Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 669 (2003) 37–43

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and characterization of cyclopentadienyl thiolato complexes of magnesium

Aibing Xia, Mary Jane Heeg, Charles H. Winter *

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

Received 5 November 2002; received in revised form 11 December 2002; accepted 11 December 2002

Abstract

Treatment of Cp_2Mg with 2-methyl-2-propanethiol, cyclohexanethiol, and 2-propanethiol in toluene at ambient temperature afforded the tetrameric cyclopentadienyl thiolato complexes $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^t\text{Bu})]_4$ (97%), $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}(C_6H_{11}))]_4$ (92%), and $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^i\text{Pr})]_4$ (83%) as colorless crystalline solids. Treatment of $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^t\text{Bu})]_4$ with tetrahydrofuran or *tert*-butylpyridine in dichloromethane/hexane afforded the dimeric solvated complexes $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(\text{THF})]_2$ (78%) or $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(^t\text{Bupy})]_2$ (60%) as colorless crystals. The crystal structures of $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^t\text{Bu})]_4$, $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(\text{THF})]_2$, and $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(^t\text{Bupy})]_2$ were determined by X-ray diffraction methods. In the solid-state structure, $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^t\text{Bu})]_4$ contains one η^5-cyclopentadienyl ligand per magnesium and one cubic core of Mg_4S_4 that features a mirror plane of symmetry along one diagonal Mg_2S_2 plane. $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(\text{THF})]_2$ contains one η^5-cyclopentadienyl ligand per magnesium and one bent Mg_2S_2 core with a mirror plane along thiolato bridges. $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(^t\text{Bupy})]_2$ contains one η^5-cyclopentadienyl ligand per magnesium and a planar Mg_2S_2 core with a center of symmetry.

Keywords: Magnesium; Magnesocene; Cyclopentadienyl; Thiolato; Cubic

1. Introduction

Magnesium thiolato chemistry has attracted increasing attention recently. These complexes have unique structural features and can be made as solvent free monomers [1–3], solvated monomers [4–8], dimers [4,7–10], trimers [6], and tetramers [11]. The main structure determining factor is the steric bulk of the ligands. Therefore, only highly sterically hindered thiolato ligands can lead to formation of two coordinate monomeric species. With less steric bulk, thiolato bridging is common and Lewis bases are required to form monomeric structures. Most magnesium thiolato complexes have been homoleptic. Among the 21 magnesium thiolato structures that were listed in a Cambridge Crystallographic Database search (Version 5.23, April 2002), only three amido thiolato complexes reported by Ruhlandt-Senge are heteroleptic [4]. Ethyl(*tert*-butylthiolato)magnesium was isolated, but not structurally characterized [11]. Magnesium thiolato complexes have potential uses in several areas. Because they are less reducing than corresponding alkaline metal thiolato complexes, they are more suitable starting materials for the preparation of thiolato complexes of transition metal centers [8]. More importantly, recent study has shown that the magnesium ion is a useful dopant for group 12 (Zn, Cd)-group 16 (S, Se, Te) semiconductors [12–17]. Currently used precursors to these materials include elemental magnesium [13], magnesocene [16] or methyl-substituted magnesocene [12,14,15], elemental zinc [13] or dimethylzinc [12,14–16], diethylsulfide [12], di-*tert*-butylsulfide [14–16], or 2-

---

* Corresponding author. Tel.: +1-313-577-5224; fax: +1-313-577-8289.

E-mail address: chw@chem.wayne.edu (C.H. Winter).

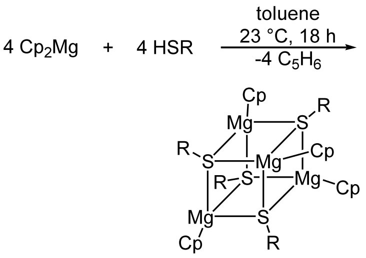
0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(02)02194-0

methyl-2-propanethiol [14,16], elemental selenium [13], di-*tert*-butylselenium [14–16], or dimethylselenium [12]. Given the fact that magnesocene and 1,1′-dimethylmagnesocene are the most common dopant source compounds for magnesium in semiconductor doping, it is surprising that virtually nothing is known about reactions of magnesocenes with sulfur source compounds. Herein we report reactions of magnesocene and several alkanethiols, which yield the first magnesium complexes featuring mixed cyclopentadienyl and thiolato ligand sets. X-ray crystallography demonstrates tetrameric or dimeric structures with or without the presence of Lewis bases such as tetrahydrofuran and *tert*-butylpyridine.

2. Results

2.1. Synthesis and characterization of cyclopentadienyl thiolato complexes

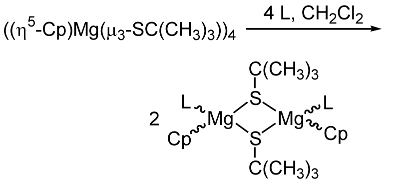
Treatment of magnesocene (Cp_2Mg) with the alkanethiols 2-methyl-2-propanethiol, cyclohexanethiol, or 2-propanethiol at ambient temperature in toluene afforded $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^t\text{Bu})]_4$ (**1**, 97%), $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}(C_6H_{11}))]_4$ (**2**, 92%), or $[(\eta^5\text{-Cp})Mg(\mu_3\text{-S}^i\text{Pr})]_4$ (**3**, 83%) as colorless crystalline solids (Eq. (1)). The compositions were based on the spectral and analytical data. The solid-state structure of **1** was determined by X-ray crystallography and is described below. In the solid state, **1** is tetrameric with a Mg_4S_4 core. Spectral and solubility similarity as well as analytical data suggests similar cubic structure assignments for **2** and **3**. Complexes **1**–**3** are stable under inert atmosphere and no decomposition was observed after several days in dichloromethane-d_2 solutions sealed under an argon atmosphere during NMR study. The ^{1}H-NMR spectra of **1**–**3** contain cyclopentadienyl singlets ranging from δ 6.24 to 6.37, which are close to that of Cp_2Mg (δ 6.19, dichloromethane-d_2). The $^{13}C\{^1H\}$-NMR spectra contain cyclopentadienyl singlets ranging from 106.98 to 107.45 ppm, which are again similar to that of Cp_2Mg (107.71 ppm, dichloromethane-d_2).



(1)

1, R = $C(CH_3)_3$, 97%
2, R = C_6H_{11}, 92%
3, R = $CH(CH_3)_2$, 83%

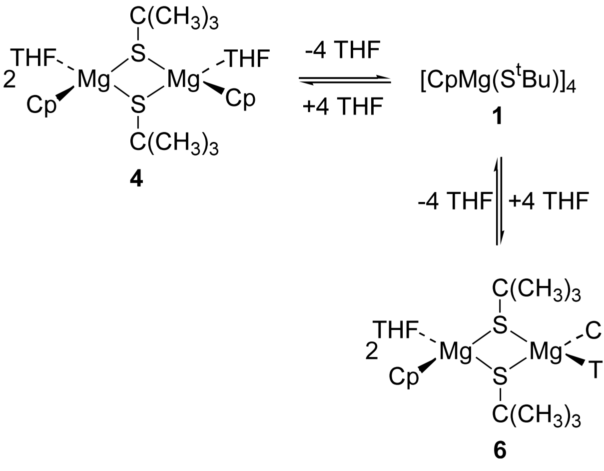
Treatment of **1** with tetrahydrofuran or *tert*-butylpyridine in dichloromethane, followed by recrystallization, afforded colorless crystals of $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(THF)]_2$ (**4**, 78%) or $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(^t\text{Bupy})]_2$ (**5**, 60%) (Eq. 2). The structural assignments were based on the spectral and analytical data as well as X-ray crystal structure determinations. In the solid state, compounds **4** and **5** are both dimeric with Mg_2S_2 cores. Their molecular structures are described below. The ^{1}H-NMR spectrum of analytically pure **4** at ambient temperature exhibits three cyclopentadienyl resonances at δ 6.23, 6.29, and 6.37 with a ratio of 34:59:7. In addition to the cyclopentadienyl resonances, three *tert*-butyl resonances appear at δ 1.43, 1.48, and 1.74 in a similar ratio. The $^{13}C\{^1H\}$-NMR spectrum contains three cyclopentadienyl resonances at 106.04, 106.73, and 107.45 ppm. The pair of resonances at δ 6.37 and 1.74 is identical to those of **1**, suggesting a minor equilibrium in which dissociation of tetrahydrofuran from **4** leads to the formation of **1**. The ^{1}H-NMR spectrum of **5** contains cyclopentadienyl singlet at δ 6.17, while its $^{13}C\{^1H\}$-NMR spectra contains a cyclopentadienyl singlet at 106.38 ppm. These resonances are shifted slightly upfield from those of the tetrameric **1**, reflecting the influence of the electron-donating *tert*-butylpyridine ligand.



(2)

4, L = THF, 78%
5, L = 4-tert-butylpyridine, 60%

Variable temperature ^{1}H-NMR spectra for **4** were recorded between 20 and −40 °C in dichloromethane-d_2. Upon cooling, the pair of resonances at δ 6.29 (Cp) and 1.43 (^{t}Bu) increased in intensity at the expense of the other two pairs of Cp and ^{t}Bu resonances. At −20 °C, the resonances at δ 6.29 and 1.43 became the most dominant and the ratio of the three cyclopentadienyl resonances was 75:22:3. Single crystals of **4** grown at −20 °C in preparative experiments adopt a solid-state structure with *syn*-cyclopentadienyl ligands, and **4** is probably the major species in solution at this temperature. The minor species has resonances consistent with **1**. At −30 °C, the ratio of the cyclopentadienyl ligands increased to 82:16:2. Further cooling led to precipitation. Because the pairs of resonances for **1** (δ 6.37 and 1.74) decreased in intensity as the temperature was lowered, the presence of **1** suggests an equilibrium process instead of an impurity. As outlined in Eq. 3, these NMR experiments are consistent with an equilibrium mixture of *syn*-$[(\eta^5\text{-Cp})Mg(\mu\text{-S}^t\text{Bu})(THF)]_2$ (**4**), *anti*-$[(\eta^5\text{-Cp})Mg(\mu\text{-S}^t\text{Bu})(THF)]_2$ (**6**), and **1**.



(3)

2.2. Crystal structures

To establish the solid-state geometries, the X-ray structures of **1**, **4**, and **5** were determined. Crystallographic data are summarized in Table 1. Selected bond distances and angles are given in Tables 2–4. Perspective views of **1**, **4**, and **5** are presented in Figs. 1–3.

Complex **1** crystallizes as a tetramer, with the four cyclopentadienyl magnesium fragments being held together by four μ_3-2-methyl-2-propanethiolato ligands. The two halves of the Mg_4S_4 cube are related by a diagonal Mg_2S_2 plane. The cyclopentadienyl ligands are bonded to the magnesium centers in an η^5-fashion, with magnesium–carbon bond lengths ranging from 2.364(5) to 2.412(4) Å. The magnesium-cyclopentadienyl centroid distances are 2.094(6) and 2.100(6) Å. The magnesium–sulfur bond lengths range from 2.566(2) to 2.602(2) Å.

Table 1
Crystal data and collection parameters for **1**, **4**, and **5**

	1	4	5
Empirical formula	$C_{36}H_{56}Mg_4S_4$	$C_{26}H_{44}Mg_2O_2S_2$	$C_{36}H_{54}Mg_2N_2S_2$
Fw	714.28	501.35	627.55
Space group	*C*2/*m*	*Pnma*	$P2_1/n$
a (Å)	17.485(8)	17.760(2)	10.625(1)
b (Å)	12.334(6)	18.239(2)	17.464(2)
c (Å)	20.362(10)	9.243(1)	21.150(2)
β (°)	111.604(12)		95.598(3)
V (Å^3)	4083(3)	2994(1)	3906(1)
Z	4	4	4
Temp (K)	295(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073
Calc. (g cm^{-3})	1.162	1.112	1.067
μ (mm^{-1})	0.317	0.239	0.193
$R(F)^a$ (%)	4.94	5.75	6.06
$R_w(F^2)^b$ (%)	11.33	17.95	16.98

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for $I > 2\sigma(I)$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths (Å)			
Mg(4)–S(1)	2.594(2)	Mg(6)–S(2)	2.602(2)
Mg(4)–S(2)	2.585(2)	Mg(6)–S(3)	2.584(2)
Mg(4)–S(3)	2.585(2)	Mg(5)–S(1)	2.566(2)
Mg(5)–S(3)	2.602(2)	S(1)–C(1)	1.863(4)
S(2)–C(4)	1.865(4)	S(3)–C(7)	1.865(3)
Bond angles (°)			
Mg(4)–S(1)–Mg(5)	96.86(5)	Mg(4)–S(1)–Mg(4A)	94.74(7)
Mg(4)–S(3)–Mg(5)	96.20(5)	Mg(4)–S(2)–Mg(4A)	94.97(7)
Mg(4)–S(2)–Mg(6)	96.08(4)	Mg(4)–S(3)–Mg(6)	96.66(5)
Mg(5)–S(3)–Mg(6)	95.47(5)	S(1)–Mg(4)–S(3)	83.09(4)
S(1)–Mg(5)–S(3)	83.29(5)	S(2)–Mg(6)–S(3)	83.27(5)
S(2)–Mg(4)–S(3)	83.51(5)	S(3)–Mg(5)–S(3A)	83.64(6)
S(3)–Mg(6)–S(3A)	84.37(6)		

Table 3
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths (Å)			
Mg(1)–S(1)	2.504(1)	Mg(1)–S(2)	2.503(1)
S(1)–C(1)	1.843(4)	S(2)–C(4)	1.848(4)
Mg(1)–O(1)	2.075(2)		
Bond angles (°)			
Mg(1)–S(1)–Mg(1A)	92.85(5)	Mg(1)–S(2)–Mg(1A)	92.90(5)
Mg(1)–S(1)–C(1)	123.32(9)	Mg(1)–S(2)–C(4)	123.18(10)
S(1)–Mg(1)–S(2)	79.09(3)		

Table 4
Selected bond lengths (Å) and angles (°) for **5**

Bond lenghts (Å)			
Mg(1)–S(1)	2.505(1)	Mg(1)–S(1A)	2.492(1)
S(1)–C(1)	1.828(4)	Mg(1)–N(1)	2.160(3)
Bond angles (°)			
Mg(1)–S(1)–Mg(1A)	99.69(4)	Mg(1)–S(1)–C(1)	123.44(13)
Mg(1A)–S(1)–C(1)	126.14(14)	S(1)–Mg(1)–S(1A)	80.31(4)

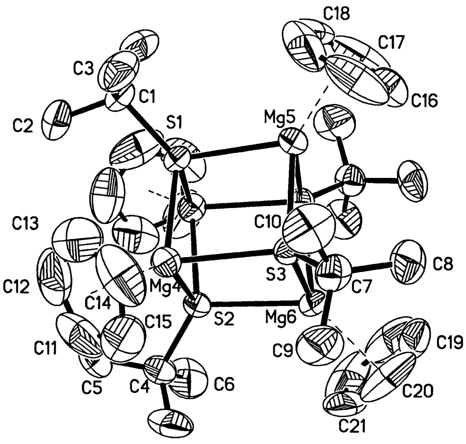


Fig. 1. Perspective view of **1** with 50% probability ellipsoids.

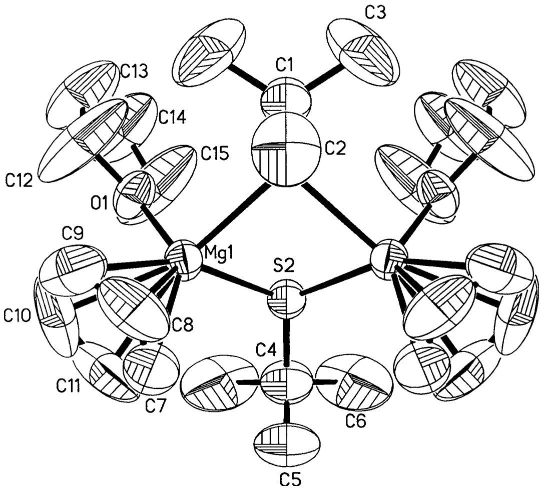


Fig. 2. Perspective view of **4** with 50% probability ellipsoids.

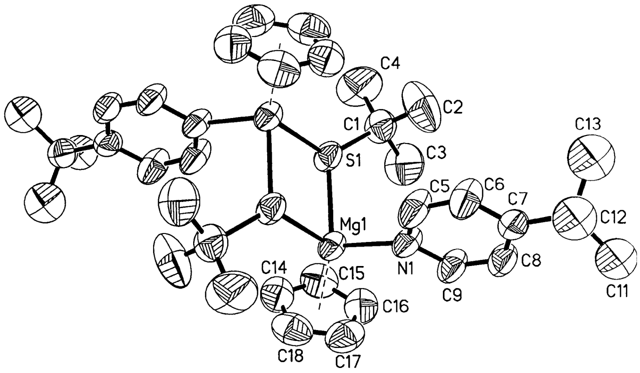


Fig. 3. Perspective view of **5** with 50% probability ellipsoids.

Complex **4** crystallizes as a dimer, with the two cyclopentadienyl magnesium fragments being held together by two μ_2-2-methyl-2-propanethiolato ligands. The two halves of the bent Mg_2S_2 core are related by a mirror plane of thiolato bridges, yielding a butterfly structure. The sum of angles in the Mg_2S_2 core is 343.93°. The cyclopentadienyl ligands are bonded to the magnesium centers in an η^5-fashion, with magnesium–carbon bond lengths ranging from 2.391(4) to 2.427(4) Å. The magnesium–sulfur bond lengths range from 2.503(1) to 2.504(1) Å. These values are slightly shorter than the related bonds in **1** and indicated a slight easing of the steric congestion in the dimeric structure of **4** in comparison to the tetrameric structure of **1**. The magnesium-cyclopentadienyl centroid distances are 2.135(4) Å.

Complex **5** crystallizes as a dimer, with the two cyclopentadienyl magnesium fragments being held together by two μ_2-2-methyl-2-propanethiolato ligands. The two halves of the Mg_2S_2 core are related by an inversion center. The cyclopentadienyl ligands are bonded to the magnesium centers in an η^5-fashion, with magnesium–carbon bond lengths ranging from 2.434(4) to 2.492(1) Å. The magnesium–sulfur bond lengths range from 2.492(1) to 2.505(1) Å. These values are slightly shorter than the related bonds in **1** but almost identical to those of **4**. The magnesium-cyclopentadienyl centroid distances are 2.154(4) and 2.155(4) Å.

3. Discussion

This work presents the first description of magnesium complexes with mixed cyclopentadienyl and thiolato ligand sets. The interaction of magnesocene and alkanethiols led to the formation of stable cyclopentadienyl magnesium thiolato complexes **1**–**3**. In the solid state, **1** is tetrameric with a Mg_4S_4 cubic core and is the first structurally characterized magnesium chalcogenide that adopts a cubic core structure. As mentioned in the introduction section, (ethyl)(*tert*-butylthiolato)magnesium was proposed to have the cubic tetrameric structure $[EtMg(S^tBu)]_4$, but it was not structurally characterized [11]. Compounds **1**–**3** showed no evidence for redistribution to Cp_2Mg and $Mg(S^tBu)_2$ at ambient temperature in solution or the solid state. A previous study by Coates has shown that heteroleptic thiolato complexes have varied stability [11]. For example, $[MeMgS^tBu(OEt_2)]_2$ decomposes to dimethylmagnesium and bis(*tert*-butylthiolato)magnesium upon removal of diethyl ether, and reaction of $^tBu_2Mg$ and 2-methyl-2-propanethiol resulted in the formation of bis(*tert*-butylthiolato)magnesium either from diethyl ether solution or in the presence of tetrahydrofuran. On the other hand, the above discussed (ethyl)(*tert*-butylthiolato)magnesium can be obtained free from diethyl ether.

Treatment of **1** with tetrahydrofuran and *tert*-butylpyridine led to formation of dimeric solvated complexes **4** and **5**. The magnesium–sulfur bond lengths of 2.49–2.60 Å in **1**, **4**, and **5** are comparable to those reported values for the bridging Mg–S distances (2.52–2.53 Å for $[Mg(THF)(N(SiMe_3)_2)(SPh)]_2$ [4], 2.50–2.53 Å for $[Mg(THF)_2(N(SiMe_3)_2)(S\text{-}2,4,6\text{-}^iPr_3C_6H_2)]_2$ [4], 2.51 Å for $[Mg(THF)(S\text{-}2,4,6\text{-}^tBu_3C_6H_2)(\mu\text{-}S\text{-}2,4,6\text{-}^tBu_3C_6H_2)]_2$ [4], 2.58–2.67 Å for $Mg_3(\mu_2\text{-}SPh)_6(py)_6$ [6], 2.46–2.47 Å for $[Mg(S\text{-}2,4,6\text{-}Ph_3C_6H_2)_2]_2$ [8]).

Tetrameric chalcogenides with cubic structures are prevalent in transition metal chemistry [18], among which the iron chalcogenides are the most intensively studied because of their importance in biological systems [19]. However, the corresponding tetrameric cubic chalcogenides of main group metals are much less investigated and only a limited number of such complexes have been reported among main group metals. The structurally characterized examples are limited to the group 13 metals (Al, Ga, In) [20]. Tetrameric cubic structures have been proposed for beryllium and magnesium complexes of the formula RM(SR′) [11,21].

We recently investigated the reactivity of amines toward Cp_2Mg and found that anilines such as diphenylamine react slowly to protonate one cyclopentadienyl ligand to afford cyclopentadienyl amido magnesium complexes [22]. Primary and secondary alkyl amines form stable adducts with Cp_2Mg, and no cyclopentadienyl elimination was observed even at elevated temperatures [23]. By contrast, alkanethiols react readily with Cp_2Mg at ambient temperature to afford stable cyclopentadienyl thiolato magnesium complexes as described herein. The difference in the reactivity of thiols and amines towards Cp_2Mg are attributed to the marked differences in their pK_a values (~ 10 for thiols, ~ 15 for CpH, and ~ 40 for amines) [24].

The final issue involves relating the results described herein to the activation of Cp_2Mg by 2-methyl-2-propanethiol under CVD conditions. Magnesocenes are the most commonly used doping sources in several CVD processes and 2-methyl-2-propanethiol is often used as the sulfur precursor [14,16]. The results of this study provide structural models for some of the gas phase and surface species that may be important in CVD processes of sulfide semiconductor materials.

4. Experimental

4.1. General considerations

All reactions were performed under an inert atmosphere of argon using either glovebox or Schlenk line techniques. Toluene, tetrahydrofuran, and hexane were distilled from sodium. CH_2Cl_2 was distilled over P_2O_5. 2-Methyl-2-propanethiol, cyclohexanethiol, 2-propanethiol, and *tert*-butylpyridine were purchased from Aldrich Chemical Company and were used as received. Cp_2Mg was prepared according to literature procedure [25].

^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra were obtained in dichloromethane-d_2. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Desert Analytics, Tucson, Arizona. Melting points were obtained on a Haake–Buchler HBI digital melting point apparatus and are uncorrected.

4.2. Synthesis of tetrameric cyclopentadienyl magnesium thiolato complexes

*4.2.1. Preparation of [(η^5-Cp)Mg(μ_3-S^{t}Bu)]$_4$ (**1**)*

Treatment of Cp_2Mg (0.927 g, 6.00 mmol) with 2-methyl-2-propanethiol (0.82 ml, 6.0 mmol) in toluene (30 ml) at ambient temperature led to immediate precipitation of a white solid. The mixture was stirred for 18 h and the solvent was removed under reduced pressure to afford **1** as a white solid (1.036 g, 97%): m.p. 210 °C (dec.); IR (Nujol, cm^{-1}) 3084 (w), 1604 (w), 1305 (m), 1215 (m), 1157 (m), 1010 (m), 764 (s), 728 (s); ^{1}H-NMR (dichloromethane-d_2, δ): 6.37 (s, 20H, C_5H_5), 1.75 (s, 36H, $C(CH_3)_3$); ^{13}C{^{1}H}-NMR (dichloromethane-d_2, ppm): 107.45 (s, C_5H_5), 51.16 (s, $C(CH_3)_3$), 35.46 (s, $C(CH_3)_3$).

Anal. Calc. for $C_{36}H_{56}Mg_4S_4$: C, 60.53; H, 7.90. Found: C, 60.30; H, 7.75.

*4.2.2. Preparation of [(η^5-Cp)Mg(μ_3-S(C_6H_{11}))]$_4$ (**2**)*

In a fashion similar to the preparation of **1**, treatment of Cp_2Mg (0.927 g, 6.00 mmol) with cyclohexanethiol (0.73 ml, 6.00 mmol) afforded **2** as a white solid (1.128 g, 92%): m.p. 253 °C (dec.); IR (Nujol, cm^{-1}) 3085 (w), 1602 (w), 1303 (w), 1259 (m), 1152 (w), 1008 (m), 766 (s), 727 (s); ^{1}H-NMR (dichloromethane-d_2, δ): 6.24 (s, 20H, C_5H_5), 2.96 (m, 4H, CH), 2.29–1.33 (m, 40H, CH_2); ^{13}C{^{1}H}-NMR (dichloromethane-d_2, ppm): 106.98 (s, C_5H_5), 46.08 (s, SCH), 38.48, 28.00, 25.90 (s, CH_2).

Anal. Calc. for $C_{44}H_{64}Mg_4S_4$: C, 64.57; H, 7.88. Found: C, 64.48; H, 8.10.

*4.2.3. Preparation of [(η^5-Cp)Mg(μ_3-S^{i}Pr)]$_4$ (**3**)*

In a procedure similar to the preparation of **1**, treatment of Cp_2Mg (0.463 g, 3.00 mmol) with 2-propanethiol (0.28 ml, 3.00 mmol) afforded **3** as a white solid (0.410 g, 83%): m.p. 304 °C (dec.); IR (Nujol, cm^{-1}) 3085 (w), 1605 (w), 1305 (m), 1261 (m), 1242 (m), 1153 (m), 1050 (m), 1008 (m), 768 (s), 725 (m), 727 (s); ^{1}H-NMR (dichloromethane-d_2, δ): 6.27 (s, 20H, C_5H_5), 3.32 (septet, $J = 6.0$ Hz, 4H, $CH(CH_3)_2$), 1.61 (d, $J = 6.0$ Hz, 24H, $CH(CH_3)_2$); ^{13}C{^{1}H}-NMR (dichloromethane-d_2, ppm): 107.05 (s, C_5H_5), 37.67 (s, $CH(CH_3)_2$), 28.09 (s, $CH(CH_3)_2$).

Anal. Calc. for $C_{32}H_{48}Mg_4S_4$: C, 58.39; H, 7.35. Found: C, 58.03; H, 7.64.

4.3. Synthesis of dimeric solvated cyclopentadienyl magnesium thiolato complexes

*4.3.1. Preparation of [(η^5-Cp)Mg(μ_2-S^{t}Bu)(THF)]$_2$ (**4**)*

Treatment of **1** (0.100 g, 0.14 mmol) with tetrahydrofuran (0.1 ml, 1.5 mmol) in dichloromethane (5 ml), followed by addition of hexane (15 ml) and crystallization at −20 °C, afforded **4** as colorless crystals (0.110 g, 78%): m.p. 190 °C (dec.); IR (Nujol, cm^{-1}) 3086 (w), 1603 (w), 1357 (m), 1306 (m), 1262 (m), 1155 (s), 1029 (m), 1011 (m), 876 (m), 969 (s), 744 (s), 727 (m); the ^{1}H-NMR spectrum in dichloromethane-d_2 indicated an equilibrium mixture in a 34:59:7 ratio according to the cyclopentadienyl resonances at δ 6.23, 6.29, 6.36, the tetrahydrofuran ligand gives broad peaks at δ 1.92 and 3.86. Assignments for cyclopentadienyl and *tert*-butyl ligands: (1) δ 6.23 (s, C_5H_5), 1.43 (s, $C(CH_3)_3$); (2) δ 6.29 (s, C_5H_5), 1.48 (s, $C(CH_3)_3$); (3) δ 6.36 (s, C_5H_5), 1.74 (s, $C(CH_3)_3$). The ^{13}C{^{1}H}-NMR (dichloromethane-d_2) spectrum also shows three Cp-containing species as well as a pair of tetrahydrofuran resonances at 25.84 and 69.18 ppm: Assignments for cyclopentadienyl and *tert*-butyl ligands: (1) 106.04 (s, C_5H_5), 37.11 (s, $C(CH_3)_3$); (2) 106.73 (s, C_5H_5), 36.86 (s, $C(CH_3)_3$); (3) 107.45 (s, C_5H_5), 35.45 (s, $C(CH_3)_3$). The quaternary carbons were not observed.

Anal. Calc. for $C_{26}H_{44}Mg_2O_2S_2$: C, 62.29; H, 8.85. Found: C, 62.22; H, 9.00.

4.3.2. Preparation of $[(\eta^5\text{-Cp})Mg(\mu_2\text{-S}^t\text{Bu})(^t\text{Bupy})]_2$ (**5**)

In a fashion similar to the preparation of **4**, treatment of **1** (0.100 g, 0.14 mmol) with *tert*-butylpyridine (0.208 g, 1.5 mmol) afforded colorless crystals of **5** (0.106 g, 60%): m.p. 220 °C (dec.); IR (Nujol, cm^{-1}) 3079 (w), 1616 (m), 1505 (m), 1306 (m), 1277 (m), 1231 (m), 1155 (m), 1071 (m), 1019 (m), 1008 (m), 758 (s), 741 (m), 728 (s); ^{1}H-NMR (dichloromethane-d_2, δ): 8.72 (bs, 4H, NC*H*), 7.43 (bs, 4H, C*H*), 6.17 (s, 10H, C_5H_5), 1.39 (s, 18H, $C(CH_3)_3$), 1.35 (s, 18H, $NC(CH_3)_3$); $^{13}C\{^1H\}$-NMR (dichloromethane-d_2, ppm): 149.24 (C_α of pyridine), 125.32 (C_γ of pyridine), 121.75 (C_β of pyridine), 106.38 (C_5H_5), 42.48 ($SC(CH_3)_3$), 37.02 ($SC(CH_3)_3$), 35.29 ($C(CH_3)_3$ of ^{t}Bupy), 30.37 ($C(CH_3)_3$ of ^{t}Bupy).

Anal. Calc. for $C_{36}H_{54}Mg_2N_2S_2$: C, 68.90; H, 8.67; N, 4.46. Found: C, 69.26; H, 8.76, 4.48.

4.4. X-ray crystallographic structure determinations

Crystalline samples were mounted in sealed thin wall capillaries under nitrogen atmosphere for X-ray data collection. All crystal structure data were collected at room temperature on a Bruker P4/CCD diffractometer equipped with Mo radiation. For each collection, a full sphere of data was collected at 10 s frame^{-1} with 0.2° or 0.3° between each frame. The frame data were integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program [26] and the structure was solved and refined using the programs of SHELXL-97 [27]. Crystal structures of **1** consist of tetrameric neutral complexes with no associated solvent or ions. The asymmetric unit of **1** contains half of a tetrameric complex; the internal symmetry element is a mirror plane through two magnesium and two sulfur atoms. Crystals of **4** and **5** consist of dimeric complexes with two coordinated solvent ligands. Complex **4** crystallizes with asymmetric units containing a half dimer related by a mirror plane. The asymmetric until of **5** contains two half dimers related by inversion centers. All three complexes show typical ligand disorder. The crystals were colorless and formed plates (**1**) or rods (**4** and **5**). Hydrogen atoms were placed in calculated positions and were constrained to ride on their carbon atoms.

5. Supporting information available

X-ray crystallographic files reported in this paper in CIF format for the structure determinations of **1**, **4**, and **5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 196706 for **1**, no. 196707 for **4**, and no. 196708 for **5**. Copies of this information may be obtained free of charge from The Director, 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).

Acknowledgements

We are grateful to the Office of Naval Research (grant no. N00014-99-1-0957) for support of this research.

References

[1] M. Niemeyer, P.P. Power, Inorg. Chim. Acta 263 (1997) 201.
[2] P. Ghosh, G. Parkin, Chem. Commun. (1996) 1239.
[3] J.J. Ellison, P.P. Power, Inorg. Chem. 33 (1994) 4231.
[4] W. Teng, U. Englich, K. Ruhlandt-Senge, Inorg. Chem. 39 (2000) 3875.
[5] S. Chadwick, U. Englich, K. Ruhlandt-Senge, Inorg. Chem. 38 (1999) 6289.
[6] S. Chadwick, U. Englich, M.O. Senge, B.C. Noll, K. Ruhlandt-Senge, Organometallics 17 (1998) 3077.
[7] B. Srinivas, C.-C. Chang, C.-H. Chen, M.Y. Chiang, I.-T. Chen, Y. Wang, G.-H. Lee, J. Chem. Soc. Dalton Trans. (1997) 957.
[8] K. Ruhlandt-Senge, Inorg. Chem. 34 (1995) 3499.
[9] C. Strohmann, B.C. Abele, D. Schildbach, K. Strohfeldt, Chem. Commun. (2000) 865.
[10] M.D. Janssen, R. van der Rijst, A.L. Spek, D.M. Grove, G. van Koten, Inorg. Chem. 35 (1996) 3436.
[11] G.E. Coates, J.A. Heslop, J. Chem. Soc. (A) (1968) 631.
[12] D.W. Parent, A. Rodriguez, J.E. Ayers, F.C. Jain, J. Cryst. Growth 224 (2001) 212.
[13] C.W. Chang, H.C. Yang, C.H. Chen, H.J. Chang, Y.F. Chen, J. Appl. Phys. 89 (2001) 3725.
[14] U.W. Pohl, M. Straßburg, I.L. Krestnikov, R. Engelhardt, S. Rodt, D. Bimberg, J. Cryst. Growth 214–215 (2000) 717.
[15] A.B. Krysa, Y.V. Korostelin, V.I. Kozlovsky, P.V. Shapkin, H. Kalisch, R. Rüland, M. Heuken, K. Heime, J. Cryst. Growth 214–215 (2000) 355.
[16] R. Engelhardt, U.W. Pohl, D. Bimberg, D. Litvinov, A. Rosenauer, D. Gerthsen, J. Appl. Phys. 86 (1999) 5578.
[17] T.P. Hanusa, Chem. Rev. 93 (1993) 1023.
[18] (a) M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46;
(b) S. Kabashima, S. Kuwata, M. Hidai, J. Am. Chem. Soc. 121 (1999) 7837;
(c) V.P. Fedin, I.V. Kalinina, D.G. Samsonenko, Y.V. Mironov, M.N. Sokolov, S.V. Tkachev, A.V. Virovets, N.V. Podberezskaya, M.R.J. Elsegood, W. Clegg, A.G. Sykes, Inorg. Chem. 38 (1999) 1956;
(d) R. Hernández-Molina, A.G. Sykes, Dalton (1999) 3137and references therein..
[19] (a) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., Wiley, New York, 1999, p. 791;

(b) D.J. Evans, R.A. Henderson, B.E. Smith, in: J. Reedijk, E. Bouwman (Eds.), Bioinorganic Catalysis, Marcel Dekker, New York, 1999;

(c) G.J. Leigh, in: J. Silver (Ed.), The Chemistry of Iron, Chapman and Hall, London, 1992.

[20] (a) A.H. Cowley, R.A. Jones, P.R. Harris, D.A. Atwood, L. Contreras, C.J. Burek, Angew. Chem. Int. Ed. Engl. 30 (1991) 1143;

(b) C.J. Harlan, E.G. Gillan, S.G. Bott, A.R. Barron, Organometallics 15 (1996) 5479;

(c) C. Schnitter, A. Klemp, H.W. Roesky, H.-G. Schmidt, C. Röpken, R. Herbst-Irmer, M. Noltemeyer, Eur. J. Inorg. Chem. (1998) 2033 (and references therein).

[21] G.E. Coates, A.H. Fishwick, J. Chem. Soc. A (1968) 635.

[22] A. Xia, M.J. Heeg, C.H. Winter, Organometallics 21 (2002) 4718.

[23] A. Xia, M.J. Heeg, C.H. Winter, J. Am. Chem. Soc. 124 (2002) 11264.

[24] F.G. Bordwell, Acc. Chem. Res. 21 (1988) 456.

[25] B.J. Wakefield, Organomagnesium Methods in Organic Synthesis, Academic Press, New York, 1995, p. 48.

[26] G.M. Sheldrick, SADABS, Program for the Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.

[27] G.M. Sheldrick, SHELXS-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.