Ab Initio Structure Determination of Two Polymorphs of Cyclopentadienylrubidium in a Single Powder Pattern

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Abstract

The structures of two polymorphic phases of solid RbC_5H_5 have been solved *ab initio* by high-resolution powder X-ray diffraction measured in a single powder pattern. The compound crystallizes in space group *Pbcm* (phase I), $Z = 8$, with unit-cell parameters $a = 9.3396\,(1)$, $b = 10.9666\,(1)$, $c = 10.5490\,(1)$ Å, and in space group *Pnma*, $Z = 4$ (phase II), with unit-cell parameters $a = 10.7990\,(2)$, $b = 8.6923\,(2)$, $c = 5.7061\,(2)$ Å. Both phases show polymeric zigzag chains, so-called bent-polydecker sandwich structures, with an average Rb—Cp_z (Cp-ring-centroid) distance of 2.97 Å. Phase II contains a single chain along the *a* axis, whereas phase I contains two similar but crystallographically independent chains perpendicular to each other along the *b* axis and along the *c* axis, leading to a more complex coordination sphere around the Rb atoms. The chains are bent with Cp_z—Rb—Cp_z angles ranging from 123.5 to 136.5°.

1. Introduction

The cyclopentadienyl anion $C_5H_5^-$ (Cp) is the most important ligand in organometallic chemistry (Stalke, 1994). Cp can form compounds with virtually any metallic element. Complexes exist with transition metals, *e.g.* ferrocene $Fe(Cp)_2$ (Eiland & Pepinsky, 1952), *p*-block elements, *e.g.* $PbCp_2$ (Jutzi, 1990a,b; Grenz, Hahn, du Mont & Pickard, 1984; Almenningen, Haaland & Motzfeldt, 1967; Panattoni, Bombieri & Croatto, 1966), *s*-block metals, *e.g.* $CaCp_2$ (Hanusa, 1993; Zerger & Stucky, 1974), as well as with lanthanides (Hanusa, 1993; Evans, Hughes & Hanusa, 1984). The basic compounds in organometallic synthesis are MCp ($M =$ Li, Na, K and Tl) and $MgCp_2$. Theoretical interest exists because of the special type of bond between the metal atom and the π-electrons delocalized on the five C atoms of Cp. Quantum chemical calculations have not reproduced the experimental geometries in a reliable way (Kaupp, Schleyer, Dolg & Stoll, 1992; Blom, Faegri & Volden, 1990) and only at the most sophisticated level of

approximation there is a chance to obtain the correct model for this type of bond (Park & Almlöf, 1991).

The structures of the alkaline-earth metallocenes $M(C_5H_5)_2$ ($M =$ Be, Mg, Ca) and $M[C_5(CH_3)_5]_2$ ($M =$ Ba, Sr) have been studied by gas-phase electron diffraction as well as by single-crystal diffraction studies (Stalke, 1994). A marked feature of these studies was that for $M =$ Ba or Sr, the two $C_5(CH_3)_5^-$ anions (often denoted as Cp*) were found in a noncoplanar arrangement, termed the bent conformation (Hanusa, 1993). It is this feature, as well as the correct metal-to-carbon distance, which is difficult to reproduce in quantum chemical studies.

Alkali metallocenes are special in the sense that these molecules with monovalent anions contain only one Cp molecule and the sandwich is not completed. Because of this, the molecules are highly unstable and can only exist when the metal side is complexed by a Lewis base. In the solid state alkali metallocenes may form polymeric chains $[MCp]_\infty$, for example, as is found for $K(Me_3Si)C_5H_4$ (Jutzi, Leffers, Hampel, Pohl & Saak, 1987). Still another way to stabilize alkali metallocenes is compound formation with the complex cation $[MCp_2]^-$ (Harder & Prosenc, 1994).

Crystallographic studies have focused on the analysis of the scattering of single crystals. However, the metallocenes with pure Cp have a poor solubility† and single crystals are difficult to grow. The way out of this problem was to use substituted Cp molecules, such as the pentamethylcyclopentadienyl anion $C_5(CH_3)_5^-$, which led to more soluble compounds (Jutzi, 1989, 1990a,b). Obviously, the properties of metallocenes with Cp and substituted Cp need not be identical. The characteristics of the special metal-to-π-bond will produce the most pronounced influence on the properties of Cp-containing metallocenes. Furthermore, quantum chemical calculations can be performed much easier on the compounds with Cp itself, due to the smaller sizes of these complexes. Therefore, the structures of the Cp-containing metallocenes are of particular interest.

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† When they dissolve they generally decompose too.

Alkali metallocenes can be synthesized as powders. To determine their structures we have undertaken a series of high-resolution synchrotron radiation powder diffraction experiments and it turned out to be possible to make an *ab initio* determination of these structures from the powder pattern. The structures of LiCp, NaCp and KCp have been solved previously and will be described elsewhere (Dinnebier & Olbrich, 1997). Here we report on the RbCp sample. Two different crystalline modifications have been found with exactly the same chemical composition. To our knowledge, it is the first time that such an observation has been made for a metallocene. These results are a noteworthy illustration of the power of high-resolution X-ray powder diffraction, because the structures of both modifications have been determined from a single powder spectrum.* An analysis is given of the bonding in these crystals and the origin of the bent *versus* coplanar conformations is discussed in terms of interatomic distances.

2. Experimental

All manipulations of solvents and substances were carried out under an atmosphere of dry argon using standard Schlenk and vacuum techniques. Cyclopentadienylrubidium was prepared similar to the method described in the literature (Fritz & Schaefer, 1964). Rubidium metal reacted with monomeric cyclopentadiene in tetrahydrofuran at room temperature. The colorless solution was filtered and most of the solvent was distilled off until the product started to precipitate. Cyclopentane was added to complete precipitation. The white product was dried at 348 K and 3×10^{-3} Torr. The yield was 75%.

For the powder X-ray diffraction experiments the air- and moisture-sensitive samples were sealed in glass capillaries of 0.7 mm diameter. High-resolution powder diffraction data were collected at room temperature at the SUNY X3B1 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. X-rays of wavelength 1.15 Å were selected by a double Si(111) monochromator. The diffracted beam was analyzed with a Ge(111) crystal and detected with a Na(Tl)I scintillation counter with a pulse height discriminator in the counting chain. The incoming beam was monitored by an ion-chamber for normalization for the decay of the primary beam. In this parallel beam configuration the resolution is determined by the analyzer crystal rather than by slits. Data were taken for 15 s at each 2θ in steps of $0.01°2\theta$ from $2°$ to $56°2\theta$ over a single bunch time (maximum 100 mA current).

Although θ scans did not show serious crystallite size effects, the sample was rotated during measurement for

better statistics. Low-angle diffraction peaks from RbCp had a full width at half-maximum (FWHM) of $0.015°2\theta$ for phase I and $0.07°2\theta$ for phase II, the latter significantly broader than the resolution of the spectrometer.

At first indexing the reflections with a single lattice was tried. All attempts failed, using various methods (Visser, 1969; Werner, 1964). Inspection of the peak width in the low-angle region where the reflections are reasonably well separated revealed that they largely fell into two populations: narrow peaks which are essentially resolution-limited and others which are at least three times broader at all angles. The widths were determined with the correct geometric correction for low-angle asymmetry due to axial divergence (Finger, Cox & Jephcoat, 1994; Stephens, unpublished). The width of those peaks which were sufficiently resolved from their neighbors are plotted in Fig. 1. The set of narrow peaks could be indexed to an orthorhombic cell (I, Table 1). A preliminary le Bail fit (le Bail, Duroy & Fourquet, 1988) using the program *FULLPROF* (Rodriguez-Carvajal, 1990) worked well after fixing the lattice parameters. The difference curve now clearly showed the second phase which could be used in a second indexing process, resulting in a different orthorhombic cell (II, Table 1). Once the two phases were indexed, we went back to the data in Fig. 1 and found that several of the peaks consisted of unresolved overlaps (marked with open circles in Fig. 1). When these are removed the division between the two phases by diffraction peak width is extremely clean. The fitted FWHM's from the
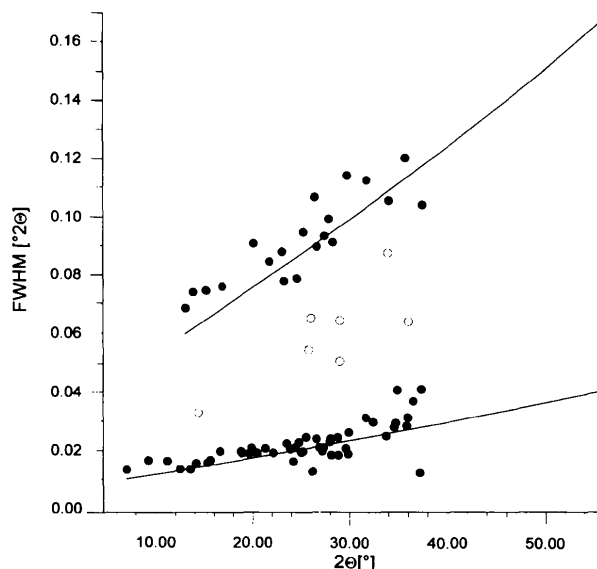

Fig. 1. Plot of individually fitted FWHM *versus* 2θ for both phases of RbC$_5$H$_5$. The FWHM ratio between phase I and phase II is approximately 3 over the entire angular range, enabling a clear separation of the two phases. The open circles denote peaks which cannot be clearly separated due to severe overlap.

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* The numbered intensity of each measured point on the profile has been deposited with the IUCr (Reference: SE0204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystallographic parameters of the two phases of RbC₅H₅*

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	RbC_5H_5 (I)	RbC_5H_5 (II)
a (Å)	9.3396 (1)	10.7990 (2)
b (Å)	10.9666 (1)	8.6923 (2)
c (Å)	10.5490 (1)	5.7061 (2)
V (Å³)	1080.46 (1)	535.63 (2)
V/Z (Å³)	135.06	133.91
Z	8	4
Space group	*Pbcm*	*Pnma*
M_r	1204.52	602.26
ρ_{calc} (g cm⁻³)	1.851	1.867
R_p	0.047	0.047
R_{wP}	0.061	0.061
R_F	4.3	4.5
R_{F^2}	6.3	6.9
No. of reflections	342	171

Rietveld refinement for the two phases are plotted as smooth curves in Fig. 1.

Since the ratio of the two unit-cell volumes was almost 2, a mixture of two polymorphs was anticipated. The space group and number of formula units per unit cell (Z) were found by applying the extinction rules and geometrical considerations. Approximately 340 peaks of phase I and ~170 peaks of phase II were extracted using the le Bail technique. These were used as input for the direct methods program *SIRPOW*92 (Cascarano, Favia & Giacovazzo, 1992) with which it was possible to detect the positions of the Rb and all the C atoms for both polymorphs. It was possible to Rietveld-refine (Rietveld, 1969) these structures to Bragg R factors around 25%, keeping the positions of the C atoms as found in the direct methods fixed. Since the shape of the Cp ring is known within very narrow limits, this additional information was used to stabilize the refinement by setting up rigid bodies. In the most general case this reduces the number of refinable parameters for the C atoms from 15 to six (three translational, three rotational). The length of the C—C vector can be refined as an additional parameter to allow the Cp ring
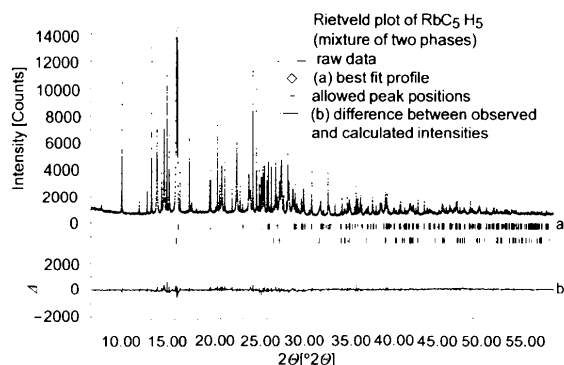

Fig. 2. Rietveld plot of the two orthorhombic phases of RbC₅H₅ [$R_p = 0.047$, $R_{wp} = 0.061$, R_F(I) = 0.043, R_F(II) = 0.045]. The asymmetric unit contains 14 atoms (eight non-H) for phase I and seven atoms (four non-H) for phase II.

Table 2. *Fractional atomic coordinates, equivalent isotropic displacement parameters ($Å^2$) and anisotropic displacement parameters*

	x	y	z	U_{iso}/U_{eq}
(a) RbC_5H_5 (phase I)				
Rb1	0.5357 (2)	0.1208 (2)	1/4	0.0507
Rb2	−0.1170 (2)	0.1574 (3)	3/4	0.0449
C11	0.6652 (8)	1/4	0.0	0.014 (4)
C12	0.5788 (7)	0.3412 (3)	0.0458 (6)	0.014 (4)
C13	0.4389 (7)	0.3064 (2)	0.0283 (4)	0.014 (4)
H11	0.7776 (8)	1/4	0.0	0.025
H12	0.6135 (7)	0.4233 (6)	0.0869 (11)	0.025
H13	0.3480 (7)	0.3571 (3)	0.0537 (7)	0.025
C21	0.1219 (9)	0.3564 (9)	3/4	0.008 (3)
C22	0.0443 (8)	0.3888 (6)	0.6447 (2)	0.008 (3)
C23	−0.0813 (9)	0.4411 (8)	0.6849 (1)	0.008 (3)
H21	0.2229 (10)	0.3144 (14)	3/4	0.025
H22	0.0755 (8)	0.3758 (7)	0.5500 (2)	0.025
H23	−0.1630 (10)	0.4752 (11)	0.6264 (1)	0.025
(b) RbC_5H_5 (phase II)				
Rb	0.8628 (2)	1/4	0.9639 (3)	6.4
C1	0.5729 (7)	1/4	0.9224 (10)	2.4 (3)
C2	0.6026 (7)	0.3778 (3)	0.7926 (8)	2.4 (3)
C3	0.6508 (8)	0.3290 (2)	0.5827 (8)	2.4 (3)
H1	0.5341 (9)	1/4	1.0912 (11)	4.0
H2	0.5907 (7)	0.4927 (3)	0.8448 (8)	4.0
H3	0.6821 (10)	0.4000 (2)	0.4461 (9)	4.0

(c) Rb in RbC_5H_5 (phases I and II)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1 (phase I)	0.043 (3)	0.019 (2)	0.073 (3)	0.001 (2)	0	0
Rb2 (phase I)	0.064 (3)	0.051 (2)	0.037 (2)	0.014 (2)	0	0
Rb (phase II)	0.040 (1)	0.080 (2)	0.071 (2)	0.000 (3)	−0.003 (2)	0

to relax within the plane. We used the program package *GSAS* (Von Dreele & Larson, 1990) for the final Rietveld refinements, shown in Fig. 2. The peak profile function was modeled using a multiterm Simpson's rule integration of the pseudo-Voigt function (Thompson, Cox & Hastings, 1987). The strong asymmetry in the low-angle region was modeled by a recently implemented function (Finger, Cox & Jephcoat, 1994), which accounts for the asymmetry due to axial divergence, leading to an strongly improved fit and therefore better profile R factors. Inclusion of H atoms in the Cp plane, located 1.06 Å from each carbon, reduced the profile R factors typically by 0.5%, which can be considered as significant (Lightfoot, Metha & Bruce, 1993). All non-H) positional parameters of Cp remained close to their rigid-body positions after turning them loose in a final cycle of refinement. The R values are listed in Table 1. The coordinates (using rigid bodies for Cp) are given in Table 2. A selection of intra- and intermolecular distances is given in Table 3.

3. Description of the structures

In the structures of the two RbCp polymorphs (Figs. 3*a* and *b*) the main features are polymeric chains consisting of an infinite array of bent sandwiches [RbCp]∞. Phase II forms with a single type of chain

Table 3. *Selected bond and shortest intramolecular distances (Å) of the two phases of RbC₅H₅*

	RbC₅H₅ (phase I)	RbC₅H₅ (phase II)
Rb1—Rb1 (intrachain)	5.987	
Rb2—Rb2 (intrachain)	5.903	5.92
Rb1—Rb1 (interchain)	5.524	
Rb2—Rb2 (interchain)	5.652	5.277
Rb1—Rb2 (interchain)	4.054	
Rb1—C11	3.229　　　(2×)	
Rb1—C12	3.173, 3.263 (2×)	
Rb1—C13	3.174, 3.229 (2×)	
Rb2—C21	3.301　　　(2×)	3.159, 3.139
Rb2—C22	3.153, 3.221 (2×)	3.173, 3.174 (2×)
Rb2—C23	3.204, 3.086 (2×)	3.196, 3.228 (2×)
Rb1—C (median)	3.214 ± 1.5%	
Rb2—C (median)	3.193 ± 3.4%	3.184 ± 1.4%
Rb1—Cp centroid	2.994	
Rb2—Cp centroid	2.944, 2.962	2.957, 2.967
Angle (Cp—Rb1—Cp)	123.50°	
Angle (Cp—Rb2—Cp)	136.54°	131.55°
Rb1—C (interchain)	3.705	
Rb2—C (interchain)	3.482	3.726
Rb1—H (intrachain)	3.660	
Rb2—H (intrachain)	3.540	3.624
Rb1—H (interchain)	3.006	
Rb2—H (interchain)	2.993	3.082
C—C (ring)	1.373	1.373
C1—C1 (intrachain)	4.309	
C2—C2 (intrachain)	4.621	4.609
C—C (interchain)	3.715	3.877
C—H (ring)	1.05 (fixed)	1.05 (fixed)
C1—H1 (intrachain)	3.991	
C2—H2 (intrachain)	4.396	4.312
C—H (interchain)	3.152	3.144
H1—H1 (intrachain)	3.440	
H2—H2 (intrachain)	3.981	4.0248
H—H (interchain)	2.637	2.644

along the *a* axis, whereas phase I consists of two crystallographically independent chains which are perpendicular to each other and run along the *b* and *c* axes. The structure of the chain along the *b* axis (type *A*) in phase I is almost identical to the structure of the chain in phase II. In this chain the symmetry of the sandwich is *m* with the mirror plane intersecting Rb and the centers of the Cp rings. The sandwich of the second chain (type *B*) in phase I has almost *mm*2 symmetry, with one mirror plane placed similarly as in type *A* chains and with the second mirror plane passing through Rb, making the two Cp rings images of each other.* Despite the different orientation of the rings, the coordination spheres of the crystallographically independent Rb atoms were found to be similar. The bond distances to the C atoms show very little variation (Table 3) and the maximum deviation within one ring is between 1.4 and 3.4%, whereas for all rings it is of the order 4%. This leads to a quite perfect (η^5-Cp)—Rb bonding. The large coordination

* The result is that the type *A* coordination of Rb1 is a distorted pentagonal prism, while in type *B* Rb2 shows a distorted pentagonal antiprism coordination by carbon.

sphere of Rb⁺ cannot be satisfied completely by the two 'face-on' bonded Cp ligands. In addition, 'side-on' van der Waals contacts to C and/or H atoms exist. Their number and type differ between the two different types of chains (Table 3, Figs. 4*a*, *b* and *c*). The general formula for the chains of type *B* is $_1^\infty[Rb^{(1)}\eta_5^{(2)}\eta_1^2H^{(4)}]$ for phase I and $_1^\infty[Rb^{(1)}\eta_5^{(2)}H^{(5)}]$ for type *A* in both phases I and II. The bent angles (Cp-ring-centroid)—Rb—(Cp-ring-centroid) for phase I are 123.5 and 136.5°, whereas for phase II an angle of 131.6° is observed. The angles are in the same range as those found for several alkali-earth or lanthanide cyclopentadienides (Harder & Prosenc, 1996; Stalke, 1994; Hanusa, 1993). The typical distance between Rb ions is ~5.9 Å along the chains and 5.6 Å between neighboring chains of the same type. Noteworthy is that the Rb—Rb distance in phase I is only ~4 Å between atoms in chains *A* and *B*, respectively, indicating a much larger Coulomb repulsion. For our particular sample, the quantitative Rietveld analysis revealed a weighted fraction of 40% for phase I and 60% for phase II.
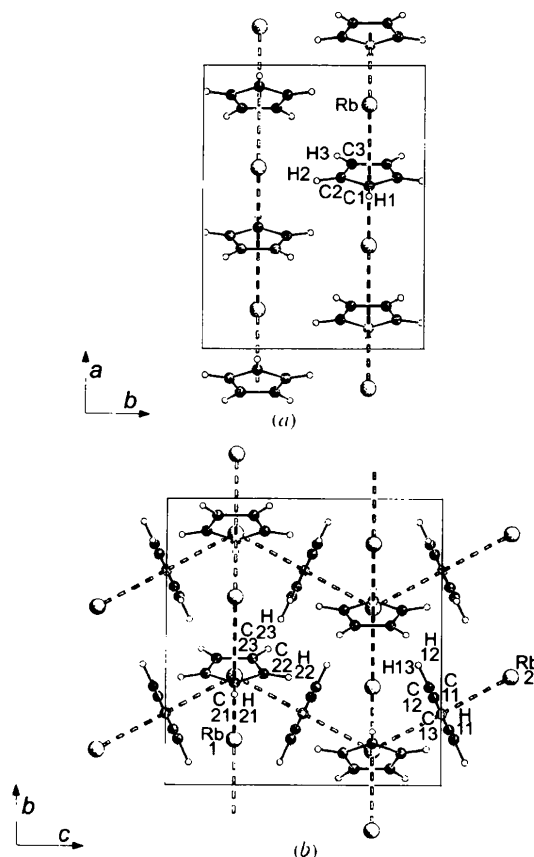

Fig. 3. (*a*) Structure plot of orthorhombic RbC₅H₅ (phase I). The chain directions are parallel to the *b* and *c* axes. (*b*) Structure plot of orthorhombic RbC₅H₅ (phase II). The chain direction is parallel to the *a* axis.
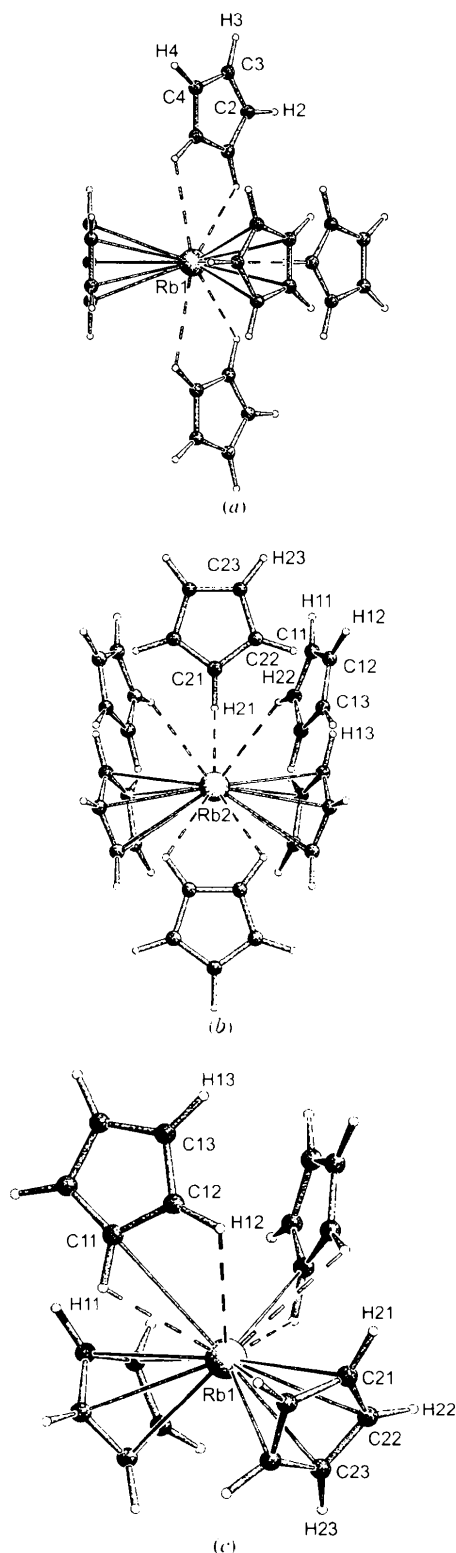
(a)

(b)

(c)

Fig. 4. (a) Coordination sphere around Rb1 in orthorhombic RbC$_5$H$_5$ (phase I). (b) Coordination sphere around Rb2 in orthorhombic RbC$_5$H$_5$ (phase I). (c) Coordination sphere around Rb in orthorhombic RbC$_5$H$_5$ (phase II).

4. Discussion

Classical metallocene is the molecule MCp$_2$ and it has been found for transition metals, alkaline-earths as well as lanthanides. The stoichiometry compound for the alkalines is MCp, which only exists as a polymer. In the solid state this coordination can be achieved by the formation of infinite [MCp]$_\infty$ polymeric chains, as is found here to be the crystal structure of RbCp. The major question in understanding the bonding in metallocenes is why for some compounds the MCp$_2$ molecule is bent (Fig. 5). For the alkaline earth and lanthanide compounds, the bent configuration has been found for molecules in the gas phase and, therefore, some intrinsic property of this bond must favor the bent conformation (Hanusa, 1993). Alternatively, crystal packing forces do influence the molecular conformation, as bent angles generally are smaller in crystals than in the gas phase (Hanusa, 1993). Obviously, for the alkaline metallocenes there is no meaningful comparison with the gas-phase conformation, but we do find strong bending in the [M-Cp]$_\infty$ polymeric chains for M = Rb, K, while for M = Li, Na the Cp ligands are coplanar (Dinnebier & Olbrich, 1997).

Several models have been proposed to explain the bent conformation. A large polarizability (Guido & Gigli, 1976) and the participation of metal d-orbitals (Hayes, 1966; Hassett & Marsden, 1990) both favor a bent conformation. In this case, the negatively charged Cp rings induce a dipole in the large polarizable Rb cation favoring a bent geometry. The importance of both effects increases with increasing atom number and either explanation is in accordance with the observed variation of the bent angle with atom number (Hanusa, 1993). The same holds for the alkali metallocenes, where LiCp and NaCp are not bent and the bent angle of RbCp (~131°) deviates more from 180° than that of KCp [~138° (Dinnebier & Olbrich, 1997)].

Alternatively, it was proposed that ligand–ligand attractive interactions are responsible for the bent conformations (Hollis, Burdett & Bosnich, 1993; Timofeeva, Lii & Allinger, 1995). For the calculated geometries of alkaline-earth and lanthanide metallo-
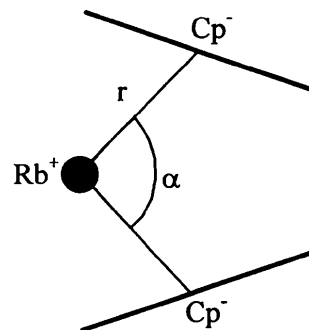

Fig. 5. Schematic drawing of the bent polymeric RbCp molecule.

cenes, Hollis, Burdett & Bosnich (1993) find a shortest carbon–carbon distance between the ligands sandwiching the metal atom of 3.6 ± 0.1 Å, twice the van der Waals radius of carbon (Bondi, 1964). For RbCp we find for the corresponding distances 4.6 (chain A) and 4.3 Å (chain B), well beyond the contact distance. Therefore, Cp—Cp van der Waals attractions can be ruled out as the origin for the bent conformations in alkali metallocenes.

Born repulsion between ligands will prevent bending beyond a certain maximum deviation from 180°. However, in RbCp as well as linear LiCp and NaCp (C—C 4.1 Å) this limit is not reached and also the absence of bending in the Li and Na compounds must have a different origin than steric interactions.

Finally, crystal packing forces do influence the configuration around the metal centers. Bending makes room for other ligands, and for RbCp and KCp (Dinnebier & Olbrich, 1997) additional coordination is found for the metal center by H and C atoms of Cp molecules of neighboring chains (Table 3; previous section).

The occurrence of two polymorphs within the same batch suggests a small difference in energy between them. This can be understood from the structural characteristics of the two compounds: (i) the density of the polymorphs is almost the same (Table 1); (ii) the coordinations of the two crystallographically independent Rb atoms in phase I and of Rb in phase II are similar (previous section; Table 3); (iii) the nonbonded contact distances between Cp molecules in neighboring chains are comparable.

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