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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, $Mg(C_5Me_5)_2$ (**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 = Ca, Sr, Ba) as determined in the gas phase or in the solid state. Structural trends of **1** in comparison to the isoelectronic species $[LiCp^*_2]^-$, $BeCp^*_2$, and $[AlCp^*_2]^+$ 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 $[Cp_2Li]^-$,[5] $BeCp^*_2$,[6] and the aluminocenium cation, $[AlCp^*_2]^+$.[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 = Ca, Sr, Ba),[9−11] exhibiting nonparallel rings even in the gas phase (Figure 1).

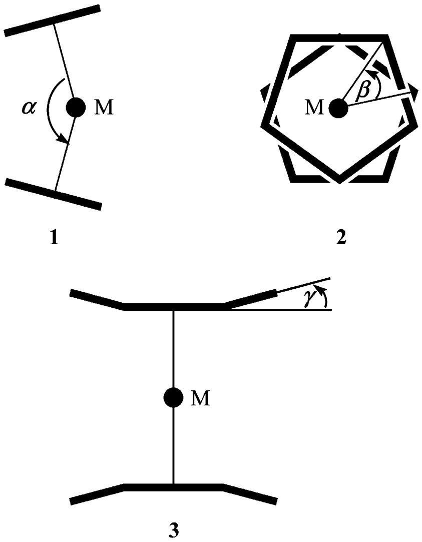

Figure 1. Schematic illustration of the structural parameters for permethylated alkaline-earth metallocenes: (1) definition of the tilt angle, α; (2) definition of the stagger angle, β; (3) definition of the out-of-plane angle, γ.

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 phase[14] as well as in the solid phase[15]—may be considered a parent compound of main-group sandwich com-

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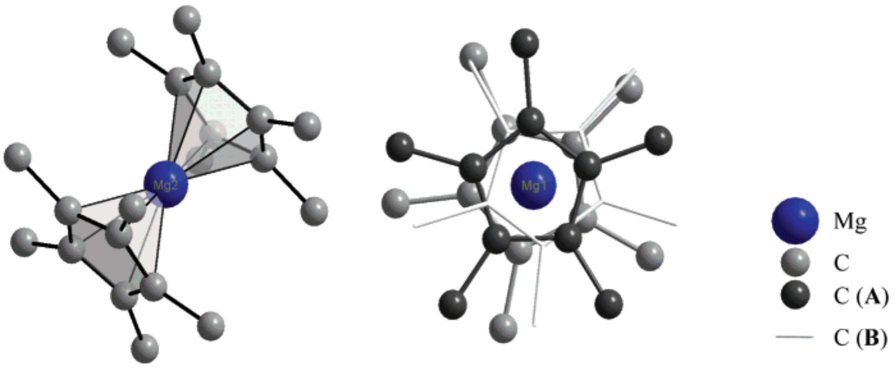
[11] For $BaCp^*_2$ α amounts to 148°: Blom, R.; Faegri, K., Jr.; Volden, H. V. *Organometallics* **1990**, *9*, 372.

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

[13] For $SrCp^{3i}_2$ (Cp^{3i} = 1,2,4-triisopropylcyclopentadienyl) a THF-containing species has been characterized: Burkey, D. J.; Hanusa, T. P. *Acta Crystallogr.* **1996**, *C52*, 2452.

10.1021/om0301031 CCC: $25.00



1a **1b**

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 $[AlCp^*_2]^+$ ion,[7,17] and about 3 years later we were able to prepare an unusual compound containing two different valence isoelectronic sandwich species $[LiCp^b_2]^-$ (Cp^b = pentabenzylcyclopentadienyl) and $[AlCp^*_2]^+$ in the same crystal[18] exhibiting the expected elongated distances between the Cp^b rings in the $[LiCp^b_2]^-$ compound of 380 pm in comparison to 356 pm between the Cp* rings in $[AlCp^*_2]^+$. 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 Jutzi[19] 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 experiments 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 $1^1/_2$ 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** (Mg2), features the magnesium atom on a center of inversion and therefore with **1** in a staggered conformation ($\beta = 36°$). For the second molecule, **1b** (Mg1), 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 Mg−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 X−Mg−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 Mg−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 ($\bar{\beta} = 23.6°$) and the conformer **B** ($\bar{\beta} = 11.9°$) as between eclipsed and staggered. $\bar{\beta}$ is the average stagger angle between C−X−X′-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

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[17] Nearly 10 years after our first detection and description of some spectroscopic properties and structural data of $[AlCp^*_2]^+$, 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.

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[21] Crystal data for **1**: $C_{20}H_{30}Mg$, fw 294.75, space group $P2_1/c$, $a = 9.9027(8)$ Å, $b = 12.7901(8)$ Å, $c = 23.028(2)$ Å, $\beta = 90.578(11)°$, $Z = 6$, $V = 2916.4(4)$ Å^3, $D_{calcd} = 1.007$ g cm^{-3}, $T = 200(2)$ K, Mo Kα radiation, graphite monochromator, Stoe-IPDS area detector, 12 147 reflections, 4472 unique ($R_{int} = 0.0473$), structure solution by direct methods, refinement on F^2 ($2\theta_{max} = 47.96°$), 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 $BeCp^*_2$, $[AlCp^*_2]^+$, 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 $[AlCp_2]^+$ 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 $[AlCp^*_2]^+$.[24]

The weak interaction between the two Cp* rings in **1** is also in line with a small deviation from planarity of the $C_5(CH_3)_5$ ring moiety ($\bar{\gamma} = 1.8°$ 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 $[AlCp^*_2]^+$ also a slight deviation of the methyl groups of $\bar{\gamma} = 2°$ [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 experimentally[16] 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 $\bar{\beta}$ in **1b** (**A**) is very close to that predicted by Burdett for the isolated molecule, while for the other conformer a value of $\bar{\beta} = 11.9°$ 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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(23) This distance for **1** is equal to that found in the sterically less demanding $Mg(C_5Me_4H)_2$: 394 pm. Schumann, H.; Gottfriedsen, J.; Glanz, M.; Dechert, S.; Demtschuk, J. *J. Organomet. Chem.* **2001**, *617/618*, 588.

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(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 $[Cp^*BBr]^+$ cation. A recent analysis of our previously obtained data shows that $\bar{\gamma} = -6°$ and not $\bar{\gamma} = -3.9°$ as published in: Dohmeier, C.; Köppe, R.; Robl, C.; Schnöckel, H. *J. Organomet. Chem.* **1995**, *487*, 127.

(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]

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