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The remarkable crystal structure of the dimeric species [bis(*ortho*-anisyl)magnesium · THF]$_2$ *

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Abstract

The crystal structure of dimeric bis(*ortho*-methoxyphenyl)magnesium tetrahydrofuranate, **1**, has been determined, and found to be remarkably unsymmetrical. The magnesium atoms in **1** have different coordination numbers and are connected by two *ortho*-methoxyphenyl groups each bridging in a unique fashion.

Introduction

The use of regioselective *ortho*-lithiation reactions of aromatic substrates has become widespread in organic and organometallic synthesis, since many of them proceed easily with high selectivity and good yields [1,2]. Several effects are thought to account for the ease of such reactions. In most cases, the hetero atom makes the adjacent proton more acidic and thus favours metallation. Coordination of the organometallic reagent to the hetero atom(s) of the substrate brings the reactants together in an initial complex, and makes subsequent conversion a favoured "intramolecular" reaction. In the transition state the coordinating hetero atoms will assist in minimizing the energy barrier for the reaction. Finally thermodynamic stabilization of the product drives the reaction to completion; the formation of intramolecular coordinative bonds and/or dipolar interactions is energetically favourable.

ortho-Metallated methoxybenzenes proved to be appropriate complexes for a study of this last-mentioned stabilizing effect. The first thermochemical results on

* Dedicated to Prof. Dr. E. Weiss, on the occasion of his 65th birthday, in grateful appreciation of many years of friendship and stimulating contacts.

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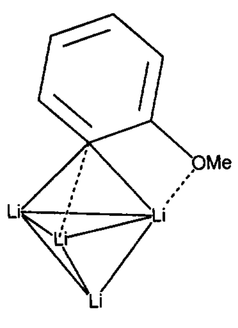
ortho-, *meta*- and *para*-lithioanisole, presented by Beak and Siegel [3], showed the *ortho*-compound to be stabilized with respect to the *para*-isomer. In the hydrolysis reactions in di-n-butyl ether and TMEDA, values for $\Delta\Delta H_{para-ortho}$ of -34.7 (2.2) and -11.7 (2.7) kJ mol^{-1}, respectively were found. The effect was confirmed by Sinnige [4] using sec-butanol instead of absolute ethanol as a proton donor in di-n-butyl ether as the solvent ($\Delta\Delta H_{para-ortho} = -14.7$ (3.5) kJ mol^{-1}). Thermochemical investigation of Grignard reagent *ortho*-methoxyphenylmagnesium bromide in THF solution showed a $\Delta\Delta H_{para-ortho}$ of -11.5 (2.8) kJ mol^{-1} for the hydrolysis with acetic acid [5]; the corresponding bis(*ortho*-methoxyphenyl)magnesium showed $\Delta\Delta H = -11.2$ (2.3) kJ mol^{-1} [6].

Since it is known that arylmagnesium species are generally monomeric in THF solution [7], the interaction between the magnesium atom and the methoxy substituent will proceed via the formation of a kind of four-membered chelate ring. Owing to conformational restrictions (the orientation of the σ Mg–C bond relative to the aromatic plane is almost fixed) the Mg–O distance must be relatively large. There will be no direct Mg–O "contact", the coordination of the carbon-bound magnesium atom with the methoxy group involves an electrostatic (dipole–dipole) long-range interaction. The methoxy substituent can be expected to optimize its orientation towards the magnesium atom, with the methyl group turned away from the metal atom. A structural investigation of this situation by a crystal structure determination of a monomeric bis(*ortho*-methoxyphenyl)magnesium complex showing this effect would be of much interest.

The situation will be different with associated species, as has been demonstrated previously by the recently obtained crystal structures for *ortho*-lithioanisole (**1**) [8,9] and (2,6-dimethoxyphenyl)lithium (**2**) [10]. Tetrameric aggregates are found, in which each aryl *ipso*-carbon μ^3-bridges three atoms of the central Li_4 cluster in the manner shown in Fig. 1 (left side). An *ortho*-methoxy substituent can be easily directed towards one of these metal atoms, since a μ-bridging *ipso*-carbon atom permits a relatively small C–C–M angle inside the coordinative four-membered ring. In the crystal structure of the solvent-free [*ortho*-lithioanisole]$_4$ (**1a**) [9], this results in Li–O bond lengths in the normal range of 1.93–2.01 Å.



1a

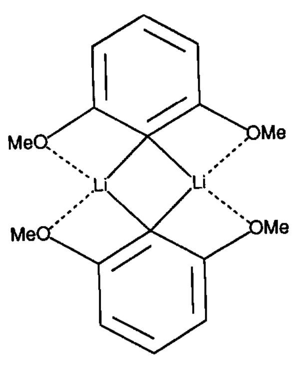


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Fig. 1. Schematical representations of the four-center two-electron μ^3 C_{ipso}–Li_3 bond in *o*-anisyllithium tetramers (left); and the dimeric subunit in the bis(2,6-dimethoxyphenyl)lithium tetramer.

Clearly, a shorter metal–oxygen distance and therefore a stronger intramolecular coordination can be achieved in associated species. The Li–C bond lengths of the μ^3-bridging *ipso*-carbon atoms in **1a** show a rather large variation (2.18–2.51 Å), and the four-center two-electron bonds are in some cases distorted in the direction of a three-center two-electron bond. This effect becomes much more pronounced in the structure of [2,6-dimethoxyphenyllithium]$_4$ (**2a**), which has coordinating methoxy groups in both *ortho* positions [10]. As a result, the tetrameric **2a** becomes separated into two relatively weakly associated dimers. In each dimer, the lithium atoms are surrounded, in approximately square planar fashion, by two carbon and two oxygen ligands (see Fig. 1, right side).

As is demonstrated by **1a** and **2a**, under suitable conditions interesting complexes of *ortho*-methoxy substituted phenyllithium compounds can be obtained and structurally characterized. For comparison, a crystal structure of an oligomeric bis-(*ortho*-methoxyphenyl) magnesium complex seemed desirable. By analogy with **1** and **2**, η^1-bridging of the aryl groups between the central magnesium atoms of the complex will permit the orientation of their methoxy substituents towards the metal centra. This will facilitate the formation of intramolecular coordinative bonds, possibly replacing associated ether molecules and/or enlarging the coordination number of the metal atoms. Thermochemical results clearly show a stabilizing effect of an *ortho*-methoxy group, which must be reflected in the molecular structure. Bis(*ortho*-methoxyphenyl)magnesium (**3**) was thus prepared and its crystal structure determined.

Results and discussion

A solution of pure **3** was prepared by stirring of a solution of bis(*ortho*-methoxyphenyl)mercury (**5**) in THF with magnesium metal. The completeness of the reaction was checked by titration of an aliquot of known volume for total base and Mg^{2+}. In order to demonstrate the reliability of the method, the reaction was also performed on an NMR scale (about 10 mg of **5**) in THF-d_8; subsequent analysis of the resulting solution by ^1H and ^{13}C NMR spectroscopy proved the presence of **3** and the absence of any side product.

A monomeric nature of **3** (= **3a**) in a THF solution was found by association measurements, in the concentration range of 3.9–11.8 mmol L^{-1}, using the stationary distillation technique described by Van Vulpen [11,12]. In this respect, the behavior of **3** does not deviate from that of other diorganylmagnesium compounds, which are generally monomeric in THF solution. The presence of a large excess of strongly coordinating THF solvent molecules effectively prevents oligomerization.

In THF solution, the structure of **3a** probably involves a tetrahedral magnesium atom with two THF ligands. For the parent compound diphenylmagnesium, two crystal structures of monomeric complexes are known which may serve as an illustration of this situation namely $Ph_2Mg \cdot TMEDA$ [13] and $Ph_2Mg \cdot [THF]_2$ [14]. Still, it is highly desirable to isolate crystals of **3a**, since the stabilizing effect found by the thermochemical measurements must be accompanied by a weak Mg–O interaction. Alignment of the methoxy groups towards the magnesium atoms would be expected. Unfortunately, all attempts to isolate crystals of **3a** from a solution of **3** in pure THF, either by cooling or concentrating, were unsuccessful.

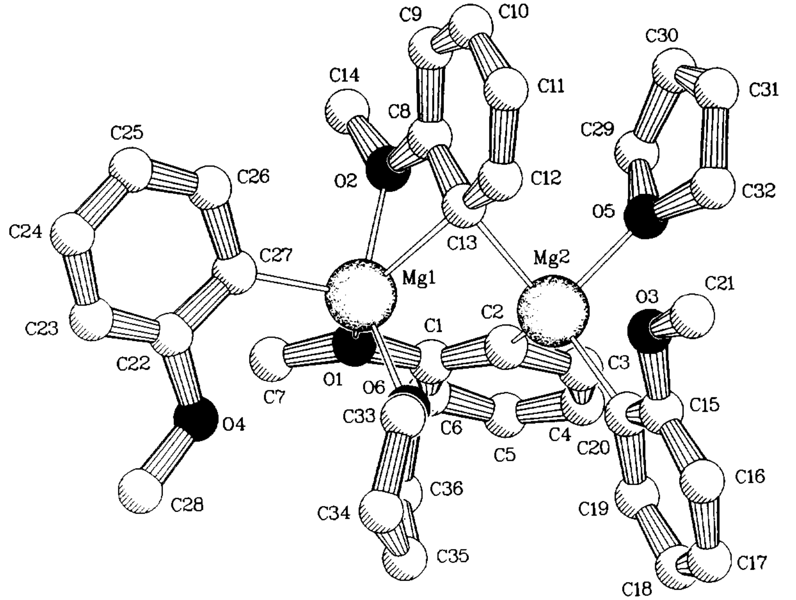

Fig. 2. PLUTON drawing of the molecular structure of **3b**, with the adopted numbering. H atoms have been omitted for clarity.

Addition of an apolar solvent to a THF solution of **3** would be expected to increase the degree of association; dissociation of one of the coordinating THF molecules from **3a** would result in the formation of a dimeric species. Such a species was in fact isolated by crystallization of **3** from an n-hexane solution containing a relatively small amount (< 10%) of THF; ^{1}H NMR characterization of the crystals in C_6D_6 showed the presence of one THF ligand per diarylmagnesium unit, which suggests the formation of a dimeric complex $[Aryl_2Mg \cdot THF]_2$ (**3b**). The NMR solution was unstable at room temperature; during several months an amorphous white solid slowly separated and the THF to diarylmagnesium ratio in solution increased to 2 : 1. This phenomenon must be interpretated as the dissociation of **3b** into the normal monomeric complex bis(*ortho*-methoxyphenyl)magnesium · $(THF)_2$ (**3a**) and polymeric, insoluble [bis(*ortho*-methoxyphenyl)magnesium]$_n$. In a ^{13}C NMR spectrum of a freshly prepared (clear) solution of crystalline **3b** in toluene-d_8, only six aryl carbon signals and one methoxy signal were visible. This result could be explained in terms of a fast interchange between the non-identical aryl groups (bridging and terminal), which must exist in a dimeric structure. When the temperature was lowered to 223 K the signals broadened but there was no further change in the spectrum. The instability of a benzene solution of **3b** prevented an association measurement, and so the presence of a dimeric species in solution could not be confirmed. At the concentration needed for the Van Vulpen technique a fast precipitation of oligomeric material occurred.

A crystal structure determination of **3b** confirmed the formation of a dimeric complex (Fig. 2); relevant structural data can be found in Table 1. At first sight, **3b** shows some resemblance to the dimeric structure of [bis(*p*-tolyl)-magnesium · THF]$_2$ (**6**) [14]. In **6**, two tetracoordinated magnesium atoms are connected by two

Table 1. Bond distances (Å) and angles (deg) for **3b**

Mg(1)–O(1)	2.056(5)	O(5)–C(29)	1.424(9)	C(15)–C(20)	1.37(1)
Mg(1)–O(2)	2.166(4)	O(5)–C(32)	1.439(9)	C(16)–C(17)	1.39(1)
Mg(1)–O(6)	2.064(5)	O(6)–C(33)	1.454(8)	C(17)–C(18)	1.37(1)
Mg(1)–C(13)	2.327(6)	O(6)–C(36)	1.444(7)	C(18)–C(19)	1.38(1)
Mg(1)–C(27)	2.132(6)	C(1)–C(2)	1.393(9)	C(19)–C(20)	1.41(1)
Mg(2)–O(5)	2.099(5)	C(1)–C(6)	1.389(9)	C(22)–C(23)	1.39(1)
Mg(2)–C(2)	2.199(7)	C(2)–C(3)	1.39(1)	C(22)–C(27)	1.40(1)
Mg(2)–C(13)	2.305(6)	C(3)–C(4)	1.40(1)	C(23)–C(24)	1.38(1)
Mg(2)–C(20)	2.147(7)	C(4)–C(5)	1.37(1)	C(24)–C(25)	1.36(1)
O(1)–C(1)	1.406(7)	C(5)–C(6)	1.37(1)	C(25)–C(26)	1.38(1)
O(1)–C(7)	1.442(9)	C(8)–C(9)	1.378(9)	C(26)–C(27)	1.402(9)
O(2)–C(8)	1.392(8)	C(8)–C(13)	1.391(9)	C(29)–C(30)	1.47(1)
O(2)–C(14)	1.41(1)	C(9)–C(10)	1.37(1)	C(30)–C(31)	1.46(1)
O(3)–C(15)	1.390(9)	C(10)–C(11)	1.38(1)	C(31)–C(32)	1.46(1)
O(3)–C(21)	1.40(1)	C(11)–C(12)	1.394(9)	C(33)–C(34)	1.48(1)
O(4)–C(22)	1.401(9)	C(12)–C(13)	1.390(9)	C(34)–C(35)	1.42(1)
O(4)–C(28)	1.424(9)	C(15)–C(16)	1.39(1)	C(35)–C(36)	1.51(1)
O(1)–Mg(1)–O(2)	87.4(2)	O(2)–C(8)–C(13)	111.4(5)		
O(1)–Mg(1)–O(6)	95.9(2)	C(9)–C(8)–C(13)	126.1(7)		
O(1)–Mg(1)–C(13)	130.8(2)	C(8)–C(9)–C(10)	116.7(7)		
O(1)–Mg(1)–C(27)	111.0(2)	C(9)–C(10)–C(11)	121.8(7)		
O(2)–Mg(1)–O(6)	148.4(2)	C(10)–C(11)–C(12)	118.4(7)		
O(2)–Mg(1)–C(13)	61.4(2)	C(11)–C(12)–C(13)	123.5(7)		
O(2)–Mg(1)–C(27)	100.2(2)	Mg(1)–C(13)–Mg(2)	80.0(2)		
O(6)–Mg(1)–C(13)	94.1(2)	Mg(1)–C(13)–C(8)	86.8(4)		
O(6)–Mg(1)–C(27)	107.7(2)	Mg(1)–C(13)–C(12)	146.0(4)		
C(13)–Mg(1)–C(27)	111.3(2)	Mg(2)–C(13)–C(8)	122.5(4)		
O(5)–Mg(2)–C(2)	100.2(2)	Mg(2)–C(13)–C(12)	107.9(5)		
O(5)–Mg(2)–C(13)	91.1(2)	C(8)–C(13)–C(12)	113.4(5)		
O(5)–Mg(2)–C(20)	104.5(2)	O(3)–C(15)–C(16)	120.8(7)		
C(2)–Mg(2)–C(13)	109.5(2)	O(3)–C(15)–C(20)	114.0(6)		
C(2)–Mg(2)–C(20)	112.1(3)	C(16)–C(15)–C(20)	125.1(7)		
C(13)–Mg(2)–C(20)	131.6(3)	C(15)–C(16)–C(17)	118.0(8)		
Mg(1)–O(1)–C(1)	119.9(3)	C(16)–C(17)–C(18)	120.0(8)		
Mg(1)–O(1)–C(7)	121.0(4)	C(17)–C(18)–C(19)	120.0(8)		
C(1)–O(1)–C(7)	119.1(5)	C(18)–C(19)–C(20)	122.9(7)		
Mg(1)–O(2)–C(8)	93.4(3)	Mg(2)–C(20)–C(15)	124.8(5)		
Mg(1)–O(2)–C(14)	136.8(5)	Mg(2)–C(20)–C(19)	121.0(5)		
C(8)–O(2)–C(14)	121.8(5)	C(15)–C(20)–C(19)	114.1(6)		
C(15)–O(3)–C(21)	119.5(6)	O(4)–C(22)–C(23)	122.8(7)		
C(22)–O(4)–C(28)	118.5(6)	O(4)–C(22)–C(27)	112.8(6)		
Mg(2)–O(5)–C(29)	125.0(5)	C(23)–C(22)–C(27)	124.4(7)		
Mg(2)–O(5)–C(32)	123.6(4)	C(22)–C(23)–C(24)	119.0(7)		
C(29)–O(5)–C(32)	108.3(5)	C(23)–C(24)–C(25)	119.5(8)		
Mg(1)–O(6)–C(33)	118.6(4)	C(24)–C(25)–C(26)	120.3(7)		
Mg(1)–O(6)–C(36)	123.2(4)	C(25)–C(26)–C(27)	124.0(6)		
C(33)–O(6)–C(36)	109.8(5)	Mg(1)–C(27)–C(22)	126.0(5)		
O(1)–C(1)–C(2)	113.8(5)	Mg(1)–C(27)–C(26)	121.0(5)		
O(1)–C(1)–C(6)	121.5(6)	C(22)–C(27)–C(26)	112.9(6)		
C(2)–C(1)–C(6)	124.6(6)	O(5)–C(29)–C(30)	105.8(7)		
Mg(2)–C(2)–C(1)	142.7(5)	C(29)–C(30)–C(31)	108.4(7)		
Mg(2)–C(2)–C(3)	104.4(5)	C(30)–C(31)–C(32)	105.4(8)		
C(1)–C(2)–C(3)	112.7(6)	O(5)–C(32)–C(31)	106.5(7)		
C(2)–C(3)–C(4)	125.2(7)	O(6)–C(33)–C(34)	104.8(6)		
C(3)–C(4)–C(5)	118.2(7)	C(33)–C(34)–C(35)	108.1(7)		
C(4)–C(5)–C(6)	120.1(7)	C(34)–C(35)–C(36)	105.3(7)		
C(1)–C(6)–C(5)	119.2(7)	O(6)–C(36)–C(35)	105.4(6)		
O(2)–C(8)–C(9)	122.4(6)				

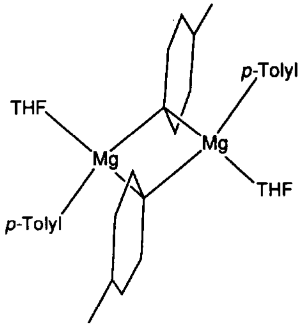

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Fig. 3. Schematic drawing of the dimeric structure of [p-tolyl$_2$Mg·THF]$_2$.

η^1-bridging p-tolyl groups. Each magnesium atom bears one σ-bonded aryl group and one THF molecule as terminal ligands (Fig. 3).

A more detailed examination, however, reveals that the situation in **3b** is different from that in **6**. The remarkable feature of the structure of **3b** is the way in which the two magnesium atoms are connected by two bridging aryl groups. One of the methoxyphenyl groups bridges the two metal atoms through the *ipso*-carbon in a normal μ^2 fashion, but the angle between the plane of this aryl group and the plane through Mg(1), Mg(2) and C(13) is diminished in order to facilitate the formation of an intramolecular four-membered chelate ring. The other aryl group bridges in a completely different way between the two magnesiums: it is σ bonded to Mg(2) through its carbon (Mg(2)–C(2) 2.199(7) Å) and to Mg(1) through its oxygen (Mg(1)–O(1) 2.056(5) Å). The structure contains one five-coordinate (Mg(1)) and one tetrahedral (Mg(2)) magnesium. The two magnesium atoms do not have the same number of bonds to carbon: Mg(1) has a full σ bond to one aryl group (Mg(1)–C(27) 2.132(6) Å), but shares the other one (Mg(1)–C(13) 2.327(6) Å) in a three-center two-electron fashion with Mg(2) (Mg(2)–C(13) 2.305(6) Å); Mg(2) is further bonded to its two aryl groups Mg(2)–C(2), (Mg(2)–C(20) 2.147(7) Å). Thus, Mg(2) gains partial magnesate character, while, in turn, Mg(1) formally carries a positive charge, which is compensated by coordination to three oxygens (Mg(1)–O(1), Mg(1)–O(2) 2.166(4) Å, Mg(1)–O(6) 2.064(5) Å). All the methoxy groups are coplanar with their aryl rings and each is oriented in such a way that its dipole has the best possible orientation towards a magnesium atom; only the methoxy group of the μ-bridging methoxyphenyl group forms a chelate bond to Mg(1), but the resulting four-membered ring is not planar.

Experimental

General remarks

In order to prevent contamination by hydrolysis or oxidation products, all manipulations involving **3** were performed in sealed and evacuated glass apparatus. Solvents were predried by storage over NaOH and distilled from Na/K alloy unless otherwise stated. NMR spectra were recorded with a Bruker WH-90 (^{1}H, 90 MHz) or a Bruker WM-250 (^{1}H, 250 MHz; ^{13}C, 62.89 MHz). The mass spectra were recorded on a Varian CH5-DF mass spectrometer, equipped with an electron impact source operating at 70 eV (direct inlet). The elemental analyses were carried out at the Organic Chemical Institute TNO, Zeist (The Netherlands). Concentrations of total base and Mg^{2+} of organomagnesium solutions were determined by acid–base titration [15] or titration with EDTA complexon [16], respectively. The starting materials 2-bromoanisole (Janssen) and mercuric bromide (Merck, z.a.) were commercial samples.

Synthesis of bis(o-methoxyphenyl)mercury (5)

2-Bromoanisole (15.0 g, 80 mmol) was converted into the corresponding Grignard reagent by reaction with magnesium (2.4 g, 100 mmol) in THF (120 mL, dried by distillation from $LiAlH_4$). The excess of magnesium was filtered off, and the completeness of the reaction was checked by titration of an aliquot of known volume on total base and Mg^{2+}. To the Grignard reagent, a solution of mercuric bromide (31.7 g, 88 mmol) in THF (100 mmol, dried by distillation from $LiAlH_4$) was added dropwise. The mixture was heated under reflux for one hour. After cooling and addition of water/THF (1:1, 50 mL) and brine (50 mL), the organic layer was separated, washed twice with brine, dried ($MgSO_4$), and filtered. Evaporation of the solvent yielded crude *ortho*-methoxyphenylmercury bromide (**7**) as an amorphous colourless solid.

Reduction of **7** (25.2 g, 65 mmol) to the corresponding symmetrical diarylmercury compound **5** was carried out by stirring with a caustic stannous chloride solution, as described by Sawatzky and Wright [17], after dissolution in dichloromethane. The reaction product was isolated from the reaction mixture by extraction with dichloromethane. The solution obtained was dried ($MgSO_4$), filtered, and evaporated to dryness. Residual water was removed by adding dry benzene (100 mL, dried by azeotropic distillation) and evaporating to dryness again. Final drying was carried out in a vacuum desiccator over P_2O_5.

Crude **5** was further purified by sublimation (80–90 °C/5 × 10^{-3} mbar). The obtained colourless solid (9.6 g, 72% yield, m.p. 106–107 °C, lit. 108 °C [18] and 106–108 °C [19]) was characterized by ^1H and ^{13}C NMR spectroscopy, mass spectroscopy and elemental analysis. ^{1}NMR (250 MHz, THF-d_8, ref. THF-d_7 = 1.75 ppm) δ 3.79 (s, 6H, OMe), 6.89 (d, ^3J = 8 Hz, 2H, aryl-H), 7.00 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 2H, aryl-H), 7.20 (dd, ^3J = 8 Hz, ^3J = 7 Hz, 2H, aryl-H), 7.37 (d, ^3J = 7 Hz, 2H, aryl-H). ^{13}C NMR (THF-d_8, ref. THF-d_8 = 25.2 ppm) δ 55.1 (q, ^1J(C–H) = 143 Hz, 2C, OMe), 110.5 (dd, ^1J(C–H) = 158 Hz, ^3J(C–H) = 8 Hz, 2C, aryl-C(3)), 121.7 9ddd, ^1J(C–H) = 158 Hz, ^3J(C–H) = 7 Hz, ^2J(C–H) = 3 Hz, 2C, aryl-C(5)), 129.2 (dd, ^1J(C–H) = 159 Hz, ^3J(C–H) = 9 Hz, 2C, aryl-C(4)), 137.9 (ddd, ^1J(C–H) = 158 Hz, ^3J(C–H) = 9 Hz, ^2J(C–H) = 3 Hz, 2C, aryl-C(6)), 158.5 (s, 2C, aryl-C(1)), 165.2 (s, 2C, aryl-C(2)). Mass spectrum (direct inlet), m/z (intensity) 416 (M^+, 29), 121 (46), 107 (32), 91 (38), 77 (100), 64 (12). Exact mass measurement, M^+ found 416.0671. $C_{14}H_{14}{}^{202}HgO_2$ calculated: 416.0700. Anal. Found: C, 40.53; H, 3.40; Hg, 48.35. Calc.: C, 40.53; H, 3.39; Hg, 48.81%.

Synthesis of bis(o-methoxyphenyl)magnesium (3)

A small amount (about 10 mg) of **5** was stirred with magnesium (triply sublimed, 50 mg) in THF-d_8 (500 μL). After two weeks, the magnesium amalgam was allowed to settle and the clear solution was decanted into a 5 mm NMR tube. ^1H and ^{13}C

NMR spectroscopy revealed the quantitative formation of the expected diarylmagnesium compound **3**.

^{1}H NMR (250 MHz, THF-d_8, ref. THF-d_7 = 1.75 ppm) δ 3.70 (s, 6 H, OMe), 6.54 (d, ^3J = 8 Hz, 2H, aryl-H(3)), 6.69 (ddd, ^3J = 7 Hz, ^3J = 6 Hz, ^4J = 2 Hz, 2H, aryl-H(5)), 6.90 (ddd, ^3J = 8 Hz, ^3J = 7 H, 2H, aryl-H(4)), 7.50 (dd, ^3J = 6 Hz, ^4J = 2 Hz, aryl-H(6)). ^{13}C NMR (ref. THF-d_8 = 25.2 ppm) δ 54.4 (q, ^1J(C–H) = 141 Hz, 2C, OMe), 106.8 (dd, ^1J(C–H) = 152 Hz, ^3J(C–H) = 7 Hz, 2C, aryl-C(3)), 120.8 (ddd, ^1J(C–H) = 154 Hz, ^3J(C–H) = 6 Hz, ^2J(C–H) = 4 Hz, 2C, aryl-C(5)), 125.7 (dd, ^1J(C–H) = 154 Hz, ^3J(C–H) = 8 Hz, 2C, aryl-C(4)), 141.2 (ddd, ^1J(C–H) = 152 Hz, ^3J(C–H) = 8 Hz, ^2J(C–H) = 1 Hz, 2C, aryl-C(6)), 156.3 (d, ^3J(C–H) = 7 Hz, 2C, aryl-C(1)), 168.8 (d, ^3J(C–H) = 12 Hz, 2C, aryl-C(2)).

For further experiments, a larger amount of **3** was prepared. A solution of **5** (7.5 g, 18 mmol) in THF (180 mL) was stirred with an excess of magnesium (1 g, 42 mmol, triply sublimed) for 2–3 weeks. After settling of the magnesium dust, the clear solution was separated by decanting it into a second ampoule. The completeness of the reaction was checked by titration of an aliquot of known volume on total base and Mg^{2+}.

The degree of association of 3 in THF

The degree of association of **3** in solution (pure THF, 25 °C, concentration range 3.92–11.77 mmol L^{-1}) was determined by the Van Vulpen technique (stationary isothermal distillation) [11,12]. Obtained data: formal concentration (calculated association), 3.92 (0.982), 5.89 (0.948), 7.85 (0.949), 9.81 (0.948), 11.77 (0.954). A solution of crystalline **3** (with 1 equiv. THF/Mg) in benzene proved to be unstable, the formation of an amorphous colourless precipitate prevented determination of the degree of association in this apolar solvent.

Crystallization and characterization of 3

A solution of **3** (1 mmol, in 1 mL THF) was diluted with n-hexane (10 mL) to give a clear solution. Colourless crystals were formed when the solution was kept at 5 °C for several weeks, and isolated by decanting the mother liquor and dried by pumping. Their identity was checked by ^{1}H NMR spectroscopy (90 MHz, toluene-d_8); a THF to diarylmagnesium ratio of 1 : 1 was found by integration. The solid material was transferred to a glove-box (Braun, Garsching, Germany, with built-in microscope, and filled with nitrogen containing less than 1 ppm H_2O and oxygen). The best crystals were selected and mounted in a Lindemann capillary. The remaining solid was hydrolyzed; titration showed the presence of base and Mg^{2+} in a ratio of 2 : 1.

Upon storage of the above-mentioned NMR solution at room temperature, a colourless precipitate (probably polymeric, THF-free **3**) was slowly formed. This process continued until, after several months, two THF molecules per diarylmagnesium unit were available in solution. ^{1}H NMR (250 MHz, toluene-d_8, ref. toluene-d_7 = 2.32 ppm) δ 2.63 (s, 6 H, OMe), 6.83 (d, ^3J = 7 Hz, 2H, aryl-H(3)), 7.37 (ddd, ^3J = 7 Hz, ^3J = 7 Hz, ^4J = 2 Hz, 2H, aryl-H(5)), 7.47 (dd, ^3J = 7 Hz, ^3J = 7 Hz, 2H, aryl-H(4)), 8.12 (dd, ^3J = 7 Hz, ^4J = 2 Hz, aryl-H(6)).

A freshly prepared solution of crystalline **3** in toluene-d_8 was analyzed with ^{13}C NMR spectroscopy before the precipitate separated. At room temperature one OMe signal and 6 aryl-C signals were visible; the low symmetry of the crystal structure was not reflected in the ^{13}C NMR spectrum of the dissolved complex. ^{13}C NMR (toluene-d_8, ref. tol.-C(1) = 137.4 ppm) δ 55.5 (q, ^1J(C–H) = 144 Hz, 2C, OMe), 108.5 (d, ^1J(C–H) = 147 Hz, 2C, aryl-C(3)), 122.5 (d, ^1J(C–H) = 155 Hz, 2C, aryl-C(5)), 125.3 (d, ^1J(C–H) = 159 Hz, 2C, aryl-C(4)), 141.9 (d, ^1J(C–H) = 154 Hz, 2C, aryl-C(6)), 152.4 (s, 2C, aryl-C(1)), 167.6 (s, 2C, aryl-C(2)). Broadening of all the signals, especially the aryl-C(1) signal, occurs upon lowering of the temperature to 223 K.

Structure determination and refinement of $[C_{14}H_{14}O_2Mg \cdot C_4H_8O]_2$

A colourless block-shaped crystal was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf–Nonius CAD4 diffractometer for data collection. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections with $8.3 < \theta < 13.0°$. The crystal reflected

Table 2

Crystal data and details of the structure determination

(a) Crystal Data	
Formula	$C_{36}H_{44}Mg_2O_6$
Mol. wt	621.35
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a, b, c (Å)	11.100(1), 11.983(1), 14.317(2)
α, β, γ(°)	67.41(1), 83.30(1), 87.59(1)
V (Å^3)	1746.2(4)
Z	2
D_{calc} (g cm^{-3})	1.182
F(000)	664
μ(cm^{-1})	1.0
Crystal size (mm)	0.50×0.35×0.15
(b) Data collection	
Temperature (K)	294
θ_{min}, θ_{max} (°)	1.55, 25.0
Radiation	Mo-K_α (Zr-filtered), 0.71073 Å
Scan type	$\omega/2\theta$
$\Delta\omega$(°)	$0.65 + 0.35 \tan\theta$
Hor. and vert. aperture (mm)	3.0, 4.0
Dist. cryst. to detector (mm)	173
Reference reflections	2 0 0, 1 1 −2, 1 1 4
Data set	h −13:13; k −14:0; l −17:15
Total data	6438
Total unique data	6116
Observed data	2703 [$I > 2.5\sigma(I)$]
DIFABS correction range	0.742–1.388
(c) Refinement	
No. of refined parameters	410
Weighting scheme	$w = 1.0/\sigma^2(F)$
Final R, wR, S	0.064, 0.081, 1.13
$(\Delta/\sigma)_{av}$ in final cycle	0.019
Min. and max. resd. dens., e/Å^3	−0.27, 0.30

rather poorly and showed relatively broad reflection profiles. The unit cell parameters were checked for the presence of higher lattice symmetry [20]. Data were corrected for Lorentz polarization, for a linear decay (0.2%) of the intensity control reflections during the 121 hours of X-ray exposure time and for absorption (using

Table 3

Final coordinates and equivalent isotropic thermal parameters and their esd in parentheses for **3**

Atom	x	y	z	U_{eq} [a] (Å^2)
Mg(1)	0.7415(2)	0.5243(2)	0.2328(1)	0.0475(7)
Mg(2)	0.6500(2)	0.2712(2)	0.3133(2)	0.0504(7)
O(1)	0.5699(4)	0.5965(3)	0.2255(3)	0.055(2)
O(2)	0.7222(4)	0.5006(4)	0.3916(3)	0.062(2)
O(3)	0.8155(5)	0.0625(4)	0.2775(4)	0.089(2)
O(4)	0.8067(5)	0.7362(4)	0.0122(3)	0.091(2)
O(5)	0.6129(4)	0.1539(4)	0.4661(3)	0.065(2)
O(6)	0.7305(3)	0.4505(4)	0.1254(3)	0.054(1)
C(1)	0.4682(5)	0.5197(5)	0.2635(4)	0.041(2)
C(2)	0.4971(6)	0.3972(5)	0.3000(4)	0.050(2)
C(3)	0.3952(6)	0.3234(6)	0.3332(5)	0.063(3)
C(4)	0.2750(7)	0.3640(7)	0.3306(5)	0.073(3)
C(5)	0.2549(7)	0.4865(8)	0.2939(5)	0.070(3)
C(6)	0.3509(6)	0.5652(6)	0.2612(4)	0.059(3)
C(7)	0.5518(8)	0.7255(6)	0.1825(7)	0.095(3)
C(8)	0.8075(6)	0.4082(6)	0.4172(4)	0.054(2)
C(9)	0.8773(6)	0.3868(6)	0.4958(5)	0.068(3)
C(10)	0.9614(7)	0.2960(7)	0.5108(6)	0.081(3)
C(11)	0.9786(6)	0.2325(6)	0.4482(5)	0.068(3)
C(12)	0.9073(6)	0.2617(6)	0.3681(5)	0.062(2)
C(13)	0.8166(5)	0.3487(5)	0.3502(4)	0.051(2)
C(14)	0.6980(8)	0.5749(8)	0.4479(6)	0.092(3)
C(15)	0.7194(7)	0.0760(5)	0.2199(5)	0.064(3)
C(16)	0.7157(8)	0.0113(6)	0.1579(6)	0.082(3)
C(17)	0.619(1)	0.0314(7)	0.1002(6)	0.096(4)
C(18)	0.5302(8)	0.1116(8)	0.1066(5)	0.089(3)
C(19)	0.5383(7)	0.1748(6)	0.1687(5)	0.076(3)
C(20)	0.6347(6)	0.1595(5)	0.2285(5)	0.058(2)
C(21)	0.8986(9)	−0.0315(8)	0.2867(7)	0.115(4)
C(22)	0.8940(7)	0.7463(6)	0.0718(6)	0.068(3)
C(23)	0.9889(8)	0.8291(6)	0.0331(6)	0.078(3)
C(24)	1.0710(7)	0.8323(6)	0.0969(7)	0.081(3)
C(25)	1.0574(7)	0.7551(6)	0.1963(6)	0.069(3)
C(26)	0.9627(6)	0.6737(6)	0.2325(5)	0.056(2)
C(27)	0.8759(5)	0.6633(5)	0.1726(5)	0.052(2)
C(28)	0.8212(9)	0.8074(9)	−0.0941(6)	0.122(4)
C(29)	0.5676(8)	0.1901(7)	0.5474(6)	0.089(3)
C(30)	0.632(1)	0.1155(9)	0.6345(6)	0.141(5)
C(31)	0.7025(9)	0.0247(8)	0.6072(6)	0.115(4)
C(32)	0.6668(8)	0.0363(6)	0.5088(6)	0.088(3)
C(33)	0.8420(6)	0.4139(7)	0.0809(5)	0.068(3)
C(34)	0.8239(8)	0.4460(9)	−0.0271(6)	0.106(4)
C(35)	0.6971(7)	0.456(1)	−0.0351(6)	0.105(4)
C(36)	0.6429(6)	0.4888(6)	0.0522(4)	0.065(3)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U matrix.

the DIFABS [21] method). The structure was solved by direct methods (SHELXS86; [22]). Refinement on F was carried out by full-matrix least-squares techniques. H-atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters; H-atoms with one common isotropic thermal parameter ($U = 0.121(4)$ Å^2). Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.064$.

Crystal data and numerical details of the structure determination are given in Table 2. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 3. Neutral atom scattering factors were taken from ref. 23 and corrected for anomalous dispersion [24]. All calculations were performed with SHELX76 [25] and the EUCLID package [26] (geometrical calculations and illustrations) on a MicroVAX cluster.

Supplementary material available. Anisotropic thermal parameters, H-atom parameters, lists of bond lengths, bond angles, torsion angles, an ORTEP plot for **3** and lists of observed and calculated structure factor amplitudes (38 pages) are available from A.L.S.

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