

**Experiment title:**

High pressure powder diffraction studies of alkaline-cyclopentadienides

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HS-1094

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Shifts:

18

Local contact(s):

Michael Hanfland

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**Robert E. Dinnebier*¹, Stefan Carlson*², Markus Wunschel*¹¹Laboratory of Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany²High Pressure Group, ESRF, B. P. 220, F-38043 Grenoble Cedex, France**Report:**

The cyclopentadienyl anion $C_5H_5^-$ (Cp), is the most important ligand in organometallic chemistry. Cp can form compounds with virtually any metallic element. Alkaline-Cp's in particular are basic compounds in organometallic synthesis. Theoretical interest exists, because of the special type of bond between the metal atom and the p-electrons delocalized on the five carbon atoms of Cp. The alkali-metallocenes with pure Cp have a poor solubility, and single-crystals are impossible to grow. As a common feature, the crystal structures of all alkaline Cp's show polymeric multidecker chains. The chains of LiCp and NaCp are linear, whereas those of the higher homologs are bent¹, leading to more complex coordination spheres. The bent angle is highly correlated with the radius and polarizability of the cation. Diffraction studies at high pressures provide an opportunity to probe the behavior of the chemical bonding of alkaline Cp's as a function of decreasing inter-atomic separation, without the complications introduced by changing chemistry.

In this work, *in situ* measurements were performed at high pressure for LiCp and KCp using a DAC at room temperature. An angle dispersive powder diffraction technique at $\lambda = 0.43133 \text{ \AA}$ with an online fast readout 2D MAR345 detector was used. Data reduction was performed using the programs FIT2D (by Andy Hammersley, ESRF) and GUF1 (by Dinnebier). The quality of the powder patterns of KCP was high enough to perform Rietveld refinements up to 5 GPa (Fig. 1) using the program GSAS. The dependence of several intramolecular parameters from pressure could be refined (Fig 2).

1. R. E. Dinnebier, U. Behrens & F. Olbrich 1997, *Organometallics* 16, 3855-3858; R. E. Dinnebier, F. Olbrich, S. van Smaalen and P. W. Stephens, 1997, *Acta Cryst B*53, 153-158; R. E. Dinnebier, F. Olbrich, & G. M. Bendele, 1997, *Acta Cryst. C*53, 699-701.

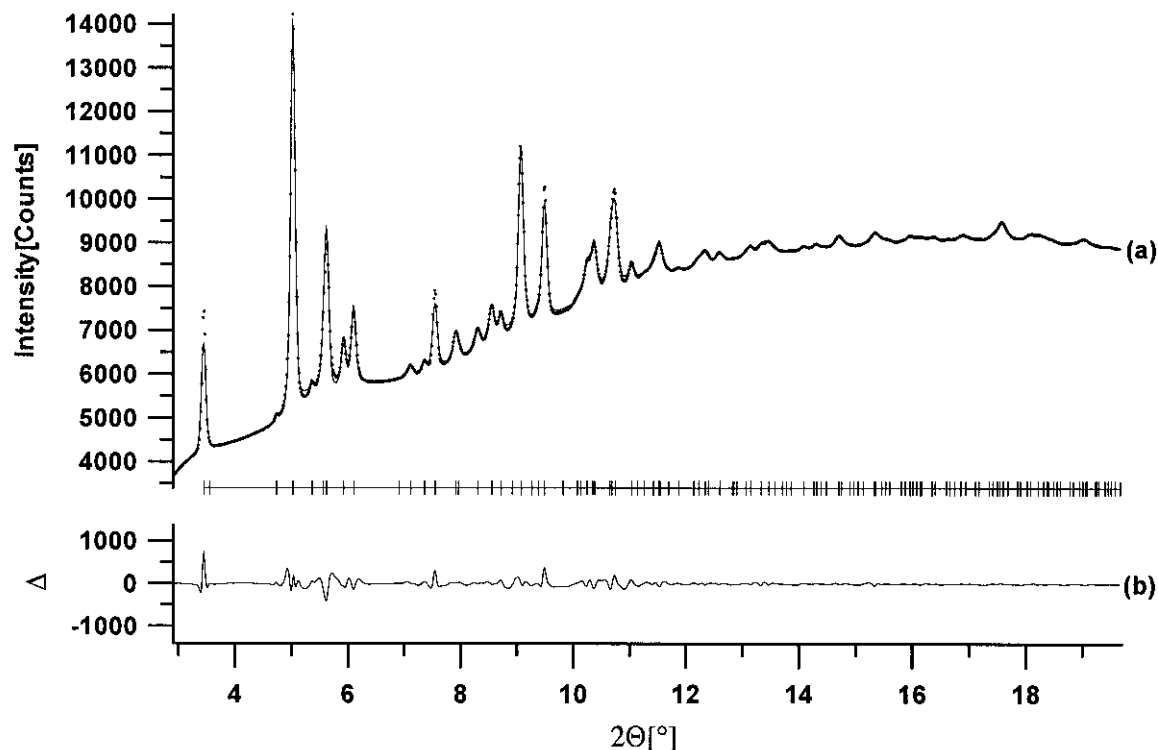


Fig. 1: Rietveld plot of potassium cyclopentadienide (KCp) at 0.35 GPa.

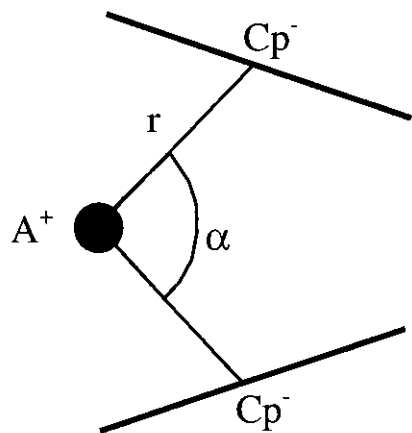


Fig. 2a:
Schematic view of the bonding between an alkaline cation (A^+) and two cyclopentadienyl anions (Cp^-) at distance r with bent angle α .

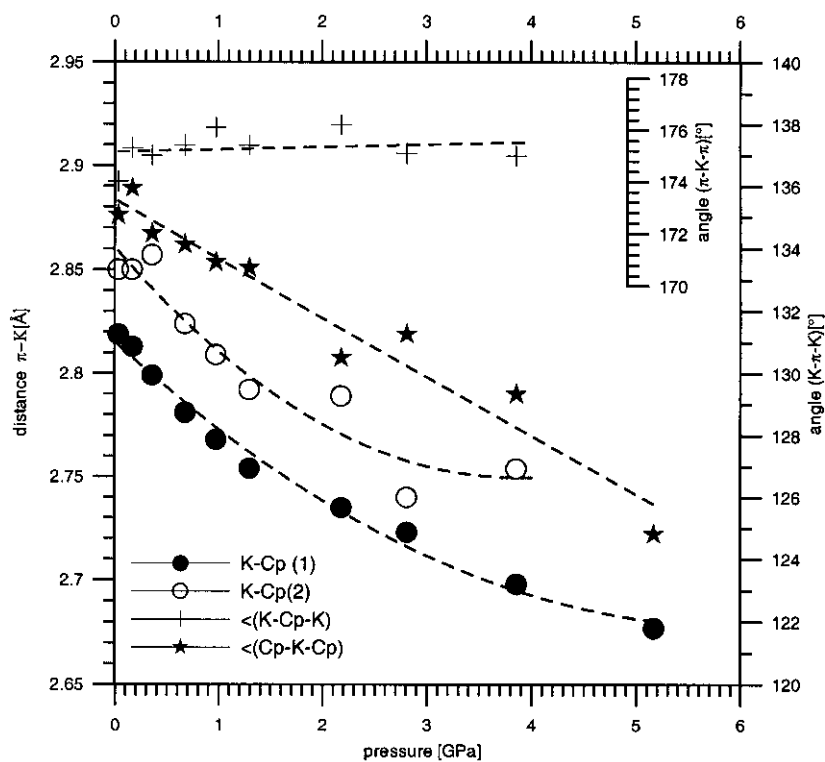


Fig. 2b:
Variation of structural parameters of potassium cyclopentadienide (KCp) with pressure up to 3.86 (resp. 5.17 GPa)