

Chiral *cis*-octahedral Grignard reagents

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Abstract

Three chiral *cis*-octahedral Grignard reagents have been synthesized and structurally characterized by X-ray diffraction methods. Crystals of *cis*-[(*n*-Pr)MgBr(dme)₂] (**1**), *cis*-[(*i*-Pr)MgBr(dme)₂] (**2**) and *cis*-[(allyl)MgBr(dme)₂] (**3**) were prepared from neat 1,2-dimethoxyethane (DME) and are all racemic. Synthesis and structural characterization of *trans*-[MgBr₂(tmeda)₂] (**4**) and *cis*-[MgBr₂(dme)₂] (**5**) indicated that bidentate tertiary amino ligands may be less well suited for the preparation of *cis*-octahedral Grignard reagents. On the other hand, the crystal structures of *cis*-[MgBr₂(trigly)] (**6**) and [Mg₂(μ-Br)₂(trigly)₂][Mg₂(μ-Me)₂Br₄] (**7**) {trigly = triglyme}, suggest that the triglyme ligand may be ideally suited for this purpose.

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1. Introduction

Grignard reagents are usually considered to be four-coordinate in the solid state, [1–6] with five-coordinate [CH₃MgBr(thf)₃] [7] as a notable exception that can be explained by the small size of the methyl group [8–10]. Even higher coordination numbers in RMgX and MgR₂ reagents normally require R groups with substituents that can form intramolecular coordinate bonds. We have, however, found that *trans*-[Mg(thienyl)₂(thf)₄] is six-coordinate in the solid state [11] and we could also prepare and determine the crystal structure of octahedral *cis*-[(thienyl)MgBr(dme)₂] and *cis*-[(vinyl)MgBr(dme)₂], where dme = 1,2-dimethoxyethane [11]. The latter two complexes were prepared and crystallized from neat DME, and since the solvent and the neutral bidentate ligands are identical, labile complexes may form. Complexes of the [MAB(LL)₂] type, where LL denotes a bidentate neutral ligand, exist as *cis*- and *trans*-isomers, and the *cis*-isomers have stereogenic metal atoms, i.e. they are “chiral at metal” (see Fig. 1). Octahedral RMgX and MgR₂ reagents are thus attractive since they can be made configurationally chiral by simple solvation if the solvent is bidentate

like DME. They are also likely to retain their solid state structure in DME or THF solution, since EXAFS and LAXS measurements [12–15] have shown that octahedral monomers, at least when R is vinyl, dominate in THF. Indeed, ¹H-NMR data show that *cis*-[(thienyl)MgBr(dme)₂] [11] seems to retain its solid-state structure in toluene solution. Moreover, racemization between the Δ and Λ enantiomers is rapid in solution, which means that if the reagent crystallizes as a conglomerate, then one of the enantiomers can be obtained in 100% yield and enantiomeric excess, theoretically [16]. Grignard reagents that are chiral at magnesium, should give strong asymmetric induction and if their chirality can be controlled or predetermined, they have a promising potential in stereoselective syntheses. Consequently, it is important to determine which monodentate R and X ligands (and bidentate LL ligands) that are appropriate to use in the design of *cis*-octahedral Grignard reagents.

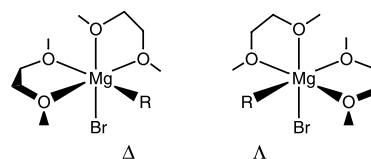


Fig. 1. The magnesium atom in *cis*-[RMgBr(dme)₂] complexes is stereogenic. The Δ- and Λ-enantiomers are stereochemically labile.

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2. Experimental

2.1. General

All operations were carried out under nitrogen or argon using Schlenk and low temperature [17] techniques. Solvents were distilled from sodium/benzophenone shortly prior to use. Neutral ligands such as *N,N,N',N'*-tetramethylethylenediamine (tmeda) and triglyme (trigly) were deoxygenated and dried with 4 Å molecular sieves. Commercial (Aldrich) Grignard reagents and organohalides were used as delivered.

2.2. Preparation of *cis*-[(*n*-Pr)MgBr(dme)₂] (1)

1-Bromopropane (0.91 ml, 10 mmol) was added dropwise into a stirred Schlenk vessel containing magnesium turnings (0.350 g, 14.4 mmol) and diethyl ether (DEE) (10 ml). The reaction mixture was stirred for 1 h. The solvent was evaporated from the greyish brown solution and DME (10 ml) was added to the residue. A grey precipitate formed. The stirring continued for 1 h and the vessel was then stored at –80 °C. After a few days, colorless crystals of **1** formed. Approximate yield: 1.0 g, 31%.

2.3. Preparation of *cis*-[(*i*-Pr)MgBr(dme)₂] (2)

2-Bromopropane (0.91 ml, 10 mmol) was added in small portions to magnesium turnings (0.325 g, 13.4 mmol) and DEE (10 ml) during stirring. After 1 h the grey solution was evaporated to dryness and DME (10 ml) was added. The solids dissolved and a grey precipitate was formed shortly after. The suspension was stirred for 1 h. Colorless crystals of **2** formed after several days at –80 °C. Approximate yield: 1.0 g, 31%.

2.4. Preparation of *cis*-[(allyl)MgBr(dme)₂] (3)

The solvent was evaporated from commercial allylmagnesium bromide in DEE (10.0 ml, 10.0 mmol). The residual solids were dried briefly under vacuum and redissolved in DME (10 ml) during stirring. From the resulting green solution a green precipitate was formed almost instantaneously. When no more precipitate was formed the reaction mixture was kept at –80 °C and after 12 h green crystals of **3** formed. Yield: 1.13 g, 35%.

2.5. Preparation of *trans*-[MgBr₂(tmeda)₂] (4)

Magnesium turnings (0.355 g, 14.6 mmol), bromobenzene (1.05 ml, 10 mmol) and DEE (10 ml) were allowed to react during stirring. After 1 h the solvent was evaporated from the brown solution. Most of the oily residue was redissolved in TMEDA (10 ml), by

heating if necessary. After a few hours, colorless crystals of **4** formed. Approximate yield: 1.5 g, 72%.

2.6. Preparation of *cis*-[MgBr₂(dme)₂] (5)

Bromobenzene (1.05 ml, 10 mmol) was added to a Schlenk vessel containing DEE (10 ml) and magnesium turnings (0.362 g, 14.9 mmol) during stirring. After the addition, the reaction mixture was allowed to stand for 1 h at ambient temperature. The brown solution was evaporated to dryness. DME (10 ml) was added, which dissolved most of the remaining solids. After a few hours at ambient temperature, colorless crystals of **5** formed. Approximate yield: 1.0 g, 54%.

2.7. Preparation of *cis*-[MgBr₂(trigly)] (6)

Magnesium turnings (0.290 g, 11.9 mmol) and 4-bromotoluene (1.71 g, 10.0 mmol) were stirred for 1 h in DEE (10 ml). After removal of the solvent by evaporation, triglyme (10 ml) was added whereafter the solids dissolved. The resulting clear brown solution was kept at ambient temperature and after a short period of time, light brown crystals of **6** formed. Approximate yield: 1.0 g, 56%.

2.8. Preparation of [Mg₂(μ-Br)₂(trigly)₂][Mg₂(μ-Me)₂Br₄] (7)

Commercial methylmagnesium bromide in DEE (5.0 ml, 15.0 mmol) was evaporated to dryness. Triglyme (5 ml) was added slowly to the solid residue. The mixture was kept at ambient temperature for 24 h. Colorless crystals of **7** formed during this time. Approximate yield: 1.5 g, 31%.

2.9. X-ray crystallography

Crystal and experimental data for **1–7** are summarized in Table 1. All crystals were selected and mounted under nitrogen in a glass capillary at low temperature [17] and transferred in liquid nitrogen to either a Rigaku AFC6 diffractometer (**1–5**; **7**) or a Rigaku R-AXIS IIc image plate system (**6**). Diffracted intensities were measured at –120 °C (AFC6) or –150 °C (R-AXIS), using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation from a RU200 rotating anode operated at 50 kV and 90 (R-AXIS) or 180 mA (AFC6). Using the AFC6 diffractometer, stationary background counts were recorded on each side of a reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections (*I* < 10.0σ(*I*)) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability during the

Table 1
Crystallographic data for 1–7

Compound	<i>cis</i> -[(<i>n</i> -Pr)MgBr(dme) ₂] (1)
Empirical formula	C ₁₁ H ₂₇ BrMgO ₄
Formula weight	327.55
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (# 14)
Unit cell dimensions	
<i>a</i> (Å)	8.755(4)
<i>b</i> (Å)	11.7960(19)
<i>c</i> (Å)	16.145(3)
α (°)	90
β (°)	101.51(2)
γ (°)	90
<i>V</i> (Å ³)	1633.8(8)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.332
Absorption coefficient (mm ⁻¹)	2.556
Crystal size (mm ³)	0.3 × 0.2 × 0.15
Theta range for data collection (°)	2.15–24.99
Reflections collected	3073
Independent reflections	2873 [<i>R</i> _{int} = 0.0786]
Completeness to theta = 24.99° (%)	100.0
Data/restraints/parameters	2873/0/154
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.0872
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1626, <i>wR</i> ₂ = 0.1165
Largest difference peak and hole (e Å ⁻³)	0.521 and -0.594
Compound	<i>cis</i> -[(<i>i</i> -Pr)MgBr(dme) ₂] (2)
Empirical formula	C ₁₁ H ₂₇ BrMgO ₄
Formula weight	327.55
Crystal system	Orthorhombic
Space group	<i>Pbca</i> (# 61)
Unit cell dimensions	
<i>a</i> (Å)	19.258(4)
<i>b</i> (Å)	13.074(4)
<i>c</i> (Å)	12.952(2)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	3261.2(14)
<i>Z</i>	8
<i>D</i> _{calc} (Mg m ⁻³)	1.334
Absorption coefficient (mm ⁻¹)	2.561
Crystal size (mm ³)	0.15 × 0.15 × 0.15
Theta range for data collection (°)	2.12–25.00
Reflections collected	2876
Independent reflections	2876
Completeness to theta = 25.00° (%)	99.8
Data/restraints/parameters	2876/0/154
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.0783
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2531, <i>wR</i> ₂ = 0.1206
Largest difference peak and hole (e Å ⁻³)	0.535 and -0.737
Compound	<i>cis</i> -[(allyl)MgBr(dme) ₂] (3)
Empirical formula	C ₁₁ H ₂₅ BrMgO ₄
Formula weight	325.53
Crystal system	Orthorhombic
Space group	<i>Pbca</i> (# 61)
Unit cell dimensions	
<i>a</i> (Å)	20.625(4)
<i>b</i> (Å)	12.919(4)
<i>c</i> (Å)	12.029(6)
α (°)	90

Table 1 (Continued)

β (°)	90
γ (°)	90
<i>V</i> (Å ³)	3205(2)
<i>Z</i>	8
<i>D</i> _{calc} (Mg m ⁻³)	1.349
Absorption coefficient (mm ⁻¹)	2.605
Crystal size (mm ³)	0.10 × 0.10 × 0.10
Theta range for data collection (°)	2.52–24.99
Reflections collected	2819
Independent reflections	2819
Completeness to theta = 24.99° (%)	99.9
Data/restraints/parameters	2819/0/154
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0444, <i>wR</i> ₂ = 0.0873
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2512, <i>wR</i> ₂ = 0.1368
Largest difference peak and hole (e Å ⁻³)	0.553 and -0.604
Compound	<i>trans</i> -[MgBr ₂ (tmeda) ₂] (4)
Empirical formula	C ₆ H ₁₆ BrMg _{0.50} N ₂
Formula weight	208.27
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (# 14)
Unit cell dimensions	
<i>a</i> (Å)	7.998(3)
<i>b</i> (Å)	13.063(4)
<i>c</i> (Å)	9.079(4)
α (°)	90
β (°)	100.20(3)
γ (°)	90
<i>V</i> (Å ³)	933.6(6)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.482
Absorption coefficient (mm ⁻¹)	4.370
Crystal size (mm ³)	0.2 × 0.2 × 0.2
Theta range for data collection (°)	2.76–24.99
Reflections collected	1753
Independent reflections	1632 [<i>R</i> _{int} = 0.0734]
Completeness to theta = 24.99° (%)	99.4
Data/restraints/parameters	1632/0/80
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1077
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1196, <i>wR</i> ₂ = 0.1335
Largest difference peak and hole (e Å ⁻³)	0.552 and -0.549
Compound	<i>cis</i> -[MgBr ₂ (dme) ₂] (5)
Empirical formula	C ₈ H ₂₀ Br ₂ MgO ₄
Formula weight	364.37
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (# 2)
Unit cell dimensions	
<i>a</i> (Å)	7.519(3)
<i>b</i> (Å)	14.616(4)
<i>c</i> (Å)	7.468(3)
α (°)	91.28(3)
β (°)	117.29(3)
γ (°)	81.51(2)
<i>V</i> (Å ³)	720.4(5)
<i>Z</i>	2
<i>D</i> _{calc} (Mg m ⁻³)	1.680
Absorption coefficient (mm ⁻¹)	5.663
Crystal size (mm ³)	0.15 × 0.15 × 0.20
Theta range for data collection (°)	2.82–25.00
Reflections collected	2731
Independent reflections	2524 [<i>R</i> _{int} = 0.1237]

Table 1 (Continued)

Completeness to theta = 25.00° (%)	99.7
Data/restraints/parameters	2524/0/136
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0540, <i>wR</i> ₂ = 0.1135
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2885, <i>wR</i> ₂ = 0.1826
Largest difference peak and hole (e Å ⁻³)	0.858 and -0.907
Compound	<i>cis</i> -[MgBr ₂ (trigly)] (6)
Empirical formula	C ₈ H ₁₈ Br ₂ MgO ₄
Formula weight	362.35
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (#14)
Unit cell dimensions	
<i>a</i> (Å)	8.393(2)
<i>b</i> (Å)	13.183(3)
<i>c</i> (Å)	12.788(3)
α (°)	90
β (°)	108.930(7)
γ (°)	90
<i>V</i> (Å ³)	1338.5(5)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.798
Absorption coefficient (mm ⁻¹)	6.096
Crystal size (mm ³)	0.2 × 0.2 × 0.2
Theta range for data collection (°)	2.57–27.50
Reflections collected	10 418
Independent reflections	3040 [<i>R</i> _{int} = 0.0690]
Completeness to theta = 27.50° (%)	98.8
Data/restraints/parameters	3040/0/136
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0358, <i>wR</i> ₂ = 0.0875
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0472, <i>wR</i> ₂ = 0.0924
Largest difference peak and hole (e Å ⁻³)	0.644 and -0.749
Compound	[Mg ₂ (μ-Br) ₂ (trigly) ₂][Mg ₂ (μ-Me) ₂ Br ₄] (7)
Empirical formula	C ₉ H ₂₁ Br ₃ Mg ₂ O ₄
Formula weight	481.61
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (# 14)
Unit cell dimensions	
<i>a</i> (Å)	7.363(3)
<i>b</i> (Å)	15.957(3)
<i>c</i> (Å)	15.339(3)
α (°)	90
β (°)	93.02(3)
γ (°)	90
<i>V</i> (Å ³)	1799.5(9)
<i>Z</i>	4
<i>D</i> _{calc} (Mg m ⁻³)	1.778
Absorption coefficient (mm ⁻¹)	6.797
Crystal size (mm ³)	0.2 × 0.2 × 0.2
Theta range for data collection (°)	2.66–25.00
Reflections collected	3415
Independent reflections	3156 [<i>R</i> _{int} = 0.0656]
Completeness to theta = 25.00° (%)	99.7
Data/restraints/parameters	3156/0/172
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.1034
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1792, <i>wR</i> ₂ = 0.1415
Largest difference peak and hole (e Å ⁻³)	0.919 and -0.943

diffraction experiment. Cell constants were obtained by least-squares refinement from the setting angles of 20 reflections. An empirical correction for the effects of absorption was made based on several psi-scans for **1**, **4** and **7**. For **2**, **3** and **5**, no correction was made for the effects of absorption owing to lack of suitable reflections for which azimuthal scans could be collected. With the R-AXIS IIC detector, 90 oscillation photos with a rotation angle of 2° were collected and processed using the CRYSTALCLEAR software package. An empirical absorption correction was applied using the REQAB program under CRYSTALCLEAR. Crystal and refinement data for compounds **1–7** are summarized in Table 1. All structures were solved by direct methods (SIR-97) [18] and refined using full-matrix least-squares calculations on *F*² (SHELXL-97) [19] operating in the WINGX program package [20]. Anisotropic thermal displacement parameters were refined for all the non-hydrogen atoms, except in **4** where the ligand atoms are disordered on double sites. Structural illustrations have been drawn with ORTEP-3 for WINDOWS [21].

3. Results and discussion

Which R groups and neutral bidentate ligands (LL) can be used in order to obtain chiral octahedral reagents of the [RMgBr(LL)₂] type? First of all, the *trans*-isomer must be avoided since it is achiral. Octahedral *trans* coordination has previously been reported [22–24] in MgR₂ complexes like the TMEDA complexes of bis(phenylethynyl)magnesium and bis(*tert*-butylethynyl)magnesium. On the other hand, no *trans*-octahedral RMgX complexes have been reported, and the crystal structures of *cis*-[(thienyl)MgBr(dme)₂] and *cis*-[(vinyl)MgBr(dme)₂] [11] suggest that the chiral *cis*-isomer is favored when the bidentate ligand (LL) is dme. This geometry has also been found in *cis*-[MgCl₂(dme)₂] [25]. It, therefore, seemed reasonable to start the investigation by trying to prepare reagents of the [RMgBr(dme)₂] type by reacting a variety of organobromides with magnesium in neat DME. Alternatively, the Grignard reagents can first be prepared in DEE or THF, the solvent evaporated, and the solids redissolved in neat DME. One problem is that the Schlenk equilibrium produces [MgBr₂(dme)₂] and [MgR₂(dme)₂] molecules, which compete with [RMgBr(dme)₂] during crystallization. Especially [MgBr₂(dme)₂] precipitates easily, *vide infra*, but sometimes this process can be reversed when crystals of [RMgBr(dme)₂] once have started to form. Another problem is the obvious risk that too bulky R groups will lead to four- or five-coordination.

Two chiral *cis*-octahedral Grignard reagents, i.e. [(*n*-Pr)MgBr(dme)₂] (**1**) and [(*i*-Pr)MgBr(dme)₂] (**2**), derived from 1-bromopropane and 2-bromopropane, respec-

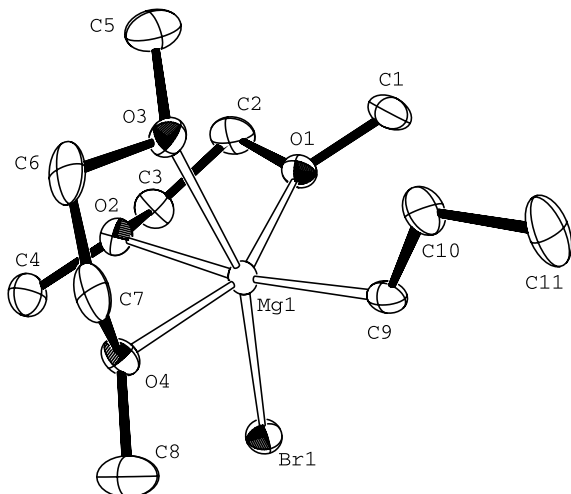


Fig. 2. ORTEP drawing of *cis*-[(*n*-Pr)MgBr(dme)₂] (**1**). Only the Λ -enantiomer is shown, but the Δ -enantiomer is also present in crystals of **1**.

tively, could be prepared and structurally characterized by X-ray diffraction. A third reagent, *cis*-[(allyl)MgBr(dme)₂] (**3**) was prepared from commercial allylmagnesium bromide. They all display similar molecular structures (see Figs. 2–4) and they all crystallize in centrosymmetric space groups (see Table 1), i.e. both Δ and Λ enantiomers are present in all crystals. Crystals of **1–3** are thus racemic, and the Δ - and Λ -enantiomers have to be resolved if these octahedral Grignard reagents are to be useful in stereoselective synthesis [16].

It is interesting to compare bond distances and angles for the closely related complexes **1–3** (see Tables 2–4). The Mg–C distances in **1** (2.16 Å), **2** (2.19 Å) and **3** (2.21 Å) are normal despite the high coordination number, while the Mg–Br distances of 2.69, 2.67 and 2.63 Å, respectively, are significantly longer than the typical

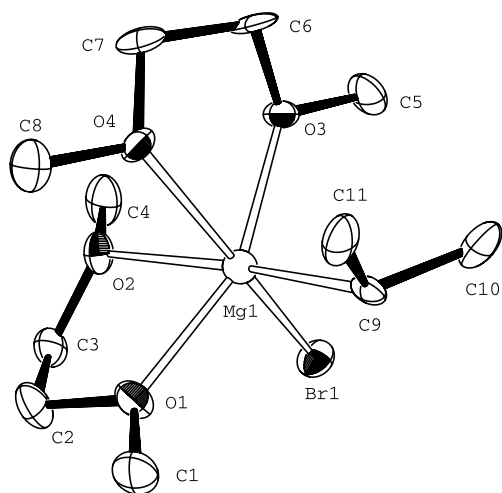


Fig. 3. ORTEP drawing of *cis*-[(*i*-Pr)MgBr(dme)₂] (**2**). Only the Λ -enantiomer is shown, but the Δ -enantiomer is also present in crystals of **2**.

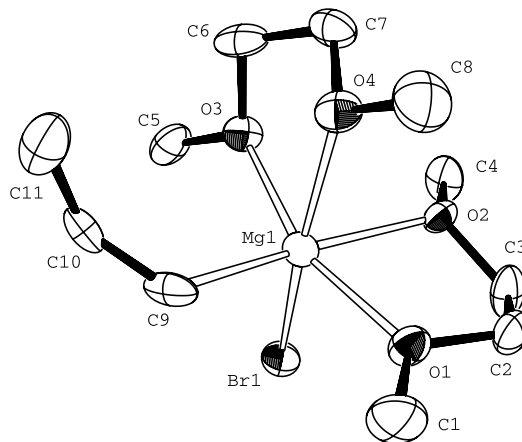


Fig. 4. ORTEP drawing of *cis*-[(allyl)MgBr(dme)₂] (**3**). Only the Λ -enantiomer is shown, but crystals of **3** are racemic.

Table 2

Bond lengths (Å) and angles (°) for *cis*-[(*n*-Pr)MgBr(dme)₂] (**1**)

Bond lengths			
Mg(1)–O(1)	2.141(4)	Mg(1)–C(9)	2.158(6)
Mg(1)–O(4)	2.166(4)	Mg(1)–O(2)	2.203(5)
Mg(1)–O(3)	2.295(4)	Mg(1)–Br(1)	2.693(2)
O(1)–C(2)	1.440(7)	O(1)–C(1)	1.441(7)
O(2)–C(3)	1.432(7)	O(2)–C(4)	1.437(7)
O(3)–C(5)	1.432(7)	O(3)–C(6)	1.447(7)
O(4)–C(8)	1.437(7)	O(4)–C(7)	1.445(7)
C(2)–C(3)	1.514(8)	C(6)–C(7)	1.497(9)
C(9)–C(10)	1.528(8)	C(10)–C(11)	1.525(8)
Bond angles			
O(1)–Mg(1)–C(9)	100.0(2)	O(1)–Mg(1)–O(4)	156.77(19)
C(9)–Mg(1)–O(4)	98.7(2)	O(1)–Mg(1)–O(2)	73.70(17)
C(9)–Mg(1)–O(2)	171.7(2)	O(4)–Mg(1)–O(2)	86.24(17)
O(1)–Mg(1)–O(3)	90.42(17)	C(9)–Mg(1)–O(3)	94.2(2)
O(4)–Mg(1)–O(3)	74.54(16)	O(2)–Mg(1)–O(3)	80.61(16)
O(1)–Mg(1)–Br(1)	95.80(14)	C(9)–Mg(1)–Br(1)	100.52(17)
O(4)–Mg(1)–Br(1)	94.20(13)	O(2)–Mg(1)–Br(1)	85.70(12)
O(3)–Mg(1)–Br(1)	162.74(14)	C(2)–O(1)–C(1)	113.3(5)
C(2)–O(1)–Mg(1)	118.7(3)	C(1)–O(1)–Mg(1)	125.2(4)
C(3)–O(2)–C(4)	110.0(5)	C(3)–O(2)–Mg(1)	111.5(4)
C(4)–O(2)–Mg(1)	124.0(4)	C(5)–O(3)–C(6)	111.0(5)
C(5)–O(3)–Mg(1)	125.5(4)	C(6)–O(3)–Mg(1)	110.9(4)
C(8)–O(4)–C(7)	111.0(5)	C(8)–O(4)–Mg(1)	120.4(4)
C(7)–O(4)–Mg(1)	111.2(3)	O(1)–C(2)–C(3)	107.1(5)
O(2)–C(3)–C(2)	107.2(5)	O(3)–C(6)–C(7)	106.6(5)
O(4)–C(7)–C(6)	107.0(5)	C(10)–C(9)–Mg(1)	122.4(4)
C(11)–C(10)–C(9)	116.3(6)		

values of 2.4–2.5 Å in four-coordinate RMgBr complexes [1,2]. In all three complexes, the Mg–O distances that is *cis* to both monodentate ligands (R and Br) are significantly shorter than the other two Mg–O distances, a geometry that has precedence in *cis*-octahedral [MgAB(LL)₂] complexes [26]. This effect is stronger when the bidentate ligand has a small bite angle, and the dme ligands in **1–3** exhibit bite angles between 73 and 75°, resulting in a distorted coordination figure. More-

Table 3
Bond lengths (Å) and angles (°) for *cis*-[(*i*-Pr)MgBr(dme)₂] (**2**)

Bond lengths			
Mg(1)–O(1)	2.158(6)	Mg(1)–O(3)	2.178(6)
Mg(1)–C(9)	2.186(8)	Mg(1)–O(4)	2.262(6)
Mg(1)–O(2)	2.263(6)	Mg(1)–Br(1)	2.665(3)
O(1)–C(2)	1.438(9)	O(1)–C(1)	1.440(9)
O(2)–C(3)	1.422(8)	O(2)–C(4)	1.431(9)
O(3)–C(5)	1.433(9)	O(3)–C(6)	1.434(9)
O(4)–C(8)	1.422(9)	O(4)–C(7)	1.436(9)
C(2)–C(3)	1.491(11)	C(6)–C(7)	1.505(11)
C(9)–C(10)	1.505(10)	C(9)–C(11)	1.529(10)
Bond angles			
O(1)–Mg(1)–O(3)	157.2(3)	O(1)–Mg(1)–C(9)	98.0(3)
O(3)–Mg(1)–C(9)	100.7(3)	O(1)–Mg(1)–O(4)	91.3(2)
O(3)–Mg(1)–O(4)	74.5(2)	C(9)–Mg(1)–O(4)	93.8(3)
O(1)–Mg(1)–O(2)	73.0(2)	O(3)–Mg(1)–O(2)	86.6(2)
C(9)–Mg(1)–O(2)	168.0(3)	O(4)–Mg(1)–O(2)	78.8(2)
O(1)–Mg(1)–Br(1)	94.71(17)	O(3)–Mg(1)–Br(1)	93.53(19)
C(9)–Mg(1)–Br(1)	103.7(2)	O(4)–Mg(1)–Br(1)	160.5(2)
O(2)–Mg(1)–Br(1)	85.22(17)	C(2)–O(1)–C(1)	111.7(6)
C(2)–O(1)–Mg(1)	119.5(5)	C(1)–O(1)–Mg(1)	125.9(5)
C(3)–O(2)–C(4)	111.8(7)	C(3)–O(2)–Mg(1)	110.9(4)
C(4)–O(2)–Mg(1)	122.2(5)	C(5)–O(3)–C(6)	111.3(7)
C(5)–O(3)–Mg(1)	126.0(5)	C(6)–O(3)–Mg(1)	114.1(5)
C(8)–O(4)–C(7)	112.2(6)	C(8)–O(4)–Mg(1)	126.5(5)
C(7)–O(4)–Mg(1)	112.1(5)	O(1)–C(2)–C(3)	107.5(7)
O(2)–C(3)–C(2)	110.0(7)	O(3)–C(6)–C(7)	108.2(7)
O(4)–C(7)–C(6)	108.0(7)	C(10)–C(9)–C(11)	109.0(7)
C(10)–C(9)–Mg(1)	113.6(5)	C(11)–C(9)–Mg(1)	113.9(5)

Table 4
Bond lengths (Å) and angles (°) for *cis*-[(allyl)MgBr(dme)₂] (**3**)

Bond lengths			
Mg(1)–O(3)	2.146(6)	Mg(1)–O(1)	2.166(6)
Mg(1)–C(9)	2.210(8)	Mg(1)–O(4)	2.216(6)
Mg(1)–O(2)	2.221(6)	Mg(1)–Br(1)	2.632(3)
O(1)–C(2)	1.411(10)	O(1)–C(1)	1.444(9)
O(2)–C(4)	1.429(8)	O(2)–C(3)	1.431(9)
O(3)–C(6)	1.430(9)	O(3)–C(5)	1.434(10)
O(4)–C(8)	1.417(10)	O(4)–C(7)	1.440(10)
C(2)–C(3)	1.471(10)	C(6)–C(7)	1.490(12)
C(9)–C(10)	1.377(11)	C(10)–C(11)	1.347(11)
Bond angles			
O(3)–Mg(1)–O(1)	160.9(3)	O(3)–Mg(1)–C(9)	101.1(3)
O(1)–Mg(1)–C(9)	94.2(3)	O(3)–Mg(1)–O(4)	74.4(2)
O(1)–Mg(1)–O(4)	93.9(2)	C(9)–Mg(1)–O(4)	91.5(3)
O(3)–Mg(1)–O(2)	89.2(2)	O(1)–Mg(1)–O(2)	73.8(2)
C(9)–Mg(1)–O(2)	165.1(3)	O(4)–Mg(1)–O(2)	80.9(2)
O(3)–Mg(1)–Br(1)	92.69(19)	O(1)–Mg(1)–Br(1)	94.70(18)
C(9)–Mg(1)–Br(1)	104.2(2)	O(4)–Mg(1)–Br(1)	161.4(2)
O(2)–Mg(1)–Br(1)	85.78(17)	C(2)–O(1)–C(1)	113.6(7)
C(2)–O(1)–Mg(1)	117.8(5)	C(1)–O(1)–Mg(1)	127.6(5)
C(4)–O(2)–C(3)	111.3(6)	C(4)–O(2)–Mg(1)	123.2(5)
C(3)–O(2)–Mg(1)	111.5(5)	C(6)–O(3)–C(5)	111.5(7)
C(6)–O(3)–Mg(1)	116.1(5)	C(5)–O(3)–Mg(1)	124.0(5)
C(8)–O(4)–C(7)	113.3(7)	C(8)–O(4)–Mg(1)	124.3(6)
C(7)–O(4)–Mg(1)	110.8(5)	O(1)–C(2)–C(3)	109.2(7)
O(2)–C(3)–C(2)	109.9(7)	O(3)–C(6)–C(7)	107.0(8)
O(4)–C(7)–C(6)	106.9(7)	C(10)–C(9)–Mg(1)	115.7(6)
C(11)–C(10)–C(9)	129.6(9)		

over, it has been shown [26] that the *cis*-octahedral stereoisomer is stabilized compared with the *trans*-octahedral isomer when the ligand has a small bite angle in [MgAB(LL)₂] complexes. Comparing the R groups, the C–C distances in **1** and **2** differ insignificantly and lie in the 1.50–1.53 Å range. The allyl ligand in **3** displays only a small difference between the two C–C distances of 1.38 and 1.35 Å. Magnesium and the dme ligands in **1**–**3** form five-membered rings, which exhibit chiral conformations. In all molecules in crystals of **1**–**3**, one of these rings has λ-conformation while the other has δ-conformation, i.e. all of the enantiomers can be designated as either Δλδ or Λδλ. This pattern of ring conformations is the same as in crystals of [(thienyl)MgBr(dme)₂] and [(vinyl)MgBr(dme)₂] [11]. There are several short intermolecular C–H···Br* contacts in **1** (2.91 Å), **2** (2.99 Å) and **3** (2.87 Å), as well as short intermolecular C–H···O* contacts, the shortest being 2.54 Å (in **1**).

In an effort to extend the range of potential *cis*-octahedral chiral organomagnesium reagents beyond bidentate oxygen donor ligands, we attempted to use a bidentate nitrogen donor ligand such as, e.g. *N,N,N',N'*-tetramethylethylenediamine (tmeda). Previously characterized complexes with bidentate amino ligands seem confined to four-coordinate species, often for the simple reason that only one equivalent of the

ligand was added during synthesis. We, therefore, prepared Grignard reagents in THF or DEE, evaporated the solvent under reduced pressure and redissolved the residues in neat TMEDA, thus ensuring a large excess of nitrogen donor ligand. In our hands, all attempts to crystallize a six-coordinate organomagnesium/tmeda adduct failed (only four-coordinate [MgR₂(tmeda)] [27] could be isolated), and instead large amounts of crystalline [MgBr₂(tmeda)₂] (**4**) precipitated,

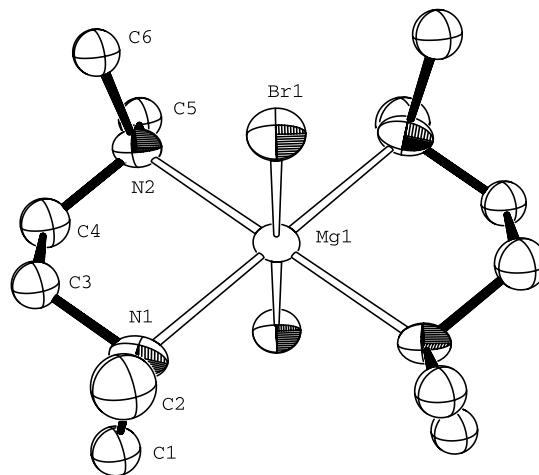


Fig. 5. ORTEP drawing of *trans*-[MgBr₂(tmeda)₂] (**4**). The ligands are disordered corresponding to δ and λ ring conformations.

Table 5
Bond lengths (Å) and angles (°) for *trans*-[MgBr₂(tmeda)₂] (**4**)

Bond lengths			
Mg(1)–N(2)	2.334(5)	Mg(1)–N(1)	2.356(6)
Mg(1)–Br(1)	2.6709(9)	N(1)–C(2)	1.447(9)
N(1)–C(1)	1.522(15)	N(1)–C(3)	1.579(15)
N(2)–C(6)	1.505(13)	N(2)–C(5)	1.509(16)
N(2)–C(4)	1.567(15)	C(3)–C(4)	1.51(2)
Bond angles			
N(2)–Mg(1)–N(1)	80.95(19)	N(2)–Mg(1)–Br(1)	90.19(13)
N(1)–Mg(1)–Br(1)	89.84(13)	C(2)–N(1)–C(1)	110.8(8)
C(2)–N(1)–C(3)	96.6(8)	C(1)–N(1)–C(3)	104.6(12)
C(2)–N(1)–Mg(1)	117.0(4)	C(1)–N(1)–Mg(1)	120.1(6)
C(3)–N(1)–Mg(1)	103.7(5)	C(6)–N(2)–C(5)	104.7(12)
C(6)–N(2)–C(4)	103.9(9)	C(5)–N(2)–C(4)	101.9(14)
C(6)–N(2)–Mg(1)	120.0(6)	C(5)–N(2)–Mg(1)	118.8(6)
C(4)–N(2)–Mg(1)	104.9(6)	C(4)–C(3)–N(1)	111.4(12)
C(3)–C(4)–N(2)	109.9(12)		

presumably formed according to the Schlenk equilibrium. An X-ray crystal structure determination of **4** (see Fig. 5) revealed the centrosymmetric *trans*-stereoisomer rather than the chiral *cis*-isomer. As seen in Table 5, the bite angle of the tmeda ligands in **4** is almost 81°, which is considerably larger than the dme bite angles in **1–3**, and thus in accord with the argument that small bite angles favor the *cis*-isomer. The ligand in **4** is disordered on double sites for all atoms, corresponding to the λ and δ ring conformations formed with the magnesium atom. On account of this disorder, the accuracy of the geometrical data is low and a detailed discussion on bond lengths and angles is not meaningful.

The molecular structure of **4** was not encouraging from the viewpoint of being able to use tertiary amine ligands in *cis*-octahedral Grignard reagents, but perhaps the molecule adopts the unwanted *trans* geometry primarily due to intramolecular Br–Br interactions in *cis*-[MgBr₂(tmeda)₂], which renders it unstable. In order to investigate this, we prepared the corresponding dme complex, i.e. [MgBr₂(dme)₂] (**5**) and determined its crystal structure. Compound **5** can be easily prepared from, e.g. PhMgBr, taking advantage of the Schlenk equilibrium. Interestingly, the use of dme ligands results in exclusively *cis*-[MgBr₂(dme)₂] (see Fig. 6) which thus is isostructural with the chloro analogue [25]. Apparently, two bromo ligands fit nicely in an octahedral *cisoid* magnesium coordination geometry, which leads to the conclusion that bidentate tertiary amino ligands (or at least tmeda) are less well suited for preparing *cis*-octahedral Grignard reagents. The molecular structure of **5** is similar to the Grignard reagents, but the Mg–Br distances in **5** (see Table 6) is somewhat shorter and the Br–Mg–Br angle in **5** (98.3°) is smaller than the C–Mg–Br angles in **1–3** (mean 102.8°), suggesting that the steric crowding is less obvious in **5**. In **5** also, the Mg–O distances that are *cis* to the monodentate bromo ligands

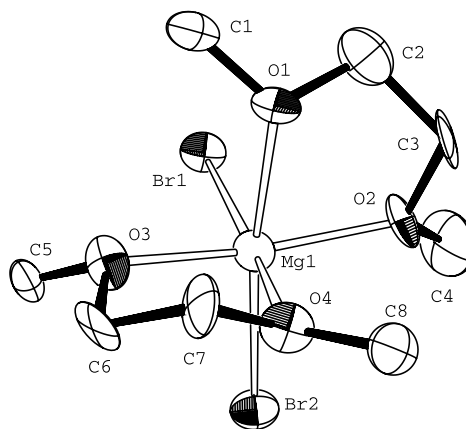


Fig. 6. ORTEP drawing of *cis*-[MgBr₂(dme)₂] (**5**). Only the Λ-enantiomer is shown, but the Δ-enantiomer is also present in crystals of **5**.

Table 6
Bond lengths (Å) and angles (°) for *cis*-[MgBr₂(dme)₂] (**5**)

Bond lengths			
Mg(1)–O(2)	2.105(11)	Mg(1)–O(3)	2.109(11)
Mg(1)–O(4)	2.160(11)	Mg(1)–O(1)	2.217(10)
Mg(1)–Br(2)	2.559(5)	Mg(1)–Br(1)	2.603(5)
O(1)–C(1)	1.432(16)	O(1)–C(2)	1.435(19)
O(2)–C(4)	1.404(19)	O(2)–C(3)	1.428(17)
O(3)–C(5)	1.449(16)	O(3)–C(6)	1.457(17)
O(4)–C(8)	1.423(17)	O(4)–C(7)	1.435(16)
C(2)–C(3)	1.54(2)	C(6)–C(7)	1.50(2)
Bond angles			
O(2)–Mg(1)–O(3)	161.2(5)	O(2)–Mg(1)–O(4)	90.4(5)
O(3)–Mg(1)–O(4)	77.0(5)	O(2)–Mg(1)–O(1)	76.8(4)
O(3)–Mg(1)–O(1)	87.9(4)	O(4)–Mg(1)–O(1)	84.0(4)
O(2)–Mg(1)–Br(2)	96.7(4)	O(3)–Mg(1)–Br(2)	97.4(3)
O(4)–Mg(1)–Br(2)	90.8(3)	O(1)–Mg(1)–Br(2)	171.6(4)
O(2)–Mg(1)–Br(1)	94.6(3)	O(3)–Mg(1)–Br(1)	95.6(3)
O(4)–Mg(1)–Br(1)	169.0(4)	O(1)–Mg(1)–Br(1)	87.7(3)
Br(2)–Mg(1)–Br(1)	98.29(17)	C(1)–O(1)–C(2)	111.2(12)
C(1)–O(1)–Mg(1)	123.0(9)	C(2)–O(1)–Mg(1)	110.8(9)
C(4)–O(2)–C(3)	114.9(13)	C(4)–O(2)–Mg(1)	125.2(11)
C(3)–O(2)–Mg(1)	115.5(10)	C(5)–O(3)–C(6)	112.8(11)
C(5)–O(3)–Mg(1)	120.3(8)	C(6)–O(3)–Mg(1)	113.4(9)
C(8)–O(4)–C(7)	113.3(12)	C(8)–O(4)–Mg(1)	128.1(10)
C(7)–O(4)–Mg(1)	110.3(10)	O(1)–C(2)–C(3)	106.7(14)
O(2)–C(3)–C(2)	109.5(13)	O(3)–C(6)–C(7)	108.0(12)
O(4)–C(7)–C(6)	105.7(14)		

are significantly shorter than the other two Mg–O distances, and the dme ligands in **5** exhibit bite angles of ca. 77°, resulting in a distorted octahedron. As in **1–3**, magnesium and the dme ligands in **5** form five-membered rings, which exhibit chiral conformations. One of these rings has λ-conformation while the other has δ-conformation, i.e. all of the enantiomers can be designated as either Δλδ or Λδλ.

The Grignard reagents **1–3** (as well as **5**) all decompose rapidly when isolated, even under an inert atmosphere, due to loss of dme ligands. In an attempt to prepare more robust reagents, we realized that joining the two dme ligands in **1**, **2** or **3** with a new C–C bond

would create a tetradentate ligand-triglyme—that should enhance the stability of the resulting complex on account of the chelate effect. Experiments, both by performing the synthesis in neat triglyme or by adding excess of triglyme to a DME or DEE solution, resulted in large amounts of *cis*-[MgBr₂(trigly)] (**6**), (trigly = triglyme) (see Fig. 7). When the R group was methyl, [Mg₂(μ-Br)₂(trigly)₂][Mg₂(μ-Me)₂Br₄] (**7**) could be isolated (see Figs. 8 and 9) which may be regarded as a “lower order” Grignard reagent with a composition corresponding to R_{0.5}MgX_{1.5}, and supports the notion that solutions of Grignard reagents are complex and may contain several species with unusual stoichiometries and structures. The molecular structures of **6** and **7** show that the triglyme ligand fits well in a *cis*-octahedral coordination geometry. Unfortunately, also crystals of **6** decompose rapidly when isolated and it is consequently uncertain if *cis*-octahedral Grignard reagents based on triglyme will prove much easier to handle as compared with **1–3**. The molecular structure of **6** resembles that of **5** closely. As seen from Table 7, the bite angles (mean ca. 76°) and Mg–Br distances are similar, as well as the Br–Mg–Br angles. There are three rings formed by Mg–dme interactions in **6**, and the Δ enantiomer has the δλδ ring conformations, while the Λ enantiomer has the λδλ ring conformations. The same pattern of ring conformations (Δδλδ and Λλδλ) returns in the cation of **7** (see Fig. 8) but since the molecule is dimeric and displays an inversion center, both enantiomers are present in the same molecule, which consequently is a *meso* form. As seen from Table 8, the fact that the bromide ligands are bridging two magnesium ions in the cation of **7**, does not change the Mg–Br distances significantly, and the similarity to mononuclear **6** is striking, although the Br–Mg–Br angle of 90.3° in **7** is more acute. The anion

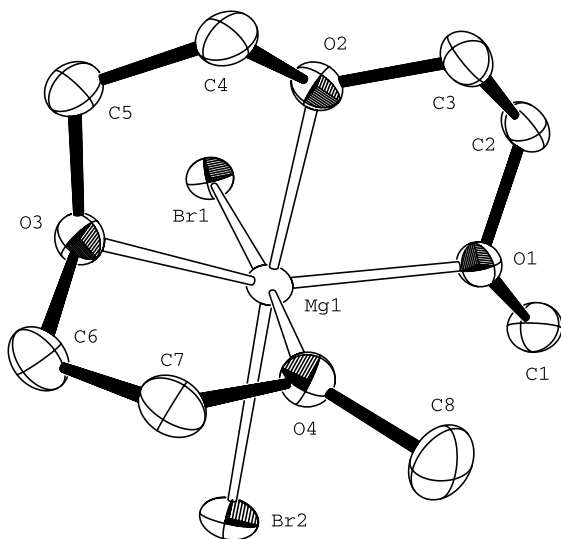


Fig. 7. ORTEP drawing of *cis*-[MgBr₂(trigly)] (**6**). Only the Λ-enantiomer is shown, but the Δ-enantiomer is also present in crystals of **6**.

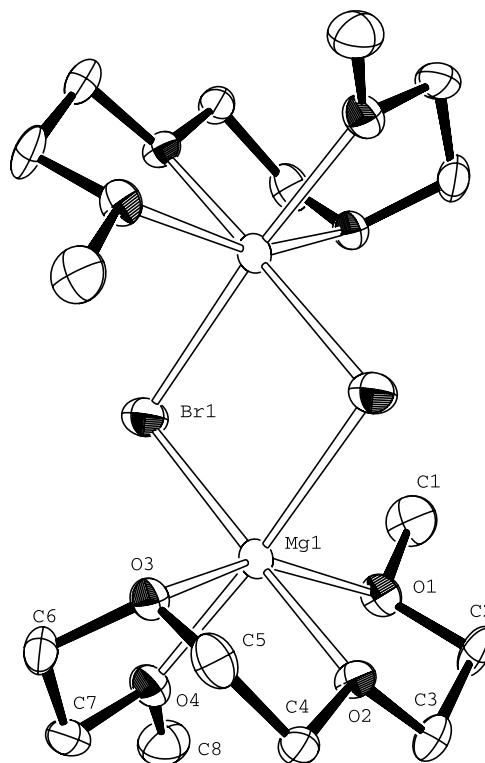


Fig. 8. ORTEP drawing of [Mg₂(μ-Br)₂(trigly)₂]²⁺, the cation of **7**. Since the molecule is centrosymmetric, one of the magnesium atoms (the lower) has the Λ configuration, while the other (the upper) has the Δ configuration.

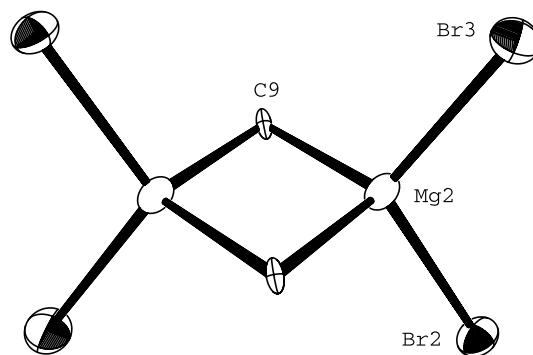


Fig. 9. ORTEP drawing of [Mg₂(μ-Me)₂Br₄]²⁻, the anion of **7**.

of **7** (see Fig. 9 and Table 8) displays a new organo-magnesium species with RMgX₂ stoichiometry and considering its charge and lack of steric hindrance, it should be highly reactive in nucleophilic additions. The coordination geometry around magnesium is tetrahedral and the bridging methyl groups result in a somewhat longer Mg–C distance (2.28 Å) as compared with the terminal R groups previously encountered. The bromo ligands are, on the other hand, coordinated at a somewhat shorter distance (mean 2.46 Å) in the anion of **7**.

In conclusion, chiral *cis*-octahedral Grignard reagents can be easily prepared when common R groups and dme

Table 7
Bond lengths (Å) and angles (°) for *cis*-[MgBr₂(trigly)] (6)

Bond lengths			
Mg(1)–O(1)	2.113(2)	Mg(1)–O(2)	2.124(2)
Mg(1)–O(3)	2.124(2)	Mg(1)–O(4)	2.173(2)
Mg(1)–Br(2)	2.5388(11)	Mg(1)–Br(1)	2.5515(11)
O(1)–C(2)	1.438(4)	O(1)–C(1)	1.440(4)
O(2)–C(3)	1.423(4)	O(2)–C(4)	1.435(3)
O(3)–C(6)	1.433(4)	O(3)–C(5)	1.443(4)
O(4)–C(8)	1.421(4)	O(4)–C(7)	1.437(4)
C(2)–C(3)	1.495(4)	C(4)–C(5)	1.497(5)
C(6)–C(7)	1.499(5)		
Bond angles			
O(1)–Mg(1)–O(2)	76.07(8)	O(1)–Mg(1)–O(3)	149.48(10)
O(2)–Mg(1)–O(3)	76.80(8)	O(1)–Mg(1)–O(4)	89.68(9)
O(2)–Mg(1)–O(4)	85.15(9)	O(3)–Mg(1)–O(4)	74.33(9)
O(1)–Mg(1)–Br(2)	102.36(7)	O(2)–Mg(1)–Br(2)	172.03(8)
O(3)–Mg(1)–Br(2)	102.56(7)	O(4)–Mg(1)–Br(2)	87.03(7)
O(1)–Mg(1)–Br(1)	95.95(7)	O(2)–Mg(1)–Br(1)	91.07(7)
O(3)–Mg(1)–Br(1)	98.27(7)	O(4)–Mg(1)–Br(1)	172.28(7)
Br(2)–Mg(1)–Br(1)	96.88(3)	C(2)–O(1)–C(1)	111.6(2)
C(2)–O(1)–Mg(1)	112.45(18)	C(1)–O(1)–Mg(1)	121.49(19)
C(3)–O(2)–C(4)	113.8(2)	C(3)–O(2)–Mg(1)	114.41(18)
C(4)–O(2)–Mg(1)	114.15(17)	C(6)–O(3)–C(5)	117.5(2)
C(6)–O(3)–Mg(1)	109.63(19)	C(5)–O(3)–Mg(1)	112.63(17)
C(8)–O(4)–C(7)	112.8(2)	C(8)–O(4)–Mg(1)	128.3(2)
C(7)–O(4)–Mg(1)	117.00(19)	O(1)–C(2)–C(3)	107.0(2)
O(2)–C(3)–C(2)	105.9(2)	O(2)–C(4)–C(5)	105.2(2)
O(3)–C(5)–C(4)	110.5(3)	O(3)–C(6)–C(7)	111.6(2)
O(4)–C(7)–C(6)	108.0(2)		

ligands are used. That also larger R groups can be accommodated remains to be proven, but since secondary R groups like isopropyl can be used, it is probably more a question of finding the right synthetic method (and crystallization conditions), rather than a question of steric hindrance. Tertiary diamine ligands are inappropriate as neutral bidentate ligands, since they seem to prefer the *trans*-octahedral coordination geometry. On the other hand, tetradentate neutral ligands with oxygen donor atoms, such as triglyme, fit well in a *cis*-octahedral environment and may be ideally suited for the preparation of “chiral at metal” Grignard reagents.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 206248 for compound **1**, CCDC 206249 for compound **2**, CCDC 206250 for compound **3**, CCDC 206251 for compound **4**, CCDC 206252 for compound **5**, CCDC 206253 for compound **6**, and CCDC 206254 for compound **7**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Table 8
Bond lengths (Å) and angles (°) for [Mg₂(μ-Br)₂(trigly)₂][Mg₂(μ-Me)₂Br₄] (7)

Bond lengths			
Mg(1)–O(2)	2.075(7)	Mg(1)–O(1)	2.086(7)
Mg(1)–O(3)	2.115(7)	Mg(1)–O(4)	2.141(7)
Mg(1)–Br(1)	2.546(4)	Mg(1)–Br(1)#1	2.624(3)
Mg(1)–Mg(1)#1	3.648(6)	Mg(2)–C(9)#2	2.258(13)
Mg(2)–C(9)	2.280(14)	Mg(2)–Br(3)	2.458(3)
Mg(2)–Br(2)	2.475(3)	Mg(2)–Mg(2)#2	2.721(7)
Br(1)–Mg(1)#1	2.624(3)	O(1)–C(2)	1.438(11)
O(1)–C(1)	1.444(12)	O(2)–C(4)	1.415(10)
O(2)–C(3)	1.418(10)	O(3)–C(5)	1.434(12)
O(3)–C(6)	1.466(12)	O(4)–C(8)	1.426(12)
O(4)–C(7)	1.451(11)	C(2)–C(3)	1.493(14)
C(4)–C(5)	1.490(13)	C(6)–C(7)	1.494(14)
Bond angles			
O(2)–Mg(1)–O(1)	76.7(3)	O(2)–Mg(1)–O(3)	76.9(3)
O(1)–Mg(1)–O(3)	151.8(3)	O(2)–Mg(1)–O(4)	91.6(3)
O(1)–Mg(1)–O(4)	93.3(3)	O(3)–Mg(1)–O(4)	77.7(3)
O(2)–Mg(1)–Br(1)	178.8(2)	O(1)–Mg(1)–Br(1)	103.1(2)
O(3)–Mg(1)–Br(1)	103.5(2)	O(4)–Mg(1)–Br(1)	89.6(2)
O(2)–Mg(1)–Br(1)#1	88.6(2)	O(1)–Mg(1)–Br(1)#1	94.1(2)
O(3)–Mg(1)–Br(1)#1	95.0(2)	O(4)–Mg(1)–Br(1)#1	172.5(2)
Br(1)–Mg(1)–Br(1)#1	90.26(11)	O(2)–Mg(1)–Mg(1)#1	132.8(2)
O(1)–Mg(1)–Mg(1)#1	102.1(2)	O(3)–Mg(1)–Mg(1)#1	103.0(2)
O(4)–Mg(1)–Mg(1)#1	135.1(3)	Br(1)–Mg(1)–Mg(1)#1	45.99(8)
Br(1)#1–Mg(1)–Mg(1)#1	44.27(8)	C(9)#2–Mg(2)–C(9)	106.3(4)
C(9)#2–Mg(2)–Br(3)	109.1(4)	C(9)–Mg(2)–Br(3)	112.0(3)
C(9)#2–Mg(2)–Br(2)	106.9(3)	C(9)–Mg(2)–Br(2)	109.4(4)
Br(3)–Mg(2)–Br(2)	112.82(13)	C(9)#2–Mg(2)–Mg(2)#2	53.5(3)
C(9)–Mg(2)–Mg(2)#2	52.8(3)	Br(3)–Mg(2)–Mg(2)#2	125.82(19)
Br(2)–Mg(2)–Mg(2)#2	121.29(19)	Mg(1)–Br(1)–Mg(1)#1	89.74(11)

Symmetry code; $-x+2, -y+2, -z$ (#1) and $-x+1, -y+2, -z+1$ (#2).

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References

- [1] F. Bickelhaupt, J. Organomet. Chem. 475 (1994) 1.
- [2] F. Bickelhaupt, in: H.G. Richey (Ed.), Grignard Reagents—New Developments, Wiley, Chichester, 2000, p. 318.
- [3] P.R. Markies, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, A.L. Spek, Adv. Organomet. Chem. 32 (1991) 147.
- [4] P.R. Markies, G. Schat, S. Griffioen, A. Villena, O.S. Akkerman, F. Bickelhaupt, Organometallics 10 (1991) 1531.

- [5] E. Weiss, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1501.
- [6] C.E. Holloway, M. Melnik, *J. Organomet. Chem.* 465 (1994) 1.
- [7] M. Vallino, *J. Organomet. Chem.* 20 (1969) 1.
- [8] H. Viebrock, E. Weiss, *J. Organomet. Chem.* 464 (1994) 121.
- [9] J. Toney, G.D. Stucky, *J. Organomet. Chem.* 28 (1971) 5.
- [10] D. Steinborn, T. Ruffer, C. Bruhn, F.W. Heinemann, *Polyhedron* 17 (1998) 3275.
- [11] M. Vestergren, B. Gustafsson, O. Davidsson, M. Hakansson, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 3435.
- [12] A. Wellmar, A. Hallberg, I. Persson, *J. Organomet. Chem.* 415 (1991) 167.
- [13] A. Wellmar, I. Persson, *J. Organomet. Chem.* 415 (1991) 155.
- [14] T.S. Ertel, H. Bertagnolli, *Polyhedron* 12 (1993) 2175.
- [15] I. Abraham, W. Horner, T.S. Ertel, H. Bertagnolli, *Polyhedron* 15 (1996) 3993.
- [16] M. Vestergren, J. Eriksson, M. Hakansson, *Chem. Eur. J.*, in press.
- [17] M. Hakansson, *Inorg. Synth.* 32 (1998) 222.
- [18] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [19] G.M. Sheldrick, *SHELX-97—Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- [20] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [21] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [22] M. Geissler, J. Kopf, E. Weiss, *Chem. Ber.* 122 (1989) 1395.
- [23] M. Perucaud, J. Ducom, M. Vallino, *C. R. Acad. Sci. Paris C* 264 (1967) 571.
- [24] B. Schubert, U. Behrens, E. Weiss, *Chem. Ber.* 114 (1981) 2640.
- [25] B. Neumueller, G. Stieglitz, K. Dehnicke, *Z. Naturforsch. B* 48 (1993) 1151.
- [26] D.L. Kepert, *Prog. Inorg. Chem.* 23 (1977) 1.
- [27] H. Viebrock, E. Weiss, *J. Organomet. Chem.* 464 (1994) 121.