

Synthesis and structural characterization of the homoleptic magnesium bis zincate complex $\text{Mg}(\text{thf})_6[\text{Zn}(\text{CH}_2\text{Ph})_3]_2$ ¹

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Abstract

The addition of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{thf})_2$ to a thf solution of $\text{Zn}(\text{CH}_2\text{Ph})_2$ yields the zincate complex $\text{Mg}(\text{thf})_6[\text{Zn}(\text{CH}_2\text{Ph})_3]_2$ (**1**), which has been characterized by X-ray crystallography and NMR. Complex **1** is cleaved by tmeda into a 1:2 mixture of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{tmeda})$ and $\text{Zn}(\text{CH}_2\text{Ph})_2(\text{tmeda})$. © 1997 Elsevier Science S.A.

Keywords: Anionic complex; Magnesium; Organozinc; Zincate

1. Introduction

In contrast to Grignard reagents and diorganomagnesium compounds, diorganozinc compounds do not tend to disproportionate spontaneously into organozinc cations and anions. However, the formation of such anions, i.e. organozincates, may be brought about by reacting diorganozinc compounds with organometallic compounds of more electropositive metals [1]. A limited number of well-characterized organozincate complexes MZnR_3 [2,3] or M_2ZnR_4 [4,5] ($\text{M} = \text{Li}, \text{Na}, \text{K}$) have been reported that were obtained in that way.

Although in situ prepared magnesium organozincates have found applications as selective reagents in organic synthesis [6], to our knowledge the only evidence for the existence of such complexes in solution comes from ¹H NMR studies on solutions containing ZnR_2 and MgR_2 ($\text{R} = \text{Me}, \text{Et}$) whether or not in the presence of azacrown ethers, like 14N4 (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) or 15-crown-5 [1].

Here we report the synthesis and characterization of the first magnesium bis(tribenzylzincate) complex $\text{Mg}(\text{thf})_6[\text{Zn}(\text{CH}_2\text{Ph})_3]_2$ (**1**), which is obtained quantita-

tively from the reaction of $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{thf})_2$ with two equivalents of $\text{Zn}(\text{CH}_2\text{Ph})_2$.

2. Experimental section

2.1. General data

All experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled from Na/benzophenone prior to use. *N,N,N',N'*-tetramethylethylenediamine (tmeda) (Aldrich Chemical Co.) was dried on molecular sieves (4 Å) and distilled prior to use. $\text{Mg}(\text{CH}_2\text{Ph})_2(\text{thf})_2$ and $\text{Zn}(\text{CH}_2\text{Ph})_2$ were prepared by published procedures [7]. $[\text{Mg}(\text{CH}_2\text{Ph})_2(\text{thf})_2]$ was obtained by evaporation of a thf solution of the Et_2O adduct of $\text{Mg}(\text{CH}_2\text{Ph})_2$, prepared according to the standard procedure described in Ref. [2], p. 197.] ¹H and ¹³C NMR spectra were recorded on a Bruker AC 200 spectrometer in C_6D_6 at 298 K. ¹H and ¹³C NMR chemical shifts are in ppm relative to external SiMe_4 . Conductivity measurements were carried out using a Philips PW 9512/00 microcell with a Consort K720 conductometer. Elemental analyses were obtained from Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

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¹ Dedicated to celebrate the 60th birthday of Professor Dr. Gottfried Huttner.

² Crystallography.

2.2. Synthesis of $Mg(thf)_6[Zn(CH_2Ph)_3]_2$ (**1**)

To a stirred solution of $Zn(CH_2Ph)_2$ (1.71 g, 6.90 mmol) in thf (25 ml) at room temperature was added a solution of 0.5 equiv. $Mg(CH_2Ph)_2(thf)_2$ (1.20 g, 3.42 mmol) in thf (25 ml). After stirring for 10 min a white precipitate formed. The suspension was stirred for another 10 min. Subsequently the solvent was removed in vacuo. The white solid was washed with hexanes (2×20 ml) and dried in vacuo to afford **1** as a white powder, yield 3.69 g (95%). Crystallization of **1** from thf afforded the product as white needles. Crystals of $1 \cdot thf$ and $1 \cdot C_6H_6$, suitable for X-ray diffraction studies, were obtained by recrystallization at room temperature from thf and C_6H_6 respectively. 1H NMR: δ 7.15 (ddd, 12 H, ArH_3); 7.04 (d, 12 H, ArH_2); 6.86 (t, 6 H, ArH_4); 3.35 (m, 24 H, thf); 1.83 (s, 12 H, $ArCH_2$); 1.25 (m, 24 H, thf). ^{13}C NMR: δ 150.7, 120.0, 128.6, 126.1 (ArC); 68.4 (thf); 25.4 (thf); 22.8 ($ArCH_2$). M.p. 88°C. Anal. Found: C, 69.69; H, 8.08. $C_{66}H_{90}O_6MgZn_2$ Calc.: C, 69.87; H, 8.00%.

2.3. Reaction of **1** with tmeda

To a stirred suspension of **1** (3.69 g, 3.25 mmol) in thf (50 ml) at room temperature was added tmeda (1.45 ml, 9.61 mmol). A clear colourless solution was formed immediately. After stirring for 30 min the solution was evaporated to dryness in vacuo. The remaining white solid was washed with hexanes (50 ml) and dried in vacuo to afford 3.25 g of a white powder. 1H and ^{13}C NMR showed this powder to be a 1:2 mixture of $Mg(CH_2Ph)_2(tmeda)$ (**2**) and $Zn(CH_2Ph)_2(tmeda)$ (**3**).

2.4. Synthesis of $Mg(CH_2Ph)_2(tmeda)$ (**2**)

To a stirred solution of $Mg(CH_2Ph)_2(thf)_2$ (0.86 g, 2.47 mmol) in C_6H_6 at room temperature was added tmeda (0.4 ml, 2.7 mmol). After stirring for 15 min the solution was evaporated to dryness in vacuo. The remaining white powder was washed with hexanes (2×15 ml), affording 0.64 g (79%) of **2**. Crystallization from toluene at $-30^\circ C$ gave the product as colourless needles. 1H NMR: δ 7.15 (m, 8 H, ArH); 6.77 (t, 2 H, ArH_4); 1.70 (s, 4 H, $ArCH_2$); 1.58 (s br, 12 H, NMe_2); 1.40 (s br, 4 H, CH_2N). ^{13}C NMR: δ 156.9, 116.7, 128.5, 124.2 (ArC); 55.6 (CH_2N); 45.9 (NMe_2); 23.3 ($ArCH_2$). Anal. Found: C, 74.49; H, 9.33; N, 8.64. $C_{20}H_{30}N_2Mg$ Calc.: C, 74.42; H, 9.37; N, 8.68%.

2.5. Synthesis of $Zn(CH_2Ph)_2(tmeda)$ (**3**)

To a stirred solution of $Zn(CH_2Ph)_2$ (1.22 g, 4.93 mmol) in C_6H_6 at room temperature was added 1 equiv. of tmeda (0.8 ml, 5.3 mmol). After stirring for 15 min the solution was evaporated to dryness in vacuo.

The remaining white powder was washed with hexanes (2×15 ml), affording 1.68 g (94%) of **3**. Crystallization from toluene at $-30^\circ C$ afforded the product as colourless needles. 1H NMR: δ 7.22 (m, 8 H, ArH); 6.91 (t, 2 H, ArH_4); 1.85 (s, 4 H, $ArCH_2$); 1.68 (s br, 12 H, NMe_2); 1.54 (s br, 4 H, CH_2N). ^{13}C NMR: δ 153.9, 119.4, 128.3, 126.6 (ArC); 56.8 (CH_2N); 46.9 (NMe_2); 21.3 ($ArCH_2$). Anal. Found: C, 65.88; H, 8.26; N, 7.78. $C_{20}H_{30}N_2Zn$ Calc.: C, 66.02; H, 8.31; N, 7.70%.

2.6. Conductivity measurements

In a typical experiment, the conductivity (A_m) of a solution of **1** (ca. 10^{-2} M) in thf at room temperature was found to be $2.76 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$. For comparison $Zn(CH_2Ph)_2$ and $Mg(CH_2Ph)_2(thf)_2$ were measured in the same system, which gave molar conductivity values of 0.006 and $0.017 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ respectively.

2.7. X-ray structure determination and refinement of $1 \cdot C_6H_6$ and $1 \cdot thf$

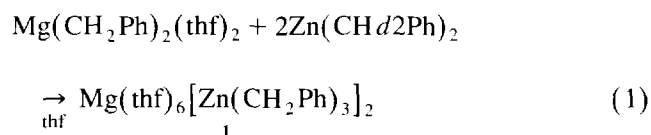
Crystal data for compound $1 \cdot C_6H_6$. $C_{21}H_{21}Zn \cdot 0.5C_{24}H_{28}MgO_6 \cdot 0.5C_6H_6$, $M_r = 606.32$, colourless, block-shaped crystal ($0.50 \times 0.50 \times 0.75 \text{ mm}^3$), monoclinic, space group $P2_1/c$ (No. 14) with $a = 13.4971(7)$, $b = 15.5495(8)$, $c = 18.2640(4) \text{ \AA}$, $\beta = 124.121(6)^\circ$, $V = 3173.3(4) \text{ \AA}^3$, $Z = 4$, $D_x = 1.269 \text{ g cm}^{-3}$, $F(000) = 1296$, $\mu(\text{Mo K}\alpha) = 8.3 \text{ cm}^{-1}$, 11341 reflections measured, 7238 independent, ($1.31^\circ < \theta < 27.50^\circ$, $\omega/2\theta$ scan, $\Delta\omega = 0.91 + 0.35 \tan \theta^\circ$, $T = 150 \text{ K}$, $\text{Mo K}\alpha$ radiation, graphite monochromator; $\lambda = 0.71073 \text{ \AA}$) on an Enraf Nonius CAD4 Turbo diffractometer on rotating anode. Data were corrected for Lp effects, a linear decay of 3% of the reference reflections, and for absorption (DIFABS, correction range 0.856–1.088). The structure was solved by automated Patterson methods (DIRDIF92). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during refinement. Refinement converged at a final wR_2 value of 0.0793, $w = 1/[\sigma^2(F^2) + (0.0332P)^2 + 1.62P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$, $R_1 = 0.0317$ (for 6299 reflections with $F_o > 4\sigma(F_o)$) $S = 1.040$, for 374 parameters. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The thf group containing O(2) displays conformational disorder and was refined with a model consisting of two components, the occupancy ratio was refined. All non-hydrogen atoms were refined with anisotropic thermal parameters; except those belonging to the minor disorder component. Hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.2 times the value of the equivalent isotropic displacement parameter of their carrier atoms. A final difference Fourier showed no residual density outside -0.51 and 0.39 e \AA^{-3} .

Crystal data for compound **1**·thf. The same procedure has been followed as for compound **1**·C₆H₆. Pertinent data are as follows: C₂₁H₂₁Zn·0.5C₂₄H₂₈MgO₆·0.5C₄H₈O, *M_r* = 603.31, colourless, block-shaped crystal (0.2 × 0.2 × 0.5 mm³), monoclinic, space group *P*2₁/*c* (No. 14) with *a* = 13.568(2), *b* = 15.901(3), *c* = 18.220(2) Å, β = 126.003(11)°, *V* = 3180.0(9) Å³, *Z* = 4, *D_x* = 1.260 g cm⁻³, *F*(000) = 1292, μ(Mo Kα) 8.2 cm⁻¹, 13644 reflections measured, 6550 independent (1.28° < θ < 27.48°), Δω = 0.72 + 0.35 tan θ°. Data were not corrected for absorption. The solvent thf molecule, located on a crystallographic inversion centre, is disordered over two positions. Refinement converged at a final *wR*₂ value of 0.1614, *w* = 1/[σ²(*F*²) + (0.0122 *P*)²], *R*₁ = 0.0792 (for 1919 reflections with *F*_o > 4σ(*F*_o)) *S* = 0.960, for 365 parameters. A final difference Fourier showed no residual density outside -0.39 and 0.44 e Å⁻³. Atomic coordinates, bond lengths and angles and thermal parameters of both structure determinations may be obtained from one of the authors.

3. Results and discussion

The reaction of Mg(CH₂Ph)₂(thf)₂ with Zn(CH₂Ph)₂ in a 1:2 molar ratio in thf at room temperature affords the magnesium bis(tribenzylzincate) complex Mg(thf)₆[Zn(CH₂Ph)₃]₂ (**1**) quantitatively. Complex **1** is a colourless, air- and moisture-sensitive solid, which is stable at room temperature when stored under a nitrogen atmosphere. Attempts to isolate other homologues of **1** [8], e.g. Mg(CH₂Ph)(thf)_{*n*}Zn(CH₂Ph)₃ or Mg(thf)_{*n*}Zn(CH₂Ph)₄, from the reaction of

Mg(CH₂Ph)₂(thf)₂ and Zn(CH₂Ph)₂ in a 1:1 molar ratio failed as was indicated by the selective crystallization of **1** while an equimolar amount of Mg(CH₂Ph)₂(thf)₂ remained in solution.



To establish the molecular geometry of **1**, an X-ray structure determination was carried out. After recrystallization from thf or C₆H₆ two different types of crystals were obtained, which turned out to be **1**·thf and **1**·C₆H₆ respectively. The geometries of both zinc complexes in the solid state are identical within experimental error. Geometrical data given in this paper refer to the crystal structure of **1**·C₆H₆, unless stated otherwise. The crystal structure of **1**·C₆H₆ comprises the packing of two discrete [Mg(thf)₆]²⁺ dications each located on a crystallographic inversion centre and four [Zn(CH₂Ph)₃]⁻ monoanions in addition to two C₆H₆ solvate molecules also located on a crystallographic inversion centre in the unit cell. Fig. 1 presents a thermal motion ellipsoid plot of the molecular geometry of **1**·C₆H₆ and selected atomic bond lengths and angles are presented in Table 1.

The molecular structure of **1**·C₆H₆ in the solid state shows a magnesium zincate, in which the doubly positively charged magnesium cation is completely separated from the two monoanionic zincate counterions. The zinc atom is three-coordinate with a distorted trigonal planar geometry at zinc. The Zn–C distances (ranging from 2.032(2)–2.0582(19) Å) are comparable to those found in MZn(CH₂CMe₃)₃ (M = K, Na) and

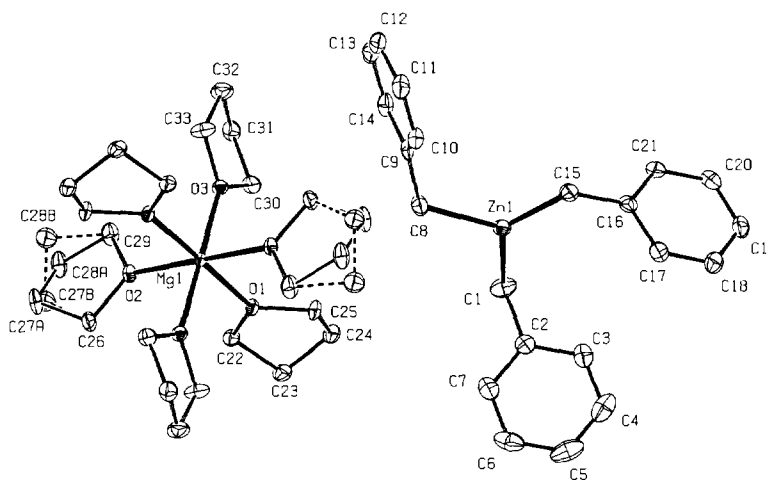


Fig. 1. Thermal motion ellipsoid plot [9] (ORTEP at 30% probability level) of the molecular structure of **1**·C₆H₆ together with the adopted numbering scheme. The hydrogen atoms and the solvent molecule have been omitted for clarity.

Table 1
Selected bond distances (Å) and bond angles (°) for $1 \cdot C_6H_6$ ^a

Bond distances			
Zn(1)–C(1)	2.051(3)	Mg(1)–O(1)	2.0673(13)
Zn(1)–C(8)	2.0582(19)	Mg(1)–O(2)	2.1094(11)
Zn(1)–C(15)	2.032(2)	Mg(1)–O(3)	2.1097(9)
Bond angles			
C(1)–Zn(1)–C(8)	112.78(10)	O(1)–Mg(1)–O(2)	90.48(5)
C(1)–Zn(1)–C(15)	128.20(9)	O(1)–Mg(1)–O(3)	89.24(4)
C(8)–Zn(1)–C(15)	118.99(11)	O(2)–Mg(1)–O(3)	89.48(4)

^a The estimated standard deviations are given in parentheses.

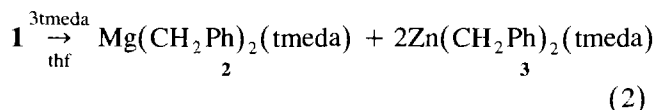
$KZn(CH_2SiMe_3)_3$, which are in the range of 2.03(1) to 2.129(5) Å [3]. The zinc atom deviates 0.02293(15) Å from the plane defined by the three C_α atoms of the three monoanionic ligands. A deviation from a perfect trigonal planar geometry at the zinc atom is also reflected in the dissimilar C–Zn–C bond angles, most likely caused by crystal packing effects. The magnesium atom in the hexa-coordinate dication is well shielded by interaction with the oxygen lone pairs of six molecules of thf, excluding contacts shorter than 5.0 Å between the magnesium atom and the C_α atoms of the zincate moiety. The O–Mg–O bond angles indicate a nearly perfect octahedral geometry of the magnesium atom, similar to that reported for $Mg(thf)_6[Sn(\eta^3-C_5H_5)_3]_2$, which also has an unassociated structure [10]. In $1 \cdot thf$ the oxygen atom of the disordered thf solvent molecule acts as an acceptor of a C–H \cdots O interaction donated by one of the CH_2 groups of a magnesium-coordinated thf molecule. In $1 \cdot C_6H_6$ this interaction is replaced by a C–H \cdots π interaction donated by a benzylic C–H and accepted by the ordered benzene solvate. The magnesium-coordinated thf molecule, which is no longer involved in any intermolecular interactions other than Van der Waals, now displays conformational disorder.

The 1H NMR spectrum of **1** in C_6D_6 at room temperature shows one resonance pattern for the benzylic ligands in addition to the resonances of coordinated thf in a 1:1 molecular ratio, similar to the $Mg(CH_2Ph)_2(thf)_2$ precursor. However, the presence of **1** is evident from the low field shift of the methylene hydrogen signal at 1.83 ppm, which is significantly lower than that of $Mg(CH_2Ph)_2(thf)_2$ at 1.62 ppm.

The ionic character of **1** in thf solution was confirmed by a conductivity measurement. The molar conductivity $\Lambda_m = 2.76 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ for **1** in thf at room temperature is 160 times larger than that of the starting materials. Unfortunately, a cryoscopic molecular weight determination in C_6H_6 was hampered by the insolubility of **1** in C_6H_6 at low temperature.

Additional evidence for the composition of **1** was obtained by the reaction with *N,N,N',N'*-tetramethylethylenediamine (tmeda) (Eq. (2)). The reaction products were identified as a 1:2 mixture of

$Mg(CH_2Ph)_2(tmeda)$ (**2**) and $Zn(CH_2Ph)_2(tmeda)$ (**3**) by comparison with separately prepared samples of **2** and **3**.



Most likely, the first step is the substitution of the six thf molecules by three tmeda molecules in **1**, which subsequently disproportionates into the apparently more stable complexes **2** and **3**. This disproportionation under the influence of tmeda is unprecedented for both zincates [5] and the closely related magnesiates [11].

4. Concluding remarks

The first example of a magnesium zincate complex has been structurally characterized in solution and in the solid state. This magnesium zincate complex can be used as a model compound for active species in various zinc-catalyzed nucleophilic addition reactions of Grignard reagents, and the present results reveal that the actual structure of a magnesium organozincate is more complicated than is justified by representations like $MZnR_3$ or M_2ZnR_4 . The reaction with tmeda shows that the actual structure of these zincates will always be dependent on the presence of Lewis donor molecules, e.g. substrates or additional ligands.

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