



# Insight in cyclopentadienyl metal complexes with superbulky ligands: The crystal structure of $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$

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## ABSTRACT

Reaction of  $(4-n\text{Bu-C}_6\text{H}_4)_5\text{CpH}$  ( $=\text{Cp}^{\text{BIG}}\text{H}$ ) with KH in THF and subsequent recrystallization from hexane/Et<sub>2</sub>O gave the solvent-free product  $\text{Cp}^{\text{BIG}}\text{K}$  in good crystalline yield (55%). Crystal structure determination revealed the one-dimensional coordination polymer  $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$ . Despite the steric bulk of the  $\text{Cp}^{\text{BIG}}$  ligands, the chains are not perfectly linear. They can be pictured as an array of highly symmetric  $(\text{Cp}^{\text{BIG}})_2\text{K}^-$  sandwiches bridged by  $\text{K}^+$  ions at an angle of  $167.7(2)^\circ$ . The C–K bond distances are much shorter than those in other cyclopentadienyl potassium complexes. This is explained by networks of attractive C–H...C( $\pi$ ) interactions between neighbouring  $\text{Cp}^{\text{BIG}}$  ligands. In all cases the C–H donors and C acceptors are represented by the *ortho*-CH units in the aryl substituents. The C–H...C( $\pi$ ) networks within the supersandwich are less distinct than those observed in the metallocene sandwich complexes  $(\text{Cp}^{\text{BIG}})_2\text{M}$  (M = Ca, Sr, Ba, Yb, Sm). Significant out-of-plane bending of the aryl substituents indicates that, within the supersandwich chain, pairs of tighter C–H...C( $\pi$ ) networks exist. Large displacement factors for the  $\text{K}^+$  ions are explained by assuming induced polarization of these soft metals. This results in enforcement of the  $\text{Cp}^{\text{BIG}}\text{--K}$  interactions.

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## 1. Introduction

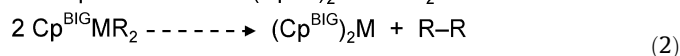
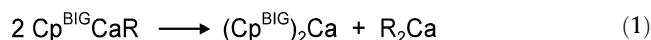
Although the sterically congested cyclopentadienyl (Cp) ligand  $\text{Ph}_5\text{CpH}$  is one of the cheapest commercially available substituted Cp ligands, its organometallic chemistry has hardly been developed [1]. Until recently, only few metallocene complexes  $(\text{Ph}_5\text{Cp})_2\text{M}$  have been structurally characterized (M = Sn [2], Fe [3]) and a handful of structures for ionic metallocenes  $[(\text{Ph}_5\text{Cp})_2\text{M}^+][\text{X}^-]$  were known [4]. Neglect of this bulky Cp ligand is mainly due to the extreme insolubility of its highly symmetrical complexes.

These problems have been circumvented by slight modification of the ligand: substituents in the aryl ring greatly increase the solubility of the organometallic complexes [5–8]. Also, modification of the synthetic procedures gave access to single crystals of  $(\text{Ph}_5\text{Cp})_2\text{Ca}$ ,  $(\text{Ph}_5\text{Cp})_2\text{Ba}$  and  $(\text{Ph}_5\text{Cp})_2\text{Yb}$  [9].

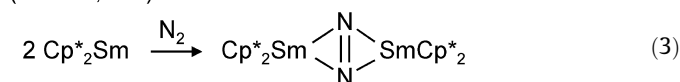
We could observe great solubilisation of *deca*-arylmatalocenes by using *n*-butyl substituents in the *para*-position of the aryl rings.

The ligand  $(4-n\text{Bu-C}_6\text{H}_4)_5\text{Cp}$ , which we abbreviate as  $\text{Cp}^{\text{BIG}}$ , gave access to various sandwich complexes (**1-Ca**, **1-Sr**, **1-Ba**, **1-Yb** and **1-Sm**) which are well-soluble in hexane at room temperature [7,8]. All complexes crystallize from this solvent isomorphously and their crystal structures show surprisingly ordered *n*Bu-substituents.

Attempted isolation of half-sandwich complexes gave in all most cases the metallocene products **1-M** (Eqs. (1) and (2)). For Yb and Sm we even observed spontaneous reduction of the metals from their most stable oxidation +3 stable to the “hot” oxidation state +2 (Eq. (2)). As  $\text{Cp}_2^*\text{Sm(II)}$  oxidizes even under nitrogen atmosphere to  $\text{Cp}_2^*\text{Sm(III)-}\mu\text{N}_2\text{-Sm(III)Cp}_2^*$  (Eq. (3)) [10], spontaneous  $\text{Sm(III)} \rightarrow \text{Sm(II)}$  reduction is surprising ( $E_{1/2} \text{Sm}^{3+}/\text{Sm}^{2+} = -1.55 \text{ V}$  [11]). The mechanism is likely related to that proposed for the sterically-induced-reduction process observed in lanthanide chemistry (SIR) [12].

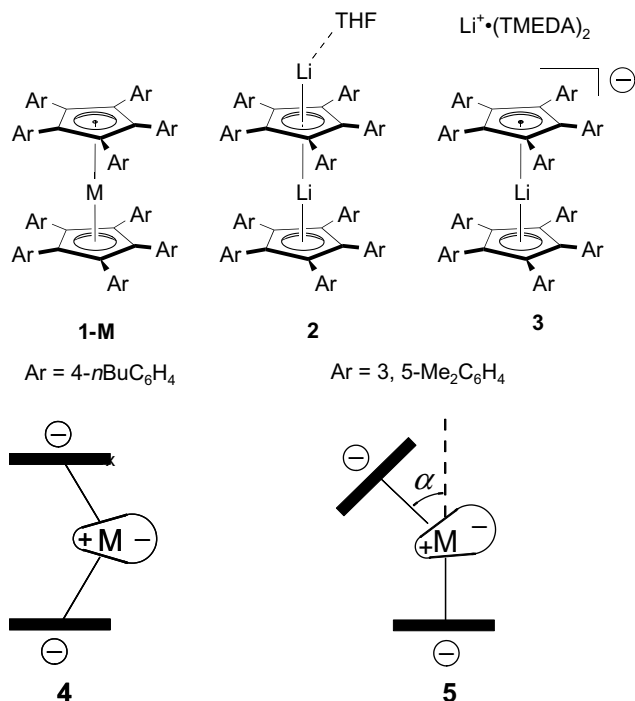


(M = Yb, Sm)



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This unexpected formation of the sandwich complexes **1-M** must be due to the remarkable stability of these sterically overloaded metallocenes. Instead of the anticipated repulsive ligand··ligand interactions, a “merry-go-round” network of attractive C–H··C(π) interactions can be observed (Fig. 1). This network of non-classical hydrogen bonds represents a circular form of the typical herringbone structure of crystalline benzene [13]. Although these ligand··ligand interactions had never been taken into consideration before, following evidence has been obtained: (i) short C··H distances are observed (<2.90 Å, *i.e.* the sum of the van der Waals radii for C and H; for the smaller metals these distances can be as short as 2.41 Å [7]), (ii) the aryl substitu-

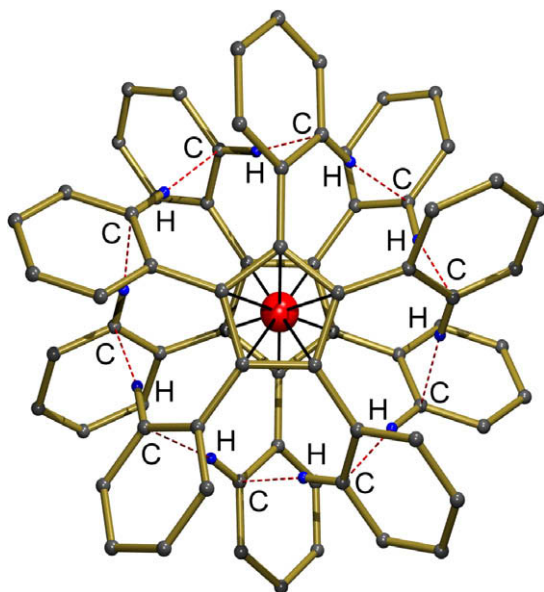


Fig. 1. The “merry-go-round” C–H··C(π) network observed in the sandwich complexes **1-M** (*n*Bu-substituents omitted for clarity).

ents typically bend out of the Cp-plane away from the metal, however, for large metals like Sm and Ba significant bending towards the metal is observed (3.5(1)° and 5.3(2)°, respectively). This out-of-plane bending angle is linearly correlated to the size of the metal [8]. Although C–H··C(π) hydrogen bonds are generally weak, the presence of 10 such interactions could contribute significantly to the stability of the metallocene.

In this contribution, we extend our work with investigations on the use of the Cp<sup>BIG</sup> ligand in alkali metal chemistry. Hitherto, two crystal structures of *penta*-arylcyclopentadienyllithium complexes are known (**2,3**) [14]. Both crystallized from THF or THF/TMEDA solutions as sandwich complexes. Under these conditions cyclopentadienyl lithium compounds generally crystallize as monomeric solvated compounds [15]. It is likely that the spontaneous formation of sandwich structures originates from similar ligand··ligand attraction as observed in (Cp<sup>BIG</sup>)<sub>2</sub>M complexes. Careful examination of the structure for **3** (the structure of **2** is plagued by disorder) indeed shows that a “merry-go-round” network with 10 C–H··C(π) interactions is operative also for metallocenes with the (3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>5</sub>Cp ligand: H··C distances in the range of 2.732–2.845 Å (average 2.791 Å) can be found.

As this network of C–H··C(π) interactions always involves two neighbouring ligands of opposite propeller chirality, the question arises how *penta*-aryl Cp ligands behave in polymeric supersandwich structures. Here, we report on the synthesis and structure of the linear supersandwich [Cp<sup>BIG</sup>K]<sub>∞</sub>.

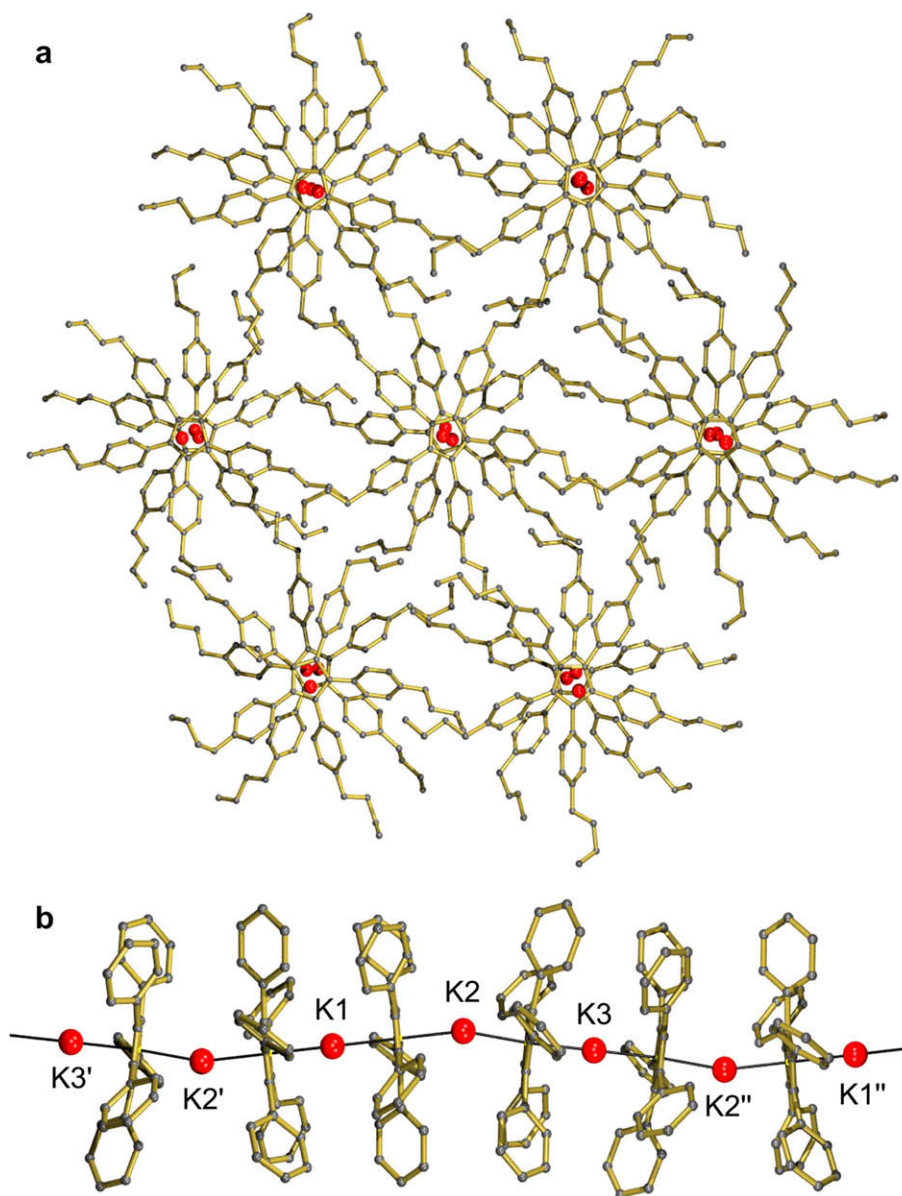
## 2. Results and discussion

Reaction of Cp<sup>BIG</sup>H with KH in THF at 60 °C resulted in the evolution of H<sub>2</sub>. Evaporation of all solvents and recrystallization of the residue from hexane/Et<sub>2</sub>O gave well-formed colourless blocks of solvent-free Cp<sup>BIG</sup>K.

The complex crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c*. Crystal structure determination revealed one-dimensional polymeric chains of [Cp<sup>BIG</sup>K]<sub>∞</sub> which are arranged parallel to each other in the direction of the *ac*-diagonal. Each chain is surrounded by six neighbouring chains that form a nearly perfect hexagon: distances between parallel running chains vary from 15.9–16.2 Å (Fig. 2a). This arrangement allows for favourable interactions between the lipophilic outershells (some of the *n*Bu-substituents are heavily disordered). The steric bulk of the Cp<sup>BIG</sup> ligand rules out interactions between K<sup>+</sup> ions and Cp<sup>-</sup> rings of neighbouring chains (these interactions are typical for chain structures of cyclopentadienyl potassium complexes with less substituted Cp rings [16–18]).

The one-dimensional polymer chain (Fig. 1b) contains three crystallographically unique K<sup>+</sup> ions. Two of these ions, K1 and K3, are located on inversion centers. The chain is not perfectly linear but slightly bent around K2 which is not located on a special crystallographic position (deviation from linearity: 12.3(2)°). As K1 and K3 represent crystallographic inversion centers, the K2··K1··K2' and K2··K3··K2'' axes are perfectly linear. Thus the chain can be pictured as an array of centrosymmetric (Cp<sup>BIG</sup>)<sub>2</sub>K<sup>-</sup> sandwiches (around K1 and K3), with perfectly coplanar Cp<sup>BIG</sup> anions, that are bridged by K<sup>+</sup> ions (K2).

Asymmetry within the chain is also observed in the K–C bond distances (Table 1). The K–C bond distances for K1 and K3 (2.894(4)–2.948(4) Å) are in a somewhat narrower range than those for K2 (2.887(4)–2.993(4) Å), however, all Cp–K interactions can be considered as η<sup>5</sup>. The Cp<sub>cent</sub>–K distances (Cp<sub>cent</sub> represents the geometrical center of the Cp ring) within the sandwich units (Cp<sub>cent</sub>–K1 2.6464(17) Å; Cp<sub>cent</sub>–K3 2.6601(16) Å) are marginally shorter than those to the bridging K2 cation (average Cp<sub>cent</sub>–K2 2.6738(19) Å). The Cp<sub>cent</sub>–metal contacts are of similar length to those reported for (Cp<sup>BIG</sup>)<sub>2</sub>Ba (2.667(1) Å) and (Ph<sub>5</sub>Cp)<sub>2</sub>Ba



**Fig. 2.** (a) Packing of parallel running chains of [Cp<sup>BIG</sup>K]<sub>∞</sub> (view along the chains); hydrogen atoms not shown for clarity. (b) Chain structure for [Cp<sup>BIG</sup>K]<sub>∞</sub>; hydrogen atoms and nBu-substituents not shown for clarity.

**Table 1**

K–C bond distances in [Cp<sup>BIG</sup>K]<sub>∞</sub> (Å); Cp<sub>cent</sub> = Cp ring center, ⟨C⟩ = average K–C distance.

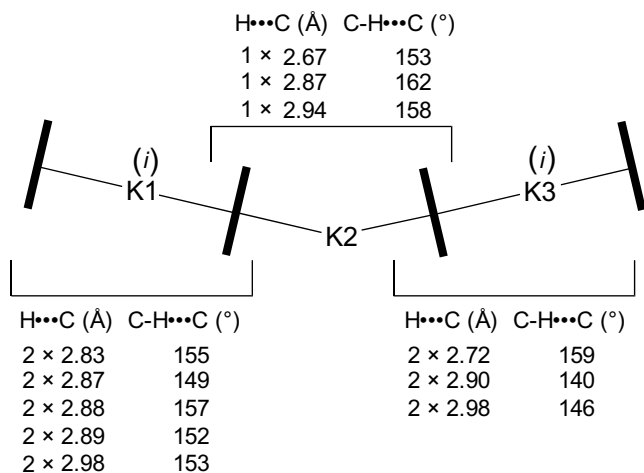
K1	K2	K2	K3
C1 2.894(4)	C1 2.950(4)	C6 2.897(4)	C6 2.935(3)
C2 2.920(4)	C2 2.925(4)	C7 2.887(4)	C7 2.901(4)
C3 2.929(4)	C3 2.912(4)	C8 2.940(4)	C8 2.900(4)
C4 2.917(3)	C4 2.925(3)	C9 2.993(4)	C9 2.923(4)
C5 2.894(4)	C5 2.949(4)	C10 2.969(4)	C10 2.948(4)
⟨C⟩ 2.911(4)	⟨C⟩ 2.932(4)	⟨C⟩ 2.937(4)	⟨C⟩ 2.921(4)
Cp <sub>cent</sub> 2.6464(17)	Cp <sub>cent</sub> 2.670(2)	Cp <sub>cent</sub> 2.6775(19)	Cp <sub>cent</sub> 2.6601(16)

(2.670(1) Å). This is in good agreement with comparable ionic radii for K<sup>+</sup> (1.33 Å) and Ba<sup>2+</sup> (1.34 Å).

It should be noticed that the Cp<sub>cent</sub>–K distances in [Cp<sup>BIG</sup>K]<sub>∞</sub> (average 2.664(2) Å) are significantly shorter than those reported for similar linear cyclopentadienyl potassium chains: e.g. [CpK]<sub>∞</sub> 2.816 Å [16a], [Me<sub>3</sub>SiCpK]<sub>∞</sub> 2.787 Å [17], [(1, 2, 4-Me<sub>3</sub>Si)<sub>3</sub>CpK]<sub>∞</sub>

2.751 Å [18]. At first sight it might seem odd that the Cp<sub>cent</sub>–K distance decreases with increasing Me<sub>3</sub>Si-substitution, however, interchain interactions should be taken into account for the less bulky cyclopentadienyl potassium complexes. Both, [CpK]<sub>∞</sub> and [Me<sub>3</sub>SiCpK]<sub>∞</sub> display short contacts between K<sup>+</sup> and Cp<sup>-</sup> rings of neighbouring chains. However, [(1, 2, 4-Me<sub>3</sub>Si)<sub>3</sub>CpK]<sub>∞</sub> forms zig-zag chains (average bending angle 8.5°) that are completely shielded by a protective shell of Me<sub>3</sub>Si-substituents. The linear chains [(1, 2, 4-Me<sub>3</sub>Si)<sub>3</sub>CpK]<sub>∞</sub> and [Cp<sup>BIG</sup>K]<sub>∞</sub> are the only examples so far of unsolvated cyclopentadienyl potassium complexes that lack interchain K<sup>+</sup>⋯Cp<sup>-</sup> contacts. Despite the more extensive substitution in Cp<sup>BIG</sup>, Cp<sub>cent</sub>–K distances in [Cp<sup>BIG</sup>K]<sub>∞</sub> are on average 0.087 Å shorter than those in [(1, 2, 4-Me<sub>3</sub>Si)<sub>3</sub>CpK]<sub>∞</sub>. The average Cp<sub>cent</sub>–K distance in [Cp<sup>BIG</sup>K]<sub>∞</sub> of 2.664(2) Å is even significantly shorter than that in a high pressure modification of CpK (2.73 Å at 4 GPa) [16b].

It seems unlikely that these record short Cp<sup>BIG</sup>–K distances [19] are due to a higher electron density in its Cp ring. In fact, on ac-



Scheme 1.

count of charge delocalization into the aryl substituents the opposite is expected [1,20]. As the aryl rings in  $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$  make an average angle of  $50.5^{\circ}$  with the Cp-plane, charge delocalization is not completely shut off. It therefore seems that the short  $\text{Cp}^{\text{BIG}}\text{-K}$  distances originate from a similar ligand...ligand attraction as has been observed in the sandwich complexes **1-M** ( $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Yb}, \text{Sm}$ ).

Indeed, neighbouring  $\text{Cp}^{\text{BIG}}$  ligands are always of opposite propeller chirality and fit like gear-wheels. This allows for a network of attractive  $\text{C-H}\cdots\text{C}(\pi)$  interactions (Scheme 1). The  $\text{Cp}^{\text{BIG}}$  rings that sandwich K1 are connected via 10  $\text{C-H}\cdots\text{C}(\pi)$  contacts shorter than  $3.0 \text{ \AA}$  [21]. In all contacts the C-H donors and C acceptors are represented by the *ortho*-CH unit in the aryl substituent. Thus a similar “merry-go-round” network as in Fig. 1 is described. The  $\text{C-H}\cdots\text{C}(\pi)$  distances are somewhat longer than those found for the barocene ( $\text{Cp}^{\text{BIG}}_2\text{Ba}$ ) ( $2.81 \text{ \AA}$  [8]) and, therefore, values slightly higher than the usual  $2.90 \text{ \AA}$  cut-off value (*i.e.* the sum of the van der Waals radii for C and H) have been taken. The average value for the here observed  $\text{C-H}\cdots\text{C}(\pi)$  contacts ( $2.89 \text{ \AA}$ ) is just below this cut-off value. The  $\text{C-H}\cdots\text{C}(\pi)$  network between ligands sandwiching K3 is less regular and six contacts  $<3.0 \text{ \AA}$  have been observed. The smallest number of contacts is observed for K2. This is due to the bent arrangements of the  $\text{Cp}^{\text{BIG}}\text{-K2-Cp}^{\text{BIG}}$  unit which allows close contact at one side at cost of complete loss of contacts at the open side. Indeed, one very short  $\text{H}\cdots\text{C}$  contact of  $2.67 \text{ \AA}$  has been measured at the shorter separation.

Like in  $(\text{Cp}^{\text{BIG}})_2\text{Ba}$ , the aryl substituents are bent out of the Cp-plane to enforce attractive  $\text{C-H}\cdots\text{C}(\pi)$  contacts. The  $\text{Cp}^{\text{BIG}}$  ligands around K1 show bending angles between  $0.5(3)^{\circ}$  and  $4.0(3)^{\circ}$  all towards the metal K1. The  $\text{Cp}^{\text{BIG}}$  ligands around K3 show bending angles in the range  $1.4\text{--}6.3^{\circ}$  towards the metal, except for one substituent which bends towards K2 by  $2.4(3)^{\circ}$ . These values underscore the observation that ligand...ligand attraction in  $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$  operates pair-wise and is probably strongest around the metals K1 and K3. As can be seen in a space-filling model of the chain (Fig. 3), this pair-wise attraction also influences the entanglement of the *n*Bu-substituents which show similar pairing in their van der Waals attraction.

Another point of interest is the observation of excessively large displacement factors for the  $\text{K}^+$  ions. Like in **1-Sr**, **1-Ba**, **1-Yb** and **1-Sm** the metals are slightly disordered within a plane parallel to the Cp rings (Fig. 4). This disorder seems to increase with the polarizability of the metal and suggests that the more polarizable metals prefer to be slightly off-center. As pointed out earlier [7,8], induced metal polarization could enforce Cp-metal attraction (4). A similar

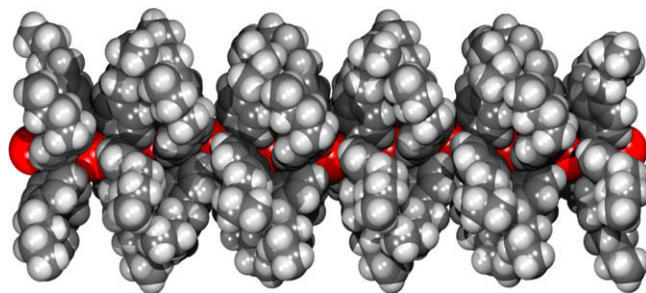


Fig. 3. Space-filling model of the chain  $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$  showing the pair-wise attraction of  $\text{Cp}^{\text{BIG}}$  ligands. Starting from the left, the  $\text{K}^+$  atoms are labeled: K1, K2, K3, K2', K1', K2'', K3'...etc.

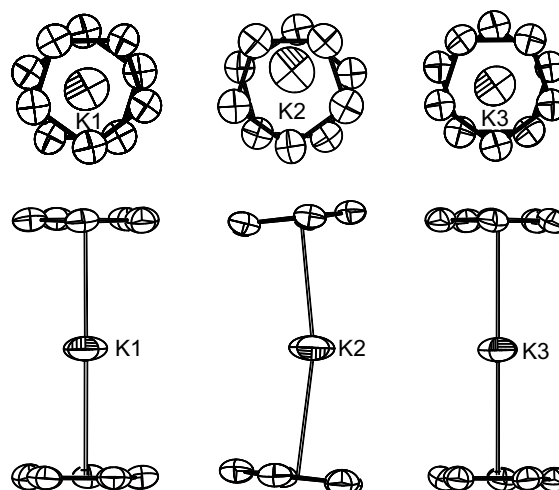


Fig. 4. ORTEP plots (50% probability) for the partial sandwich units within  $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$ . The  $U_{\text{eq}}$  for K1, K2 and K3 are 0.0634, 0.0684 and 0.0554, respectively.

induced-polarization-model (5) is in use to explain the typically observed bending of heavier alkaline-earth and lanthanide metallocenes [22].

### 3. Conclusion

In summary, the easily prepared  $\text{Cp}^{\text{BIG}}\text{K}$  crystallizes from a polar solvent as a solvent-free coordination polymer  $[\text{Cp}^{\text{BIG}}\text{K}]_{\infty}$ . Despite the steric bulk of the  $\text{Cp}^{\text{BIG}}$  ligands, these one-dimensional chains are not perfectly linear but contain centrosymmetric  $(\text{Cp}^{\text{BIG}})_2\text{K}^-$  units (around K1 and K3), which inherently show parallel Cp rings, as well as bent  $(\text{Cp}^{\text{BIG}})_2\text{K}^-$  units (around K2). The chain can be pictured as an array of highly symmetric  $(\text{Cp}^{\text{BIG}})_2\text{K}^-$  sandwiches bridged by  $\text{K}^+$  ions. All C-K bond distances and  $\text{Cp}_{\text{cent}}\text{-K}$  contacts are considerably shorter than those in comparable cyclopentadienyl potassium structures. As neighbouring  $\text{Cp}^{\text{BIG}}$  ligands show opposite propeller chirality and fit like gear-wheels, short  $\text{Cp}^{\text{BIG}}\text{-K}$  contacts are explained by networks of attractive  $\text{C-H}\cdots\text{C}(\pi)$  interactions between two such ligands (Fig. 1). These networks are less distinct as those observed in metallocene sandwich complexes **1-M**. This is likely due to the chain character of these supersandwiches. Significant out-of-plane bending of the aryl substituents indicate that within this supersandwich pairs of tighter  $\text{C-H}\cdots\text{C}(\pi)$  networks exist (around K1 and K3). The large displacement factors for the  $\text{K}^+$  ions are explained by assuming induced polarization of these soft metals. This results in enforcement of the  $\text{Cp}^{\text{BIG}}\text{-K}$  interactions.



## 4. Experimental

### 4.1. General procedures

All experiments were carried out under argon using dry solvents and Schlenk techniques. The ligand Cp<sup>BiGH</sup> was prepared according to a literature procedure [23]. NMR spectra were recorded on a Bruker DPX300 (300 MHz) spectrometer. The crystal was measured on a Siemens Smart diffractometer with APEXII area detector system. The structures were solved by Direct Methods (SHELXS-97) and refined with SHELXL-97 [24]. All geometry calculations and graphics were performed with PLATON [25].

### 4.2. Synthesis and crystallization of Cp<sup>BiGK</sup>

Cp<sup>BiGH</sup> (250 mg, 344 μmol) and KH (41.4 mg, 1.03 mmol) were dissolved in THF (5 mL) and stirred at 60 °C for 18 h. After centrifugation the solvent was removed in vacuo and the residue was dried (25 °C, 1 Torr, 30 min). The sticky residue was washed with hexane (3 × 3 mL) to leave a light brown powder. The product crystallized from hexane/diethylether (1:1) in form of large colourless blocks. Yield: 145 mg (55%). M.p. 160 °C (dec). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 300 MHz, 20 °C): 0.92 (t, 15H, CH<sub>3</sub>), 1.34 (m, 10H, CH<sub>2</sub>), 1.54 (m, 10H, CH<sub>2</sub>), 2.46 (t, 10H, CH<sub>2</sub>), 6.66 (m, 20H, Ar) ppm. <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 20 °C): 14.4, 23.2, 34.8, 36.2, 120.6, 127.3, 132.3, 136.4, 140.0 ppm. Anal. Calc. for C<sub>55</sub>H<sub>65</sub>K: C, 86.33; H, 8.56. Found: C, 86.12; H, 8.72%.

### 4.3. Crystal structure determination for Cp<sup>BiGK</sup>

Air-sensitive colourless block (0.4 × 0.2 × 0.2 mm<sup>3</sup>), monoclinic, *a* = 20.1748(7) Å, *b* = 27.4754(9) Å, *c* = 18.6994(6) Å, *V* = 9450.8(6) Å<sup>3</sup>, space group *P*2<sub>1</sub>/*c*; formula (C<sub>110</sub>H<sub>130</sub>K<sub>2</sub>), *M* = 1530.35, *Z* = 4, ρ<sub>calc</sub> = 1.076 g cm<sup>-3</sup>, μ(Mo Kα) = 0.146 mm<sup>-1</sup>; 126555 reflections were measured (Mo Kα = 0.71073 Å, graphite monochromator, *T* = -90 °C) on an Enraf Nonius CAD4 diffractometer, 15047 unique reflections (*R*<sub>int</sub> = 0.077, θ<sub>max</sub> = 24.1°), 8861 observed reflections with *I* > 2.0σ(*I*). The structure was solved by direct methods. Full matrix least-squares refinement on *F*<sup>2</sup> gave *R*<sub>1</sub> = 0.0849, *wR*<sub>2</sub> = 0.2565 and *S* = 1.04 (1182 parameters), min/max residual electron density -0.52/+0.60 e Å<sup>-3</sup>. The somewhat higher *R*-values can be ascribed to partial disorder of the *n*Bu-substituents and the 3 K<sup>+</sup> ions. In some cases a satisfying disorder model could be found. In other cases disorder was treated by refinement with large anisotropic parameters. The hydrogen atoms of the *n*Bu-substituents have been placed at idealized calculated positions and were refined in a riding mode. Hydrogen atoms on the aryl rings have been located in the difference-Fourier and were refined with isotropic displacement factors. Analysis of the C-H...C(π) network has been done on a structure in which the hydrogen atoms have been placed at 1.08 Å positions [21].

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## Appendix A. Supplementary material

CCDC 703299 contains the supplementary crystallographic data for Cp<sup>BiGK</sup>. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.073.

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