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Synthesis and Structure of $[\mathrm{Mg(dmso)_6}]^{2+}[\mathrm{C_5H_5}]^-{}_2$ and $[\mathrm{Mg}(\eta^1\text{-}\mathrm{C_5H_5})(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{thf})_2]$ (dmso = dimethylsulfoxide, thf = tetrahydrofuran)

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Summary: Dicyclopentadienylmagnesium, $\mathrm{Mg(C_5H_5)_2}$, reacts with dimethyl sulfoxide, dmso, to afford the ionic compound $[\mathrm{Mg(dmso)_6}]^{2+}[\mathrm{C_5H_5}]^-{}_2$ with "naked" uncoordinated cyclopentadienyl rings; the reaction of $\mathrm{Mg(C_5H_5)_2}$ with tetrahydrofuran, thf, leads to the neutral complex $[\mathrm{Mg(C_5H_5)_2(thf)_2}]$ with an η^1- and η^5-coordinated cyclopentadienyl ring.

Introduction

Solvent-separated ion pairs (SSIPs) are practically not known in the organometallic chemistry of the alkaline-earth metals. To our knowledge there is no example of a compound with a "naked" uncoordinated cyclopentadienyl anion and a solvated Be, Mg, Ca, Sr, or Ba cation. Only two substances with a free fluorenyl anion are known: $[(\mathrm{pmdta})\mathrm{Mg}(\mu\text{-}\mathrm{Me})_2\mathrm{Mg}(\mathrm{pmdta})]^{2+}[\mathrm{fluorenyl}]^-{}_2$ in Mg chemistry and $[\mathrm{Ca(thf)_6}]^{2+}[\mathrm{Me_3Si(fluorenyl)}]^-{}_2$ in Ca chemistry.[1] In the organometallic chemistry of the alkali metals SSIPs with the cyclopentadienyl ring are more familiar,[2−4] e.g., $[\mathrm{K(15\text{-}crown\text{-}5)_2}]^+[\mathrm{C_5H_5}]^-$, $[\mathrm{Rb_2(C_5H_5)(18\text{-}crown\text{-}6)_2}]^+[\mathrm{C_5H_5}]^-$, $[\mathrm{Rb(15\text{-}crown\text{-}5)_2}]^+[\mathrm{C_5H_5}]^-$, and with substituted cyclopentadienyl rings, [5−7] $[\mathrm{Li(12\text{-}crown\text{-}4)_2}]^+[\mathrm{C_5H_2(SiMe_3)_3}]^-$, $[\mathrm{Na(diglyme)_2}]^+[\mathrm{C_5HPh_4}]^-$, $[\mathrm{Na(triglyme)_2}]^+[\mathrm{C_5HPh_4}]^-$, $[\mathrm{Na_2(18\text{-}crown\text{-}6)_3}]^{2+}[\mathrm{C_5HPh_4}]^-{}_2$, $[\mathrm{K\text{-}cryptand(2.2.2)}]^+[\mathrm{isodiCp}]^-$. In addition there are some alkali metal compounds with a free fluorenyl anion.[8]

In this study, we report on the first example of a magnesium complex, $[\mathrm{Mg(dmso)_6}]^{2+}[\mathrm{C_5H_5}]^-{}_2$ (**1**), with dissociated $\mathrm{C_5H_5}^-$ anions. Furthermore, a neutral Mg complex, $[\mathrm{Mg(C_5H_5)_2(thf)_2}]$ (**2**), is described with an η^1- and an η^5-coordinated cyclopentadienyl ligand.

Results and Discussion

The compounds $[\mathrm{Mg(dmso)_6}]^{2+}[\mathrm{C_5H_5}]^-{}_2$ (**1**) and $[\mathrm{Mg(C_5H_5)_2(thf)_2}]$ (**2**) were synthesized from $\mathrm{Mg(C_5H_5)_2}$ and dimethyl sulfoxide or tetrahydrofuran, respectively. Complex **1** forms a colorless crystalline powder that is thermally stable up to 60 °C. Several compounds with "naked" $\mathrm{C_5H_5}^-$ anions can be isolated and handled only at low temperatures.[9] Even more stable than **1** seems to be the recently synthesized complex $[\mathrm{K(15\text{-}crown\text{-}5)_2}]^+[\mathrm{C_5H_5}]^-$.[2] Compound **2** forms light yellow crystals that are stable up to 107 °C, where they melt. Both compounds can be handled in air only for short periods (some seconds). In solution they decompose immediately when exposed to air.

The stoichiometry of **1** and **2** was ascertained by elemental analysis and NMR spectroscopy. The ^{1}H NMR spectrum of compound **1** shows a singlet at 5.45 ppm, which is diagnostic for uncoordinated cyclopentadienyl rings. Complex **2** has its resonance for the coordinated cyclopentadienyl rings at 5.86 ppm. The singlet observed indicates dynamic behavior of the five-membered rings or η^5-coordination of both in solution.

The crystal and molecular structures of **1** and **2** were determined by single-crystal structural analysis. The structures are illustrated in Figures 1 and 2, where relevant bond lengths and angles are also given. Compound **1** crystallizes in the space group $P\bar{1}$, with the magnesium atom on an inversion center. Only one free $\mathrm{C_5H_5}^-$ anion is crystallographically independent. Interestingly, the $\mathrm{C_5H_5}$ moiety is not disordered. Often free $\mathrm{C_5H_5}$ rings are heavily disordered.[9] Thus reliable values for the C−C distances within the $\mathrm{C_5H_5}$ ring could be obtained (average value 139.8 pm; range 139.3−140.0(2) pm). The C−C distances in the planar $\mathrm{C_5H_5}$ ring are in good agreement with data previously observed for compounds with free $\mathrm{C_5H_5}^-$ rings.[9] In the $[\mathrm{Mg(dmso)_6}]^{2+}$ cation, which was not known before, the metal atom is octahedrally coordinated by the oxygen atoms of the

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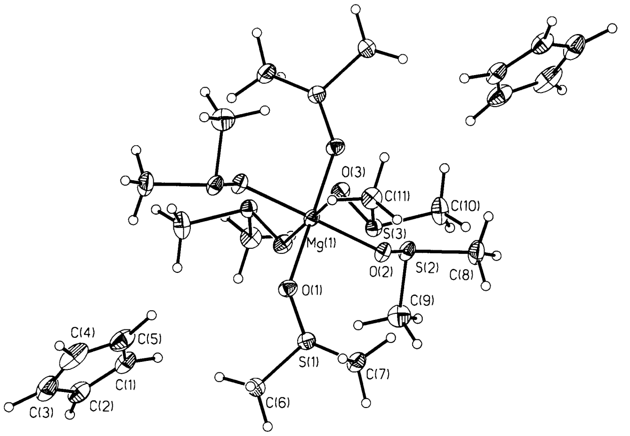

Figure 1. View of the structure of $[Mg(dmso)_6]^{2+}[C_5H_5]^-{}_2$ (**1**) with atomic numbering scheme (50% thermal ellipsoids). Selected bond lengths (pm) and angles (deg): Mg−O 206.9−209.0(1), S−O 152.0−152.5(1), S−C 177.7−1.784(2), C−C 139.3−140.0(2), av.139.8; O−Mg−O 88.81−91.19(3), Mg−O−S 120.7−123.1(1), O−S−C 104.9−105.7-(1), C−S−C 97.9−98.6(1), C−C−C 107.9−108.1(2)°.

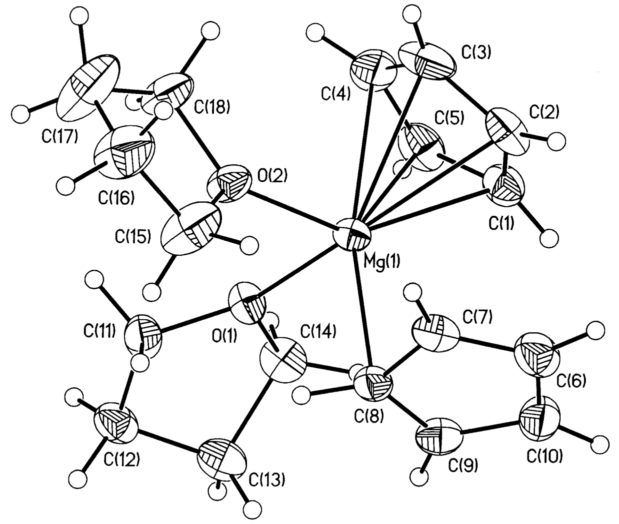

Figure 2. View of the molecular structure of $[Mg(C_5H_5)_2(thf)_2]$ (**2**) with atomic numbering scheme (50% thermal ellipsoids). Selected bond lengths (pm) and angles (deg): Mg−O 208.8, 209.8(2), Mg−C(η^5-C_5H_5) 241.7−247.9(3), Mg−(η^5-C_5H_5) 213.7(1), Mg−C(η^1-C_5H_5) 228.2(2), C−C(η^5-C_5H_5) 139.6−141.6(6), av 140.3, C−C(η^1-C_5H_5) 141.6(C8−C9), 138.8(C9−C10), 140.1(C6−C10), 138.5(C6−C7), 143.1-(C7−C8)(5); O−Mg−O 90.2(1), O−Mg−C8 93.0, 94.3(1), (η^5-C_5H_5)−Mg−O 113.6(1), 116.8(1), (η^5-C_5H_5)−Mg−C8 137.7(1).

dimethyl sulfoxide ligands (Mg−O 206.9−209.0(1) pm; O−Mg−O 88.81−91.19(3)° or 180°). The average S−O and S−C distances within the pyramidal dmso ligands are 152.2 and 178.0 pm. In uncoordinated dimethyl sulfoxide 151.3 and 178.8 pm are observed.[10] There is an intermolecular hydrogen bond network present in the crystal structure of compound **1**. The shortest contact is between a methyl hydrogen atom at C(6) of the dmso ligand and an oxygen atom [O(1)′] of an adjacent cation [H(6a)···O(1)′ 246 pm; C−H···O 176° (C−H fixed at 108 pm)]. Important hydrogen bonds are also between the “naked” $C_5H_5^-$ anion and the methyl groups of adjacent $[Mg(dmso)_6]^{2+}$ cations, e.g., H(8c)···Cp-center 248 pm and H(11b)···Cp-center 251 pm; angle H···Cp···H 176°.

Complex **2** (Figure 2) crystallizes in the acentric space group $P2_1$ with one molecule as asymmetric unit. The complexation of two tetrahydrofuran molecules to $[Mg(C_5H_5)_2]$ results in a change of the coordination of one C_5H_5 ligand from η^5 to η^1. Most probably, this change in coordination is steric in origin. The Mg−C-(η^5-C_5H_5) bond lengths are between 241.7 and 247.9(3) pm (average 244.7 pm), and the Mg−C(η^1-C_5H_5) bond length is 228.2(3) pm. The other Mg−C distances are greater than 270 pm. Within the η^1- C_5H_5 ring variable C−C bond lengths are found, indicating a cyclopentadiene-like structure with three longer and two shorter bonds. The closest known structure available for comparison with **2** is that of [Mg(η^5-C_5H_5)(η^1-C_5H_5)(thf)-(t-BuNH$_2$)] (**3**).[11] Here the Mg−O bond length is 206.7 pm (cf. **2**: 208.8 and 209.8(2) pm), the average Mg−C(η^5-C_5H_5) distance 246 pm, and the Mg−C-(η^1-C_5H_5) bond length 237.0 pm. Thus, in our complex **2** the Mg−C(η^1-C_5H_5) distance (228.2 pm) is a good deal shorter (8.8 pm) owing to the minor donor properties of the two tetrahydrofuran ligands in **2** in comparison with the amine and ether ligand in **3**.

Conclusion

To generate an uncoordinated “naked” cyclopentadienyl ring in alkali metal chemistry, it is necessary to encapsulate the alkali metal ion by crown ether ligands.[2−4] The magnesium cation is already satisfied by six DMSO ligands to liberate its cyclopentadienyl rings. THF as ligand is not strong enough to generate free $C_5H_5^-$, but a change to η^1-coordination of one cyclopentadienyl ligand is observed.

Experimental Section

Dicyclopentadienylmagnesium was purchased from Strem Chemicals. All manipulations were performed using conventional Schlenk techniques under an atmosphere of argon.

Synthesis of $[Mg(dmso)_6]^{2+}[C_5H_5]^-{}_2$ (1). To a solution of 0.15 g (0.97 mmol) of $[Mg(C_5H_5)_2]$ in 2 mL of tetrahydrofuran was added 4 mL of dimethyl sulfide. A white precipitate was obtained, which was redissolved by heating of the mixture. On cooling, colorless crystals of **1** appeared, which were washed with hexane and dried in a vacuum. Yield: 0.48 g (0.77 mmol, 80%). The compound (mp 133 °C) is insoluble in hexane and toluene, slightly soluble in tetrahydrofuran, and easily soluble in acetonitrile, dichloromethane, and dmso. ^1H NMR (200 MHz, CD_3CN):[12] δ 5.45 (s, C_5H_5), 2.51 (s, dmso) ppm. Anal. Found: C 41.5, H 6.5. Calcd: C 42.4, H 7.4.

Synthesis of $[Mg(C_5H_5)_2(thf)_2]$ (2). To a solution of 0.20 g (1.3 mmol) of $[Mg(C_5H_5)_2]$ in 5 mL of tetrahydrofuran was added 1 mL of hexane. The yellow powder obtained was redissolved by heating the mixture. The solution was evaporated to 2 mL and cooled to 5 °C. Slightly yellow crystals of **2** were obtained and dried in a vacuum. Yield: 0.24 g (0.80 mmol, 62%). The compound (mp 107 °C) is insoluble in hexane and toluene, but soluble in acetonitrile, dichloromethane, thf, and dmso. ^1H NMR (200 MHz, CD_3CN): δ 5.86 (s, C_5H_5), 3.65

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[12] NMR analysis of crystalline **1** showed that the C_5H_5/dmso ratio was generally too low. This is due to partial H/D exchange of the $C_5H_5^-$ anion with the deuterated solvent.

(m, thf), 1.83 (m, thf) ppm. Anal. Found: C 73.2, H 7.4. Calcd: C 72.4, H 8.8.

X-ray Structure Determination of 1 and 2. In the syntheses of **1** and **2** crystals suitable for X-ray crystal structural analysis were obtained. The crystals were mounted on glass fibers in rapidly cooled mineral oil.

Crystal Data. For **1**: $C_{22}H_{46}MgO_6S_6$, $M = 623.26$, triclinic, space group $P\bar{1}$, $a = 837.50(5)$ pm, $b = 938.22(5)$ pm, $c = 1102.30(6)$ pm, $\alpha = 74.027(1)°$, $\beta = 73.267(1)°$, $\gamma = 88.710(1)°$, $U = 795.93(8)$ Å, $Z = 1$, $D_c = 1.300$ g cm^{-3}, μ(Mo Kα) = 0.482 mm^{-1}. Bruker SMART-CCD diffractometer (2θ limit 55.0°). Crystal dimensions: 0.8/0.24/0.12 mm, 3273 observed data [$I > 2\sigma I$)] of 3554 independent data measured ($T = 153$ K). Refinement (on F^2) to $R_1 = 0.032$ and $wR_2 = 0.083$. No. of refined parameters: 166. For **2**: $C_{18}H_{26}MgO_2$, $M = 298.70$, monoclinic, space group $P2_1$, $a = 905.0(1)$ pm, $b = 889.2(1)$ pm, $c = 1054.8(1)$ pm, $\beta = 105.74(1)°$, $U = 817.0(2)$ Å, $Z = 2$, $D_c = 1.214$ g cm^{-3}, μ(Mo Kα) = 0.111 mm^{-1}. P4 Siemens diffractometer (2θ limit 55.0°). Crystal dimensions: 0.5/0.4/0.25 mm, 1853 observed data [$I > 2\sigma I$)] of 1997 independent data measured ($T = 173$ K). Refinement (on F^2) to $R_1 = 0.048$ and $wR_2 = 0.120$. No. of refined parameters: 190. In both structures all atoms (excluding hydrogens) were refined using anisotropic displacement parameters (riding model for hydrogens). The structures were solved by direct methods (SHELXS-97 and SHELXL-97).[13] CCDC 187582/3.

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Note Added in Proof. A noncrystallographically characterized unstable tetrahydrofuran adduct of magnesocene was described by Lehmkuhl, H.; Mehler, K.; Benn, R.; Rufinska, A.; Krueger, C. *Chem. Ber.* **1986**, *119*, 1054.

Supporting Information Available: X-ray crystallographic information for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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