After washing of zeolite Cs,Na-Y/CsOH723, the product being denoted as Cs,Na-Y/CsOH723*, a pattern of characteristic lines is recorded in addition to the diffuse background (Figs. 82(d) and (e)). Indexing results in a cubic structure with a cell constant $a = 13.647(4)$ Å, which is assigned to that of mineral pollucite ($CsAlSi_2O_6$), see Fig. 82(c).

The present investigation has shown that the conditions of the preparation of basic zeolites Y and X by Cs exchange, impregnation with CsOH, and subsequent calcination are very crucial for obtaining suitable catalyst materials. The X-ray powder diffraction technique proved to be a powerful tool in these studies and clearly reveals that both, a too high loading with CsOH acting as guest compound and a too high calcination temperature cause damage and partial transformation of zeolite crystals. The results could be of interest for a preparation of mesoporous systems by a controlled local damage of the zeolite framework.

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The effect of crystal packing on the structures of polymeric metallocenes

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The bend angle (α) in metallocenes is defined as the angle between the bonds from a metal atom towards the centers of the cyclopentadienyl (Cp) ligands sandwiching this metal atom (Fig. 84). The bend angle assumes different values in different compounds. 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.

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. Alternatively, it was proposed that the bend conformation is due to attractive ligand–ligand interactions. 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.

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. This is even more severe for crystalline materials, like the polymeric alkali Cp compounds, because quantum chemical calculations on solids can only be done at much lower levels of sophistication than it can be done for molecules.

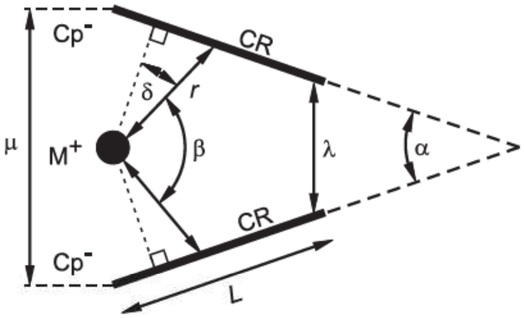

Figure 84: Schematic view of the bonding between an alkaline cation and two cyclopentadienyl anions. Indicated are the distance (r) between the metal cation (M^+) and the centers (CR) of the cyclopentadienyl rings (Cp^-), the bend angle (α), the tilt angle (δ), the angle CR–M^+–CR (β), the diameter of 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 M^+ onto the plane of the Cp ring.

In the present 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. Pressure is an interesting variable, because it allows 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.

The air and moisture sensitive samples of LiCp, KCp, and CsCp were loaded inside a glove box into membrane driven diamond-anvil cells (DAC), with degassed silicon oil as pressure medium. High pressure X-ray powder diffraction data were collected at room temperature at beamline ID9 of the European Synchrotron Radiation Facility (ESRF).

Lattice parameters have been determined as a function of pressure for the polymeric metallocenes LiCp (up to 12.2 GPa), KCp (up to 5.3 GPa), and CsCp (up to 2.0 GPa). Both, the X-ray powder diffraction data as well as the lattice parameters do not give any indications for phase transitions. The volumes V of the unit cells of LiCp and KCp are decreased by approximately 24% at 5 GPa, in case of CsCp the decrease is 10% at 2 GPa, indicating that all three compounds are soft and highly compressible. Vinet-type equations of state (EOS) 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, employing the computer program EOSFIT.

The crystal structures of MCp ($M = $ Li, Na, K, Rb, Cs) comprise of polymeric chains $[M\text{–}Cp]_\infty$. With the exception of a metastable phase of RbCp, only one crystallographically independent chain exists, that 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 (Fig. 85). 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 Fig. 84) is independent of pressure (Fig. 85).

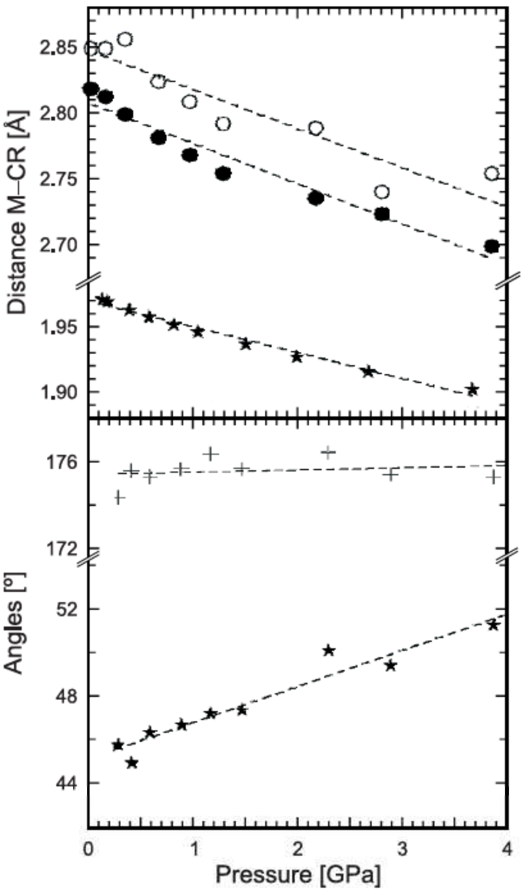

Figure 85: Pressure dependence of the geometry of MCp [M = Li, K]. (a) Distances M–CR; for M = Li one crystallographic independent distance is found (asterisk) with a value equal to $c/2$, for M = K two alternating distances along the polymeric chains are obtained (hollow and filled circles). (b) Angles K–CR–K (plus) and the bend angle α (asterisks) for KCp. The bend angle for LiCp is 0°.

Initially surprising the bend angle α in KCp increases with increasing pressure (Fig. 85). 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 towards 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 $\alpha = 0^\circ$ 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, that 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.

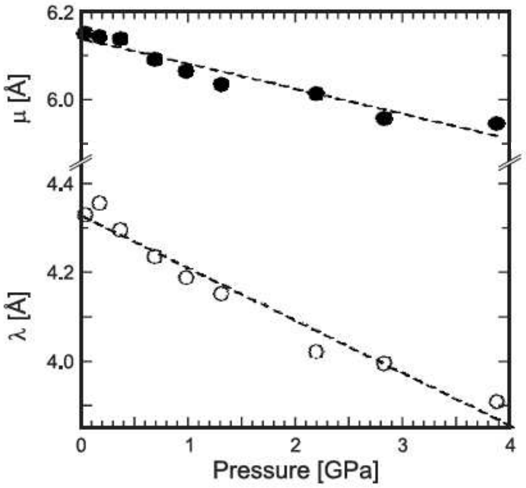

Figure 86: Pressure dependence of the distances λ and μ (as defined in Fig. 84) of KCp. λ and μ were obtained from the structural parameters by the equations $\lambda = A - B$ and $\mu = A + B$ with $A = 2r\cos(\alpha/2)$ and $B = L\sin(\alpha/2)$.

For KCp λ decreases with pressure which for an important fraction is the result of the increase with pressure of the bend angle (Fig. 86). 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.

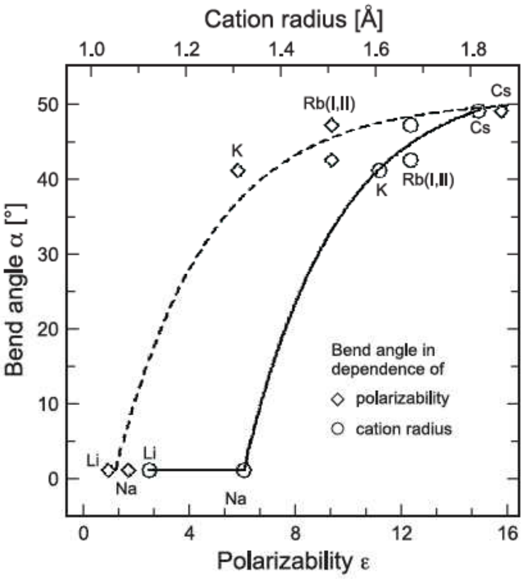

Figure 87: Bend angle α of the alkali cyclopentadienides (note the two different polymorphs for RbCp) as a function of cation radii (open circles) and as a function of cation polarizability (diamonds). The solid line represents a guide to the eye, whereas the dashed line is a Boltzmann-type of fit to the dependence on the polarizability ε: $\alpha[^\circ] = -59.244[^\circ] \cdot \exp(-0.2666 \cdot \varepsilon) + 51.937$ (R = 97%).

On the other hand, the decrease of μ with pressure 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 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 M^+ Cp^- ionic interactions 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 alkaline 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. Although the bend angle of the alkaline series show a clear correlation with the polarizability of the alkaline 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 (Fig. 87). 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.