

Synthesis and Characterization of Bis(arenethiolato)magnesium Complexes with Intramolecular Coordination. X-ray Structure of $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\}_2]_2$

Maurits D. Janssen,[†] Remco van der Rijst,[†]
Anthony L. Spek,[‡] David M. Grove,[†] and
Gerard van Koten^{*,†}

Department of Metal Mediated Synthesis, Debye Institute,
and Department of Crystal and Structural Chemistry,
Bijvoet Center, Utrecht University, Padualaan 8,
3584 CH Utrecht, The Netherlands

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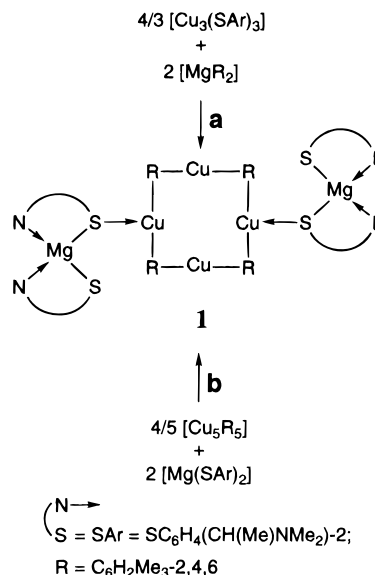
Introduction

Organomagnesium compounds and in particular Grignard reagents, RMgX , play an important role in inorganic and organic synthesis, and there is much current interest in their structures.^{1,2}

One of our interests in this field concerns the application of Grignard reagents in copper(I) arenethiolate catalyzed organic transformations.³ In the course of our studies, we have discovered that a copper(I) arenethiolate, CuSAr ($\text{Ar} = \text{C}_6\text{H}_4\text{-2-CH}(\text{Me})\text{NMe}_2$), in which there is intramolecular Cu–N coordination reacts with a diorganomagnesium reagent, R_2Mg ($\text{R} = \text{C}_6\text{H}_2\text{-2,4,6-Me}_3$), to afford a complex $[\text{Cu}_4\text{R}_4][\text{Mg}(\text{SAr})_2]_2$ (**1**),⁴ which comprises an assembly of two bis(arenethiolato)magnesium units coordinated to a tetranuclear organocopper aggregate (Scheme 1a).⁵ Obviously, the formation of **1** arises from exchange of the monoanionic ligands R and SAr, although two of the four arenethiolate ligands still remain bonded to copper through a single sulfur atom. The discovery of complex **1** is consistent with studies of the organic reactions catalyzed by CuSAr where it has been shown that the SAr monoanion is an excellent nontransferable group and that therefore the use of chiral arenethiolate ligands SAr^* can result in enantioselective C–C bond formation.³

To further investigate the formation of complexes such as $[\text{Cu}_4\text{R}_4][\text{Mg}(\text{SAr})_2]_2$ (**1**), we designed the strategy of directly reacting organocopper aggregates with preformed bis(arenethiolato)magnesium complexes (Scheme 1b). However, since very little information exists on the stability and nature of intramolecularly coordinated bis(arenethiolato)magnesium complexes, we found it necessary to study the syntheses, properties,

Scheme 1. Synthesis and Schematic Structure of $[\text{Cu}_4\text{R}_4][\text{Mg}(\text{SAr})_2]_2$ ^a



^aKey: (a) known preparation from CuSAr and MgR_2 ; (b) theoretical preparation from CuR and $\text{Mg}(\text{SAr})_2$.

and structures of these species, prior to elaborate studies on the organocopper magnesium arenethiolate assemblies.

Here we report the synthesis and characterization of the novel bis(arenethiolato)magnesium complex $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\}_2]_2$ (**3**), which is formed upon reaction of the bis(aryl)magnesium reagent $[\text{Mg}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)_2]$ (**2**)⁶ with 2 equiv of elemental sulfur.

Experimental Section

All experiments were carried out using standard Schlenk techniques under an inert nitrogen atmosphere. THF, Et_2O , and C_6H_6 were distilled from sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled from calcium hydride. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer. Melting points were determined by using a Büchi melting point apparatus. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. The known bis(aryl)magnesium starting material $[\text{Mg}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)_2]$ (**2**)⁶ was prepared by reacting $[\text{Li}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)]^7$ and $\text{MgBr}_2(\text{OEt})_2$ in Et_2O between 0 and 25 °C and was identified by ^1H and ^{13}C NMR spectroscopy.

Synthesis of $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\}_2]_2$ (3**).** To **2** (1.39 g, 4.7 mmol) in THF (50 mL) cooled at -78 °C was slowly added sublimed sulfur (0.30 g, 9.4 mmol) under vigorous stirring. After 0.5 h at -78 °C, the reaction mixture was allowed to slowly warm to room temperature over 30 min to afford a clear slightly yellow solution. After 0.5 h at 25 °C, removal of the volatiles *in vacuo* and washing with pentane (2×30 mL) yielded 1.20 g (72%, 3.36 mmol) of **3** as a white solid. Crystals suitable for X-ray structure determination were obtained by slow diffusion of pentane into a saturated solution of **3** in CH_2Cl_2 at -20 °C. Mp: 159 °C dec. ^1H NMR (C_6D_6 , 300 MHz, 297 K), δ in ppm: 1.62 (s, 12H, NMe_2), 3.22 (s, 4H, CH_2), 6.58 (d, 2H, $^3J = 7$ Hz, ArH-3), 6.74 (t, 2H, $^3J = 7$ Hz, ArH-4), 6.95 (t, 2H, $^3J = 7$ Hz, ArH-5), 7.85 (d, 2H, $^3J = 7$ Hz, ArH-6). ^{13}C NMR (C_6D_6 , 75.5 MHz, 297 K), δ in ppm: 45.2 (NMe_2), 66.5 (CH_2), 122.4 (ArH), 129.1 (ArH),

* To whom correspondence should be addressed. E-mail: vankoten@xray.chem.ruu.nl.

[†] Debye Institute.

[‡] Bijvoet Center. To whom correspondence concerning crystallographic studies should be addressed. E-mail: spea@xray.chem.ruu.nl.

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Table 1. Experimental Data for the X-ray Diffraction Study of **3**

formula	C ₃₆ H ₄₈ Mg ₂ N ₄ S ₄	V (Å ³)	1819.3(6)
space group	P2 ₁ /c	d _{calc} (g·cm ⁻³)	1.3027(4)
crystal system	monoclinic	μ(Mo Kα) (cm ⁻¹)	3.1
Z	2	radiation, λ (Å)	Mo Kα, 0.710 73 ^a
a (Å)	9.1464(14)	T (K)	150
b (Å)	20.254(5)	R ^b	0.0660
c (Å)	10.1420(15)	wR ₂ ^c	0.1494
β (deg)	104.455(12)		

^a Graphite-monochromated. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)] \}^{1/2}$.

131.1 (ArH), 136.1 (Ar-2), 137.0 (ArH), 147.0 (Ar-1). ¹³C NMR (CDCl₃, 50.3 MHz, 297 K), δ in ppm: 45.2 (NMe₂), 66.4 (CH₂), 122.7 (ArH), 129.1 (ArH), 131.0 (ArH), 135.0 (Ar-2), 136.1 (ArH), 145.1 (Ar-1). Anal. Calcd for [C₃₆H₄₈Mg₂N₄S₄]·0.5CH₂Cl₂: C, 57.98; H, 6.53; N, 7.41. Found: C, 58.14; H, 6.31; N, 7.38.

Reaction of [Mg{S(C₆H₄-2-CH₂NMe₂)₂]₂ (3**) with H₂O.** To an NMR sample of **3** in C₆D₆ was added an excess of thoroughly degassed H₂O. After 0.5 h of shaking the water was removed with a pipet and ¹H NMR analysis showed a single product, *i.e.* the arenethiol HS(C₆H₄-2-CH₂NMe₂),⁸ whose identity was substantiated by the absence of extra signals when independently prepared HS(C₆H₄-2-CH₂NMe₂) was added.

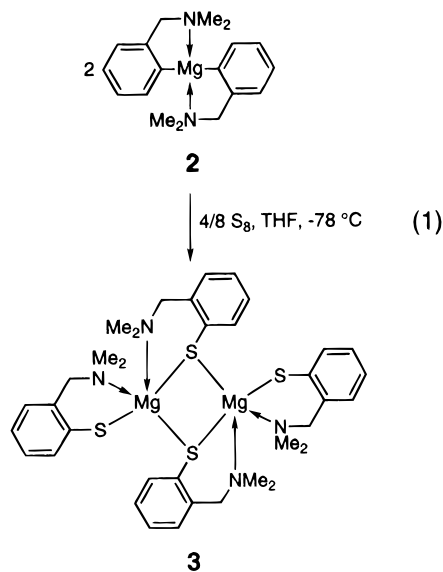
Reaction of [Mg{S(C₆H₄-2-CH₂NMe₂)₂]₂ (3**) with Me₃SiCl.** To **3** (0.57 g, 1.60 mmol based on monomer) in Et₂O (25 mL) was added an excess of Me₃SiCl (5 mL, 39.4 mmol). After 0.5 h, the volatiles were removed *in vacuo* and the product was extracted with pentane (3 × 10 mL). Removal of the pentane *in vacuo* afforded Me₃SiS(C₆H₄-2-CH₂NMe₂)⁹ in 86% yield (1.37 mmol) as a pale yellow colorless oil. The identity of this product was confirmed by ¹H NMR spectroscopy.⁹

Structure Determination and Refinement of **3.** X-ray data (total/unique reflections: 11 949/4162) were collected (Mo Kα, λ = 0.710 73 Å; ω/2θ mode; 2.0° < θ < 27.50°) on an Enraf-Nonius CAD4T/rotating anode diffractometer with a graphite monochromator, fitted with a standard Enraf-Nonius low-temperature unit, for a transparent colorless crystal (0.20 × 0.25 × 0.25 mm) glued on top of a glass fiber. Accurate unit-cell parameters and an orientation matrix were derived from the setting angles of 25 well-centered reflections (SET4¹⁰) in the range 11° < θ < 14°. The unit-cell parameters were checked for the presence of higher lattice symmetry.¹¹ Data were corrected for Lorentz-polarization effects and absorption (DIFABS¹² as implemented in PLATON;¹³ correction range 0.88–1.20). The structure was solved by direct methods (SHELXS86¹⁴), and refinement on F² (208 variables) was carried out by full-matrix least-squares techniques (SHELXL93¹⁵) using no observance criterion. Hydrogen atoms were included on calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were refined with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atom by a factor of 1.2 for the CH₂ and aromatic hydrogen atoms and a factor of 1.5 for the methyl hydrogen atoms. Weights were optimized in the final refinement cycles. No correction for extinction was found necessary. Neutral-atom scattering factors and anomalous-dispersion corrections were taken from ref 16. Geometrical calculations and illustrations were performed with PLATON.¹³ All calculations were performed on a DEC5000 cluster. Crystal data and numerical details of the structure determination and refinement are collected in Table 1.

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Results and Discussion

The bis(aryl)magnesium reagent [Mg(C₆H₄-2-CH₂NMe₂)₂] (**2**)⁶ reacts under optimal reaction conditions with 2 equiv of elemental sulfur at low temperature to afford in a smooth reaction the dimeric bis(arenethiolato)magnesium complex [Mg{S(C₆H₄-2-CH₂NMe₂)₂]₂ (**3**) (eq 1) which can be isolated



as a white powder in high yield. This crude bulk material was shown by ¹H NMR (benzene-*d*₆) to be pure **3**.

Under nonoptimal conditions, byproducts are formed which hamper the isolation of pure **3**; these byproducts, which have not been identified, are probably organo(arenethiolato)magnesium complexes (from incomplete sulfur insertion) or intermediate Mg{S_n(C₆H₄-2-CH₂NMe₂)₂} species.¹⁷

Nonrecrystallized pure **3** is a white solid which melts at 159 °C with decomposition and which is readily soluble in most common organic solvents with the exception of alkanes. The bulk material **3** after recrystallization from CH₂Cl₂ and pentane always contained some CH₂Cl₂ (elemental analysis and ¹H NMR) and would appear to contain, besides pure **3**, some dichloromethane solvate **3**·CH₂Cl₂. Solid pure **3** turns yellow to orange on exposure to air within 10 min. It has been characterized as a dimer in the solid state (*vide infra*) and as a monomer in benzene solution by cryoscopy and NMR spectroscopy (*vide infra*). The chemical formulation of **3** as a pure bis(arenethiolato)magnesium complex [Mg{S(C₆H₄-2-CH₂-NMe₂)₂]₂ has been supported by a number of characteristic chemical reactions. For example, addition of water to **3** either in the solid state or in solution leads to elimination of arenethiol HS(C₆H₄-2-CH₂NMe₂).⁸ Furthermore, aerobic decomposition of solutions of **3** occurs rapidly, and besides the formation of arenethiol, there is formation of a compound that is probably the corresponding disulfide {S(C₆H₄-2-CH₂NMe₂)₂}. Complex **3** reacts selectively in Et₂O at ambient temperature with chlorotrimethylsilane to afford in high yield the corresponding trimethylsilyl aryl thioether Me₃SiS(C₆H₄-2-CH₂NMe₂).⁹

To establish the structure of **3** in the solid state, an X-ray structure determination was carried out. The molecular structure of **3** is depicted in Figure 1, and selected geometrical data are listed in Table 2. In the crystal structure, this complex exists as a dimer in which two magnesium atoms are each S₂N₂-chelate bonded by a terminal arenethiolate with the two magnesium

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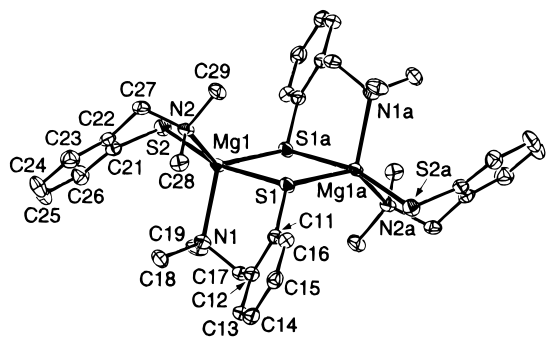


Figure 1. Molecular structure and adopted atom-labeling scheme of $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_4\text{-}2\text{-CH}_2\text{NMe}_2)\}_2]_2$ (**3**) (ORTEP, thermal ellipsoids at 50% probability) with the exclusion of the hydrogen atoms.

Table 2. Selected Geometrical Data for $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_4\text{-}2\text{-CH}_2\text{NMe}_2)\}_2]_2$ (**3**)^a

Bond Lengths (Å)			
Mg1–S1	2.5189(18)	Mg1–N2	2.239(4)
Mg1–S1a	2.5778(17)	S1–C11	1.761(4)
Mg1–S2	2.4462(18)	S2–C21	1.770(4)
Mg1–N1	2.252(3)		
Bond Angles (deg)			
Mg1–S1–Mg1a	104.11(5)	S1–Mg1–S2	164.71(7)
Mg1–S1–C11	108.16(14)	S1–Mg1–N1	89.66(9)
Mg1–S2–C21	94.22(14)	S2–Mg1–N2	90.35(9)
S1–Mg1–S1a	75.89(5)		

^a The estimated standard deviations of the last significant digits are shown in parentheses. “a” indicates the symmetry operator (1 – x, 1 – y, 1 – z).

atoms being linked through the sulfur atoms of two bridging arenethiolate ligands. Each magnesium atom acquires a five-coordinate geometry through further coordination by the nitrogen atom of one of these bridging arenethiolates.

The magnesium geometry which results has C_{2v} symmetry and is 50% along the Berry pseudorotation coordinate between trigonal bipyramidal (D_{3h}) and square planar (C_{4v}).¹⁸ In this structure, there is a central Mg_2S_2 core which, through the presence of a crystallographic inversion center, is perfectly planar.

The bridging arenethiolate ligands show almost equal Mg–S bond lengths of 2.5189(18) Å (Mg1–S1) and 2.5778(17) Å (Mg1–S1a), and the terminally bonded arenethiolate ligand forms a Mg1–S2 bond with a length of 2.4462(18) Å. These distances are significantly longer than those reported for dimeric $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3)\}_2]_2$, in which the magnesium atoms are reported to be three-coordinated by three thiolate sulfur atoms ($\text{Mg-S}^{\text{bridge}} = 2.462(5)$ Å (average), $\text{Mg-S}^{\text{terminal}} = 2.349(5)$ Å);¹⁹ since there is weak additional π -bonding of one of the phenyl *ortho* substituents, the Mg atoms may be interpreted as having a distorted pseudotetrahedral, four-coordinate, geometry. Even shorter distances are observed in the monomeric bis(arenethiolato)magnesium complex $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Bu}_3)\}_2\text{-}(\text{OEt}_2)]_2$,¹⁹ where the tetrahedral Mg coordination arises from two thiolate sulfur atoms and two oxygen Lewis bases ($\text{Mg-S}^{\text{terminal}} = 2.387(5)$ Å (average)), and therefore we conclude that the long Mg–S distances in **3** are a reflection of the five-coordination of the metal.

The angles Mg1–S1–Mg1a, Mg1–S1–C11, and Mg1a–S1–C11 of 104.11(5), 108.16(14), and 127.66(14)° indicate a tetrahedral geometry of the bridging thiolate sulfur atoms, and this is consistent with a description of each arenethiolate bridge-

bond as arising from two two-electron two-center (2e–2c) interactions. It is interesting to note that the bonding of the arenethiolate ligands in **3** is not similar to that calculated by Pappas²⁰ for the complexes $\text{M}(\text{SH})_2$ (M = Be, Mg, Ca). These calculations indicated that the Mg–S interaction is highly ionic with little covalent character, calculated bond distances and bond angles being Mg–S 2.324 Å, S–Mg–S 180°, and Mg–S–H 95.2°. However, in **3**, the Mg–S–*C*_{ipso} angle of 94.22(14)° for the terminal arenethiolate ligands and to a lesser extent the Mg–S bond length of 2.4462(18) Å are reasonably close to the calculated Mg–S–H and Mg–S values in $\text{Mg}(\text{SH})_2$.

Comparison of the M_2S_4 core of **3** (M = Mg) with those in other bis(arenethiolato)metal(II) complexes shows it to be similar to those in $[\text{Mg}\{\text{S}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3)\}_2]_2$,¹⁹ $[\text{Zn}\{\text{S}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Bu}_3)\}_2]_2$,²¹ $[\text{Fe}\{\text{S}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Bu}_3)\}_2]_2$,²² and $[\text{Fe}\{\text{S}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3)\}_2]_2$.²³ Interestingly, bis(arenethiolato)magnesium complex **3** is isostructural with the bis(phenolato)iron(II) analogue $[\text{Fe}\{\text{O}(\text{C}_6\text{H}_4\text{-}2\text{-CH}_2\text{NMe}_2)\}_2]_2$, which we prepared recently.²⁴

The ¹H NMR spectra of **3** in toluene-*d*₈ are temperature dependent. At 297 K, one obtains the fast-exchange ¹H NMR spectrum which comprises singlet resonances for the CH₂ (3.18 ppm) and NMe₂ (1.61 ppm) groups as well as four resonance patterns for the aromatic hydrogens. Below 243 K, one obtains the slow-exchange spectrum which consists of two singlet resonances for the two methyl groups of the NMe₂ unit (2.20 and 0.61 ppm), two broad signals for the CH₂ group (4.19 and 1.91 ppm), and aromatic proton resonances that are essentially identical to those in the high-temperature spectrum. The resonance pattern for the CH₂NMe₂ group is a clear indication that the nitrogen donor center is coordinated to the metal at this temperature. Furthermore, the single pattern for the arenethiolate ligands suggests that the structure of **3** is highly symmetrical in solution at this temperature, and although this could be explained by fast exchange of the bridging and terminal arenethiolate ligands, we believe this is evidence that **3** is monomeric in solution. The latter conclusion is corroborated by a cryoscopic molecular weight determination which showed **3** to be monomeric in benzene solution. This result implies that during dissolution of crystalline **3** there is aggregate breakdown with coordination of the magnesium being reduced from five-coordinate to four-coordinate.

Interpreted on the basis of these NMR data, complex **3** is at low temperature a pseudotetrahedral four-coordinate monomeric bis-*S,N*-chelated magnesium species. The fluxional process which is operational in this mononuclear species must be able to explain the singlet resonances for both the CH₂ and NMe₂ groups. If there is retention of magnesium–nitrogen coordinative bonding, then the process occurring in solution is one in which there is inversion of the tetrahedral magnesium geometry *via* a planar four-coordinate transition state. Alternatively, magnesium–nitrogen dissociation/association processes are possible, and these would involve a two- or three-coordinate magnesium center. From the decoalescence temperatures of the

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CH₂NMe₂ resonances, we have calculated the barrier of activation (ΔG^\ddagger) for the operative process to be 42.5 ± 1.0 kJ mol⁻¹.²⁵

Conclusion

The first example of a bis(arenethiolato)magnesium complex with intramolecular coordination has been synthesized and structurally characterized. The synthetic methodology employed could provide the basis for novel routes to a variety of bis(arenethiolato)magnesium-complexed organocopper aggregates. Preliminary experiments have shown that the reaction of mesitylcopper with **3** affords an aggregate like **1** of structural type [Cu₄R₄][Mg(SAr)₂]₂,⁴ and further studies are currently

(25) Eyring equation: $\Delta G^\ddagger = -RT_c \ln[2\pi h(\Delta\nu)/kT_c\sqrt{3}]$ where ΔG^\ddagger = free energy of activation (J), T_c = coalescence temperature (K), $\Delta\nu$ = chemical shift difference (Hz), and the other symbols have their usual meaning.

establishing the nature of this and related aggregated complexes. Studies of similar species prepared from intramolecularly coordinated lithium arenethiolates are ongoing.²⁶

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Supporting Information Available: Tables giving structure determination details, all atomic parameters, thermal parameters, bond lengths, and bond angles (7 pages). Ordering information is given on any current masthead page.

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