆): $\delta^1H = -0.37$ (quart. ${}^1(J^{11}B^1H) = 82.3$, BH₄), 0.41 (s, 18 H, SiMe₃), 1.27 (t, 6 H, CH₂CH₃)), 13.49 (quart, 4 H, CH₂). $-{}^{13}C = 6.1$ (SiMe), 14.4, 65.0 (Et₂O). $- \delta^{11}B$ (in diethyl ether) = -37.8 (broad). -C₁₀H₃₂NBMgSi₂ (273.67): calc. Mg 8.86, B 3.95, H⁻ 1.47; found Mg 8.54, B 3.84, H⁻ 1.30 %. **Bis(trimethylsilyI)amino-magnesium** tetrahydroborate-bis(tetrahydrofuran), (47): 46 (3.68 g, 13.5 mmol) was dissolved in thf (40 mL). The solution was then reduced in vacuo to half of its volume. Then pentane was allowed to diffuse into the solution. After 6 d crystals had separated. These were dried shortly in vacuo. They rapidly hydrolysed in air with formation of a colorless powder. Yield: 3.34 g (87.8 %), m. p. 61 – 64 °C. NMR (in C₆D₆): δ^{1} H =0.41 (s, Me₃Si), 1.29, 3.71 (thf). – δ^{13} C: 6.2 (Me₃Si), 25.2, 69.6 (thf). – C₁₄H₃₈O₂NBMgSi₂ (434.74): calc. Mg 7.07, B 3.15, H⁻ 1.17; found Mg 6.92, B 3.10.02, H⁻ 1.08 %.

Bis(trimethylsilylamino)-magnesium tetrahydroborate dimethoxyethane, 48: To 2.37 g of **46** (8.7 mmol) was added dme (30 mL). The solution was stirred for one h, then most of the volatile parts were removed in vacuo (oil pump). Pentane was allowed to diffuse into the remaining solution within a period of 5 d. Colorless need-les separated within this time. They were isolated and shortly dried in vacuo. Yield: 2.14 g (85.2 %), m. p. 63 – 65 °C. NMR (in C₆D₆): δ^{1} H = 0.01 (Me₃Si), 3.19 (H_{3} CO), 3.40 (t, C H_{2} O). – δ^{13} C = 2.7 (Me₃Si), 57.3 (H₃CO), 71.1 (CH₂O). – C₁₀H₃₂O₂NBMgSi₂ (289.67): calc. Mg 7.07, B 3.15, H⁻ 1.17; found Mg 6.92, B 3.02, H⁻ 1.08 %.

Bis(trimethylsilyl)aminomagnesium tetrahydroborate-diglyme, (49): 0 1.63 g of **46** (5 mmol) were dissolved in diglyme (30 mL). In vacuo about 10 mL of the solvents were removed, and the remaining solution stored at -18 °C for 5 d. Colorless crystals of single crystal quality formed. Yield: 1.5 g (82 %), m. p. 68 - 71 °C. NMR

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(in C₆D₆): δ^1 H = 0.11, 0.39 (s, ratio 2:1, Me₃Si), 3.10 (H₃CO). 3.41 (MeOCH₂), 3.51 (CH₂CH₂O). – δ^{13} C = 2.6, 2.9 (Me₃Si), 58.7 (CH₃O), 70.9 (MeOCH₂O), 72.3 (CH₂CH₂O). C₁₂H₃₆O₃NBMgSi₂ (333.72): calc. Mg 7.29, B 3.24, H⁻ 1.20; found Mg 7.21, B 3.17, H⁻ 1.13 %.

Trimethylsiloxomagnesium tetrahydroborate diethyl ether, (50): A solution of **46** (1.14 g, 4.0 mmol) in diethyl ether (10 mL) was kept for a week in a refrigerator at -25 °C. Within this time colorless, regularly shaped crystals separated. These were isolated, dried in a stream of N₂ and analyzed by X-ray crystallography. The crystals proved to be compound **50**. The same compound was obtained after several recrystallisations of **46** from diethyl ether. Yield: 0.52 g (65.1 %), m.p. 71–73 °C. NMR (in C₆D₆): δ^{1} H = -0.39 (quart., ${}^{1}J({}^{11}\text{B}^{1}\text{H}) = 82.4$ Hz, BH₄), 0.31 (s, Me₃Si), 0.89, 3.52 Et₂O). $-\delta^{13}$ C: 3.4 (Me₃Si), 13.9, 65.6 (Et₂O). $-\delta^{11}$ B (in THF): -39.9 (quint., ${}^{1}J({}^{11}\text{B}^{1}\text{H}) = 81.4$. $-C_7H_{23}O_2$ BMgSi (202.46): calc. C 41.53, B 5.34, Mg 12.02; H⁻ 11.45 found C 38.72, B 5.47, Mg 12.25. H⁻ 11.02 %.

X-ray Structure analysis

Reflection data were collected on a Siemens P4 diffractometer operated with graphite monochromatized MoK α radiation in the $\omega/2\theta$ mode using a scintillation counter for intensity measurements. The unit cell and the orientation matrix were determined by centering the reflection found in rotation photos. Scan time varied from 5 to 30 s depending on intensity. After data reduction the structures were solved with the program packages SHELXPLUS and SHELX 93 [29]. Relevant crystallographic data as well as information on the structure solution are summarized in Table 4. Additional crystallographic data are deposited with the Cambridge Crystallographic Data Centre as publication numbers CCD-256049-256056 and can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK Fax +44-1223-336033; email: deposit@ccdc.cam.as.uk. In figures 1 - 7 all thermal ellipsoids are depicted on a 25 % probability scale. Bond lengths are given in A, and bond angles in degrees. Estimated standard deviations are set in parenthesis.

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