# *Notes*

## Polymeric and Monomeric Barocene: Synthesis and Structure of $Ba(C_5H_5)_2 \cdot DMSO$ and $Ba(C_5H_5)_2$(18-crown-6) (DMSO = dimethylsulfoxide)

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*Summary: Dicyclopentadienylbarium,* $Ba(C_5H_5)_2$, *crystallizes from dimethyl sulfoxide in a polymeric form with four* $C_5H_5^-$ *groups surrounding tetrahedrally the central* $Ba^{2+}$ *ion; the reaction of* $Ba(C_5H_5)_2$ *with 18-crown-6 affords monomeric* $Ba(C_5H_5)_2$*(18-crown-6) with two axial* $C_5H_5^-$ *rings and an equatorial 18-crown-6 ligand at the central* $Ba^{2+}$ *ion.*

### Introduction

The solid-state structures of all cyclopentadienyl alkali metal compounds, $MC_5H_5$, have been established by X-ray diffraction methods. In the polymeric infinite multidecker structure of $LiC_5H_5$ and $NaC_5H_5$ the cyclopentadienyl rings show a parallel arrangement, whereas in $KC_5H_5$, $RbC_5H_5$, and $CsC_5H_5$ bent units are observed.[1] The alkaline earth metallocenes, $M(C_5H_5)_2$, exhibit a greater diversity in their solid-state structures. Beryllocene, $Be(C_5H_5)_2$, shows a unique “slip sandwich” structure with one ligand $\eta^5$- and the other $\eta^1$-bound to beryllium.[2] Magnesocene, $Mg(C_5H_5)_2$, adopts the normal ferrocene-type $D_{5d}$ structure.[3] In contrast, $Ca(C_5H_5)_2$ exhibits a polymeric structure with four inequivalent bridging $C_5H_5$ rings surrounding the calcium ion.[4] The solid-state structures of the heavier bis(cyclopentadienyl) alkaline earth metal compounds, $Sr(C_5H_5)_2$ and $Ba(C_5H_5)_2$, are unknown. The substituted derivatives of strontocene and barocene, $Ba(C_5Me_5)_2$, $Ba[C_5H(i\text{-Pr})_4]_2$, $Sr[C_3H_2(SiMe_3)_3]_2$, and $Ba[C_3H_2(SiMe_3)_3]_2$, show a nonparallel arrangement of the two five-membered rings attached to the central $Sr^{2+}$ or $Ba^{2+}$ ion, whereas in the sterically strained compound $Ba[C_5(i\text{-Pr})_5]_2$ the normal ferrocene-type structure is realized.[5,6]

In this study, we present the solid-state structure of the heaviest alkaline earth metallocene, $Ba(C_5H_5)_2$ (containing dimethyl sulfoxide not coordinated to barium), and the reaction of $Ba(C_5H_5)_2$ with the polydentate ligand 18-crown-6.

### Results and Discussion

Pure barocene, $Ba(C_5H_5)_2$ (**1**), can be made by cocondensation of cyclopentadiene and barium at −196 °C.[7] More convenient is the preparation of $Ba(C_5H_5)_2$ from $LiC_5H_5$ and $BaI_2$ in tetrahydrofuran (THF). But this synthesis yields only crude $Ba(C_5H_5)_2$ (ca. 80%) containing both $LiC_5H_5$ and LiI besides some THF.[8] We synthesized $Ba(C_5H_5)_2$ by reacting barium bis-hexamethyldisilazide, $Ba[N(SiMe_3)_2]_2$, with cyclopentadiene in toluene following a procedure of Hanusa.[9] The barocene thus obtained is not completely pure but contains small amounts of the hexamethyldisilazide anion (ca. 2 mol %), which can be seen from $^1H$ NMR spectroscopy (small singlet at $\delta = -0.10$ ppm) and elemental analysis (nitrogen percentage 0.4%). Barocene forms a very air-sensitive, white fine powder that is insoluble in tetrahydrofuran, toluene, and hexane but soluble in dimethyl sulfoxide (DMSO). The stoichiometry was ascertained by elemental analysis and NMR spectroscopy. The $^1H$ NMR spectrum in DMSO-$d_6$ shows a singlet at 5.51 ppm. As the uncoordinated $C_5H_5^-$ ring exhibits its resonance at 5.30 ppm[10] in DMSO, the cyclopentadienyl ring remains bound to barium in solution. We think that the polymeric structure of $Ba(C_5H_5)_2$ is broken up to yield a mononuclear complex of the form $[(C_5H_5)_2Ba(DMSO)_n]$ in DMSO solution. Complexes of this type with two substituted cyclopentadienyl rings were already described in the literature.[11]

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[10] The compound $[Mg(DMSO)_6]^{2+}(C_5H_5^-)_2$, which contains uncoordinated cyclopentadienyl rings, shows a $^1H$ NMR and $^{13}C$ NMR resonance at 5.30 and 104.4 ppm, respectively, in DMSO-$d_6$ solution: Jaenschke, A.; Paap, J.; Behrens, U. *Organometallics* **2003**, *22*, 1167.

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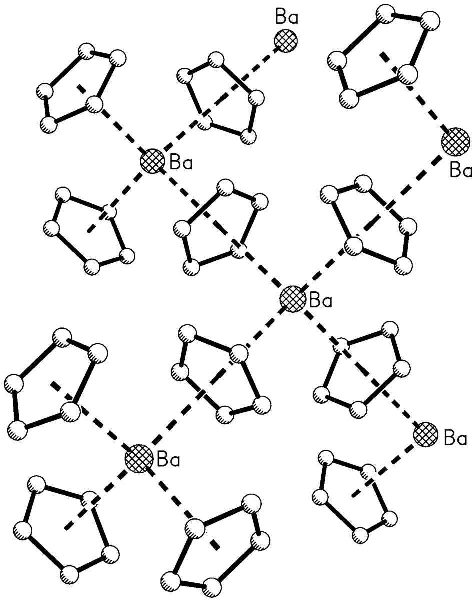

**Figure 1.** View of the polymeric structure of $Ba(C_5H_5)_2$·DMSO (**1**·DMSO). DMSO molecules that are in voids of the structure, disorder of the $C_5H_5$ rings, and H atoms are not shown. Selected bond lengths (pm) and angles (deg): Ba−C 313.8(6)−316.4(5), Ba−($\eta^5$-$C_5H_5$) 291.8(3); ($\eta^5$-$C_5H_5$)−Ba−($\eta^5$-$C_5H_5$) 108.9(3)−110.1(3).

In the $^{13}C$ NMR spectrum of $Ba(C_5H_5)_2$ the signal due to the $C_5H_5$ ring is observed at 106.5 ppm. An uncoordinated $C_5H_5^-$ ring would resonate at 104.4 ppm.[10] When the reaction of $Ba[N(SiMe_3)_2]_2$ with cyclopentadiene is carried out in THF, the $Ba(C_5H_5)_2$ precipitated contains small amounts of THF (ca. 0.2 THF per Ba) that cannot be removed by washing the product with hexane.

We were able to crystallize $Ba(C_5H_5)_2$ (**1**) from DMSO, getting crystals of the composition $Ba(C_5H_5)_2$·DMSO (**1**·DMSO). The structure was determined by X-ray diffraction and is illustrated in Figure 1, where relevant bond lengths and angles are also given. $Ba(C_5H_5)_2$·DMSO crystallizes in the orthorhombic space group *Fddd* with lattice parameters *a*, *b*, *c* that are almost equal. Indeed, the structure could also be refined in the cubic space group *Fd−3* or *Fd−3m* leading to *R* values better than 0.04. But as the lattice parameters differ significantly from each other, we decided to refine the structure in the space group *Fddd* (final *R* value 0.028). The barium atom is located on a special position ($^1/_8$, $^1/_8$, $^1/_8$) and is tetrahedrally surrounded by four $\eta^5$-coordinated $C_5H_5$ rings that show a 2-fold rotational disorder. Each $C_5H_5$ ring is bound to two Ba atoms. Thus a three-dimensional polymeric array is built up by the Ba atoms and the $C_5H_5$ rings (Figure 1), which is analogous to the ideal $\beta$-cristobalite (high-temperature form of $SiO_2$) structure. The DMSO molecules that are not coordinated to barium are in voids of the structure and are disordered (the average Ba···DMSO (midpoint) distance is 584.5 pm). The Ba−C bond lengths are quite similar and vary from 313.8(6) to 316.4(5) pm. The Ba−$C_5H_5$(midpoint) distance is 291.8(3) pm. The $C_5H_5$−Ba−$C_5H_5$ angles are between 108.9(3)° and 110.1(3)°. There is only a second X-ray structure determination of a barium compound with an unsubstituted $C_5H_5$ ligand, $[PBu_4]^+[Ba(C_5H_5)_3]^-$. The structure solution of the barate anion $[Ba(C_5H_5)_3]^-$ revealed a linear infinite chain with tetrahedrally coordinated barium and bridging and end-on $\eta^5$-coordinated $C_5H_5$ rings.[12] The barium−bridging cyclopentadienyl ring distance is 291.6(6) pm. Thus almost the same value is found as in our $Ba(C_5H_5)_2$·DMSO compound. It should be mentioned that DFT calculations at the BP86 level for monomeric bent $Ba(C_5H_5)_2$ resulted in a Ba−$C_5H_5$(midpoint) distance of only 271.9 pm.[13] Indeed, for the bent substituted derivatives of $Ba(C_5H_5)_2$ Ba−ring distances around 270 pm are found.[5a,b]

X-ray powder investigations were carried out with barocene obtained from the reaction of $Ba[N(SiMe_3)_2]_2$ with cyclopentadiene in toluene (powder **1a**) and in THF (powder **1b**). Both samples were heated to 200 °C for 5 h before taking the diffractograms at 100 K. Powder **1b**, which contains small amounts of THF (ca. 0.2 THF per Ba), gives an X-ray powder diagram that is quite similar to the calculated powder diffractogram of $Ba(C_5H_5)_2$·DMSO and identical to the calculated powder diagram of $Ba(C_5H_5)_2$ (DMSO solvent not taken into account). Hence the barocene prepared from THF crystallizes in the cubic $\beta$-cristobalite structure. The barocene prepared from toluene (powder **1a**) gives rather broad reflections in the X-ray diffractogram that shows no similarities to the calculated powder diagram of $Ba(C_5H_5)_2$·DMSO.

Treatment of barocene (**1**) with the crown ether 18-crown-6 in DMSO yields the monomeric complex $[Ba(C_5H_5)_2(18\text{-crown-}6)]$ (**2**). Compound **2** forms air-sensitive, colorless crystals that are insoluble in toluene and THF but soluble in pyridine and DMSO. The stoichiometry was ascertained by X-ray powder diffractometry and NMR spectroscopy. An experimental X-ray powder diagram of **2** is totally similar to the calculated powder diffractogram from the single-crystal investigation. The $^1H$ NMR spectrum in DMSO-$d_6$ shows a singlet at 3.59 ppm due to the crown ether ligand and a singlet at 5.52 ppm due to the coordinated $C_5H_5$ rings. In the $^{13}C$ NMR spectrum the signal due to the $C_5H_5$ ring is observed at 106.6 ppm (crown ether signal at 70.4 ppm).

Single crystals of complex **2** could be obtained from a DMSO solution. The structure was determined by X-ray diffraction (Figure 2) and could be well refined in the orthorhombic space group *Cmca* (final *R* value 0.023). The barium atom is located on a special position ($^1/_2$, $^1/_2$, $^1/_2$), which would require $C_{2h}$ symmetry for the molecule. However, as only $C_i$ symmetry is present in the molecule, it shows a 2-fold disorder in the crystal structure. Compound **2** exhibits a hexagonal-bipyramidal environment for the barium center with the two $C_5H_5$ rings at the top and bottom of the bipyramid. The center of symmetry at barium requires a *trans* angle of 180°. The six oxygen atoms of the 18-crown-6 ligand are arranged alternatively above and below the equatorial plane by 16 pm. The average barium−oxygen and barium−$C_5H_5$(carbon) separations are 280.0 and 321.7 pm, respectively. The Ba−$C_5H_5$(midpoint) distance is 298.6(2) pm and therewith longer than in $Ba(C_5H_5)_2$

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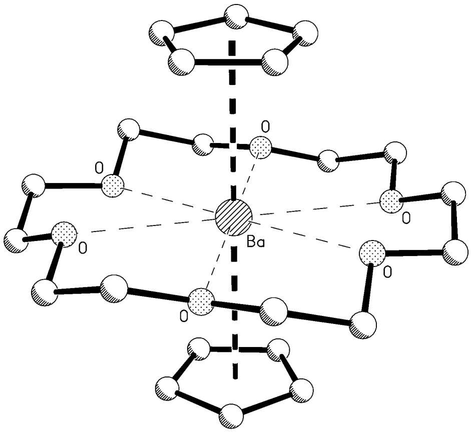

**Figure 2.** View of the molecular structure of $[Ba(C_5H_5)_2$-(18-crown-6)] (**2**). Disorder of the crown ligand, disorder of the $C_5H_5$ rings, and H atoms are not shown. Selected bond lengths (pm) and angles (deg): Ba−C 318.0(6)−325.7(7), Ba−($\eta^5$-$C_5H_5$) 298.6(2), Ba−O 277.3(4)−283.7(4); ($\eta^5$-$C_5H_5$)−Ba−($\eta^5$-$C_5H_5$) 180.0.

(**1**) (291.8(3) pm). For linear monomeric $Ba(C_5H_5)_2$ a Ba−$C_5H_5$ bond length of only 274.1 pm was calculated (DFT calculations).[13] Indeed, the complex $Ba[C_5(i\text{-Pr})_5]_2$, with two parallel arranged five-membered rings, shows a Ba−ring distance of 274.8(2) pm.[5c] There is only a second X-ray structure determination of a complex of the type $[BaR_2$(18-crown-6)] where R is an anionic organyl ligand. In the compound $[Ba(\eta^1\text{-}C{\equiv}CSiPh_3)_2$(18-crown-6)] the average Ba−O and Ba−C bond lengths are 279.9 and 285.2 pm. The C−Ba−C angle is 162.7°.[14]

## Experimental Section

Barium metal, hexamethyldisilazane, and dicyclopentadiene were purchased from Merck. All manipulations were performed using conventional Schlenk techniques under an atmosphere of argon. Solvents were dried, distilled, and degassed before use. Instrumentation: Infrared: Perkin-Elmer FT-IR PE 1720. NMR: Samples were dissolved in dried DMSO-$d_6$ (Varian Gemini-2000 and Bruker Avance 400). X-ray powder diffractometry: Samples were measured in glass capillaries (Debye−Scherrer mode) with Cu K$\alpha_1$ radiation using a Ge(111) monochromator (StadiP, Stoe & Cie GmbH).

The precursor barium bis(hexamethyldisilazide)·2THF was prepared by a standard literature method.[15]

**Synthesis of $Ba(C_5H_5)_2$ (1) and $Ba(C_5H_5)_2$·DMSO (1·DMSO).** To a solution of 1.33 g (2.2 mmol) of barium bis(hexamethyldisilazide)·2THF in 20 mL of tetrahydrofuran or toluene was added 0.33 g (5.0 mmol) of cyclopentadiene (freshly distilled). A fine, white precipitate was obtained, which was washed several times with *n*-hexane and dried in a vacuum. Yield: quantitative. The barocene (**1**) obtained from THF contains small amounts of THF (ca. 0.2 THF per Ba). Barocene obtained from toluene contains small amounts of the hexamethyldisilazide anion (ca. 2 mol %). Compound **1** is insoluble in tetrahydrofuran, toluene, and hexane but easily soluble in DMSO. Solutions in DMSO turn from light yellow to dark red within several days. Red crystals of $Ba(C_5H_5)_2$·DMSO were obtained after two weeks by putting a layer of toluene onto a concentrated solution of barocene in DMSO. $^1$H NMR (200 MHz, DMSO-$d_6$): $\delta$ 5.51 (s, $C_5H_5$) ppm. $^{13}$C NMR (50.3 MHz; DMSO-$d_6$): $\delta$ 106.5 ($C_5H_5$) ppm. IR (Nujol): $\nu$ 3088, 1592, 1075, 1011, 916, 743 cm$^{-1}$. Anal. Found (barocene (**1**) from toluene): C 44.1, H 3.8, N 0.4. Calc:C 44.9, H 3.8, N 0.0.

**Synthesis of $Ba(C_5H_5)_2$(18-crown-6) (2).** To 0.22 g (0.82 mmol) of $Ba(C_5H_5)_2$ (**1**) in 3 mL of DMSO was added under stirring a solution of 2.12 g (8.0 mmol) of 18-crown-6 in 5 mL of DMSO. After filtering, 40 mL of toluene was added to the solution in order to precipitate the product. The fine gray powder obtained was washed several times with *n*-hexane and dried in a vacuum. Yield: 0.10 g (0.19 mmol), 23%. The flesh-colored $Ba(C_5H_5)_2$(18-crown-6) (**2**) is easily soluble in DMSO and a little in pyridine, but insoluble in THF, diethyl ether, toluene, and hexane. Colorless crystals of $Ba(C_5H_5)_2$(18-crown-6) (**2**) were obtained from a dark red concentrated solution of barocene and 18-crown-6 (slight excess) in DMSO after two weeks at 20 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 5.52 (s, 10H, $C_5H_5$), 3.59 (s, 24H, $CH_2$) ppm. $^{13}$C NMR (100.6 MHz; DMSO-$d_6$): $\delta$ 106.6 ($C_5H_5$), 70.4 ($CH_2$) ppm. IR (Nujol): $\nu$ 3074, 1592, 1344, 1308, 1283, 1244, 1153, 1114, 1093, 1007, 984, 956, 831, 715 cm$^{-1}$. Anal. Found: C 44.3, H 5.8, O 19.9. Calc: C 49.7, H 6.4, O 18.1. No consistent elemental analysis was obtained for complex **2**. The difficulty in getting accurate combustion analyses seems to be typical of several types of alkaline earth compounds.[9b,16]

**X-ray Structure Determination of 1·DMSO and 2.** In the syntheses of **1**·DMSO and **2** crystals suitable for X-ray crystal structural analysis were obtained. The crystals were mounted on glass fibers in rapidly cooled mineral oil. Full spheres of diffraction data were measured at 153 K using a Bruker AXS CCD area detector instrument.

**Crystal data for 1·DMSO:** $C_{12}H_{16}BaOS$, $M = 345.65$, orthorhombic, space group *Fddd*, $a = 1346.08(6)$ pm, $b = 1347.07(6)$ pm, $c = 1350.76(6)$ pm, $U = 2449.3(2)$ Å$^3$, $Z = 8$, $D_c = 1.875$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 3.385 mm$^{-1}$. Bruker SMART-CCD diffractometer (2$\theta$ limit 55.0°). Crystal dimensions: 0.26/0.24/0.17 mm, 1028 observed data [$I > 2\sigma(I)$] of 1097 independent data measured ($T = 153$ K). Refinement (on $F^2$) to $R_1 = 0.028$ and $wR_2 = 0.063$. No. of refined parameters: 61. For **2**: $C_{22}H_{34}BaO_6$, $M = 531.83$, orthorhombic, space group *Cmca*, $a = 1224.30(10)$ pm, $b = 1353.05(11)$ pm, $c = 1359.70(11)$ pm, $U = 2252.4(3)$ Å$^3$, $Z = 4$, $D_c = 1.568$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 1.797 mm$^{-1}$. Bruker SMART-CCD diffractometer (2$\theta$ limit 55.0°). Crystal dimensions: 0.12/0.07/0.07 mm, 911 observed data [$I > 2\sigma(I)$] of 1357 independent data measured ($T = 173$ K). Refinement (on $F^2$) to $R_1 = 0.023$ and $wR_2 = 0.052$. No. of refined parameters: 117. 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).[17] CCDC 240869/70.

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**Supporting Information Available:** X-ray crystallographic information for **1**·DMSO and **2**; experimental powder diffractograms for **1** (prepared from THF) and **2**, calculated powder diffractograms for **1**·DMSO, **1** (without DMSO), and **2**; CIF data for **1**·DMSO and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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