

Notes

Bis(pentamethylcyclopentadienyl)magnesium: Unexpected Determination of the Until Now Unknown Molecular Structure of the Crystalline Compound

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Summary: The structure of bis(pentamethylcyclopentadienyl)magnesium, $\text{Mg}(\text{C}_5\text{Me}_5)_2$ (**1**), in the solid state has been determined by X-ray diffraction. The experimental results are described and discussed in comparison to structural properties of the higher alkaline-earth metallocenes MCp^*_2 ($M = \text{Ca}, \text{Sr}, \text{Ba}$) as determined in the gas phase or in the solid state. Structural trends of **1** in comparison to the isoelectronic species $[\text{LiCp}^*_2]^-$, BeCp^*_2 , and $[\text{AlCp}^*_2]^+$ are also presented.

The ferrocene-like sandwich compounds of the main-group elements have been discussed in some recent reviews,^{1–4} and lately considerable progress has been achieved in this field: e.g., with the preparation and structural characterization of the valence isoelectronic species, namely the anion $[\text{Cp}_2\text{Li}]^-$,⁵ BeCp^*_2 ,⁶ and the aluminumocenium cation, $[\text{AlCp}^*_2]^+$.⁷ On the basis of this and other recent experimental work, the bonding properties within these sandwich compounds were evaluated in several works.⁸ For the results discussed in the following, especially the trends of the neutral group II sandwich complexes BeCp_2 , MgCp_2 , CaCp_2 , SrCp_2 , BaCp_2 , and their derivatives are of interest, since some unexpected structural data, especially for the heavier elements, were disclosed: e.g., the tilt angles α (Figure 1, part 1) for the bent forms of MCp^*_2 ($M = \text{Ca}, \text{Sr}, \text{Ba}$),^{9–11} exhibiting nonparallel rings even in the gas phase (Figure 1).

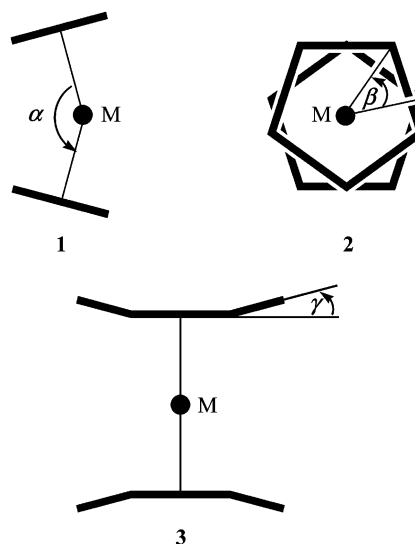


Figure 1. Schematic illustration of the structural parameters for permethylated alkaline-earth metallocenes: (1) definition of the tilt angle, α ; (2) definition of the stagger angle, β ; (3) definition of the out-of-plane angle, γ .

Herein we will restrict our discussion mainly to these structurally more shielded and more molecular decamethyl derivatives. Within this group, the crystal structures of the base-free CaCp^*_2 and BaCp^*_2 ¹² are known. For SrCp^*_2 ¹³ and MgCp^*_2 (**1**), crystal structures are still missing. This comes as a surprise, at least in the case of MgCp^*_2 , since solid **1** is commercially available and is used on a regular basis to implement Cp^* ligands under nonpolar solvent conditions: i.e., **1** together with MgCp_2 —for which α is 180° in the gas phase¹⁴ as well as in the solid phase¹⁵—may be considered a parent compound of main-group sandwich com-

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(1) Jutzi, P.; Burford, N. In *Metallocenes*; Togni, A., Haltermann, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, Chapter 1.

(2) (a) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969. (b) Jutzi, P. *Chem. Unserer Zeit* **1999**, *33*, 342.

(3) Stahlke, D. *Angew. Chem.* **1994**, *106*, 2256; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2168.

(4) (a) Hanusa, T. P. *Chem. Rev.* **1993**, *93*, 1623. (b) Hanusa, T. P. *Organometallics* **2002**, *21*, 2559.

(5) Harder, S.; Prosenc, M. H. *Angew. Chem.* **1994**, *106*, 1830; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744.

(6) Conejo, M. M.; Fernández, R.; Gutiérrez-Puebla, E.; Monge, Á.; Ruiz, C.; Carmona, E. *Angew. Chem.* **2000**, *112*, 2025; *Angew. Chem., Int. Ed.* **2000**, *39*, 1949.

(7) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem.* **1993**, *105*, 1714; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655.

(8) (a) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (b) Brigdeman, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2887. (c) Hollis, T. K.; Burdett, J. K.; Bosnich, B. *Organometallics* **1993**, *12*, 3358. (d) Kaupp, M.; Schleyer, P. R.; Dolg, M.; Stoll, H. *J. Am. Chem. Soc.* **1992**, *114*, 8202. (e) Timofeeva, T. V.; Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1995**, *117*, 7452.

(9) For CaCp^*_2 α amounts to 154° : Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Volden, H. V. *Acta Chem. Scand.* **1987**, *A41*, 24.

(10) For SrCp^*_2 α amounts to 149° : Anderson, R. A.; Blom, R.; Burns, C. J.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1987**, 768.

(11) For BaCp^*_2 α amounts to 148° : Blom, R.; Faegri, K., Jr.; Volden, H. V. *Organometallics* **1990**, *9*, 372.

(12) Williams, R. A.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1990**, *9*, 1128.

(13) For SrCp^*_{31} ($\text{Cp}^*_{31} = 1,2,4\text{-triisopropylcyclopentadienyl}$) a THF-containing species has been characterized: Burkey, D. J.; Hanusa, T. P. *Acta Crystallogr.* **1996**, *C52*, 2452.

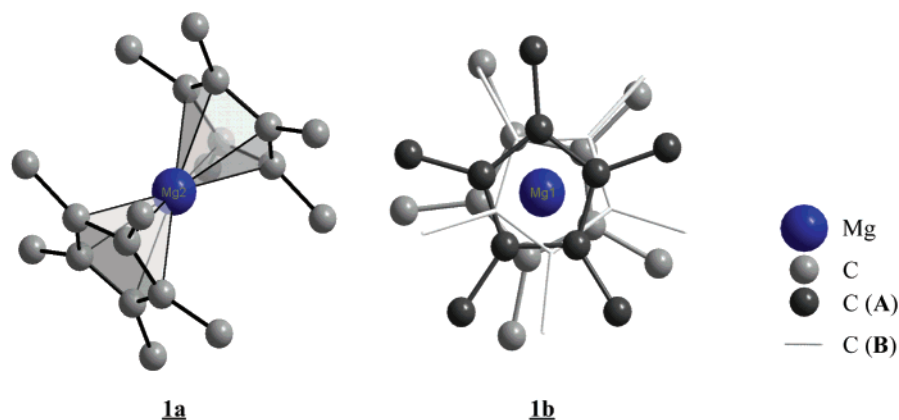


Figure 2. Structure of MgCp^*_2 (**1**) with H atoms omitted. The two crystallographically independent conformers **1a** and **1b** are illustrated. In the case of **1b** two different disordered species, **A** (80%) and **B** (20%), are present (cf. text).

plexes. Therefore, it is not surprising that 17 years ago the gas-phase structure of **1** was determined by electron diffraction.¹⁶ However, under the conditions applied in these experiments (160 °C), only an average molecular structure was obtained. Due to the expected weak bonds which allow facile rotation and bending motions of the Cp^* ligands, a more detailed look into the structural data is only possible with the help of a crystal structure. For a systematic structural discussion it is therefore absolutely necessary to fill the gap of the missing crystal structure of **1**. For us, these investigations have been a special challenge, since about 10 years ago we described the preparation and structure of the isoelectronic $[\text{AlCp}^*_2]^+$ ion,^{7,17} and about 3 years later we were able to prepare an unusual compound containing two different valence isoelectronic sandwich species $[\text{LiCp}^*_2]^-$ (Cp^b = pentabenzylcyclopentadienyl) and $[\text{AlCp}^*_2]^+$ in the same crystal¹⁸ exhibiting the expected elongated distances between the Cp^b rings in the $[\text{LiCp}^*_2]^-$ compound of 380 pm in comparison to 356 pm between the Cp^* rings in $[\text{AlCp}^*_2]^+$. In the following, the valence isoelectronic neutral species MgCp^*_2 (**1**) in the solid state is presented and discussed.

Though **1** is commercially available, we prepared this compound using the methods described by Jutzi¹⁹ and Lappert.²⁰ Since **1** has been well characterized in solution, e.g. via NMR spectroscopy, we will concentrate only on the crystal structure determination. From the reaction mixture of MgBu_2 and Cp^*H in *n*-heptane, well-shaped crystals are obtained which, however, have to be handled with caution: e.g., the transparent colorless crystals rapidly turn opaque when transferred to the diffractometer. Therefore, the crystals were picked from the cooled solution and rapidly fixed on the goniometer head under a stream of cooled nitrogen. Many experi-

ments were necessary to get a suitable data set for a proper structure determination.²¹

The crystals of **1** belong to the monoclinic system ($P2_1/c$) with $1\frac{1}{2}$ molecules of **1** in the asymmetric unit: i.e., there are two different species of **1**, for which we will use the notation **1a** and **1b** in the following. The first species, **1a** ($\text{Mg}2$), features the magnesium atom on a center of inversion and therefore with **1** in a staggered conformation ($\beta = 36^\circ$). For the second molecule, **1b** ($\text{Mg}1$), all atoms are located on general positions: i.e., no symmetry relation exists. For this conformer **1b** two different disordered species **A** (80%) and **B** (20%) are present. In Figure 2, the molecular structure of **1a** is shown. The average $\text{Mg}-\text{C}$ distance is 230.5 pm, with minimum and a maximum values of 230.0 and 230.8 pm, respectively. For the completely disordered species of **1b** the situation is more difficult to describe. A projection along the $\text{X}-\text{Mg}-\text{X}$ direction (X is the center of the Cp^* ring) is presented in Figure 2, exhibiting one fixed (gray C atoms) and one disordered Cp^* ring: i.e., the two conformers of **1b**, **A** (80%, dark C atoms) and **B** (20%, only white sticks). A closer inspection of the space-filling model of **1b** reveals differences of the surrounding atoms for the fixed and disordered Cp^* rings (**A/B**): i.e., there is less interaction for the latter, which favors the possibility of the presence of different orientations of Cp^* ring moieties in this environment.²²

For each conformer of **1b** the fixed Cp^* ring exhibits $\text{Mg}-\text{C}$ distances of 230.2 pm (minimum/maximum 229.6(2)/230.4(2) pm). The position of the fixed Cp^* ring in relation to the second Cp^* ring is also evident from Figure 2: the conformer **A** can be described as a nearly staggered species ($\bar{\beta} = 23.6^\circ$) and the conformer **B** ($\bar{\beta} = 11.9^\circ$) as between eclipsed and staggered. $\bar{\beta}$ is the average stagger angle between $\text{C}-\text{X}-\text{X}'-\text{C}'$ of two different Cp^* rings (Figure 1, part 2).

The different arrangement within the two conformers of **1** (**1a** and **1b** (**A/B**)) in the same crystal casts a light

(14) Haaland, A.; Luszyk, J.; Brunvoll, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1975**, *85*, 279.

(15) Bänder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.

(16) Andersen, R. A.; Blom, R.; Boncella, J. M.; Burns, C. J.; Haaland, A.; Volden, H. V. *J. Organomet. Chem.* **1986**, *312*, C49.

(17) Nearly 10 years after our first detection and description of some spectroscopic properties and structural data of $[\text{AlCp}^*_2]^+$, a more thorough discussion appeared recently: Schurko, R. W.; Hung, I.; Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 13204.

(18) Dohmeier, C.; Baum, E.; Ecker, A.; Köppe, R.; Schnöckel, H. *Organometallics* **1996**, *15*, 4702.

(19) (a) Kohl, F. X.; Jutzi, P. *Chem. Ber.* **1981**, *114*, 489. (b) Whitesides, M. G.; Feitler, D. *Inorg. Chem.* **1976**, *15*, 466.

(20) Duff, W. A.; Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G.; Segal, J. A. *J. Organomet. Chem.* **1985**, *293*, 271.

(21) Crystal data for **1**: $\text{C}_{20}\text{H}_{30}\text{Mg}$, fw 294.75, space group $P2_1/c$, $a = 9.9027(8)$ Å, $b = 12.7901(8)$ Å, $c = 23.028(2)$ Å, $\beta = 90.578(11)^\circ$, $Z = 6$, $V = 2916.4(4)$ Å³, $D_{\text{calc}} = 1.007$ g cm⁻³, $T = 200(2)$ K, Mo $K\alpha$ radiation, graphite monochromator, Stoe-IPDS area detector, 12 147 reflections, 4472 unique ($R_{\text{int}} = 0.0473$), structure solution by direct methods, refinement on F^2 ($2\theta_{\text{max}} = 47.96^\circ$), H atoms calculated, 326 parameters, $R1$ ($I > 2\sigma(I)$) = 0.0518, $wR2$ (all data) = 0.1495, GOF (F^2) = 0.964; computer programs SHELXS-97, SHELXL-97, Stoe IPDS-software.

(22) For a more detailed look at the closest contacts, see the Supporting Information.

on the soft dynamics within **1**, which can even be influenced by the very weak lattice forces. In the series BeCp^*_2 , $[\text{AlCp}^*_2]^+$, and MgCp^*_2 , with increasing distances between the Cp^* rings (from 331 pm through 355 pm to 394 pm),²³ the differences between the energies of the conformers (D_{5h} , D_{5d}) decrease. For the unsubstituted species differences of only 0.5 kJ mol⁻¹ for $[\text{AlCp}_2]^+$ and 0.1 kJ mol⁻¹ for MgCp_2 have been calculated.⁷ For the idealized conformers of **1** with D_{5d} and D_{5h} structures we calculate an energy difference of 1.3 kJ mol⁻¹ in comparison with 1.8 kJ mol⁻¹ for $[\text{AlCp}^*_2]^+$.²⁴

The weak interaction between the two Cp^* rings in **1** is also in line with a small deviation from planarity of the $\text{C}_5(\text{CH}_3)_5$ ring moiety ($\bar{\gamma} = 1.8^\circ$ for **1a**, 1.6° for the fixed Cp^* ring, and 3.0° for the disordered Cp^* (**A**) ring of **1b**).²⁵ $\bar{\gamma}$ is the average out-of-plane angle between the methyl group and the Cp plane (Figure 1, part 3). In $[\text{AlCp}^*_2]^+$ also a slight deviation of the methyl groups of $\bar{\gamma} = 2^\circ$ ²⁶ from the ring plane was found, although herein the Al–ring distance is shorter.²⁷

Concerning the possible change of the tilt angle α from 180° (cf. Figure 1), only the slightly larger Mg–C distances in the conformer **B** point to the direction of a possibly easier distortion of the X–M–X moiety (X being the centers of the Cp^* rings). However, the solid-state

structure of **1** described here gives no hint of a bent minimum structure like that observed for the solid CaCp^*_2 ²⁸ and BaCp^*_2 ²⁹ analogues. For heavier element containing compounds such as CaCp^*_2 ,⁹ SrCp^*_2 ,¹⁰ and BaCp^*_2 ¹¹ also in the gaseous state bent structures have been determined and confirmed by ab initio calculations.³⁰ Furthermore, for these compounds the greater M–C distances together with the bent structures of the MCp^*_2 molecules provide interactions with further Cp^* rings of other MCp^*_2 moieties in the solid state. Thus, concerning the tilt angle α , our results for **1** (even in the solid state) are in line with the calculated^{8c} and experimentally¹⁶ determined data for the isolated gaseous molecules.

However, this detailed look into the solid-state structure of **1** shows the expected weak interactions between the two Cp^* rings of **1** (with respect to the staggered angle β and the out-of-plane angle γ), which can easily be influenced by weak lattice forces. Therefore, it seems not surprising that, for example, only the average value of β in **1b** (**A**) is very close to that predicted by Burdett for the isolated molecule, while for the other conformer a value of $\beta = 11.9^\circ$ is estimated.^{8c} However, our results also show that the accuracy of these and many other X-ray structure determinations (especially for Cp compounds) has to be substantially improved (e.g. by synchrotron radiation, by measurements at very low temperatures) in order to get a more detailed insight into the soft dynamics and possibly into the electronic structure (via experimental electron density) of molecules such as **1**.

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Supporting Information Available: Lists of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **1** and additional figures presenting space-filling models from the fixed and the disordered Cp^* ring and their surrounding atoms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(28) For CaCp^* α amounts to 147.7 and 146.3° (there are two symmetrically independent molecules) and the X–M–X distance is about 472 pm (for both molecules).¹²

(29) For BaCp^*_2 α amounts to 130.9 and 131.0° (there are two symmetrically independent molecules) and the X–M–X distances are about 546 and 548 pm, respectively.¹²

(30) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Green, J. C.; Hohl, D.; Rosch, N. *J. Chem. Soc., Chem. Commun.* **1986**, 405.

(23) This distance for **1** is equal to that found in the sterically less demanding $\text{Mg}(\text{C}_5\text{Me}_4\text{H})_2$: 394 pm. Schumann, H.; Gottfriedsen, J.; Glanz, M.; Dechert, S.; Dementschuk, J. *J. Organomet. Chem.* **2001**, 617/618, 588.

(24) The quantum-chemical (DFT) calculations relied on the TURBOMOLE program package. The BP method with the SVP basis set was used for all elements. Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, 162, 165. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, 240, 283. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, 242, 652. Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. *Theor. Chem. Acta* **1997**, 97, 119. Weigend, F.; Häser, M. *Theor. Chem. Acta* **1997**, 97, 331. Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, 294, 143.

(25) All angles were determined with the tool kits *Angles* and *Torsion Angles* from the DIAMOND program package (version 2.1d, Crystal Impact GbR, 1996–2000). For the determination of the torsion angles we used a dummy atom located at the Cp ring centroid.

(26) Dohmeier, C. Dissertation, TU München, 1994.

(27) Obviously the value of the $\bar{\gamma}$ angle does not only reflect the Cp^* ring interaction caused by the different distances between the two Cp^* moieties in these compounds. In addition, for geometric reasons the different values of $\bar{\gamma}$ are caused by the specified electronic behavior of the central metal atom and its interaction with the orbital of the Cp^* ring. The predicted negative value of $\bar{\gamma}$ (bending of methyl groups in the direction of the metal) has been experimentally confirmed for the $[\text{Cp}^*\text{BBr}]^+$ cation. A recent analysis of our previously obtained data shows that $\bar{\gamma} = -6^\circ$ and not $\bar{\gamma} = -3.9^\circ$ as published in: Dohmeier, C.; Köppe, R.; Robl, C.; Schnöckel, H. *J. Organomet. Chem.* **1995**, 487, 127.