Solid-State Structures of Base-Free Rubidium and Cesium Pentamethylcyclopentadienides. Determination by High-Resolution Powder Diffraction

Ulrich Behrens,[†] Robert E. Dinnebier,[‡] Swen Neander,[†] and Falk Olbrich*[,†]

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6,
D-20146 Hamburg, Germany, and Max-Planck Institute for Solid State Research,
Heisenbergstrasse 1, D-70569 Stuttgart, Germany

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Summary: Powder diffractometry was carried out on the base-free salts MC_5Me_5 *(MCp*, M = K−Cs) at room temperature and at −120 °C. The powder patterns at room temperature and low temperature are identical for all compounds. The solid-state structures of RbCp* and CsCp* could be solved. Both compounds are isomorphous. They crystallize as "multidecker structures" in the form of polymeric zigzag chains.*

The investigation of the solid-state structures of the base-free salts MCp, MCp*, MInd, and MFl (M = Li−Cs; Cp = cyclopentadienide, Cp* = pentamethylcyclopentadienide, Ind = indenide, Fl = fluorenide), fundamental and highly important compounds in organometallic chemistry, is a very special challenge because nearly none of these compounds can be obtained in the form of single crystals suitable for single-crystal X-ray diffraction and therefore they cannot be structurally determined. Dimeric lithium fluorenide is the only exception.[1] The structures of all other salts were and are targets for investigations by powder diffraction methods, mostly with high-resolution synchrotron radiation. In this manner, the solid-state structures of MCp (M = Li−Cs),[2−4] MCp* (M = Li,[5] Na[6]), LiInd,[7] and NaFl[7] were solved. Now we continue our reports with some results on the alkali-metal pentamethylcyclopentadienides (MCp*), which were investigated for the metals potassium to cesium at room temperature and at −120 °C. It should be mentioned that the crystal structures of a few Lewis base adducts of these compounds were described in previous literature (i.e. $[NaCp^*(py)_3]$,[8] $[KCp^*(thf)_x]_n$ (x = 1, 2),[9] and [MCp*(18-crown-6)]·THF (M = K−Cs)[10,11]). A good review is given by Smith.[12]

Results and Discussion

The reaction of the alkali metals potassium, rubidium, and cesium with pentamethylcyclopentadiene in toluene (K, Rb) or tetrahydrofuran (Cs) yielded colorless, air-sensitive, microcrystalline powders. All samples were characterized by X-ray powder diffraction experiments at room temperature with synchrotron radiation and at −120 °C on a conventional powder diffractometer. The powder patterns obtained did not indicate any phase transitions at different temperatures. The solution of the structure for KCp* (**1**) failed, while the solid-state structures of RbCp* (**2**) and CsCp* (**3**) could be deduced from the synchrotron data sets. Details are given in Figure 1 and Table 2. In addition, KCp* (**1**) was prepared by a second, alternative method from potassium hexamethyldisilazide and pentamethylcyclopentadiene in diethyl ether. Although the powder pattern obtained from this sample showed much less crystallinity, the comparison of both diagrams indicated an identical crystal structure (see the Supporting Information).

Rubidium pentamethylcyclopentadienide (**2**) and cesium pentamethylcyclopentadienide (**3**) are isomorphic, show an extreme pseudotetragonal symmetry (for details see the Supporting Information), and crystallize as so-called "multidecker structures" in the form of polymeric zigzag chains (Figure 1).

Two Cp^{*-} anions are bound asymmetrically in an η^5 mode to the metal ion. Unfortunately the data sets only allowed us to refine inaccurate M−C bond lengths between 2.93(2) and 3.54(2) Å (average 3.24(2) Å) for the rubidium compound **2** and 3.19(2)−3.52(2) Å (average 3.36(2) Å) for **3**. Each zigzag chain is surrounded by four neighboring polymeric chains (Figure 2). Methyl groups of the Cp^{*-} anions of the adjacent chains are arranged to the open side of the bent Cp*−M−Cp* fragment (Figure 3). The disorder of the Cp* rings, which are located on an inversion center of the space group chosen (*C*2/*c*), and the unreliable positions of the hydrogen atoms do not allow an exact specification of the methyl−metal interactions. Nevertheless, the coordination number of the metal cations in **2** and **3** can be given as 2.

The solid-state structures of **2** and **3** are comparable to those of the polymeric zigzag chains found in KCp,[2] β-RbCp,[3] and

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* To whom correspondence should be addressed. Fax: +49(0)40/42838-2893. E-mail: olbrich@chemie.uni-hamburg.de.

[†] Universität Hamburg.

[‡] Max-Planck Institute for Solid State Research.

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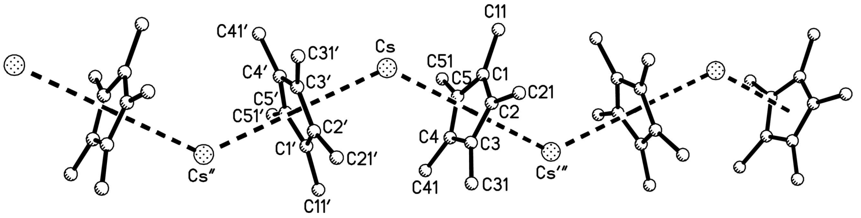

Figure 1. Polymeric zigzag chain of CsCp* (five units; H atoms and disorder of the Cp* ring not shown for clarity). Symmetry operations: (′) $x - 0.5, -y + 1.5, z - 0.5$; (″) $x - 0.5, -y + 1.5, -z$; (‴) $x + 0.5, -y + 1.5, z + 0.5$. Selected bond lengths (Å) and angles (deg): Cs−C1 = 3.24(2), Cs−C2 = 3.43(2), Cs−C3 = 3.52(2), Cs−C4 = 3.38(2), Cs−C5 = 3.21(2), Cs−C1′ = 3.47(2), Cs−C2′ = 3.28(2), Cs−C3′ = 3.19(2), Cs−C4′ = 3.33(2), Cs−C5′ = 3.50(2), Cs−C_{5c} = 3.132(2), Cs−C_{5c}′ = 3.132(2), Cs−Cs″ = 6.265(2), Cs−Cs‴ = 6.265(2); Cs″−Cs−Cs‴ = 129.2(1), Cs−C_{5c}−Cs‴ = 180.0. The drawing of RbCp* shows the same structure. Selected bond lengths (Å) and angles (deg): Rb−C1 = 3.21(2), Rb−C2 = 3.52(2), Rb−C3 = 3.46(3), Rb−C4 = 3.10(3), Rb−C5 = 2.93(2), Rb−C1′ = 3.29(3), Rb−C2′ = 2.96(2), Rb−C3′ = 3.03(2), Rb−C4′ = 3.39(2), Rb−C5′ = 3.54(2), Rb−C_{5c} = 3.017(2), Rb−C_{5c}′ = 3.017(2), Rb−Rb″ = 6.033(4), Rb−Rb‴ = 6.033(4); Rb″−Rb−Rb‴ = 131.0(1), Rb−C_{5c}−Rb‴ = 180.0.

Table 1. Selected Distances (Å) and Angles (deg) for Potassium, Rubidium, and Cesium Cyclopentadienides and Pentamethylcyclopentadienides

compd	CN	M−C(η^5)	M−C_{5c}[b]	M−M′	M′−M−M″	ref
KCp	4	2.955(5)−3.140(6)	2.816(4)	5.626(4)	138.0(1)	2
KCp*			solid state structure unknown			
α-RbCp[a]	5	3.173(6)−3.263(8)	2.994(5)	5.988(5)	123.5(1)	3
	4	3.086(8)−3.301(7)	2.953(7)	5.903(6)	136.5(1)	3
β-RbCp	4	3.139(6)−3.228(7)	2.962(5)[c]	5.926(4)	131.3(1)	3
RbCp* (**2**)	2	2.93(2)−3.54(2)	3.017(2)	6.033(4)	131.0(1)	this work
CsCp	4	3.296(6)−3.389(6)	3.140(6)[c]	6.278(2)	129.7(1)	4
CsCp* (**3**)	2	3.19(2)−3.52(2)	3.132(2)	6.265(2)	129.2(1)	this work

[a] Two crystallographically different Rb^+ ions. [b] C_{5c} denotes the center of the C_5 ring. [c] Mean.

Table 2. Selected Crystallographic Data for Rubidium (2) and Cesium (3) Pentamethylcyclopentadienides

	RbCp*	CsCp*
formula	$C_{10}H_{15}Rb$	$C_{10}H_{15}Cs$
fw	220.69	268.13
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a (Å)	10.6642(6)	10.6654(5)
b (Å)	10.6639(9)	10.6615(2)
c (Å)	10.9707(10)	11.3233(4)
β (deg)	119.036(5)	118.140(2)
V ($Å^3$)	1090.8(2)	1135.36(7)
Z	4	4
D_{calcd} (g cm^{-3})	1.344	1.569
T (°C)	20	20
λ (Å)	0.849 79(2)	0.849 79(2)
2θ range (deg)	4.0−41.0	4.0−49.0
step size (deg)	0.005	0.005
no. of rflns	326	581
no. of variables	70	57
R-p[a]	0.0704	0.0439
R-wp[a]	0.0913	0.0682
R-F^2[a]	0.0610	0.0361

[a] R-p, R-wp, and R-F^2 as defined in TOPAS.[19]

CsCp[4] (RbCp crystallizes in two different phases).[3] Selected data are given in Table 1. In RbCp*, compared to β-RbCp, the Rb−Rb′ distance is about 0.1 Å longer while the Rb′−Rb−Rb″ angle is the same (Rb−Rb′ distance in **2** 6.033(4) Å and in β-RbCp 5.926(4) Å; Rb′−Rb−Rb″ angle in **2** 131.0(1)° and in β-RbCp 131.3(1)°). For the cesium Cp/Cp* compounds a different situation for the Cs−Cs′ distance was found. Here the metal−metal distances are slightly shorter in CsCp* than in CsCp (6.265(2) Å (CsCp*) versus 6.278(2) Å (CsCp)). A comparison of the M′−M−M″ angles within the three compounds MCp (M = K, β-Rb, Cs)[2−4] indicate a decreasing tendency of the values from the smaller cation K^+ (K′−K−K″ = 138.0(1)°) to the medium-sized ion Rb^+ (Rb′−Rb−Rb″ = 131.3(1)°) to the largest ion Cs^+ (Cs′−Cs−Cs″ = 129.7(1)°). Once again, unfortunately the solid-state structure of base-free KCp* (**3**) is still unknown.

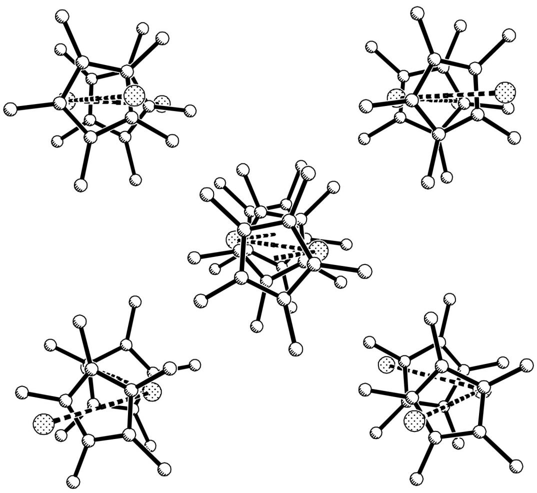

Figure 2. Drawing of a zigzag chain, which is surrounded by four adjacent polymeric chains.

The only three known Lewis base adducts of the rubidium and cesium Cp/Cp* compounds, namely RbCp·2thf[13] (5.9075(5) Å; 145.34(3)°), CsCp·RbCp(18-crown-6)·2.5thf[14] (6.3622(4) Å; 125.22(1)°), and CsCp·CsCp(18-crown-6)·2.75thf[15] (6.331(2) Å; 125.06(4)°), also show the same geometry of MCp zigzag chains. The metal−metal distances or angles (values are given in parentheses) do not differ very much from those of the base-free salts. Four complexes of this kind are known from the metal potassium: KCp·Et_2O[16] (5.536(1) Å; 145.32(2)°), KCp*·thf[9] (5.527(3) Å; 141.06(5)°), KCp*·2thf[9] (5.630(3) Å; 137.89(4)°), and KCp*·2py[8] (5.565(2) Å; 138.04(3)°). The K−K′ distances and K′−K−K″

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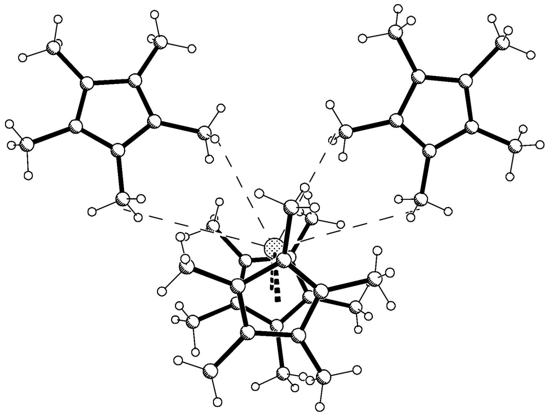

Figure 3. View of the M^+ environment of **2** and **3**. Four Cp* rings are shown.

angles for both types of compounds, Cp and Cp*, are in the same range as found for base-free KCp (5.626(4) Å; 138.0(1)°).

In this context it should be mentioned that the base-free Cp/Cp* salts of the lighter cations Li^+ and Na^+ crystallize as linear multidecker structures with M′−M−M″ angles of 180°.[2]

Experimental Section

All reactions, solvent drying procedures, and preparation of $KN(Si(CH_3)_3)_2$ (from potassium hydride and hexamethyldisilazane in toluene) were carried out as published previously.[11,17] The following instruments were used: IR spectra, Perkin-Elmer FT-IR PE 1720; X-ray powder diffraction, beamline BM16 at the European Synchrotron Radiation Facility (ESRF) and Stadi-P (Ge monochromator, Cu $K\alpha_1$ radiation), STOE & Cie GmbH.

Synthesis of Potassium Pentamethylcyclopentadienide (1). Method A. Pentamethylcyclopentadiene (4.0 mL, 3.35 g, 24.5 mmol) was added at room temperature to potassium metal (0.86 g, 22.0 mmol) in toluene (50 mL). The reaction mixture was heated for 2 h at 80 °C until the metal disappeared and a white suspension had formed. The precipitate was filtered off, washed with cyclopentane, and dried at 10^{-2} Torr. Yield: 3.05 g (79%) of product was obtained as a white, pyrophoric, very air-sensitive powder. IR (Nujol): ν 2725 (s), 1667 (w), 1579 (w), 1162 (m), 1078 (w), 1061 (w), 1000 (w), 647 (w), 461 (w) cm^{-1}.

Method B. A 1.95 g portion (9.77 mmol) of $KN(Si(CH_3)_3)_2$ was dissolved in 40 mL of diethyl ether at room temperature and filtered. Pentamethylcyclopendiene (1.6 mL, 1.39 g, 10.2 mmol) was added to the solution to yield a white precipitate after 30 s. The mixture was stirred at room temperature for 2 h, and 20 mL of cyclopentane was added. The precipitate was separated, washed three times with 20 mL of cyclopentane, and dried at 10^{-2} Torr for 7 h. Yield: 1.41 g (83 %) of white powder. IR (Nujol): ν 2726 (m), 1667 (w), 1580 (w), 1351 (m), 1265 (m), 1157 (m), 1081 (s), 1064 (s), 1001 (m), 644 (m), 457 (m) cm^{-1}. Anal. Calcd (found) for $C_{10}H_{15}K$ (174.32): C, 68.9 (68.7); H 8.7 (8.8).

Synthesis of Rubidium Pentamethylcyclopentadienide (2) and Cesium Pentamethylcyclopentadienide (3). The compounds were prepared as described in previous literature.[11]

X-ray Powder Crystallography. For the data collection the air-sensitive, colorless, and microcrystalline samples were sealed in glass capillaries of 0.7 mm diameter under argon. The temperature chosen was 20 °C for the high-resolution synchrotron radiation experiments (ESRF) and −120 °C for the transmission diffractometer. The powder patterns were indexed with the program ITO.[18] Systematic absences and crystallographic considerations led to the results provided in Table 2. For structure determination and refinement, the program TOPAS was used.[19] The Cp* ring was refined with restrained distances (rigid-body refinement, C–C(arom.) = 1.42 Å, $C-CH_3$ = 1.51 Å, H atoms in idealized positions) and held on an inversion center of the space group.

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Supporting Information Available: Text, figures, and tables giving crystallographic details, powder diffraction patterns, all bond lengths and angles, atom coordinates and equivalent thermal parameters, anisotropic thermal parameters for the metal atoms, and Rietveld plots for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, the crystal structures have been deposited at the Cambridge Crystallographic Data Centre. The following deposition numbers were allocated: **2**, CCDC-693193; **3**, CCDC-693260.

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