



Note

Synthesis and structural characterization of two donor-functionalized terphenyl magnesium compounds

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ABSTRACT

The synthesis and structural characterization of two novel donor-functionalized terphenyl magnesium compounds, namely (Danip)₂Mg (**1**) [Danip = 2,6-di(*o*-anisyl)phenyl] and [DinapOMg(THF)]₂ (Dinap = 2,6-di(*o*-2-methoxynaphthyl)phenyl; DinapO = 2-(*o*-2-methoxynaphthyl)-6-(*o*-2-naphthoxide)phenyl) is reported. Compound **1** represents a first structurally authenticated bis terphenyl magnesium compound, while the molecular structure of dimeric tetrahydrofuran solvated **2** shows a five-coordinate magnesium atom stabilized by a partially demethylated dianionic mixed aryloxy/aryloxy terphenyl ligand (= DinapO).

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1. Introduction

Like their lithium analogues, magnesium derivatives such as Grignard reagents have obvious applications as ligand transfer agents. Grignard compounds have been known for more than a hundred years and many such complexes have been structurally characterized so far [1]. There are also reports on intramolecularly coordinated arylmagnesium compounds as well as the effects on the so-called “Schlenk equilibrium” [1–3].

There is much current interest in the chemistry of terphenylic ligands. Still the vast majority of these papers focusses on such compounds of the main group elements, mostly elements from the p-block, but there are also a number of reports on s-block element compounds [4–6]. To the best of our knowledge only two structurally characterized terphenyl magnesium compounds are known, namely dimeric [Mg(μ-Br)C₆H₃-2,6-Mes₂(THF)]₂ [7] and monomeric Mg(Br)(C₆H₃-2,6-Trip₂)(THF)₂ [8]. Additionally, isolation of the impure bis terphenyl compound Mg(C₆H₃-2,6-Mes₂)₂ was reported [4,7], which was obtained from the above mentioned dimeric compound after addition of 1,4-dioxane. Actually, a first mention on a terphenyl magnesium compound, namely generation of BrMgTriph in solution and its subsequent reactions, was reported more than 70 years ago [9]. Besides these two mono terphenyl magnesium compounds a number of structurally characterized mono terphenyl derivatives of beryllium are known [4]. To the best of our knowledge no terphenyl derivatives of the

heavier group-2 elements, calcium strontium, or barium have been structurally characterized.

We have previously been exploring the accessibility of f-element compounds stabilized by different terphenylic ligand systems. Our previous work has demonstrated that stable compounds of the rare-earth elements Sm–Lu can be obtained using the donor-functionalized ligand Danip from simple salt metathesis reactions employing DanipLi and the corresponding lanthanide trichloride [10–13]. We were now interested in probing the accessibility of an alternative transfer agent for the Danip moiety and therefore attempted the synthesis of a Grignard compound of assumed composition DanipMgI(THF)_x.

2. General aspects of X-ray data collection, structure determination, and refinement for complexes **1** and **2**

Crystal, data collection, and refinement parameters are given in Table 1. Data were collected on a Bruker Apex AXS CCD system. The systematic absences in the diffraction data are uniquely consistent for the reported space groups. All crystals were mounted on glass fibers with Paratone-N oil and cooled to indicated temperatures. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix, least-squares procedures. SADABS absorption corrections were applied to all data sets. All non-hydrogen atoms except those exhibiting disorder were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

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Table 1
Crystallographic data for (Danip)₂Mg (**1**) and [DinapOMg(THF)]₂ (**2**).^a

Complex	1	2
Formula	C ₄₀ H ₃₄ MgO ₄	C ₆₉ H ₆₀ Mg ₂ O ₆
Formula weight	602.98	1033.79
space group	C2/c	P2(1)/c
<i>a</i> (Å)	15.0641(15)	10.793(3)
<i>b</i> (Å)	13.7200(13)	19.072(5)
<i>c</i> (Å)	14.7341(14)	26.8106(6)
β (°)	93.544(2)	98.207(4)
<i>V</i> (Å ³)	3039.4(5)	5319(2)
<i>Z</i>	4	4
<i>D</i> _(calcd) (g cm ⁻³)	1.318	1.291
<i>T</i> (°C)	−173(2)	−173(2)
Radiation	Mo K α (λ = 0.71073 Å)	Mo K α (λ = 0.71073 Å)
μ (Mo K α) (cm ⁻¹)	1.02	1.02
Goodness-of-fit (GOF)	1.190	1.058
<i>R</i> ₁ (%)	5.98	5.46
<i>wR</i> ₂ (%)	14.41	13.36

^a The quantity minimized was $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [(wF_o^2)^2]^{1/2}$; $R_1 = \sum \Delta / \sum (F_o)$, $\Delta = |F_o - F_c|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \text{Max}(F_o, 0)]/3$.

All software and sources of the scattering factors are contained in SHELXTL (5.10) program library (G.M. Sheldrick, Bruker XRD, Madison, WI).

3. Results and discussion

3.1. (Danip)₂Mg (**1**)

Reaction of Danip-I [14,15] with excess magnesium metal in THF solution at ambient temperature (48–72 h) produces a colorless suspension. In some cases no reaction between both components was observed and therefore the reaction mixture was initially heated to approximately 50 °C. Alternatively, addition of a catalytic amount of mercury dichloride was found to be helpful. ¹H NMR spectroscopic studies of the crude product from the reaction mixture in deuterated benzene solution indicate the presence of DanipMgI(THF) as the main product (3.51 ppm, −OMe), additionally a second singlet (3.06 ppm, −OMe) which can most likely be assigned according to the Schlenk equilibrium to (Danip)₂Mg. After standard workup procedures compound **1** crystallizes from a toluene solution in approximately 40–50% yield. We note that other than in previously studied reactions of DanipLi with LnCl₃, formation of significant amounts of Danip-H (3.20 ppm, −OMe) as a side product is always observed, presumably as a result of C–H activation, thereby reducing the yield of the title compound. The undesired side product can widely be removed by repeated washing of the crude product with warm hexanes.

Single crystalline material was obtained by slow evaporation of a toluene solution at ambient temperature inside a glove box. A single-crystal structure determination showed that the obtained product is not the expected mono terphenyl compound DanipMgI(THF), but the bis terphenyl compound (Danip)₂Mg (**1**) instead (Fig. 1). The molecular structure of **1** features a magnesium atom in a distorted octahedral coordination environment with an almost linear C–Mg–C angle of 177.89(16)°, a *trans* O–Mg–O angle of 162.96(6)°, *cis* O–Mg–O angles of 88.73(7)°, 92.74(10)°, and 94.82(11)°, respectively, and C–Mg–O angles of 81.31(8)°, 81.71(8)°, 97.24(9)°, and 99.77(9)°. Both Mg–C–C angles are 122.25(19)°. The Mg–C distance of 2.144(3) Å can favorably be compared with the corresponding interatomic separations in the other two structurally characterized terphenyl magnesium compounds, namely dimeric [Mg(μ-Br)C₆H₃-2,6-Mes₂(THF)]₂ (2.136(6) Å) [7] and monomeric Mg(Br)(C₆H₃-2,6-Trip₂)(THF)₂ (2.145(7) Å) [8]. Further comparisons of the Mg–C, as well as the Mg–O distances (2.225(2) and 2.239(2) Å) in **1**, can be made, e.g.,

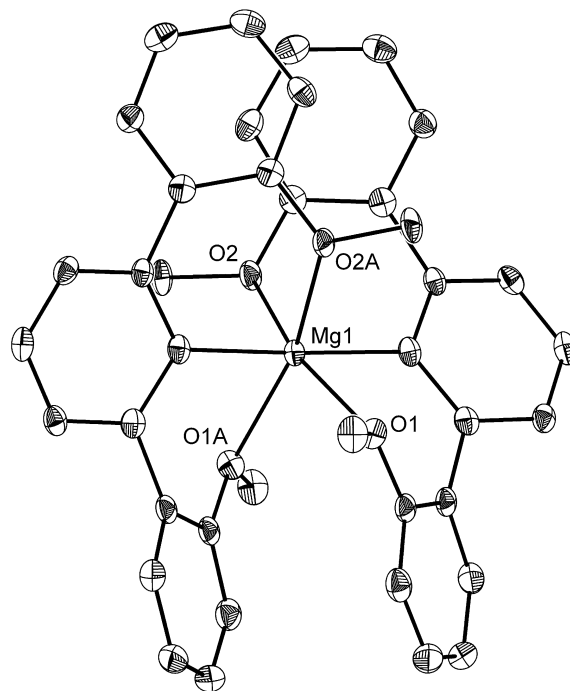


Fig. 1. Molecular structure of **1** drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

with the also six-coordinate diarylmagnesium compound Mg[C₆H₃-2,6-(CH₂OMe)₂]₂ [3] exhibiting slightly shorter Mg–C (2.093(4) and 2.105(4) Å) but noticeably longer Mg–O distances (2.282(3)–2.338(3) Å) as compared to **1**. As another example, a somewhat longer Mg–C distance of 2.216(1) Å is reported for the also six-coordinate Mg[C₆H₃-2,6-(CH₂PMe₂)₂]₂ [16]. On the other hand, a significantly shorter Mg–O(OMe) distance of 2.105(7) Å is found for five-coordinate dimeric [Mg(μ-Br)C₆H₃-2-CH₂OMe(THF)]₂ [2], while the Mg–C separation of 2.110(8) Å falls into the expected range.

3.2. [DinapOMg(THF)]₂ (**2**)

Reaction of Dinap-I [17] with excess magnesium metal under similar reaction conditions as for **1** produces a pale yellow suspension. Again, as was seen in the case of the above mentioned reaction, formation of a significant amount of the protonated terphenyl Dinap-H is observed. From the toluene extract of the crude product a pale yellow product crystallizes in approximately 30% yield. A single-crystal structure determination revealed that neither the expected Dinap-MgI(THF)_x nor (Dinap)₂Mg is formed, but instead a mono terphenyl magnesium compound of composition [DinapOMg(THF)]₂ (**2**) (Fig. 2) featuring a partially demethylated donor-functionalized terphenyl ligand (= DinapO; 3.47 ppm, −OMe (in C₆D₆)). As the other product from this reaction, the methylated terphenyl Dinap-Me was identified, confirmed by both ¹H NMR in deuterated benzene (two sets of signals in an approximate 2:1 ratio: 2.25 and 2.27 ppm, −Me; 3.41 and 3.42 ppm, −OMe) and GC/MS spectroscopy, explaining the fate of the missing methyl group in the DinapO ligand.

The molecular structure of dimeric **2** exhibits five-coordinate magnesium atoms that are complexed by a THF molecule, two bridging naphthoxide ligands, one naphthyloxy moiety, as well as the ipso carbon atom of the terphenyl substituent. The coordination geometry about the metal atom can best be described as a heavily distorted trigonal bipyramid with one of the bridging, as well as the OMe oxygen atom, occupying the *trans* positions

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