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Effect of Crystal Packing on the Structures of Polymeric Metallocenes○

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The pressure dependencies of the crystal structures of the polymeric metallocenes lithium cyclopentadienide (LiCp) and potassium cyclopentadienide (KCp) have been determined by synchrotron X-ray powder diffraction. The decrease of the volume of LiCp by 34% up to a pressure of $p = 12.2$ GPa and of KCp by 23% at $p = 5.3$ GPa as well as the bulk moduli of $K = 7.7$ GPa for LiCp and 4.9 GPa for KCp indicate a high compressibility for these compounds. The crystal structures of KCp have been determined up to $p = 3.9$ GPa. An increase of the bend angle is found from 45° at $p = 0$ GPa up to 51° at $p = 3.9$ GPa. This variation is completely explained by a model invoking attractive K^+ Cp^- interaction and repulsive nonbonded carbon–carbon interactions. It is proposed that the bend angle in the polymeric alkali metal metallocenes is the result of the optimization of the crystal packing.

Introduction

The bend angle in metallocenes is defined as the angle between the bonds from a metal atom toward the centers of the cyclopentadienyl (Cp) ligands sandwiching this metal atom (Figure 1).[1] The bend angle assumes different values in different compounds.[3−5] A complete understanding of the variation of bend angles would be tantamount to a full understanding of chemical bonding in metallocenes, which has not been achieved up to the present date.[6]

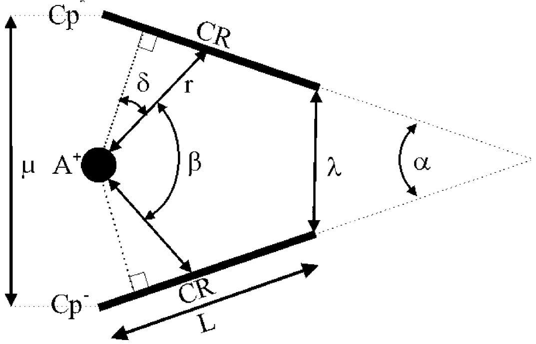

Figure 1. Schematic view of the bonding between an alkali metal cation and two cyclopentadienyl anions. Indicated are the distance (*r*) between the metal cation (A^+) and the centers (CR) of the cyclopentadienyl rings (Cp^-), the bend angle (α), the tilt angle (δ), the angle CR−A^+−CR (β), the diameter of the Cp^- rings (L), and the border to border distances (μ and λ) between neighboring Cp^- rings. Slippage is defined as the distance between CR and the perpendicular projection of the metal ion A^+ onto the plane of the Cp^- ring.[28]

Experimentally, the bend angle has been found to depend on a range of properties, like the ionic size and polarizability of the metal atoms, the size of the ligands (Cp versus substituted Cp), and the possible presence of lone pairs on the metal atom.[1,7−8] Alternatively, it was proposed that the bend conformation is due to attractive ligand−ligand interactions.[5] However, the many available crystal structures of metallocenes show that no simple relation exists between the bend angle and one or more of the above-mentioned parameters. Sapunov et al. concluded that the final structure of metallocenes depends on a "delicate balance" between ionic, π-bonding, and nonbonded interactions.[1]

○ Dedicated to Professor Martin Jansen on the occasion of his 60th birthday.

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Apart from incidental successes, the experimental geometries have not been reproduced by quantum chemical computations in a systematic way. The possible origin of this failure is the importance of electron correlation for the stability of metallocenes, which is not fully captured by state-of-the-art calculations.[9−11] This is even more severe for crystalline materials, like the polymeric alkali metal Cp compounds,[12−14] because quantum chemical calculations on solids can only be done at much lower levels of sophistication than it can be done for molecules.

In this contribution, we report on the pressure dependence of the crystal structures of LiCp and KCp. The crystal structures of LiCp, KCp, RbCp, and CsCp at ambient conditions have previously been solved from high-resolution X-ray powder diffraction data.[12−14] Pressure is an interesting variable, because it allows one to change the interatomic distances, without direct modifications of other quantities, like polarizabilities, atomic sizes, and molecular sizes. The results provide another set of experimental data on geometries of metallocenes that can be used to disentangle the different parameters that determine the bend angle in metallocenes.

Experimental Section

LiCp, KCp, and CsCp were prepared as described elsewhere.[12,14] For the X-ray powder diffraction experiments, the air- and moisture-sensitive samples were loaded inside a glovebox into membrane-driven diamond-anvil cells (DAC), with degassed silicon oil as pressure medium.[15] The DAC's were equipped with 500 μm culet diameter diamonds and a stainless steel gasket with 250 μm diameter hole. The pressure was determined by the ruby luminescence method using the wavelength shift calibration of Mao et al.[16] High-pressure X-ray powder diffraction data were collected at room temperature at beamline ID9 of the European Synchrotron Radiation Facility (ESRF). Monochromatic radiation for the high-pressure experiment was selected at 30 keV (wavelength $\lambda = 0.431\,329$ Å for LiCp and KCp; $\lambda = 0.415\,94$ Å for CsCp). The X-ray beam was collimated down to a fwhm of 80 × 80 μm^2. Diffracted intensities were recorded with a Marresearch Mar345 online image plate system. For CsCp, a set of 12 images was recorded at selected pressures between 0.0 and 2.0 GPa. For LiCp, a set of 16 images at selected pressures between 0.0 and 12.17 GPa, and for KCp, a set of 15 images at selected pressures between 0.03 and 11.13 GPa were recorded. Exposure times of the order of 1 min were chosen. Data reduction was performed using the program FIT2D,[17] resulting in diagrams of corrected intensities versus the scattering angle 2Θ. It was observed that the diffracted intensity was quite uniformly distributed over the Debye−Scherrer rings, ruling out severe grain size effects and preferred orientation.

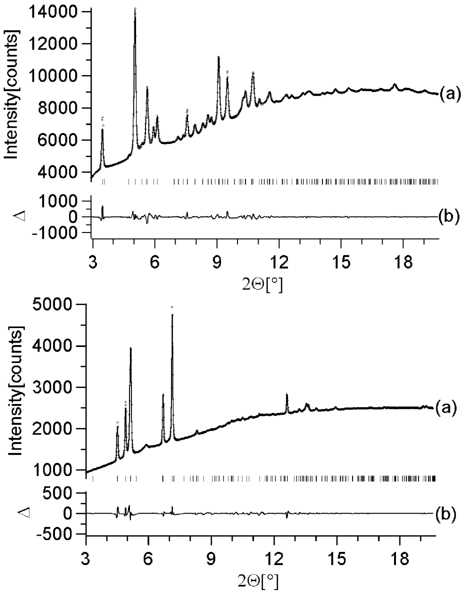

Figure 2. Top: Rietveld plot of potassium cyclopentadienide at 0.35 GP. Bottom: LeBail plot of lithium cyclopentadienide at 0.14 GPa. Drawn are the measured (◇ symbols) and calculated (solid line) powder diffraction profiles (a), the calculated peak positions, and the difference curve between measured and calculated profile (b).

Over the investigated pressure range, no phase transitions are observed for LiCp, KCp, and CsCp. For all data sets, lattice parameters as a function of pressure were obtained by Le Bail type of fits (Figure 2) using the program GSAS.[18−19] The background was modeled manually using the program GUFI.[20] The peak profile was described by a pseudo-Voigt function in combination with a special function that accounts for the asymmetry due to axial divergence.[21,22] The powder patterns of LiCp and CsCp exhibit severe anisotropic peak broadening mainly caused by lattice strain. In the case of LiCp, a uniaxial strain model (one refined parameter) with the sharpest peaks along the face diagonals of the *ab*-plane was sufficient to model the anisotropy of the fwhm, whereas in the case of CsCp the phenomenological strain model of Stephens[23] as implemented in GSAS was used (six refined parameters for the orthorhombic phase). Significant isotropic line broadening of the diffraction maxima caused by nonhydrostatic conditions due to freezing of the pressure transmitting medium was observed for pressures above 3 GPa.

The quality of the powder patterns of KCp was sufficient to perform Rietveld refinements of the crystal structure in dependence on pressure (Figure 2). For the Rietveld refinements, using the program GSAS, the lattice parameters and reflection profile parameters were first kept at the values obtained from the LeBail fits. Under the assumption that the shape of the cyclopentadienide

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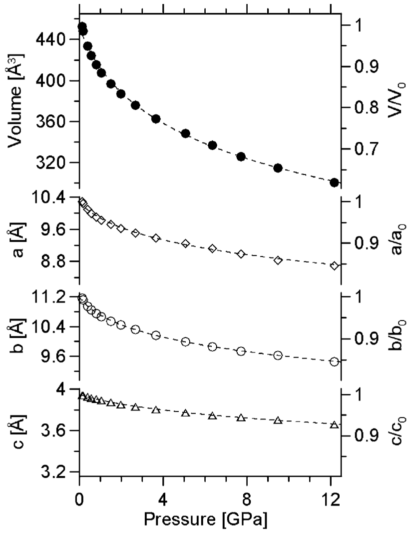

Figure 3. Pressure dependence of the lattice parameters and the unit cell volume of LiCp. The dashed lines represent Vinet equations of state. Relative values are of equal scale.

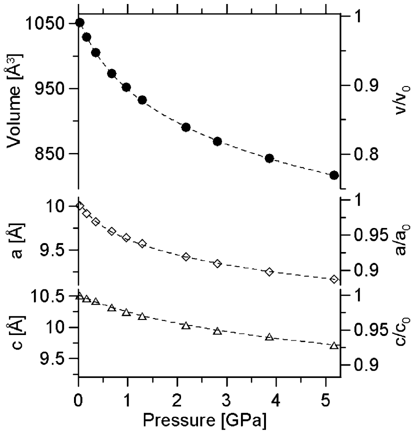

Figure 4. Pressure dependence of the lattice parameters and the unit cell volume of KCp. The dashed lines represent Vinet equations of state. Relative values are of equal scale.

anion does not depend on pressure, Cp was defined as a rigid body using the parameters as determined from the crystal structure determination of the room-temperature phase.[12] The position (3 parameters) and the orientation (3 parameters) of the rigid body as well as the position of the potassium atom (3 parameters) were refined. The quality of the Rietveld refinement against the data obtained at $p = 5$GPa was insufficient to obtain reliable structural parameters.

Results and Discussion

Equation of State. Lattice parameters have been determined as a function of pressure for the polymeric metallocenes LiCp (up to 12.2 GPa; Figure 3), KCp (up to 5.3 GPa; Figure 4), and CsCp (up to 2.0 GPa; Figure 5). Both the raw X-ray powder diffraction data and the lattice parameters do not give any indications for phase transitions. We conclude that phase transitions do not occur in the studied pressure ranges.

The volumes V of the unit cells of LiCp and KCp are decreased by approximately 24% at 5 GPa; in the case of CsCp the decrease is 10% at 2 GPa, indicating that all three compounds are soft and highly compressible. Then the equation of state (EOS) is best described by a Vinet type EOS.[25−26] Therefore, Vinet type EOS's were individually fitted to the pressure dependent data of the unit cell volumes as well as to the pressure-dependent data of the lattice parameters, for each of the three compounds, by employing the computer program EOSFIT.[27] The resulting curves describe the data well (Figures 3−5). Among others, the Vinet EOS provides a value for the zero-pressure bulk moduli of compounds (Table 1), again confirming the high compressibilities of these compounds. For CsCp, a complete fit of the EOS was not possible due to the limited size and limited quality of the data. In this case, only a linear fit (K'

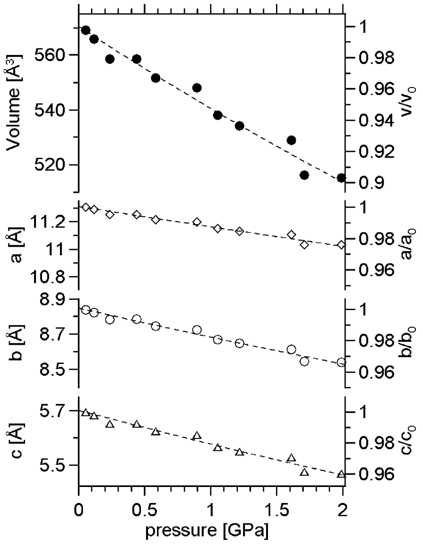

Figure 5. Pressure dependence of the lattice parameters and the unit cell volume of CsCp. The dashed lines represent Vinet equations of state. Relative values are of equal scale.

Table 1. Equations of State (EOS) for LiCp, KCp, and CsCp

	lattice params (Å, Å³) at $p = 0$ GPa		bulk modulus[a] K	K'	R_{wp} (%)
LiCp (0−12.2 GPa)	a	10.28(4)	5.8(9)	6.3(5)	5.4
	b	11.20(3)	4.8(4)	6.9(3)	2.2
	c	3.946(4)	20.7(1)	8.9(5)	2.9
	V	452.5(30)	7.7(7)	7.1(3)	2.7
KCp (0−5.3 GPa)	a	10.05(3)	3.5(6)	12.5(7)	2.1
	c	10.53(1)	8.7(8)	7.9(7)	2.9
	V	1061.6(36)	4.9(3)	11.1(4)	1.1
CsCp (0-2.0 GPa)	a	11.30(1)	25.7(24)	4.0 (fix)	16.7
	b	8.84(2)	17.0(18)	4.0 (fix)	16.6
	c	5.70(1)	14.0(14)	4.0 (fix)	15.9
	V	569.2(35)	18.0(19)	4.0 (fix)	16.4

[a] The bulk modulus is the inverse compressibility. The parameters K and K' are the two parameters in a Vinet EOS that were fitted to the pressure dependence of the unit cell volume or alternatively to the pressure dependence of the cube of a lattice parameter.[26]

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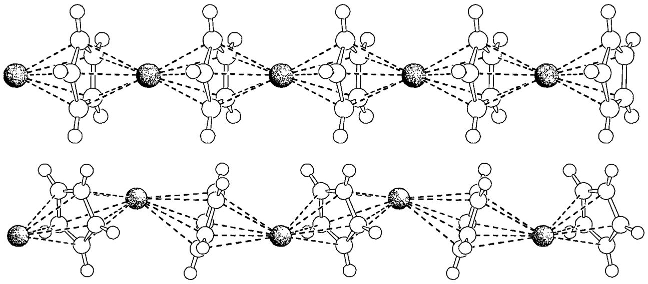

Figure 6. Single polymeric chains (supersandwich structures) of LiCp (top) and KCP (bottom) at ambient conditions.[11]

= 4.0) could be made, implying that the bulk modulus may have large errors, because it represents the derivative of the EOS at $p = 0$ GPa. Therefore, we refrain from a detailed analysis of the data on CsCp.

Pressure Dependence of the Crystal Structures. The crystal structures of MCp (M = Li, Na, K, Rb, Cs) comprise polymeric chains $[M-Cp]_\infty$ (Figure 6).[12−14] With the exception of a metastable phase of RbCp, only one crystallographically independent chain exists, which runs parallel to one crystallographic axis (the *c*-axis for M = Li, Na, K; the *a*-axis for M = Rb, Cs). At ambient conditions, either a parallel arrangement ($\alpha = 0°$ for M = Li, Na) or a bend conformation ($\alpha > 0°$ for M = K, Rb, Cs) of the $Cp-M^+-Cp^-$ sandwiches has been found. Within the pressure ranges studied here, the topologies of the crystal structures are preserved at high pressures.

The complete crystal structures at different pressures (up to $p = 4$ GPa) of KCp allow the pressure dependencies of characteristic geometric parameters to be studied. The distance between K and the centroid of the Cp ring (CR) continuously decreases with pressure. Because the Li−CR distance is smaller than the K−CR distance, the decrease with pressure of the former is smaller than the latter (Figure 7; Table 2). We believe that, apart from the covalent bonds within the Cp^- molecule, the strongest bonds are the η^5-type interactions between K^+ and Cp^- within the chains. This interpretation is supported by the observation that the slippage (see Figure 1) is independent of pressure (Figure 7; Table 2; Supporting Information).

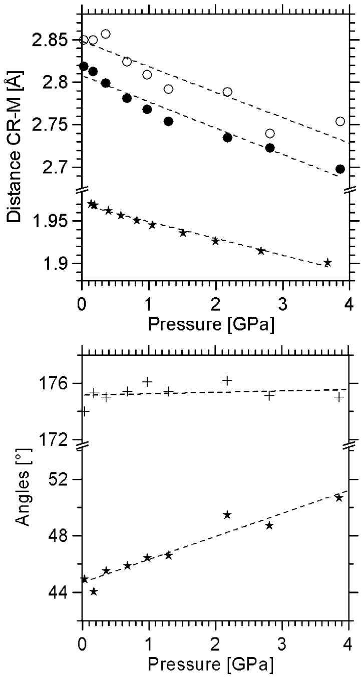

Figure 7. Pressure dependence of the geometry of MCp (M = Li, K). (a) Distances M−CR are shown; for M = Li one crystallographic independent distance is found (asterixes) with a value equal to *c*/2, and for M = K two alternating distances along the polymeric chains are obtained (hollow and filled circles). (b) Angles K−CR−K (plusses) and the bend angle α (asterisks) for KCp are shown. The bend angle for LiCp is 0°.

Table 2. Linear Fits on Selected Geometrical Parameters in Dependence on Pressure in the Range from 0 to 3.9 GPa for LiCp and KCp[a]

	value at $p = 0$ GPa	slope
Li−CR (Å)	1.9690	−0.019 80
K−CR(1) (Å)	2.8079	−0.030 9
K−CR(2) (Å)	2.8482	−0.029 95
α(KCp) (deg)	44.6998	1.624 7
K(1)−CR−K(2) (deg)	175.145	0.097 26
λ(KCp) (Å)	4.3263	−0.118 31
μ(KCp) (Å)	6.1366	−0.056 55

[a] Agreement factors are generally above 90%.

Initially surprising, the bend angle α in KCp increases with increasing pressure (Figure 7; Table 2). As shown below, this variation of the bend angle is the result of packing effects, i.e., of interchain interactions. Bend structures of the polymeric metallocenes allow denser packings than chains with parallel Cp molecules because they allow additional coordination of M^+ by η^1- or η^2-type interactions toward Cp^- molecules of neighboring chains. These interactions are limited by the opening distance μ of the bend structure and the minimum allowed nonbonded carbon−carbon distance (approximately 4.0 Å at ambient conditions). For small M−CR distances, the opening μ is not sufficiently large to accommodate molecules of neighboring chains for any accessible bend angle. Then the structure adopts $\alpha = 0°$ as observed for LiCp and NaCp. For larger M−CR distances a bend structure leads to an increased packing density and a larger coordination of M and thus to a state of lower energy than a structure without bending. The optimum bend angle will be determined by the shortest carbon−carbon distances within the chains (λ) and between the chains, which cannot become shorter than the van der Waals distance. A larger μ and therefore a smaller λ corresponds to a larger lateral packing density and therefore lower energy, and in the optimum structure, λ will be approximately equal to the carbon−carbon van der Waals distance. For KCp λ decreases with pressure which for an important fraction is the result of the increase with pressure of the bend angle (Figure 8; Table 2). This behavior corresponds to the decrease of the van der Waals distance with pressure, as is also exemplified by the shortest intrachain carbon−carbon distance of 4.45 Å at 0 GPa and of 4.01 Å at 3.9 GPa (compare with Figure 8). On the other hand, the decrease with pressure of μ is much smaller, which then allows a decrease with pressure of the interchain distance given the pressure dependence of the van der Waals distance. This is illustrated by the shortest interchain carbon−carbon distance, which is 3.86 Å at 0 GPa and 3.43 Å at 3.9 GPa. Both the shortest inter- and intrachain

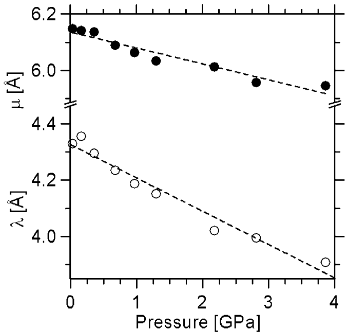

Figure 8. Pressure dependence of the distances λ and μ (as defined in Figure 1) of KCp. λ and μ were obtained from the structural parameters by the equations $\lambda = A - B$ and $\mu = A + B$ with $A = 2r \cos(\alpha/2)$ and $B = L \sin(\alpha/2)$.

carbon−carbon distances as well as λ decrease by the same amount while the decrease of μ is about half this value. Thus, the reduced pressure dependence of μ corresponds to the lateral compression of these compounds.

From this analysis we come to the conclusion that the crystal structures of polymeric MCp compounds are the result of a balance between attractive K+ Cp^- ionic interactions[11] and carbon−carbon nonbonded repulsion. Our data do not provide any evidence for attractive ligand−ligand interactions. Other types of interactions may be important in metallocenes containing metal atoms with d-electrons or lone pairs. However, packing effects will be important for those compounds too.

The proposed interpretation is in accordance with the variation of the bend angle in MCp over the alkali metal series. Alternatively, it has been proposed that the bend angle depends on the polarizability of the metal atom with larger polarizabilities favor larger bend angles.[7] Although the bend angle of the alkali metal series show a clear correlation with the polarizability of the alkali metal atoms, we believe that the presently proposed model gives an equally good explanation for the correlation of the bend angle and the size of the cation (Figure 9). The present model explains the pressure dependence of the bend angle, while a sole dependence of the bend angle on the polarizability does not explain this pressure dependence.

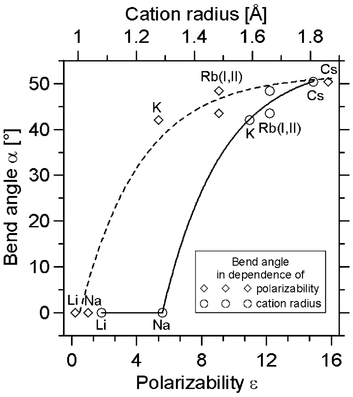

Figure 9. Bend angle α of the alkali metal cyclopentadienides (note the two different polymorphs for RbCp) as a function of cation radii (open circles) and as a function of cation polarizability (diamonds). The solid line represents a guide to the eye, whereas the dashed line is a Boltzmann type of fit to the dependence on the polarizability ϵ: $\alpha\ (\text{deg}) = -59.244° \exp(-0.2666\epsilon) + 51.937$ ($R = 97\%$).

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Supporting Information Available: Crystallographic data in CIF format for KCp at different pressures and lattice parameters for LiCp and CsCp at different pressures. This material is available free of charge via the Internet at http://pubs.acs.org.

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