Coordination Chemistry Reviews
176 (1998) 17–66

Recent developments in cyclopentadienyl-alkalimetal chemistry

Sjoerd Harder*

Department of Chemistry, University of Konstanz, Postfach 5560 M738, D-78457 Konstanz, Germany

Received 2 October 1997; accepted 19 November 1997

Contents

---

* Tel.: +49 7531 882009; fax: +49 7531 883137; e-mail: harder@dg9.chemie.uni-konstanz.de

0010-8545/98/$ - see front matter © 1998 Elsever Science S.A. All rights reserved.
PII S0010-8545(98)00113-1

Abstract

Cyclopentadienyl-alkalimetal compounds are among the first organometallic compounds prepared. Their structures have been well studied and generally show unsolvated or solvated polymer chains or solvated monomers. During the last few years there have been some interesting developments in the structural chemistry of this compound class; structures of oligomeric species and anionic metallocene sandwich complexes have been reported. This work discusses bonding in Cp-alkalimetal compounds and summarizes selected structural data of all Cp-alkalimetal compounds published up to September 1997 including our own unpublished results (the indenyl, fluorenyl and higher delocalized systems have been excluded deliberately and are only mentioned occasionally for comparison). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Cyclopentadienyl; Alkalimetal; Sandwich compounds

1. Introduction

The landmark synthesis and structure determination of bis(cyclopentadienyl)iron (‘ferrocene’) [1,2] opened an important field in chemistry: the organometallic chemistry of the transition metals, a field which is nowadays well-established and surpassed the chemistry of the main-group metals. A surprisingly large amount of modern transitionmetal compounds still contain the cyclopentadienyl ligand (Cp).

Ferrocene is often labelled as the first metallocene. However, if one takes the term ‘metallocene’ to describe a metal complex having one or more Cp ligands [16], than metallocene chemistry existed already long before the discovery of ferrocene. Ironically, the first synthetic route to ferrocene ($2CpMgBr + FeCl_2 \rightarrow Cp_2Fe + 2MgBrCl$) makes use of Cp-magnesiumbromide, a main-group metallocene. Even older than this cyclopentadienyl Grignard reagent [3] are the cyclopentadienyl complexes of the alkalimetals, which have been prepared already shortly after the isolation of cyclopentadiene itself.

The discovery of cyclopentadiene has been described in a couple of entertaining papers[1] [4,5] which show that especially the slow and reversible Diels–Alder dimerization of cyclopentadiene has been puzzling at that time. The new C_5H_6-compound has been marked as the ‘simplest indene’ [4] or was labelled ‘propentylene’ [6]. Later it was more correctly named ‘cyclopentadiene’ [5] and soon after, in

---

[1] Quoted from Roscoe and Liebigs [4] (translated from German): “In order to find a clarification for the Genesis of this hydrocarbon, I approached a friend, Mr Josiah Hardman, who kindly supplied me with about 200 liters of the most volatile fractions from 240 tons of tar. This material was carefully fractionated and yielded circa 2 liters of a low-boiling substance”.Quoted from Kraemer and Spilker [5] (translated from German): “The observation that the boiling point of the volatile fractions experience an increase after standing was already made by us in an early stadium of our research, in the course of which we sometimes experienced in our laboratory an explosion of great violence which we ascribe to the sudden decomposition of such unsaturated compounds”.

the year 1900, the first organometallic compound containing a cyclopentadienyl ligand was prepared in the form of CpNa. Thiele prepared CpNa ‘in situ’ for the use in further reactions [7], but 1 year later he synthesized and isolated pure CpK from the reaction of cyclopentadiene and potassium metal in benzene [8]. Interestingly, CpK represents the first isolated pure organoalkalimetal compound (all previous attempts to isolate pure organometallic compounds of the alkalimetals failed [9]).[2]

Although it was recognized in an early stage that Cp-alkalimetal compounds are salt-like highly ionic species, investigations on its bonding and molecular structures only started in the late 1950s. Results from IR [10,11] and NMR measurements [12–14] indicated largely ionic species in which the metal cation is bonded above the π-plane along (or close) to the fivefold axis of the Cp ligand. The first single crystal structure determinations of Cp-alkalimetal compounds date from 1976 and showed this structural type indeed to be correct (first polymeric chain structure [15,16]; first monomeric structures [17–20]). In the meantime, several structures in the Cp-alkalimetal series have been determined. These include structures of substituted and unsubstituted Cp rings with a large variety of alkalimetal/ligand combinations. In general, the structures of Cp-alkalimetal compounds belong to the categories of unsolvated linear polymers, solvated linear polymers and solvated monomers (Fig. 1).

The preference for a certain structure type depends on the combination of ring-substituents, metal and the solvent (or ligands) present. For a long time there seemed to be no more variation within this group of Cp-alkalimetal structures. However, the continuous work of main-group organometallic chemists combined with the increasing interest of transitionmetal chemists in their Cp-alkalimetal precursors, resulted in some new impulses in this field. Likewise, new developments and improvements in methods for structure determination have been of great value. This work is the first review article dealing specifically with Cp-alkalimetal compounds. It not only complements earlier review articles in which Cp-alkalimetal compounds were included [21–28], but also gives a complete summary of all Cp-alkalimetal structures and incorporates the most recent developments in this branch of chemistry.

2. Bonding in cyclopentadienyl-alkalimetal complexes

Nearly 1 century ago, Thiele isolated the first pure Cp-alkalimetal compound in the form of CpK [8]. Although Thiele was aware of the fact that double bonds next

---

[2] The most common ways to prepare organoalkali compounds were either the Zn–Na exchange reaction, $Et_2Zn + 2Na \rightarrow 2EtNa + Zn$, in which case ate-complexes are formed (Et_3Zn^-/Na^+) or the Hg–Na exchange reaction, $Et_2Hg + 2Na \rightarrow 2EtNa + Hg$, in which case the finely divided sodium amalgam could not be separated from the EtNa precipitate (polar etheral solvents to dissolve the sodium species were not used at that time).

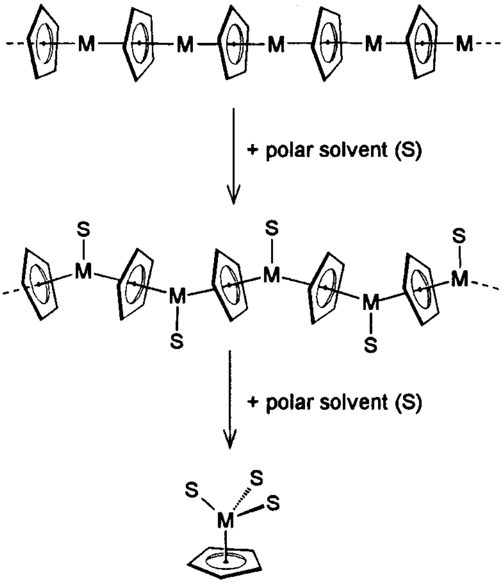


Fig. 1. Generally observed solid state structures of Cp-alkalimetal compounds. Stepwise solvation of the metal cation results in degradation of the polymer chain into monomeric units.

to a methylene or methyl group acidify this C–H unit (or in his own words: 'increase the mobility of the hydrogen atom'), he was reserved about the exact structural formula of the new Cp complex. The first sentence of his article reads (translated from German): 'One of the hydrogens in cyclopentadiene is very easily exchanged for a potassium; probably this is a methylene hydrogen which, as I recently proved, is very reactive on account of its neighbouring ethylene double bonds'. The fact that Thiele was not sure which hydrogen reacted seems amazing, however, one should consider that the concept of aromaticity and Hückel's $4n+2$ electron rule [29] were unknown at that time. Nowadays a simple ab initio calculation suffices to estimate roughly the energy differences between the isomers (Fig. 2) [30].

At present the aromaticity of the Cp anion is beyond dispute, however, the nature of the Cp-alkalimetal bond is still confusing. The bond between a highly electropositive alkalimetal and a less electropositive carbon is expected to have ionic character, but the extent of ionic character has been the subject of a longtime discussion [31–33]. Several advanced calculational methods have been applied to analyze the electron distribution in alkalimetal compounds [34–38]. At present, the value of 80–90% ionic character seems to be established [31–33]. This implies that organoalkalimetal compounds in general should be described as ion clusters in which electrostatic anion–cation attraction predominates the bonding.

The polarity of the carbon–alkalimetal bond is not only dependent on the metal

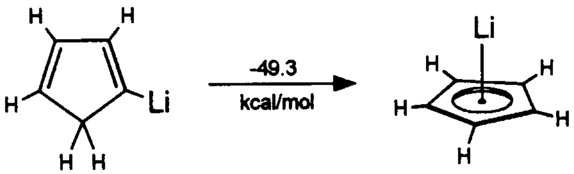
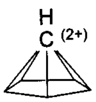


Fig. 2. The energy difference between hypothetical 2-lithio-cyclopentadiene (C_s) and aromatic (η^5)CpLi (C_{5v}), according to ab initio calculation (RHF/6-31 + G*).

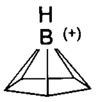
(the polarity increases along the row Li–Cs) but also depends on the nature of the organic anion. Calculations show Cp-alkalimetal bonds to be more ionic than alkyl-alkalimetal bonds (91–97% vs. 79–93% for the latter [31,32]). For this reason the Cp-alkalimetal bond should be considered as highly ionic with negligible covalent character. In analogy, its structures should be described and discussed from an electrostatic point of view. Therefore CpLi can not be considered a member in the series of aromatic 6-membered *nido*-polyhedra (**1**–**3**) for which 'aromaticity in three-dimensions' has been demonstrated and corresponding $4n + 2$ electron rules have been devised [39–41]. Instead, CpLi is better described as a contact ion-pair (**4**) without delocalization of ring electrons in the Li^+-cap and only 'two-dimensional aromaticity' in the Cp ring.

In principle, the cyclopentadienyl ligand may bind to the metal in several ways varying from η^1 to η^5. In order to determine the preferred hapticity in CpLi, a so-called calculational haptotropic search has been carried out [42]. For this purpose the Li^+ was moved above the Cp anion from one side to the other side of the ring. Constrained optimization of the different stadia along the path shows a distinct preference for (η^5)Cp–Li bonding.

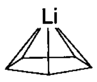
We repeated a similar haptotropic search with less constraints and a better level of theory (including correction for electron correlation) [30]. The CpLi moiety was constrained in C_s symmetry and Li^+ was moved in steps above the Cp ring (which was constrained planar but the hydrogens were allowed to move out of the plane). Several stadia of lithium coordination were optimized (Fig. 3). The energy as well as the distance between the Cp plane and Li^+ increase with decreasing hapticity: $\eta^5 < \eta^4 < \eta^3 < \eta^2 < \eta^1$. The energy difference of 19.6 kcal/mol between (η^5) and (η^1)Cp–Li bonding is substantial. Hitherto, this preferred mode of bonding is confirmed by numerous structure determinations. However, small deviations from



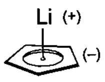
(1)



(2)



(3)



(4)

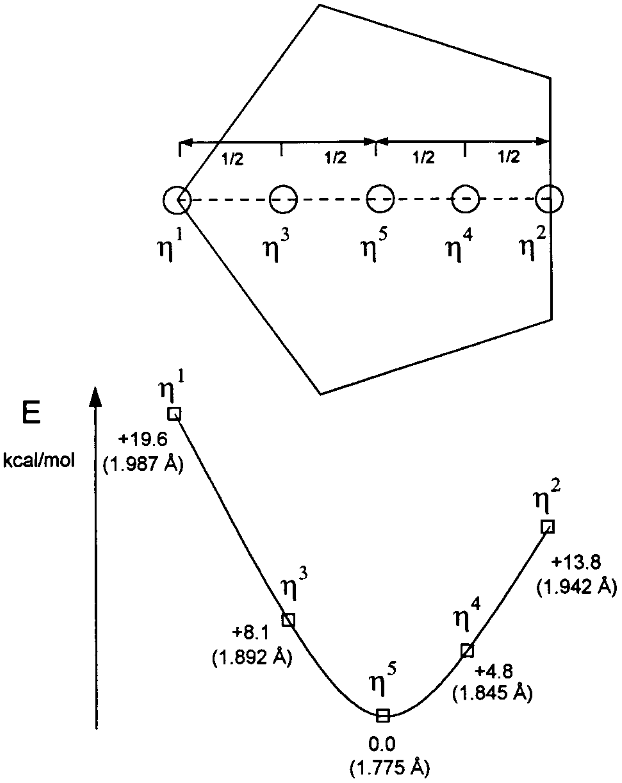
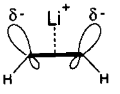


Fig. 3. A haptotropic search on CpLi (MP2/6-31+G*) (Li is shifted over the Cp plane from left to right). The energy as well as the Cp(plane)–Li distance (given in parentheses) increase with decreasing hapticity.

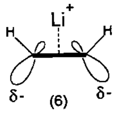
perfect (η^5)Cp–alkalimetal bonding are common. The energy curve around the η^5-minimum is rather flat (Fig. 3) and symmetry breaking ring substituents or metal bound ligands already suffice to distort a perfect (η^5)Cp-alkalimetal bonding geometry.

As has been previously calculated [39–44], the hydrogens in CpLi bend away from the metal cation. This out-of-plane bending shifts more electron density to the side of the ring facing the Li cation (**5**), whereas opposite bending would shift the negative charge to the other side of the Cp ligand (**6**). These effects are generally small: the hydrogens in CpLi are calculated to bend only 2.0° out of the plane of the Cp ring (MP2/6-31+G*). The different stadia in the haptotropic search on CpLi show that out-of-plane bending is most extreme for those C–H units closest to Li^+ (Fig. 4a). The largest bending is observed in the (η^1)Cp–Li complex for the C–H unit closest to Li^+ (15.7°).

An analysis of the atomic charges in the different stadia of the haptotropic search (Fig. 4b), shows that the position of Li^+ also has a tremendous effect on the



(5)



(6)

charge distribution in the Cp anion. The CH groups closest to Li$^+$ have the highest electron density. This is due to the strong polarizing influence of the small Li cation and the good polarizability of the Cp π-system.

Apart from the 'face-on' Cp-alkalimetal bonding described above, the Cp ligand also possesses 'side-on' bonding abilities. Such Cp$^-$ ⋯ M$^+$ interactions especially play a role in the bonding of polymeric structures of the heavier Cp-alkalimetal compounds. Two border structures for 'side-on' Cp$^-$ ⋯ Li$^+$ bonding have been calculated (Fig. 5) [30]: an 'η^1' and an 'η^2' interaction of which the latter is energetically favoured. The Cp$^-$/Li$^+$ dissociation energies are 92.7 and 123.2 kcal/mol, respectively. These interactions are characterized by very short Li$^+$ ⋯ H–C distances and for this reason sometimes labelled as agostic interac-

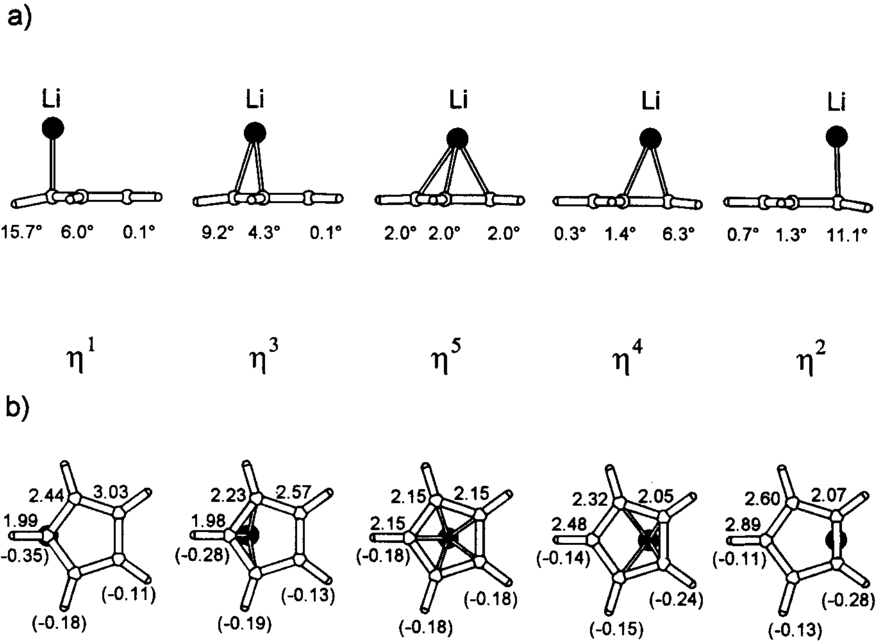


Fig. 4. The different stadia in the haptotropic search on CpLi (MP2/6-31+G*). (a) Side view which shows the hydrogen out-of-plane bending in relationship to the position of Li$^+$ above the Cp plane. (b) Top view showing the relation between the C–Li bond distances (given in Å) and the NPA group charges (i.e. charge of the carbon + attached hydrogen given in parentheses).

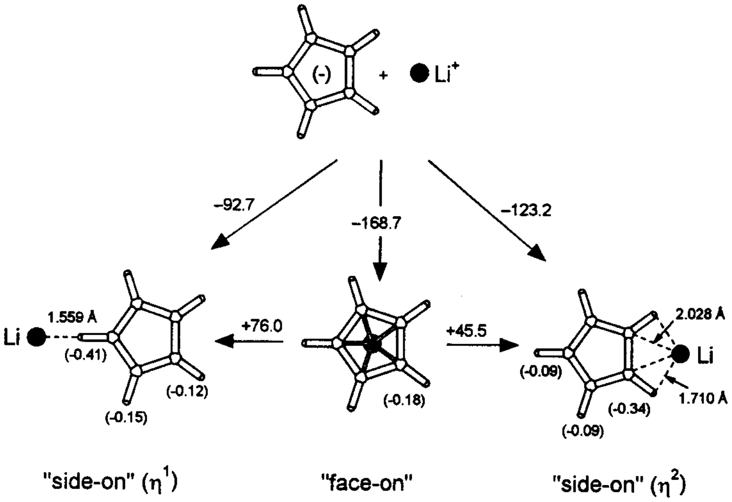
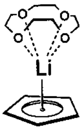


Fig. 5. 'Side-on' $Cp^- \cdots Li^+$ coordination in comparison to 'face-on' $Cp^- \cdots Li^+$ coordination (MP2/6-31+G*). Energy differences are given in kcal/mol. Charges are given in parentheses as NPA group charges (i.e. sum of the charge of the carbon and attached hydrogen).

tions [45–47]. Although C–H bonds are usually polarized $C^{\delta -}–H^{\delta +}$ and would not favourably interact with a Li^+ cation, the strong polarizing influence of a nearby Li^+ draws electron density from the ring into the C–H σ-bond. This is generally observed from a low-field shift in ^{1}H-NMR for the agostic proton [45–47]. Additionally, the π-system of the Cp anion is also strongly polarized by this 'side-on' $Cp^- \cdots Li^+$ contact. This can be concluded from the calculated charges (Fig. 5). Thus, this type of bonding can be understood as an interaction of a metal cation with the electron density and the induced dipole on the Cp ligand.

The calculations presented are performed on gas phase models of an interacting anion–cation combination, whereas in solution or in the solid state many anions and cations seek balance between Coulomb attraction and repulsion. For this reason, the relative energy differences should not be taken as absolute values. However, the fact that a 'side-on' $Cp^- \cdots Li^+$ bond is calculated to be approx. 50% weaker than the usual observed 'face-on' $(\eta^5)Cp^- \cdots Li^+$ bonding, indicates that such interactions should not be underestimated.

Cp-alkalimetal compounds are, with a few exceptions, insoluble in apolar solvents. Consequently, nearly all structure determinations have been performed on species containing polar (co)solvent molecules as a ligand for the metal cation. It is therefore appropriate to include a brief discussion on alkalimetal–ligand interactions here as well. This type of interaction is often described as an *electron-donating* ligand (or solvent molecule) bonding to an *electron-deficient* cation, a terminology dating from an era in which organoalkalimetal compounds were described from the viewpoint of a predominant covalent bonding model. It should be stressed that



(7)

alkalimetal cations are not *electron-deficient*. Ionization potentials for the alkalimetals are the lowest throughout the periodic table of elements and as Schleyer stated [48]: ‘It is hard for lithium to bind two or three electrons; eight is out of the question’. For this reason, polar solvents like THF or TMEDA are not *electron-donating* species which donate electron density in order to fill up empty valence orbitals at the alkalimetal cation. Several independent calculations [49,50] have shown the interaction between lithium and a polar solvent to be primarily electrostatic, i.e. a large electrostatic component (cation–dipole attraction) and a smaller polarization component (cation-induced dipole attraction) are involved, but negligible charge transfer from the ligand to the lithium cation is observed. Consequently, eight-electron rules do not apply to the coordination chemistry of the Group I metals. Instead, alkalimetal cations collect as many anions and dipolar ligand molecules in their coordination spheres as possible. This number is only defined by steric limits. For example, an official electron count in the complex CpLi · (12-crown-4) (**7**) [51] results in 14 valence electrons in the Li coordination sphere. The large number of Li^+-anion and Li^+-dipole contacts in this complex is merely a consequence of the favourable construction of the crown ether molecule.

In summary, Cp-alkalimetal compounds are highly ionic species of which the molecular structures should be discussed in terms of electrostatic attraction and repulsion between ion charges, induced ion dipoles and (partially induced) ligand dipole moments.

3. Structures of cyclopentadienyl-alkalimetal complexes

3.1. Polymeric cyclopentadienyl-alkalimetal complexes

Although the bond between a carbanion and an alkalimetal cation is highly ionic, organoalkalimetal compounds generally do not show the salt-like character as found for NaCl (i.e. poor solubility in organic solvents and the formation of an infinite three-dimensional structure). This distinction stems from the difference between the electron-distribution around a Cl^- and a carbanion in general. Whereas the electron density in Cl^- is distributed spherically, a carbanion commonly shows an asymmetric charge distribution in which the negative charge is localized on one side of the molecule. Obviously, these differences are reflected in the different solid state structures of NaCl and organoalkalimetal compounds (Fig.

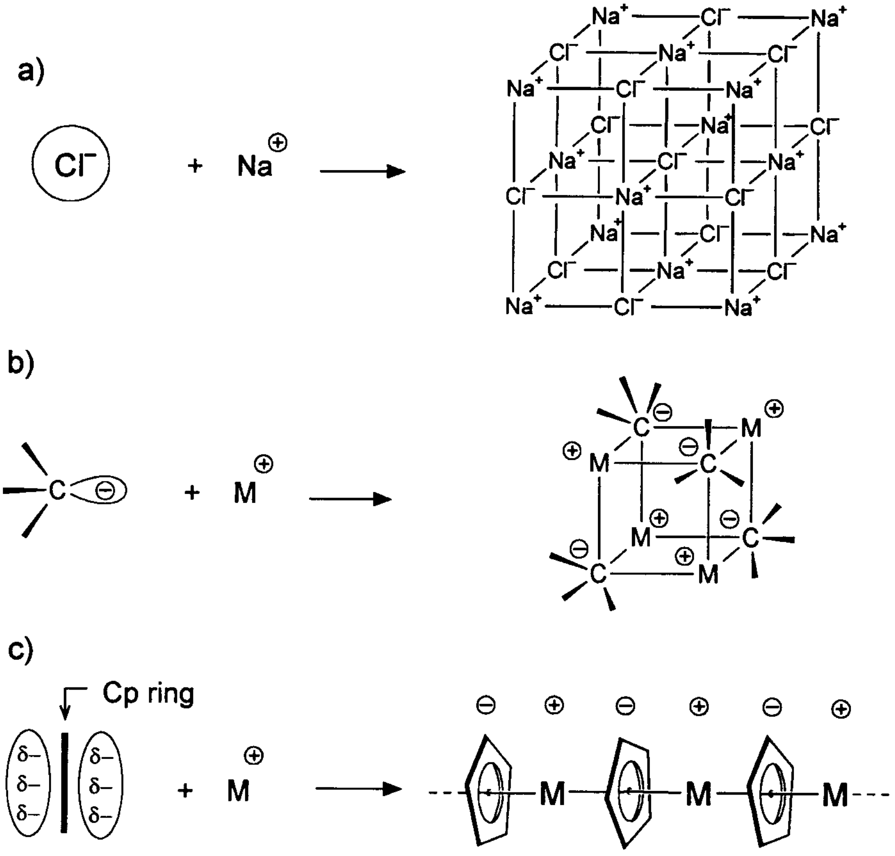


Fig. 6. The relationship between the structure of the anion and the structure of the aggregate.

6a,b) and, consequently, in their physical properties. Whereas NaCl forms an infinite three-dimensional polymeric structure, organoalkalimetal compounds generally form defined clusters in which the outside organic bulk prevents further aggregation.

The cyclopentadienyl anion differs from general carbanions in the sense that the electron distribution is evenly divided between all carbon atoms in the ring and on both sides of the Cp ring (Fig. 6c). For this reason a one-dimensional polymer-like chain structure, a supersandwich, is obvious and often observed in X-ray structures of Cp-alkalimetal compounds. All structurally known polymeric Cp-alkalimetal complexes have been summarized in Table 1.

The structures of the *unsubstituted* and *unsolvated* Cp-alkalimetal compounds (CpLi, CpNa, CpK, etc.) have always been a matter of fundamental interest. However, such compounds are generally very slightly soluble in non-coordinating apolar solvents and can only be obtained from these solvents as fine powders.

Table 1
Crystal structures of polymeric Cp-alkalimetal compounds[a]

Compound formula	Range C–M (Å)	Av. C–M (Å)	Cp_c–M[b] (Å)	CCDC code	Ref.
CpLi	2.275–2.335	2.307	1.969	–	[52]
CpNa	2.632–2.671	2.650	2.357	–	[52]
CpK	3.033–3.081	3.056	2.816	–	[52]
	2.956–3.139	3.055	2.816	–	
CpRb (phase I)	3.173–3.263	3.214	2.962	–	[53]
	3.086–3.301	3.175	2.944		
CpRb (phase II)	3.139–3.228	3.184	2.962	–	[53]
(TMS)CpLi	2.280–2.339	2.305	1.966	PAPYOU	[54]
	2.281–2.333	2.299	1.959		
	2.283–2.329	2.308	1.968		
	2.274–2.347	2.312	1.972		
	2.279–2.324	2.299	1.957		
	2.301–2.339	2.320	1.982		
(TMS)CpK	2.988–3.079	3.032	2.785	FOGMET	[55,56]
	3.002–3.073	3.035	2.788		
CpNa · TMEDA	2.856–2.964	2.914	2.667	CPNATM10	[15,16]
	2.830–3.017	2.940	2.691		
2-(THF)CH_2CpNa · THF	2.733–2.898	2.823	2.568	PIRFAX	[57]
	2.698–2.968	2.829	2.576		
(benzyl)CpNa · THF	2.728–2.836	2.784	2.515	SUDWAP	[58]
	2.661–2.897	2.774	2.506		
(cyclopentyl)CpNa · THF	2.667–2.803	2.724	2.455	SUDWET	[58]
	2.693–2.799	2.744	2.477		
$(Me_2N)_2$BCpNa · THF	2.704–2.796	2.752	2.477	ZOQLUM	[59]
	2.710–2.787	2.753	2.479		
	2.681–2.824	2.754	2.482		
	2.614–2.926	2.801	2.538		
$(Me_2N)_2$BCpNa · THP	2.662–2.778	2.720	2.441	ZOQMAT	[59]
	2.712–2.745	2.731	2.452		
(Me_2B)CpNa · $(THP)_2$	2.744–2.928	2.843	2.578	ZOQMIB	[59]
	2.714–2.745	2.731	2.452		
$(Bu^t$NHSi)CpK · THP	3.012–3.095	3.052	2.808	HACYOZ	[60]
	2.979–3.085	3.031	2.785		
Cp* K · $(pyridine)_2$	2.962–3.104	3.030	2.783	KOHZUC	[61]
	2.959–3.105	3.058	2.794		
CpK · Et_2O	2.992–3.030	3.011	2.767	NAGSUJ	[62]
	2.992–3.032	3.012	2.768		

[a] Coordinates (without S.D.) originate from the Cambridge Crystallographic Database [63].
[b] Cp_c represents the geometric center of the C_5-ring.

Developments in high-resolution powder X-ray diffraction using synchrotron radiation, however, enable the powder structure determinations of substances of growing complexity. The solid state structures of the series of simple unsubstituted and unsolvated Cp-alkalimetal compounds have been determined only very recently via X-ray powder diffraction.

Structural analyses of CpLi and CpNa powders reveal that these compounds are isomorphous, i.e. they show very similar cell parameters and possess an identical crystal system and spacegroup [52]. Both compounds can be described as one-dimensional linear supersandwiches of alternating Cp anions and metal cations (Fig. 7). Crystallographic symmetry imposes all Cp rings within each supersandwich to be coplanar and eclipsed. Likewise, equidistant Cp–M bonds are imposed by symmetry, however, the metal cations are not bound exactly on the line between the centres of two subsequent Cp rings: the angles Cp_c–Li–Cp_c and Cp_c–Na–Cp_c measure 176.4 and 177.7°, respectively. Each linear supersandwich is surrounded from six other parallel running $(CpM)_\infty$ chains (Fig. 7b). Four of these chains are positioned 'staggered' (i.e. offset by exactly halve of the *c*-axis like shown in Fig. 7a), a situation which enables 'side-on' $Cp^- \cdots M^+$ bonding (see Section 2), and two are positioned 'eclipsed'. The distances between 'eclipsed' chains (z in Fig. 7b) are longer than those between 'staggered' chains (x and y in Fig. 7b). Whereas, the 'eclipsed' chain pairs in CpLi and CpNa are situated at similar distances, the 'staggered' chains in CpLi are further apart from each other than those in CpNa. Also, the shortest interchain Li ··· H contact of 3.453 Å is longer than the shortest interchain Na ··· H contact of 3.353 Å. Apparently, the Cp rings within the $(CpLi)_\infty$ chain are so close to each other that 'side-on' $Cp^- \cdots Li^+$ bonding is effectively prohibited by interchain $Cp^- \cdots Cp^-$ repulsion. In $(CpNa)_\infty$, the larger Na^+ forces the Cp rings further apart and enables a slightly more efficient penetrating of 'staggered' chain pairs.

Whereas CpLi and CpNa form nearly linear supersandwiches which only slightly interact, the structures of the heavier cyclopentadienides, CpK [52] and CpRb [53], form bent 'zig–zag' chains of CpM units which strongly interact among each other. This nicely shows the influence of an increase in metal radius. Enlargement of the cation results in larger distances between the Cp anions within a chain. This facilitates bending of the Cp^-–M^+–Cp^- unit and enables a very efficient bonding interaction between the polymer chains. For example, strongly bending of the Cp–K–Cp unit in CpK (138°) maximizes interchain $Cp^- \cdots K^+$ bonding, while

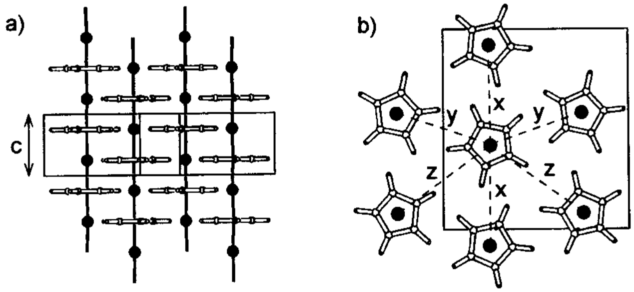


Fig. 7. (a) View perpendicular on the linear chains of CpM (M = Li or Na). (b) View along the linear chains of CpM (the distances between neighbouring chains are designated with x, y and z; for M = Li: x = 5.565 Å, y = 5.557 Å and z = 6.260 Å; for M = Na: x = 5.503 Å, y = 5.309 Å and z = 6.291 Å).

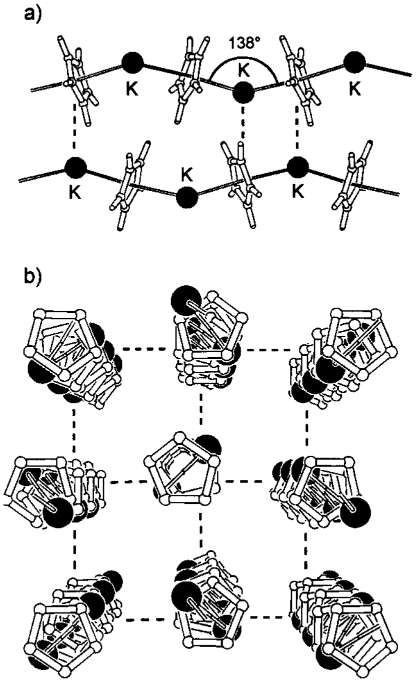


Fig. 8. (a) Two neighbouring 'zig–zag' chains of CpK units. (b) Perspective view along the interacting chains in the structure of CpK; hydrogen atoms are omitted for clarity.

minimizing the interchain $Cp^- \cdots Cp^-$ repulsive interactions (Fig. 8a). The chain direction in the structure of CpK coincides with a crystallographic fourfold inversion axis and therefore each $(CpK)_\infty$ chain interacts with four neighbouring chains (Fig. 8b).

For CpRb, two different crystal phases are found [53]. The polymer chains in both crystal phases are strongly bent (123.5–131.6°). One of the phases (phase I) differs from all other polymeric Cp–M chain structures: the structure is built-up from layers of parallel chains, however, neighbouring layers show a mutually perpendicular orientation (Fig. 9). The other structurally known phase of CpRb (phase II) shows interacting parallel chains (Fig. 10).

Although 'side-on' *inter*chain $Cp^- \cdots M^+$ contacts are generally weaker than 'face-on' $Cp^- \cdots M^+$ *intra*chain contacts, the energy of such interactions should not be neglected (see discussion in Section 2). Therefore the structures of CpK and CpRb, can be considered as a transitional form between the one-dimensional chain-like polymer structure of CpLi and an infinite three-dimensional polymer structure.

Only two cases of single crystal structure determinations of solvent free Cp-alkalimetal compounds have been described in the literature, that of (TMS)CpLi [54] and that of (TMS)CpK [55,56]. A comparison of these results with the work on

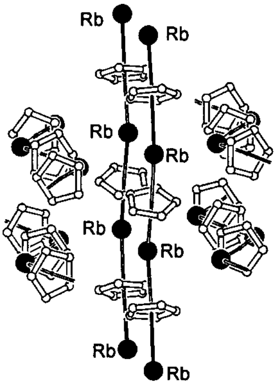


Fig. 9. CpRb (phase I) shows layers of parallel chains. Subsequent layers possess a mutually perpendicular orientation. 'Side-on' $Cp^- \cdots Rb^+$ bonding proceeds within the layers and between the layers.

Cp-alkalimetal powders nicely demonstrate the effect of ring substituents on the overall structure. The structure of (TMS)CpLi shows a linear supersandwich of alternating anions and cations similarly to the structure of CpLi (Fig. 11a). As in CpLi, no pronounced interchain interactions are observed. The Cp rings are nearly coplanar (angles between planes vary from 5 to 8°) and the TMS-substituents point in various directions around the chain (Fig. 11b).

However, the complex (TMS)CpK forms a supersandwich in which the Cp–K–Cp units are bent (150.7°) and the TMS-substituents are situated roughly on one side of the chain. This enables mutual 'side-on' Cp–K interchain contacts between neighbouring chains (Fig. 12a) and layers of coordination polymers originate. These

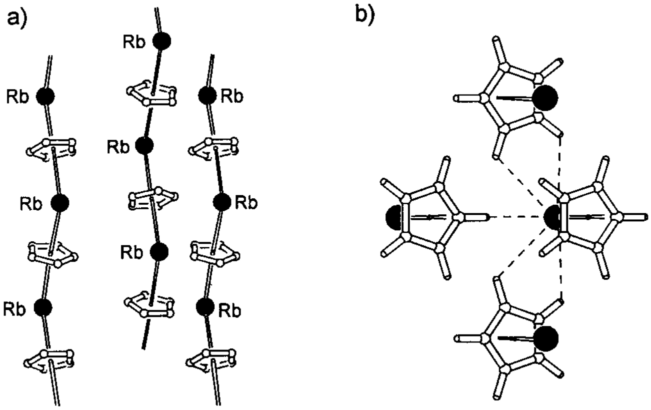


Fig. 10. The structure of one of the crystal phases of CpRb (phase II). (a) View perpendicular on the 'zig–zag' chains. (b) View along the chains showing the 'side-on' $Cp^- \cdots Rb^+$ interchain contacts for one particular Rb^+.

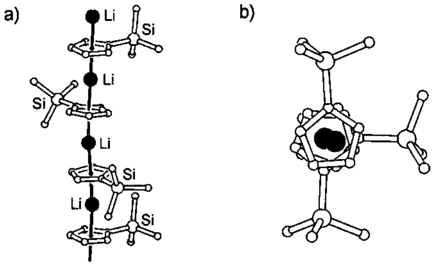


Fig. 11. (a) The crystal structure of (TMS)CpLi: a linear supersandwich of alternating anions and cations. (b) View along the linear chain.

layers are shielded on the outside by the TMS bulk (Fig. 12b) and do, except for the usual van der Waals attraction, not interact with each other. Thus, the introduction of a simple TMS-substituent breaks down the three-dimensional salt-like CpK array in two-dimensional sheets of mutually interacting linear chains. Sterically blocking of coordination sites at the metal by simple substitution of the Cp ring is therefore also related to an increased solubility of substituted Cp-alkalimetal compounds; cf. CpK is largely insoluble in toluene whereas (TMS)CpK was crystallized from this solvent.

All other polymeric Cp-alkalimetal structures which have been determined were crystallized from polar solvents and include one or more solvent molecules. Such solvated polymers crystallize as supersandwiches which all exhibit a characteristic zig–zag chain structure like in CpK · Et_2O [62] (Fig. 13).

This zig–zag structure is imposed by ligand–cation interactions which result in bending of the Cp^-–M^+–Cp^- unit. The supersandwich chains in all these compounds are isolated chains which do not mutually interact. Thus it can be concluded that ligand–cation contacts are given preference to interchain interactions.

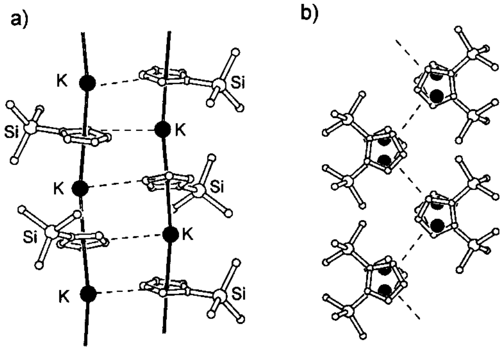


Fig. 12. The crystal structure of (TMS)CpK. (a) ‘Side-on’ $Cp^- \cdots K^+$ interaction between two neighbouring chains. (b) View along the chains showing a ‘zig–zag’ sheet of interacting chains.

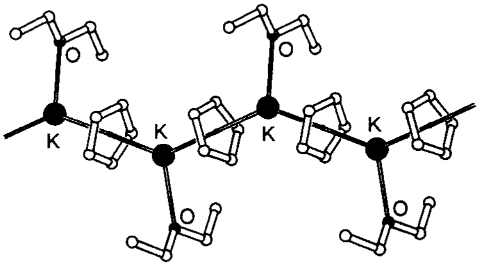


Fig. 13. The crystal structure of CpK · Et_2O: a 'zig–zag' chain typical for the structures of solvated polymeric Cp-alkalimetal complexes.

If bending of two successive Cp^{-}–M^{+}–Cp^{-} units proceeds in different planes, spiral structures like that of the CpNa · TMEDA chain can arise (Fig. 14) [15,16]. One turn in the spiral consists of four CpNa units.

Intramolecular solvation of the cation has been observed in the chain structures of $(Bu^tHN)Me_2SiCpK$ · THF [60] and 2-(THF)CH_2CpNa · THF [57] (Fig. 15a). Another remarkable structure exhibits benzyl-CpNa · THF [58] (Fig. 15b) which

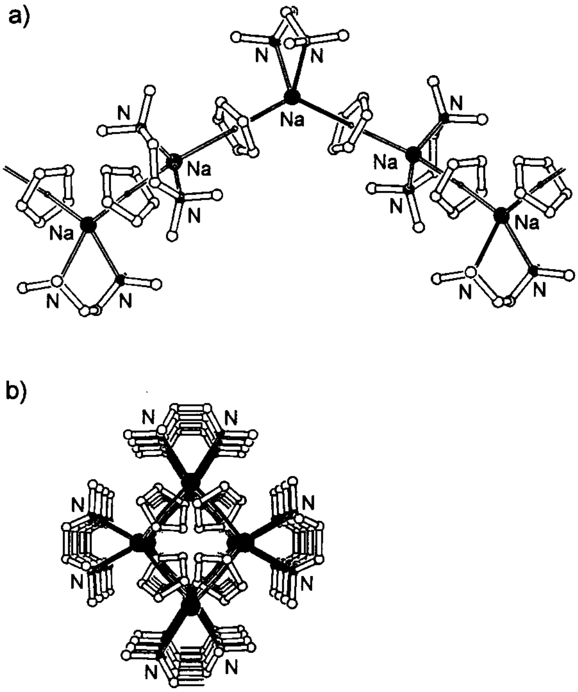


Fig. 14. The spiral chain structure of CpNa · TMEDA. (a) View perpendicular on the chain. (b) View along the spiral chain.

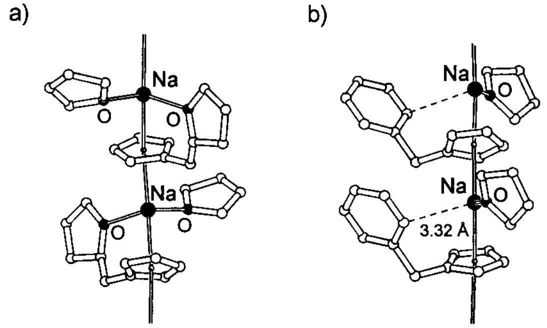


Fig. 15. Intramolecular coordination in the crystal structures of (a) 2-(THF)CH_2CpNa · THF and (b) benzyl-CpNa · THF.

forms an ordinary zig–zag chain in which Na^+ is solvated by one THF ligand. However, the position of the phenyl group is such that a weak but not insignificant interaction between its electron-rich π-system and Na^+ can be expected. The shortest (phenyl)C ··· Na^+ contact of 3.32 Å is much longer than the (Cp^-)C ··· Na^+ bond distance which in the same structure averages 2.779 Å, however, it should be noted that no sharp cut-off value for an electrostatic interaction exists: Coulomb attraction falls off slowly with a $1/r$ dependence. The striking conformity between the Na^+ coordination spheres in 2-(THF)CH_2CpNa · THF (Fig. 15a) and benzyl-CpNa · THF (Fig. 15b) justifies a (phenyl)π ··· Na^+ interaction in the latter.

3.2. Monomeric cyclopentadienyl-alkalimetal complexes

Polar solvents can break down polymeric Cp-alkalimetal structures into monomeric units. The majority of all X-ray structure determinations of Cp-alkalimetal compounds revealed monomeric structures (principal structural data are summarized in Table 2). Their relatively large number and the absence of strong intermolecular interactions between monomeric species enables a reliable evaluation of the factors determining their structures. The influences of the metal cation, coordinating ligands and ring substituents are discussed.

3.2.1. The influence of the metal cation

It is remarkable that a vast number of all structurally known monomeric Cp-alkalimetal compounds (listed in Table 2) are lithium complexes, whereas the polymeric chain structures (listed in Table 1) are nearly exclusively Cp complexes of the heavier metals Na and K. This nicely reflects the problem of coordinative saturation which is generally encountered with the larger electropositive metals (cf. organoalkalimetal structures in general [74] and also the structural chemistry of the alkaline-earth metals [75,76]). Enlargement of the metal cation increases its coordination number and results in an increased tendency for the formation of coordination polymers. For example, precipitation of Cp*Na (Me_5CpNa) from a pyridine solution results in the crystallization of the monomeric complex Cp* Na · $(pyridine)_3$, whereas Cp* K crystallizes from the same solvent as a solvated polymeric chain: $[Cp^*K \cdot (pyridine)_2]_\infty$ [61].

A monomeric CpK complex has only been observed in the case of $(benzyl)_5CpK \cdot THF_3$ [72,73] (Fig. 16), a complex in which large benzylsubstituents in the Cp ring prevent the formation of a polymeric chain structure. For similar reasons, bulky substituents are often introduced to enhance the solubility of Cp-alkalimetal compounds, e.g. it is noteworthy that 1,2,4-$(TMS)_3CpLi$ even dissolves in hexane [19,55,56].

3.2.2. The influence of the ligand (solvent)

An evaluation of the influence of the ligand on the structure of solvated Cp-alkalimetal complexes is only valid when the influences of different substituents are excluded. Table 2 shows a number of $(TMS)_3CpLi$ structures which only vary in the ligand solvating the Li cation. The structures of these compounds and their corresponding Cp_c–Li distances are listed in Fig. 17a. This series shows increasing Cp_c–Li distances with increasing solvation of Li^+. The shortest bond distances are observed for the monosolvated species $(TMS)_3CpLi$ · chinuclidin and $(TMS)_3CpLi$ · (THF). Chelation of Li^+ by TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) results in a significant increase of the Cp_c–Li distance. The crystal structure of the analogue PMDTA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) complex shows only bidentate coordination of the tridentate ligand and a similar Cp_c–Li distance. Finally, an X-ray study on crystals of $(TMS)_3CpLi$ formed in the presence of 12-crown-4 (a very efficient complexing agent for Li^+) revealed the structure of a solvent-separated ion pair in which the Cp–Li bond is broken [70]. These results show that solvation of Li^+ with external ligands competes with Cp^-–Li^+ bonding. Thus, solvation of the metal cation not only induces the gradual cutting of polymer chains into monomeric units but might even cause an extended degradation of monomers into separated ion-pairs.

Ab initio calculations confirm that progressive solvation of the metal in CpLi increases the Cp–Li bond distance (Fig. 17b) [77]. This is explained by Coulombic repulsion between the Cp anion and the directed solvent dipoles.

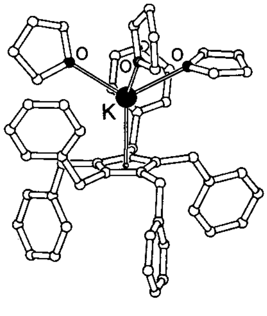


Fig. 16. The only monomeric crystal structure of a CpK compound: $(benzyl)_5CpK \cdot THF_3$.

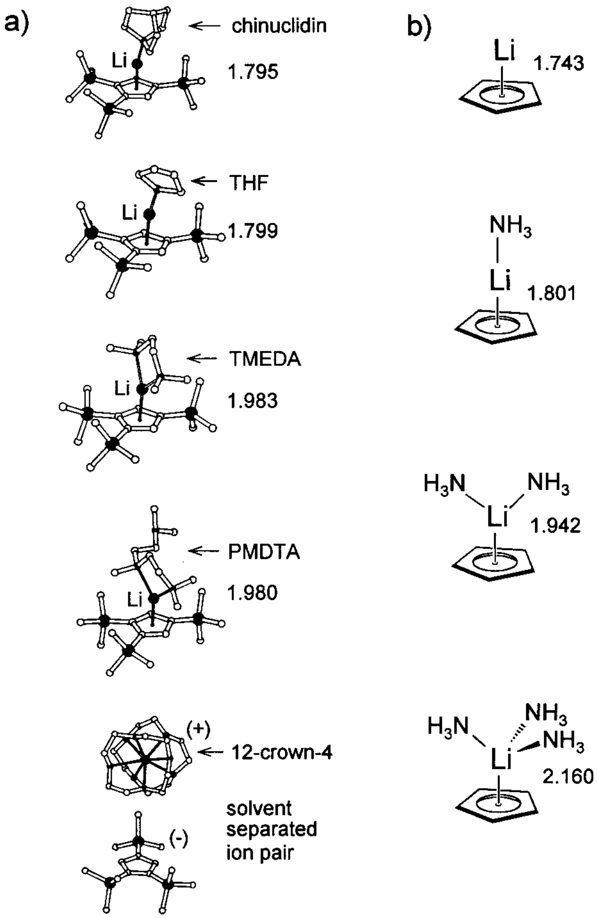


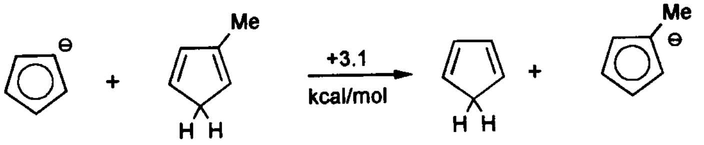
Fig. 17. (a) Crystal structures of $(TMS)_3CpLi$ complexes and their corresponding Cp_c–Li distances (Å). (b) Ab initio (RHF) calculated CpLi complexes (Cp_c–Li distances in Å) [52].

3.2.3. *The influence of ring substituents*

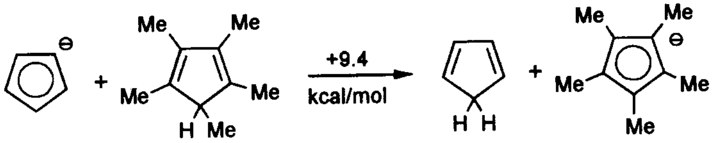
The majority of all substituted Cp-complexes include either alkyl or silyl substituted Cp rings. Therefore the influence of ring substituents on the molecular structure, electron distribution and stability of Cp-alkalimetal compounds will be discussed here for alkyl and silyl substituents in particular.

Due to the frequent use of the $(Me)_5Cp$ ligand in organometallic chemistry, the effect of alkyl substitution is well documented. Alkyl substituents increase the electron density in the Cp ligand [78–80], however, not much is known about the electronic effects of silyl substituents on the Cp ring [81].

Ab initio calculations (RHF/6-31 + g* + ZPE correction) [30] show that electron releasing alkyl substituents destabilize the Cp anion (eqs. 1–2). In contrast,



(eq. 1)

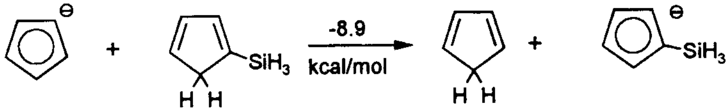


(eq. 2)

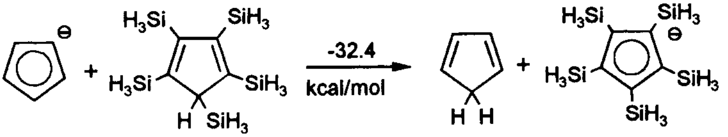
silyl substituents strongly stabilize the Cp anion (eqs. 3–4)[3]. The strong stabilization of the Cp anion by fivefold H_3Si substitution is in line with the observation that second-row elements generally stabilize adjacent anionic centres, partly through polarization effects and partly through negative hyperconjugation [82–84].

The heterolytic dissociation energies ($Cp'Li \rightarrow Cp'^{-} + Li^{+}$) for the substituted Cp compounds are (given in kcal/mol): Me_5CpLi (170.0), MeCpLi (168.8), CpLi (168.3), $H_3SiCpLi$ (160.4) and $(H_3Si)_5CpLi$ (134.5). Alkyl substitution results in slightly stronger Cp–Li bonding, whereas silyl substitution induces the opposite.

What are the effects of alkyl and silyl substituents on the Cp-alkalimetal bond length? A discussion of experimentally determined Cp–metal bond distances in differently substituted Cp-alkalimetal compounds, only makes sense when comparing compounds with the same cap, i.e. metal–ligand combination. A comparison in the series of CpLi structures with TMEDA as a solvating ligand (Fig. 18a) shows that the Cp–Li distance shortens with increased alkyl substitution in the Cp ring.



(eq. 3)



(eq. 4)

---

[3] The equations 1–4 show the MeCpH and H_3SiCpH isomers of lowest energy. The relative energies (kcal/mol) for the isomers are: 1-MeCpH (+3.5); 2-MeCpH (+0.4); 3-MeCpH (0.0) and 1-H_3SiCpH (+1.1); 2-H_3SiCpH (0.0); 3-H_3SiCpH (+0.8).

This effect is small but is in agreement with increased electron density in the Cp ligand which enhances Coulombic $Cp^{-} \cdots M^{+}$ attraction and also fits well to the calculational data in Fig. 18b[4]. On the other hand, gradual TMS-substitution results in a significant elongation of the experimentally observed CpLi bond (Fig. 18a). Calculational data (Fig. 18b), however, do not confirm the elongation of the CpLi bond with increased silyl substitution. Even fivefold H_3Si-substitution does not considerably affect the Cp–Li distance. A silyl ring substituent draws π-electron density from the Cp ring by negative hyperconjugation, but it also strongly donates electron density in the σ-system of the ring. Apparently, the overall effect balances and no large influence on the Cp–Li bond length is observed in the calculational models. The experimentally observed elongation of the Cp–Li distance with increased TMS-substitution of the Cp ring is likely controlled by steric interactions between the substituents and the Li · TMEDA cap. These interactions are especially obvious in the tris-TMS substituted CpLi compound. Steric repulsion between the substituted Cp anion and the TMEDA ligand is also reflected in the N–Li bond distances; e.g. the average N–Li bond distances in TMSCpLi · TMEDA and $(TMS)_3CpLi$ · TMEDA are 2.130 and 2.185 Å, respectively.

Table 2 includes two other compounds with an identical cap: CpLi · (12-crown-4) and $(RO)_2BCpLi$ · (12-crown-4). The slightly longer Cp–Li distance in the latter is caused by the π-electron withdrawing $(RO)_2B$ substituent. In this respect the crystal structure of the separated ion-pair $(TMS)_3Cp^{-}/Li^{+}$(12-crown-4$)_2$ is noteworthy. The contact ion pair, CpLi · (12-crown-4), and the separated ion pair, $(TMS)_3Cp^{-}/Li^{+}$(12-crown-4$)_2$, were crystallized under similar conditions (i.e. with 2 molEq. of 12-crown-4 present in a THF solution). Formation of the separated ion pair is explained by a combination of factors: (i) efficient solvation of the Li cation with a crown ether ligand; (ii) a reduced dissociation energy for the Cp–Li bond by threefold TMS substitution; and (iii) strong steric interactions between the Li(12-crown-4) cap and the $(TMS)_3Cp$ anion in a hypothetical contact ion-pair $(TMS)_3CpLi$ · (12-crown-4).

3.3. Oligomeric cyclopentadienyl-alkalimetal compounds

Apart from polymeric and monomeric Cp-alkalimetal complexes, a few cases of oligomeric solid state structures have been revealed only very recently (Table 3).

A dimeric structure of $(Ph_2P)CpNa$ · DME has been published [85] (Fig. 19). The structure represents an odd dimer in the sense that not the carbanion (the Cp^{-} moiety) bridges the metal centres but coordinative $P \cdots Na^{+}$ bonding provides the contacts between the two monomeric species, a situation which is also common in α-heteroatom substituted organolithium compounds [88,89]. Although not recognized by the authors, this case of ligand–metal bonding represents the first coordinative $R_3P \cdots Na^{+}$ bond.

---

[4] It should be noted that the calculated Cp–Li distances are shorter than the experimental values (this is due to lack of Li-solvation), but the relative effects of ring substitution can be nicely compared.

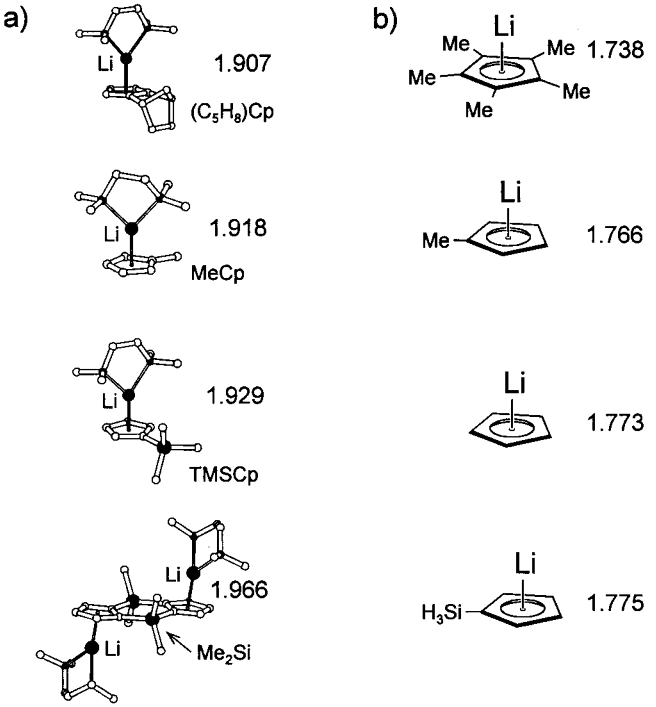
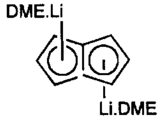
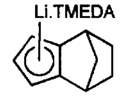
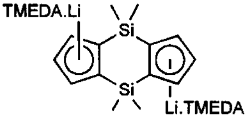


Fig. 18. (a) Crystal structures of TMEDA-solvated CpLi complexes and their corresponding Cp_c–Li distances (Å). (b) Ab initio calculated CpLi complexes (RHF/6-31 + g*) and their corresponding Cp_c–Li distances (Å). All Cp–Li bonding modes are close to η^5.

A dimer with a bridging Cp moiety has been found in a crystal structure of $(benzyl)_5CpLi$ [86]. This highly substituted CpLi compound dissolves in benzene and crystallizes as $[(benzyl)_5CpLi]_2 \cdot C_6H_6$ (Fig. 20a). The linear arranged dimer can be considered as the first intermediate in the formation of Cp-alkalimetal polymer chains. Obviously, further extension of the dimer to a polymeric $(benzyl)_5CpLi$ chain is not possible for steric reasons: in the dimer the benzyl substituents at neighbouring Cp rings point away from each other. An interesting feature in the structure of this dimer is the variety in the observed Cp–Li bond distances. The sandwiched Li^+ is not symmetrically bound between the two Cp anions (Fig. 20b) and this asymmetry was confirmed by calculation [86]. The asymmetry in the dimer is evident from electrostatic bonding considerations: the top Li^+ exerts a repulsive force on the sandwiched Li^+ (or similar, the terminal Cp anion exerts a repulsive force on the bridging Cp anion). In a symmetrical supersandwich all repulsive and attractive forces on both sides of the metal cation are equal.

An oligomer composed of four monomeric units has been found in the crystal structure of a C_1-bridged dilithio-bis(cyclopentadienide) (Fig. 21) [87]. The

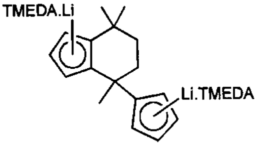
Table 2
Crystal structures of monomeric Cp-alkalimetal compounds[1]

Compound formula	Range C–M (Å)	Av. C–M (Å)	Cp_c–M[b] (Å)	CCDC code	Ref.
$1,2,4-(TMS)_3CpLi \cdot$ chinuclidin[c]	2.137–2.172 2.150–2.221	2.157 2.189	1.775 1.815	DECPOQ	[19]
$1,2,4-(TMS)_3CpLi.THF$	2.139–2.192 2.153–2.186	2.161 2.170	1.794 1.804	SEBHUC	[64]
$(Me_2HSi)_5CpL_i \cdot O=CPh_2$	2.178–2.193	2.186	1.820	PAVMEE	[65]
	2.196–2.306	2.249	1.889	DANPOX	[66]
	2.215–2.266	2.248	1.907	YEHTIO	[67]
MeCpLi · TMEDA	2.236–2.278	2.258	1.918	SIJNII	[68]
(TMS)CpLi · TMEDA	2.257–2.286	2.267	1.929	CEZTIK	[20]
	2.247–2.357	2.307	1.966	KIXMIN	[69]
$1,2,4-(TMS)_3CpLi \cdot$ PMDTA	2.303–2.349	2.324	1.980	COJROI	[17–19]
$1,2,4-(TMS)_3CpLi \cdot$ TMEDA	2.287–2.366	2.327	1.982	COJRUO10	[17–19]
	2.277–2.378	2.328	1.983		
CpLi · (12-crown-4)	2.343–2.419	2.380	2.063	VITKAK	[70]
$(RO)_2BCpLi \cdot$ (12-crown-4)	2.380–2.455	2.400	2.084	ZOQMEX	[59]
$Ph_4CpNa \cdot (DME)_2$	2.795–2.907	2.849	2.581	ZOZHOL	[71]
$Cp^* Na \cdot (pyridine)_3$	2.657–2.701	2.678	2.399	KOHZOW	[61]
$(benzyl)_5CpK \cdot (THF)_3$	2.970–3.095	3.035	2.789	SAXRAK	[72,73]

[a] Coordinates (without standard deviations) originate from the Cambridge Crystallographic Database [63].
[b] Cp_c represents the geometric center of the C_5-ring.
[c] Chinuclidin = 1-azabicyclo[2.2.2]octane (or 1-aza-adamantane).

$(RCp_2)^{2-}$ units in this tetramer are connected by four bridging Li cations reciding at the *exo*-side of the $(RCp_2)^{2-}$ unit. The remaining Li cations are bound to one Cp ring and solvated with a TMEDA ligand. This complex can be considered as a cyclic supersandwich, i.e. a chain-like polymer of which both ends interact mutu-

Table 3
Crystal structures of oligomeric Cp-alkalimetal compounds[a]

Compound formula	Range C–M (Å)	Av.C–M (Å)	Cp_c–M^b (Å)	CCDC code	Ref.
$[(Ph_2P)CpNa \cdot DME]_2$	2.703–2.752	2.728	2.452	YEZCAH	[85]
$[(benzyl)_5CpLi]_2 \cdot C_6H_6$	2.11–2.19 2.29–2.42 2.23–2.27	2.15 2.36 2.25	1.78 2.03 1.90	–	[86]
	2.212–2.348 2.317–2.379 2.344–2.379	2.287 2.347 2.356	1.952 2.019 2.030	ZIZHAR	[87]

[a] Coordinates (without standard deviations) originate from the Cambridge Crystallogrpahic Database[63].
[b] Cp_c represents the geometric center of the C_5-ring.

ally. A similar cyclic tetramer has been observed in the analogue fluorenyl chemistry of the alkalimetals. For example, fluorenylsodium in the presence of TMEDA crystallizes in a polymeric chain structure [90]. However, exchanging TMEDA for TMPDA (tetramethylpropylene-diamine, a ligand with a larger bite angle) results in the crystallization of a cyclic tetramer of fluorenylsodium [90]. Similar cyclic hexameric structures have been found in the solid state structure of $(TMS)_2CpTl^{(I)}$ [91]. In analogy to the 'sandwich' terminology, cyclic supersandwiches have been labelled as 'doughnut' complexes [91].

Certain substituted Cp-alkalimetal complexes dissolve in apolar solvents like hexane and may well be present in solution as a 'doughnut' complex (a cyclic oligomer). The observation that a hexane solution of $(TMS)_3CpLi$ stiffens at higher

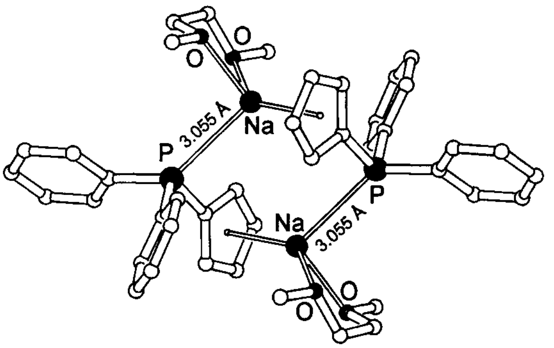


Fig. 19. The dimeric structure of $(Ph_2P)CpNa \cdot DME$.

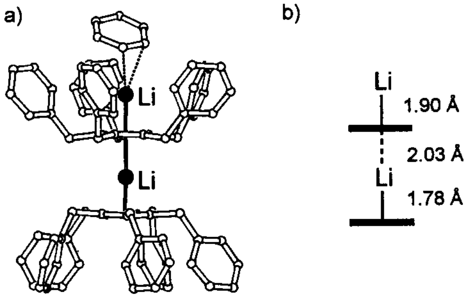


Fig. 20. (a) The dimer of (benzyl)$_5$CpLi is capped with a benzene ligand. (b) The different Cp–Li bond distances.

concentrations into a gel-like substance [55,56] argues for the presence of oligomeric units. In aromatic solvents, the end-standing metal cation of a linear oligomer can be capped with a solvent molecule (like in dimeric (benzyl)$_5$CpLi; Fig. 20), but in alkanes cyclic oligomers are more likely. The presence of oligomers with a variety of ring sizes likely hinders crystallization of defined molecular units and a gel, typical for oligomers in solution, is formed. The report that removal of the hexane solvent yields a white powder which cannot be dissolved in hexane again [64], suggests that in the solid state (TMS)$_3$CpLi forms long insoluble polymer chains which, upon solvation in alkane solvents, not reversibly break down to oligomeric units.

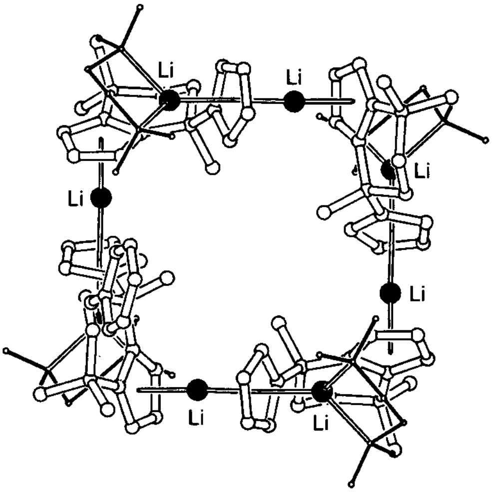


Fig. 21. The tetrameric ‘doughnut’ structure of a C$_1$-bridged dilithio-bis(cyclo-pentadienide). The TMEDA ligands are shown as thin black lines.

Table 4
Crystal structures of mixed-metal Cp-alkalimetal compounds[a]

Compound formula	Range C–M (Å)	Av. C–M (Å)	Cp_c–M[b] (Å)	CCDC code	Ref.
Cp_2Sn-CpNa · PMDTA	2.782–2.846	2.814	2.551	KUPFEG	[92,33]
(TMS_2N)CpSn-CpLi · PMDTA	2.416–2.648	2.545	2.252	PESVUE	[94]
CpTl-CpLi · PMDTA	2.342–2.685	2.517	2.226	SUMSIC	[95,96]
	2.449–2.681	2.559	2.271		

[a] Coordiantes (without S.D.) originate from the Cambridge Crystallographic Database [63].
[b] Cp_c represents the geometric center of the C_5-ring.

3.4. Mixed-metal cyclopentadienyl-alkalimetal compounds

As discussed in Section 3.1, the distribution of electron density on both sides of the Cp anion gives rise to the formation of polymeric $-Cp^{-}-M^{+}-Cp^{-}-M^{+}-$ chains. Solvation of the metal cation can break the polymeric chain into smaller units, among which the solvated monomer. The Cp anion in a solvated monomer still possesses one empty electron rich side which can dock on electrophilic metal compounds. In several cases mixed-metal complexes have been isolated (Table 4) [92–98].

The crystal structure of one of these complexes, Cp_2Sn-CpNa · PMDTA [92,93], is shown in Fig. 22. As expected, Sn ··· Cp bond distances to the terminal Cp rings are shorter than that to the docked CpNa species. Such complexes are generally considered as intermediates in nucleophilic substitution reaction at Sn^{II} centres.

4. Anionic alkalimetallocene sandwich complexes

Starting with the discovery of ferrocene, many of the elements within the periodic table have been sandwiched between the rings of cyclopentadienyl ligands. Not only a wide variety of transition metals, but also the group II alkaline-earth metals [75,76] and even group III (B [98], Al [100,101], As and Sb [102,103]) and group IV (Si [104–106], Sn [107,108]) elements have been put between the π-sys-

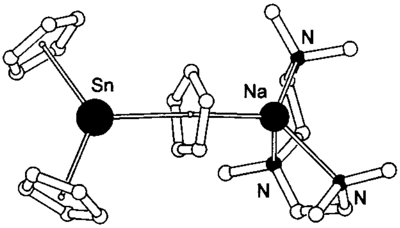
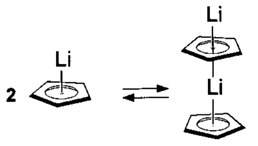
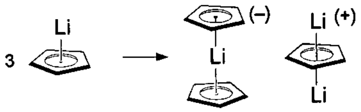


Fig. 22. The crystal structure of Cp_2Sn-CpNa · PMDTA.



(eq. 5)



(eq. 6)

tems of Cp ligands. From various experimental observations it was concluded that similar 'Cp_2M' sandwich compounds also could exist for the series of the group I alkalimetals.

(i) Already in 1962, the unexpected high conductivity of a solution of CpLi in THF raised the suspect that ionic particles exist in solution [109]. These could either be the free ions Cp^- and Li^+, but the existence of triple-ions like Cp_2Li^- was also not excluded.

(ii) Cryoscopic measurements on a solution of CpLi in liquid ammonia [110] showed that the molecular weight for the average CpLi species in solution is 1.4(±0.1) times the molecular weight of CpLi monomer. Thus, higher aggregates exist in solution. The observed aggregation factor can be explained by an equilibrium between monomers and dimers (eq. 5) or by assuming the existence of triple-ion pairs (eq. 6).

The triple cation, $CpLi_2^+$, is considered an inverse sandwich complex and such a complex was recently observed in a crystal structure determination in the form of $MeCpLi_2^+ \cdot (TMEDA)_2$ (Fig. 23) [111]. Likewise, $CpNa_2^+ \cdot THF_6$ [112] and $Bu^tCpK_2^+ \cdot (18\text{-crown-}6)_2$ [113] have been observed in solid state structures.

(iii) A recent extensive NMR study using a variety of available techniques [114] shows the existence of an anionic Cp_2Li^- sandwich in solution. In a THF solution at low temperature, monomeric lithium isodicyclopentadienide is in equilibrium

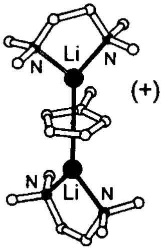
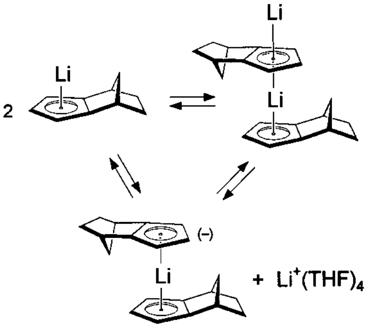


Fig. 23. A structurally confirmed inverse sandwich complex: the $MeCpLi_2^+ \cdot (TMEDA)_2$ cation.



(eq. 7)

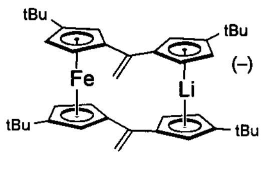
with the dimer and with a combination of a sandwich metallocene anion and THF-solvated Li^+ (eq. 7).

Comparable low temperature NMR data [114] suggest that a similar equilibrium is present for CpLi in THF, although the existence of the Cp_2Li^- species could not be proven here with absolute certainty.

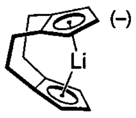
(iv) Other NMR studies provided evidence for a ferrocene-bridged Cp_2Li^- anion (**8**) [115] and the doubly CH_2CH_2-bridged Cp_2Li^- anion (**9**) [116].

Though quite some crystal structures of lithium cations sandwiched between π-systems are known [117–121], structural proof of the ‘lithocene anion’ was still lacking. However, considering Cp-alkalimetal complexes in the solid state as linear supersandwiches, one likely method for the syntheses of anionic metallocene sandwiches is obvious. Exchanging halve of the metal cations in a supersandwich array for non-coordinating cations, like ammonium or phosphonium cations, will result in the formation of isolated anionic metallocene sandwiches (Fig. 24a). Likewise, considering Cp-alkalimetal complexes in solution as monomeric species, exchanging halve of the metal cations for non-coordinating cations results in the generation of a mixture of ‘free’ Cp-anions and solvated CpM monomers. If $Cp^- \cdots M^+$ coordination competes successfully with cation solvation, the formation of an anionic metallocene sandwich is achieved (Fig. 24b).

According to this method, the lithocene anion was prepared and its structure was elucidated [122,123]. Several other anionic alkalimetallocene sandwich complexes



(8)



(9)

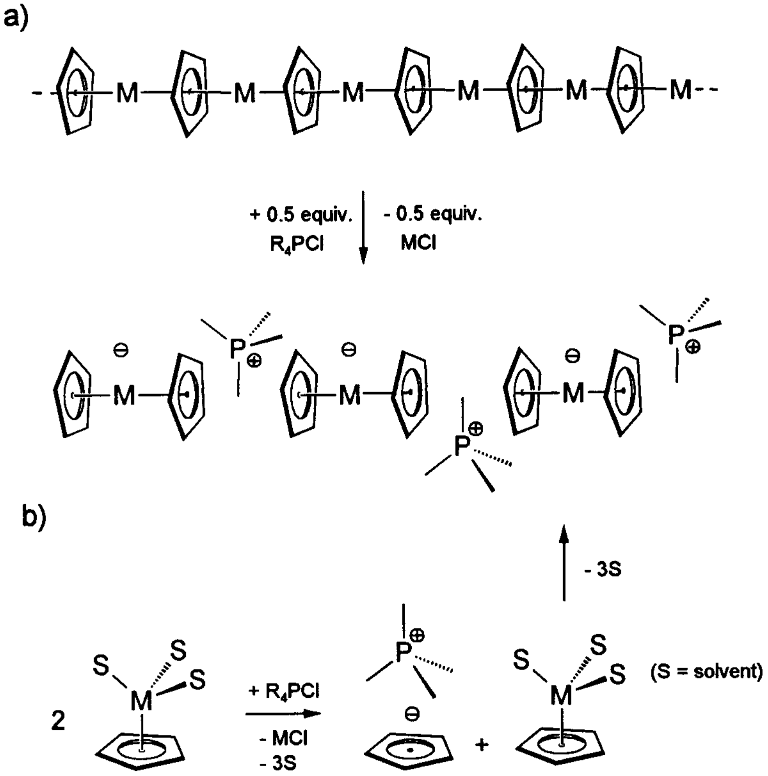


Fig. 24. Approach for the syntheses of anionic metallocene sandwich complexes.

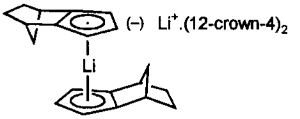
have been isolated and characterized, partially via other methods and sometimes by coincidence. These complexes and its most important data are listed in Table 5.

4.1. Syntheses and structures of anionic lithocene sandwich complexes

Large yellow crystals of $[Cp_2Li^-][Ph_4P^+]$ can easily be obtained from a solution of CpLi and Ph_4PCl (molar ratio 2:1) in THF. An X-ray structure determination [122,123] shows a monoclinic unit cell ($P2/c$ symmetry) with an alternating arrangement of $[Cp_2Li^-]$ and $[Ph_4P^+]$ ions (Fig. 25a). The phosphonium cations show C_2-symmetry with the phosphorus atom located on a crystallographic twofold axes. The lithocene anions are positioned on crystallographic inversion centres. In this respect, the crystal structure of the lithocene anion is comparable to those of magnesocene, chromocene, ferrocene, cobaltocene and nickelocene (Cp_2Mg [131]; Cp_2Cr [132]; Cp_2Fe [133]; Cp_2Co [134]; and Cp_2Ni [135]). All these compounds crystallize in centrosymmetric monoclinic spacegroups in which the metals are located on inversion centres.

The structure of the lithocene anion, $[Cp_2Li^-]$, is shown in Fig. 25b. The

Table 5
Crystal structures of anionic alkalimetallocene sandwich complexes[a]

Compound formula	Range C–M (Å)	Av. C–M (Å)	Cp_c–M[b] (Å)	CCDC code	Ref.
$[Cp_2Li^-][Ph_4P^+]$	2.262–2.366	2.318	2.009	HESJIY	[122,123]
$[Cp_2Li^-](Me_2N)_3S^+)$	2.260–2.334 2.262–2.359	2.297 2.314	1.969 1.989	SURLOG	[124,125]
$[Cp_2Na^-][Ph_4P^+]$	2.584–2.670	2.630	2.366	ZOQPUQ	[126]
$[Cp_2Na^-][Cp^-](Me_2N)_3S^+)_2$	2.596–2.640	2.615	2.329	SURLUM	[124,125]
$[Cp_3Cs_2{}^-][Ph_4P^+]$	3.313–3.385 3.300–3.360	3.350 3.330	3.134 3.100	ZOGCED	[127,128]
 (–) Li$^+$.(12-crown-4)$_2$	2.292–2.390 2.300–2.340	2.337 2.319	2.008 1.986	YEHTOU	[129]
$[tBuCp_2Li^-][Ph_2PMe_2{}^+]$	2.282–2.358 2.254–2.382	2.312 2.318	1.984 1.991	–	[130]

[a] Coordinates (without standard deviations) originate from the cambridge Crystallographic Database[63].
[b] Cp_c represents the geometric center of the C_5-ring.

coplanarity of both Cp rings is inherent to the centrosymmetric nature of the anion. The Cp_c–Li distance of 2.008(4) Å is slightly longer than the comparable distance of 1.969 Å in $(CpLi)_\infty$ [52]. The lithocene anion shows only a small variance in the C–Li bond distances [range from 2.262(3) to 2.366(4) Å; average, 2.318(4) Å] and the angle between the Cp_c–Li axis and the Cp plane is 87.1(3)°. Therefore the Cp–Li interaction can be regarded as an (η^5)Cp–Li bond which is hardly slipped.

The Cp rings in the lithocene anion are almost perfectly staggered. However, high anisotropy in the ring thermal parameters indicates substantial rotational disorder in the positions of the Cp carbon atoms (Fig. 25c). This is most likely due to small energy differences between staggered and eclipsed conformations. Recent MNDO calculations on the lithocene anion do indeed indicate essentially free rotation of the Cp rings around the longitudinal axis [114].

The lithocene anion has also been generated in the presence of the weakly coordinating cation, $(Me_2N)_3S^+$ [124,125]. Free Cp anions can be obtained according to eq. 8.

Subsequent reaction of the salt $[Cp^-][(Me_2N)_3S^+]$ with CpLi resulted in the formation of the complex $[Cp_2Li^-][(Me_2N)_3S^+]$ which was structurally characterized by X-ray diffraction [124,125]. The lithocene anion in this complex is, similar to that in $[Cp_2Li^-]$ $[Ph_4P^+]$, a staggered sandwich with approximate D_{5d} symme-

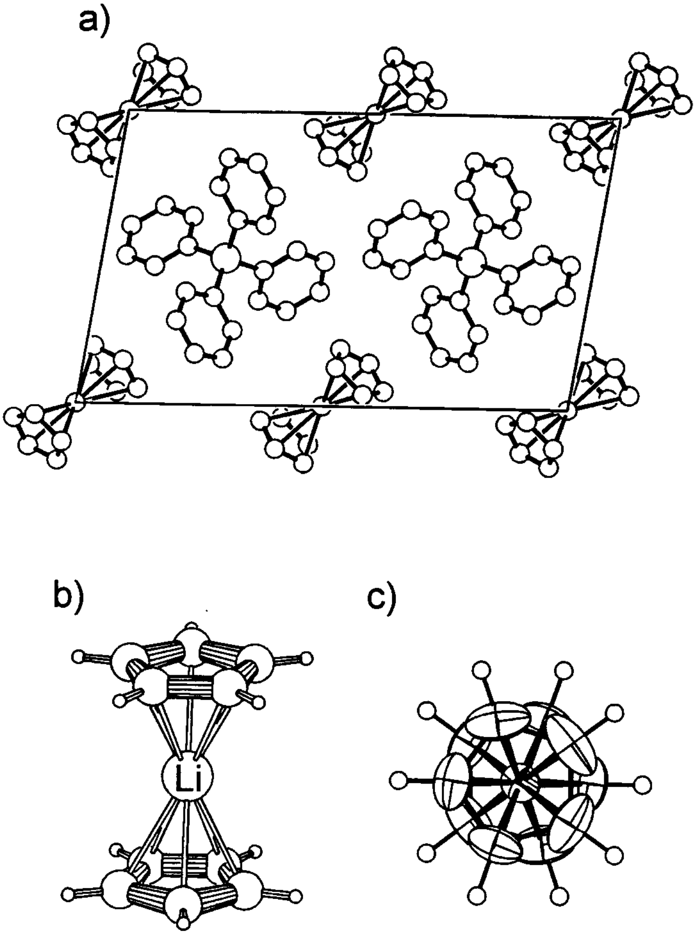
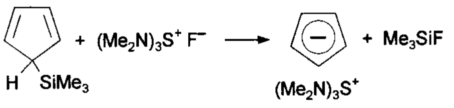


Fig. 25. Crystal structure of $[Cp_2Li^-][Ph_4P^+]$. (a) View of the monoclinic unit cell along the *b* axis (space group *P2/c*). (b) The D_{5d} 'ferrocene-like' structure of the $[Cp_2Li^-]$ anion. (c) ORTEP plot showing disorder within the planes of the Cp rings (top view; ellipsoids represent 50% probability).

try. The Cp_c–Li distance in $[Cp_2Li^-][(Me_2N)_3S^+]$ is only slightly longer than that in $[Cp_2Li^-][Ph_4P^+]$ (Table 5).

Two structures of substituted lithocene anions were published. Isodicyclopenta-



(eq. 8)

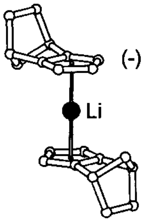


Fig. 26. The structure of [$(\text{isodiCp})_2\text{Li}^-$], a substituted lithocene anion.

dienide lithium crystallizes from THF solution in the presence of an excess of 12-crown-4 as an anionic sandwich complex [129] (Fig. 26).

In the crystal structure, one of the two Li cations is solvated with two 12-crown-4 ligands. Like the phosphonium cation, such a strongly solvated Li^+ can be considered as a non-coordinating cation. Thus, anionic alkalimetallocene sandwiches can be generated also by specific solvation of halve of the metal cations in a solution of Cp-alkalimetal species. However, ring substituents seem to have a large influence on the nature of the crystallizing species and varying structures can result when CpLi species with different substituents are crystallized under the same conditions (Fig. 27). When no substituents are present a solvated contact ion pair is formed (a) [51], whereas three TMS-substituents placed on the ring result in the

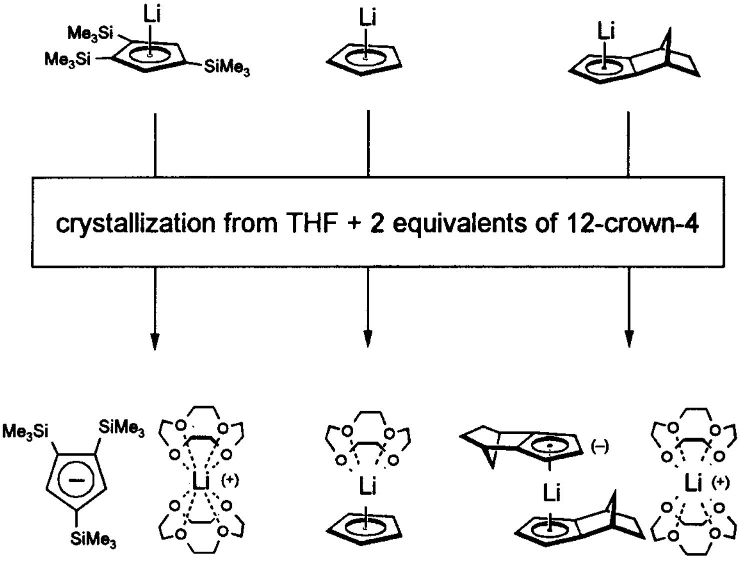
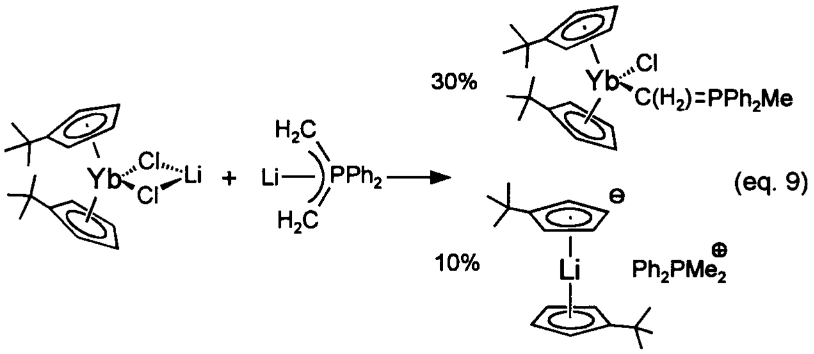


Fig. 27. The varying results when CpLi species with different substituents are crystallized in the presence of 12-crown-4.



crystallization of a ‘free’ solvent-separated ion pair (b) [51] and in the case of dialkyl substitution a lithocene anion is formed (c) [129].

Recently, the crystal structure of another substituted lithocene anion was revealed accidentally (eq. 9) [130].

The structure of the Bu^t-substituted lithocene anion is a staggered sandwich (Fig. 28) in which the Cp rings are nearly coplanar (the angle between the planes is 2.5°). The Cp–Li distances in this anion are comparable to those observed in the lithocene anions described previously (Table 5). This complex, $[(\mathrm{Bu^tCp})_2\mathrm{Li}^-][\mathrm{Ph_2PMe_2^+}]$, can also be prepared in 70% yield from the reaction of $[\mathrm{Ph_2PMe_2^+}][\mathrm{CF_3SO_3^-}]$ with 2 molEq. of Bu^{t}CpLi [130].

The Cp$_c$–Li bond distances in both alkylsubstituted lithocene anions are close to the Cp$_c$–Li bond distances in the structurally known unsubstituted lithocene anions.

4.2. Syntheses and structures of anionic sodocene sandwich complexes

In analogy to the synthesis of the lithocene anion described in Section 4.1, CpNa was reacted under similar conditions with 0.5 equivalent of $\mathrm{Ph_4PCl}$ in THF. The

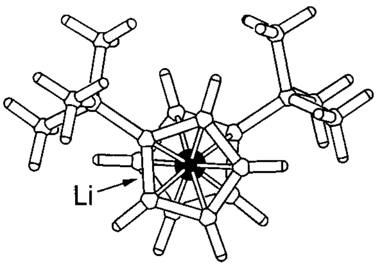
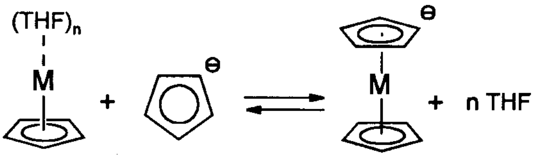


Fig. 28. Structure of the Bu^t-substituted lithocene anion, $[(\mathrm{Bu^tCp})_2\mathrm{Li}^-]$.



(eq. 10)

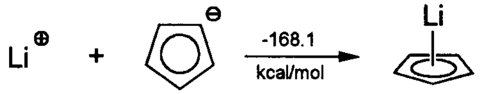
dark-red crystalline product, unexpectedly, appeared to consist of $[Cp^-][Ph_4P^+]$ instead of the desired $[Cp_2Na^-]$ $[Ph_4P^+]$ [126].

Addition of 0.5 molEq. of Ph_4PCl to a solution of CpNa in THF results in the generation of free Cp anions. These 'naked' anions were expected to function as very effective ligands and to interact with the remaining CpNa species to form $[Cp_2Na^-]$. However, in THF solution this is presumably an equilibrium (eq. 10) which will be dependent on the strength of the Na^+–THF bond and the energy involved in Cp^--Na^+ bonding.

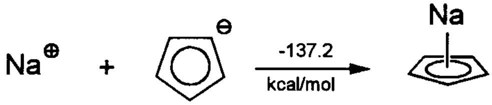
The Cp-alkalimetal bond is highly ionic and, according to Coulomb's law, weakens with increasing Cp^-–M^+ distance, i.e. along the series M = Li, Na, K (etc.). Ab initio calculations (eqs. 11, 12) indeed show that association of a free Cp anion with Li^+ is more exothermic than association with Na^+ [126] and are in agreement with results obtained earlier [31,32]. Compared to the Cp–Li bond, the weaker Cp–Na bond would imply lower stability of the sodocene anion. This could explain the observed crystallization of $[Cp^-][PPh_4^+]$ in the attempted synthesis. However, calculations on the actual metallocene anions show that bonding of a second Cp anion is more exothermic for Na^+ than for Li^+ (eqs. 13, 14).

The reason for the weaker Cp–metal bond in the lithocene anion is the stronger repulsive $Cp^- \cdots Cp^-$ interaction (due to the smaller radius of Li^+ and thus smaller $Cp^- \cdots Cp^-$ distance) which outweighs the advantage of stronger Cp^-–Li^+ bonding. This is nicely illustrated by a comparison of the Cp–metal bond lengths in the pairs $CpLi/Cp_2Li^-$ and $CpNa/Cp_2Na^-$ (see eqs. 13, 14). Coordination of a Cp anion to CpLi results in Cp–Li bond lengthening of 0.29 Å, i.e. 16%, whereas coordination of a Cp anion to CpNa induces a Cp–Na bond lengthening of 0.18 Å, i.e. only 8%.

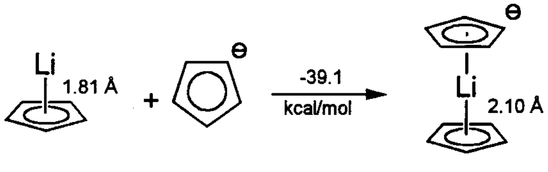
Solvation of the alkalimetal will have a dominant influence on the relative stabilities of the species in the equilibrium of eq. 10. For this reason it is not straightforward to estimate the position of this equilibrium. The possible existence of higher oligomeric CpMCpM structures or triple-decker anions, $CpMCpMCp^-$, complicates the solution equilibrium. It should also be mentioned that the crystallizing species not always is the dominant species in the solution equilibrium. The nature of the crystallizing species is also determined by the relative solubilities of all species participating in the equilibrium. For example, the sodocene anion in THF solution might be present as a THF-monosolvate (**10**), a species which represents part of the THF-solvated Na-supersandwiches described in Section 3.1 (Fig. 15). In contrast to the unsolvated lithocene anion, such a species has a dipole moment and is probably well soluble in THF.



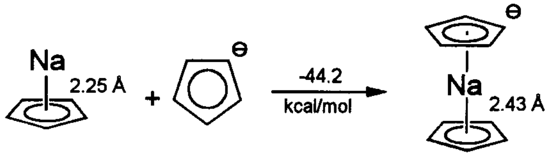
(eq. 11)



(eq. 12)



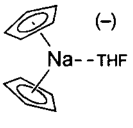
(eq. 13)



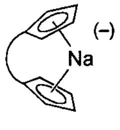
(eq. 14)

One approach to overcome withdrawal of the Cp anion from the reaction mixture is to tie this anion to the CpM fragment, i.e. to synthesize an anionic *ansa*-sodocene sandwich (**11**); such species are described in Section 4.4.

As another approach to prepare anionic sodocene sandwiches, the equilibrium in eq. 10 can be directed towards the side of the sandwich anion by varying the reactant concentrations. Increasing the overall absolute concentration favours the formation of Cp_2Na^-. Likewise, an increment of the CpNa concentration shifts the equilibrium to the side of Cp_2Na^-. A combination of both, resulted in the formation of orange needle-like crystals revealing the structure of $[Cp_2Na^-][Ph_4P^+]$ [126]. The compounds $[Cp_2Li^-][Ph_4P^+]$ and $[Cp_2Na^-][PPh_4^+]$ are isomorphous, i.e. cell dimensions, space group symmetry, crystal packing and the molecular structure are remarkably similar. Like the lithocene anion, the sodocene anion also forms a staggered sandwich complex with coplanar Cp rings (Fig. 29). The C–Na bond distances are in the narrow range of 2.584(3)–2.670(3) Å



(10)



(11)

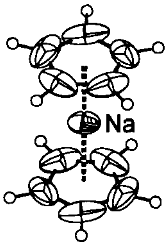


Fig. 29. ORTEP plot of the anionic sodocene sandwich (50% probability ellipsoids).

[average 2.630(3) Å]. Although high anisotropy in the ring displacement parameters indicates a small energy difference between staggered and eclipsed conformations, the average structure can be described as a $(\eta^5,\eta^5)Cp_2Na^-$ sandwich with approximate D_{5d} symmetry.

A similar Cp_2Na^- unit was found in the crystal structure of a complex consisting of a Cp_2Na^-, a Cp^- and two $(Me_2N)_3S^+$ units [124,125]. In this complex, the sodocene anion displays a similar staggered conformation with the same structural features as the anion in $[Cp_2Na^-][PPh_4^+]$ (see Table 5 for a comparison).

4.3. Synthesis and structure of an anionic cesocene sandwich complex

The X-ray structure analysis of a product obtained from a $CpCs/Ph_4PCl$ (2:1) solution revealed the product formula $[Cp_3Cs_2^-][Ph_4P^+]$ [127,128]. The $[Cp_3Cs_2^-]$ species (Fig. 30) represents a triple-decker (or in 'sandwich' terminology: a 'Big-Mac' complex). The $[Cp_3Cs_2^-]$ anion is strongly bent [Cp–Cs–Cp = 115.6(2)°] and closely resembles a recent structure of the first triple-decker of a main group metal, the $[Cp_3Tl_2^-]$ anion, in which the angle Cp–Tl–Cp is 134.2° [136]. The bridging Cp ring is positioned over a crystallographic centre of inversion and consequently is disordered in a 50:50 ratio. The centres of both disordered Cp rings are only 0.01(1) Å apart from the crystallographic center of inversion and this results in a perfect ring of electron density between the Cs cations.[5]

The Cs–C bond distances for the terminal Cp ligands are in the range of 3.313(6)–3.385(5) Å (average 3.350(5) Å) and the Cp_c–Cs distance is 3.134(5) Å. These values compare well with Cs–C bond lengths observed for the disordered bridging Cp rings which range from 3.30(2) Å to 3.38(2) Å, average 3.34(2) Å (the Cp_c–Cs distance is 3.12(2) Å). This narrow range of Cs–C bond distances shows a close to perfect (η^5)Cp–Cs bonding geometry (the largest deviation from the average Cs–C bond distance is only 1.2%). The Cp–Cs bonds are extremely long and probably the longest Cp–metal bonds ever to be encountered throughout the periodical system (apart from Cp–metal bonding in hypothetical francocene). At

---

[5] It should be mentioned that the centers of the disordered bridging Cp rings not necessarily have to coincide with the crystallographic center of inversion. A large deviation would imply that the bridging Cp–Cs bonds (or at least one of them) are highly distorted from an ideal η^5-bonding geometry.

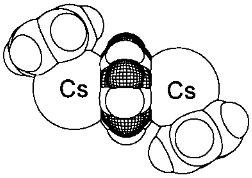


Fig. 30. A space-filling model of the strongly bent anion $[Cp_3Cs_2^-]$. The bridging Cp ring is located on a crystallographic centre of inversion and therefore disordered over two positions (each with 50% occupation).

present, there are no precedent structures of Cp–Cs compounds in order to compare the Cp–Cs bonding distances in the cesocene triple-decker. However, there is a structure known for $C_{60}^-Cs^+$ [137]. In the solid state it forms a three-dimensional polymeric structure in which Cs cations are sandwiched between C_{60}^- spheres. Partial structures in which the Cs^+ cation coordinates at a five-membered carbon ring of the C_{60}^- anion can be recognized (Fig. 31). In this respect, the C_{60}^- anion can be considered as a higher homologue in the series cyclopentadiene, indene, fluorene, etc. The C–Cs bonds in $C_{60}^-Cs^+$ vary from 3.505 to 3.696 Å and are longer than the Cp–Cs bonds observed in $[Cp_3Cs_2]^-$. This is due to delocalization of the negative charge over all 60 carbon atoms.

The bonding within the $[Cp_3Cs_2]^-$ anion should be considered as highly ionic and consequently the very long electrostatic Cp^-–Cs^+ bonds are relatively weak (for the heterolytic bond dissociation of CpCs a value of 124 kcal/mol has been calculated; cf. for CpLi this value amounts to 182 kcal/mol [31,32]). It is therefore remarkable that these loosely bonded Cp ligands show such a perfect η^5-bonding mode. Also remarkable is the similarity in the Cp–Cs bond distances for terminal and bridging Cp rings. According to electrostatic principles, larger Cp–Cs bond distances are expected for the bridging unit. Apparently, the Cs cations in the

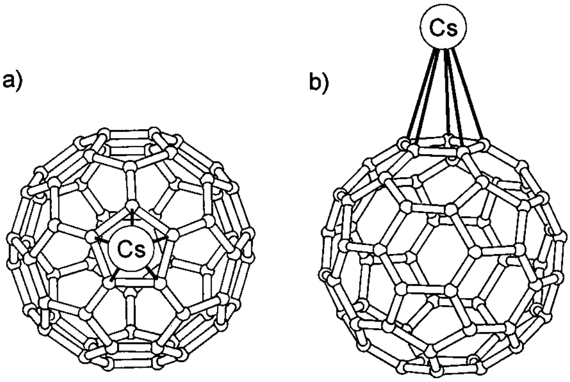


Fig. 31. Part of the crystal structure of $C_{60}^-Cs^+$ in which a Cs^+ cation is bound at the site of a five-membered carbon ring; (a) top view and (b) side view.

triple-decker are too remote [the $Cs^+ \cdots Cs^+$ distance is 6.236(3) Å] for a significant repulsive $Cs^+ \cdots Cs^+$ interaction and a concomitant elongation of the inner Cp–Cs bonds.

Another explanation for the longer than expected $Cs\text{–}Cp_{terminal}$ bond distances might be related to the participation of the terminal Cp rings in intermolecular $Cp^- \cdots Cs^+$ bonding. The huge coordination sphere of Cs^+ can not be filled with only two Cp ligands and is therefore completed by intermolecular interactions. A space-filling packing model of the structure shows that layers of $[Cp_3Cs_2^-]$ are alternated by layers of $[Ph_4P^+]$ (Fig. 32a). The shortest interaction between the layers is a (phenyl)$C \cdots Cs^+$ contact of 3.760(5) Å. More important are the short intermolecular $Cp^- \cdots Cs^+$ contacts within the layers of $[Cp_3Cs_2^-]$ anions (depicted in Fig. 32b by dotted lines). Each layer is a two-dimensional coordination polymer in which intermolecular $C \cdots Cs^+$ contacts range from 3.699(5) to 3.810(5) Å. The intermolecular $C \cdots Cs^+$ contacts are only 10% longer than the intramolecular $C \cdots Cs^+$ bond distances and should therefore be considered as significant bonding interactions.

The generation of a Cp^-/CpCs solution resulted in precipitation of the anionic triple-decker $[Cp_3Cs_2^-]$. This suggests that the remaining mother liquor might contain other species with an interesting composition: e.g. $[Cp_3Cs^{2-}]$ or $[Cp_2CsCpCsCp_2^{3-}]$. Crystallization experiments with a variety of different temperatures, absolute concentrations and relative Cp^-/CpCs concentrations all resulted in the crystallization of the anionic triple-decker $[Cp_3Cs_2^-]$ [30]. It is likely that the

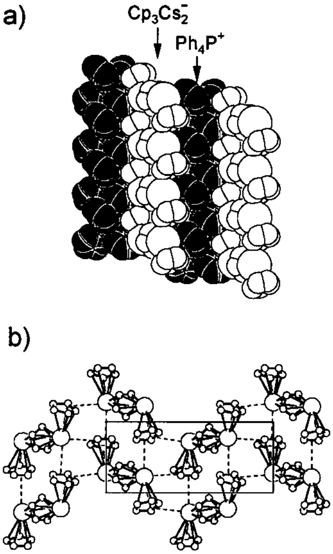


Fig. 32. (a) Packing of the alternate layers of $[Cp_3Cs_2^-]$ anions (in white) and $[Ph_4P^+]$ cations (in black). (b) The layer of $[Cp_3Cs_2^-]$ anions in which intermolecular $Cp^- \cdots Cs^+$ contacts are denoted by dashed lines.

Table 6
Crystal structures of anionic *ansa*-alkalimetallocene sandwich complexes

Compound formula	Range C–M (Å)	Av. C–M (Å)	Cp_c–M[a] (Å)	CCDC code	Ref.
$[Me_4C_2Cp_2Na^-][Ph_4P^+]$	2.614–2.705	2.664	2.381	ZOQPOK	[126]
	2.574–2.757	2.663	2.380		
	2.482–2.943	2.719	2.449		
$[(allyl)_2SiCp_2Na^-][Ph_4P^+]$	2.635–2.744	2.693	2.414	—	[138]
	2.639–2.735	2.689	2.407		
$[Me_2Si(fluorenyl)_2Li^-]$ $[Li^+\cdot THF_4]$	2.584–2.670	2.630	2.366	—	[139]

[a] Cp_c represents the geometric center of the C_5-ring.

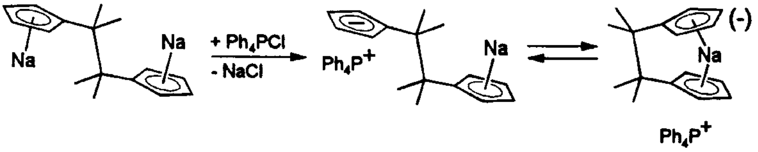
complex $[Cp_3Cs_2^-][Ph_4P^+]$ represents the species with the most advantageous intermolecular contacts and crystal packing.

4.4. Syntheses and structures of anionic ansa-alkalimetallocene sandwich complexes

A few anionic *ansa*-alkalimetallocene complexes, i.e. Cp_2M complexes with bridged Cp rings, have been isolated and were structurally characterized (Table 6).

Bis-cyclopentadienyl ligands with a $(Me_2C{-}Me_2C)$-bridge are easily available via reductive coupling of dimethylfulvene [140]. Subsequently, the bis-Na compound can be obtained quantitatively by double aromatization of the ligand with BuNa. The reaction of this bridged CpNa species with one equivalent of Ph_4PCl in THF resulted in the rapid formation of large red crystals (eq. 15) [126].

A crystal structure determination shows the composition $[Me_4C_2Cp_2Na^-\cdot THF][Ph_4P^+]$ (Fig. 33). The Na^+ is sandwiched between the bridged Cp anions. The bridge between the Cp rings enforces a bent metallocene structure (angle between the Cp planes is 60°) and enables the coordination of a THF molecule. Consequently, the average C–Na distance (2.680 Å) is longer than in the unsolvated $[Cp_2Na^-]$ species. The average Cp–Na bond distances is comparable to the Cp–metal distances in an isovalent Ca complex, $Me_4C_2Cp_2Ca$ (2.678 Å) solvated with a diimine ligand [141,142]. Likewise, the angle between the planes of the Cp rings in $[Me_4C_2Cp_2Na^-\cdot THF]$ (60°) and in $Me_4C_2Cp_2Ca$ (61.2°) are very similar. This similarity originates from the very similar ion radii of Na^+ (0.97 Å) and Ca^{2+} (0.99 Å).



(eq. 15)

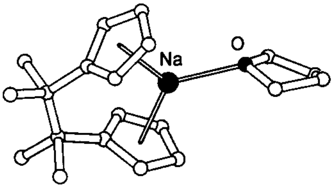


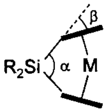
Fig. 33. The crystal structure of the C–C bridged sodocene anion solvated with one THF ligand (the bridge and one of the Cp rings is disordered over two positions of which the highest occupancy is shown here).

A single atom bridge enforces a much larger aperture in the *ansa*-metallocene ligand, e.g. it has been calculated that even the largest metal cation, Cs^+, is too small for double (η^5)Cp–Cs bonding to a fully relaxed $R_2SiCp_2^-$ ligand [139]. This leaves three possibilities for the structure of a Si-bridged alkalimetallocene complex:

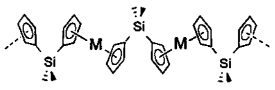
1. The Si-bridged ligand is distorted from its fully relaxed geometry similar to the Si-bridged *ansa*-metallocenes of the d-block metals (**12**): squeezing of the C–Si–C angle (α) and titling of the Cp plane in respect to the Si–C_{ipso} axis (β).
2. The Cp–M bond is distorted from its favourable (η^5)Cp–M geometry.
3. Anionic Si-bridged alkalimetallocene complexes build a polymeric structure (**13**) in which the metal cations bridge the exo-sides of the *ansa*-Cp_2 ligands (such polymers are comparable to polymers obtained after heating highly strained ferrocenophanes like Ph_2SiCp_2Fe [142]. (Fig. 18)

During our investigations on Si-bridged alkalimetallocene compounds, the complex $[(allyl)_2SiCp_2Na^-][Ph_4P^+]$ was obtained as a dark-red oil. After standing, some crystals started to precipitate and could be isolated. A crystal structure determination revealed the composition: $[(allyl)_2SiCp_2Na^-][Ph_4P^+]$ [138]. The crystal structure shows long polymeric chains which are separated by the phosphonium cations. The linear chains (Fig. 34) consist of the $R_2SiCp_2^{2-}$ species which are bridged by Na cations. All Na^+ cations are bound at the exo sides of the $R_2SiCp_2^{2-}$ ligand. Evidently, the Na^+ is too small too fit properly in the $R_2SiCp_2^{2-}$ ligand. Such a structure type is reminiscent to polymers obtained from highly strained silicon-bridged d-block metallocenes [143–145].

The two similar Cp_c–Na distances of 2.407 and 2.414 Å show a symmetric bonding of Na^+ between the Cp rings. The average Cp_c–Na distance is signifi-



(12)



(13)

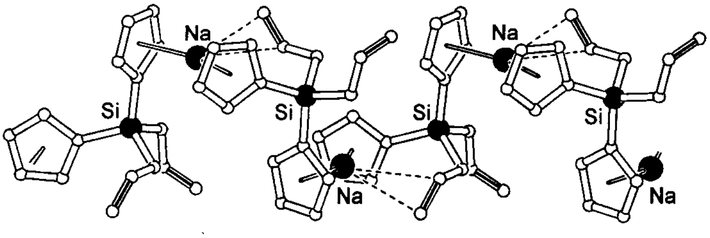


Fig. 34. The coordination polymer of [(allyl)$_2$SiCp$_2$Na$^-$] units. Weak intramolecular alkene–Na$^+$ π-interactions are indicated by dashed lines.

cantly longer than the corresponding values obtained for the structurally known sodocene anions [Cp$_2$Na$^-$] (2.329 and 2.366 Å). It is believed that an alkene–Na$^+$ π-interaction (indicated in Fig. 34 with dotted lines) is responsible for the somewhat elongated Cp$_c$–Na distances. This π-interaction likewise causes a bending of the Cp–Na–Cp unit. The Cp rings in the sodocene anion [Cp$_2$Na$^-$] are coplanar, but the Cp–Na–Cp unit in [(allyl)$_2$SiCp$_2$Na$^-$] is bent with an angle of 151.4°.

We recently reported the first structure elucidations of silicon-bridged sandwich complexes of group I and II metals [139]. Among the compounds under investigation is a dilithiated Me$_2$Si-bridged bisfluorenyl ligand. An X-ray structure determination shows that this species spontaneously crystallizes from THF solution as an ion pair which consists of an anionic lithium sandwich complex and a *tetrakis*-THF solvated Li$^+$ cation.

The structure of the anionic part (Fig. 35) shows that the Li cation is sandwiched between the fluorenyl rings and is additionally solvated from two THF ligands. The Me$_2$Si(fluorenyl)$_2$ ligand does not exhibit any of the distortions as shown in **12**. However, a severe distortion from an (η^5)fluorenyl–Li$^+$ interaction to an (η^1)fluorenyl–Li$^+$ interaction is evident from the C–Li bond distances. This nicely illustrates the major difference between cyclopentadienyl and fluorenyl alkalimetal complexes. Fluorenyl–metal coordination may vary from η^1 to η^6 and all possible coordination modes have been reported [146–152]. This rich variety of observed coordination modes is in accord with calculations on fluorenyllithium which show that the energy differences between the different modes of coordination are < 1.5 kcal/mol [147] (cf. the difference between η^1 and η^5 coordination in CpLi amounts to approx. 20 kcal/mol, see Fig. 3). It is therefore not surprising that strong deviation from ideal η^5-coordination is employed in order to fit the small lithium cation in the Si-bridged bisfluorenyl ligand.

4.5. A comparison of main-group metallocene sandwich complexes

The lithocene anion is *isoelectronic* to its structurally known first-row relatives Cp$_2$Be [153] and Cp$^*_2$B$^+$ [99]. However, these compounds are not isostructural to Cp$_2$Li$^-$ but are of the slipped sandwich type: (η^5,η^1)Cp$_2$M (Fig. 36). On the other hand, the lithocene anion is *isovalent* to its second-row relatives Cp$_2$Mg [131–135]

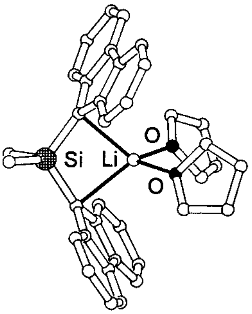


Fig. 35. The anionic part of the crystal structure of [$Me_2Si(fluorenyl)_2Li^-$] [$Li^+ \cdot (THF)_4$].

and $Cp_2^*Al^+$ [100,101], both complexes which exhibit D_{5d} sandwich structures similar to that of [Cp_2Li^-]. How can this be explained?

Preference for the geometry of a slipped sandwich complex has been discussed in terms of three-dimensional aromaticity [39–41]. A total of 12 interstitial electrons in species Cp_2Be and Cp_2B^+ with D_{5d} symmetry, would result in occupation of the degenerated (Cp_2) e_{1g} orbitals for which no bonding combination with metal s- and p-orbitals is possible. The alternative slipped sandwich complex, with six interstitial

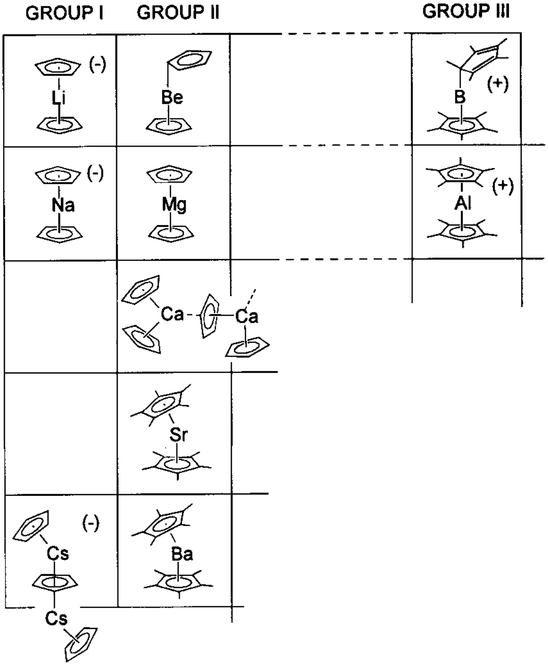


Fig. 36. A comparison of some main-group metallocene sandwich complexes.

electrons, satisfies the rules for three-dimensional aromaticity. Although such orbital rules are perfectly valid for complexes with significant covalent Cp–M bond character (like $Cp^*_2B^+$), another explanation should be forwarded for more ionic complexes like Cp_2Be. The preference for the slipped sandwiches of beryllocene and borocene can also be explained by simple size arguments. The (η^5)Cp–Be distance in the slipped sandwich of Cp_2Be amounts 1.505(6) Å. Thus, a hypothetical Cp_2Be sandwich of D_{5d} symmetry would have a Cp ··· Cp distance of approx. 3.0 Å, i.e. a ring–ring distance much shorter than the interlayer distance in graphite (the interlayer distance of 3.35 Å in graphite is commonly regarded as the equilibrium distance between two relaxing non-bonded sp^2-hybridized carbon atoms; this equals approximately twice the van der Waals radius for carbon). In a hypothetical D_{5d} $(\eta^5)Cp_2B^+$ complex, the Cp ··· Cp distance would be even shorter than 3.0 Å. For this reason Cp_2Be and $Cp^*_2B^+$ exhibit slipped sandwich structures in which unfavourable repulsions between the Cp rings are avoided. On the other hand, the Cp ··· Cp distance in $[Cp_2Li^-]$ amounts 4.012(8) Å and is well above the sum of the C ··· C van der Waals radii. Likewise, Cp_2Mg and $Cp^*_2Al^+$ show relatively long Cp ··· Cp distances of 3.96(1) and 3.67(1) Å, respectively, and staggered sandwich complexes with approximate D_{5d} symmetry are observed here as well. In fact, the structures of Cp_2Li^- and Cp_2Mg show a striking similarity. The staggered sandwich structures as well as the average C–M bond distances {$[Cp_2Li^-]$: 2.318(4) Å; Cp_2Mg: 2.304(8) Å} are very similar. This similarity in structure is born out of the very similar ionic radii for Li^+ (0.59 Å) and Mg^{2+} (0.57 Å).

The sodocene anion is *isoelectronic* and also isostructural to its second-row relatives Cp_2Mg and $Cp^*_2Al^+$. However, the diagonally related Cp_2Ca crystallizes as bent Cp_2Ca units which form a coordination polymer [154]. The bending of the Cp_2Ca unit results in coordination space at the metal cation and enables the formation of such a coordination polymer. Bending of Cp_2M units involves a shortening of the Cp ··· Cp distance and is therefore usually observed for the Cp_2M species with the larger metals. Despite the very similar ion radii of Na^+ (0.97 Å) and Ca^{2+} (0.99 Å), $[Cp_2Na^-]$ and Cp_2Ca crystallize as different structures. A possible explanation for the formation of a structure with isolated sodocene anions might be the presence of the phosphonium cations. The alternate packing of anions and cations, as observed in the crystal structure of $[Cp_2Na^-][Ph_4P^+]$, seems to be preferred. Another (or additional) explanation may be found in the twofold charge on Ca^{2+} when compared to Na^+. This implies that intermolecular M ··· Cp Coulomb attraction is stronger between bent Cp_2Ca units than between bent $[Cp_2Na^-]$ units.

The structure of Cp^*_2Ca shows a monomeric complex with an average C–Ca bonding distance of 2.640 Å [155]. This is very close to the average C–Na bond distance in $[Cp_2Na^-][Ph_4P^+]$ of 2.630 Å. However, the monomeric Cp^*_2Ca complex forms a bent sandwich structure (the angle Cp_c–Ca–Cp_c is 147°), whereas the Cp ligands in the $[Cp_2Na^-]$ unit are arranged perfectly coplanar. It is not excluded that $[Cp_2Na^-]$ has a shallow bending energy profile similar to that of Cp_2Ca. In that case the perfectly linear structure of $[Cp_2Na^-]$ is just a coincidence which is caused by crystallization of this compound in a centrosymmetric spacegroup with the [Cp_2Na^-] units on crystallographic inversion centres.

The structure of the triple-decker [$Cp_3Cs_2^-$] shows considerable bending of the Cp–Cs–Cp unit (115.6°). Similar, the powder diffraction structures of Cp_2Rb exhibit bent units (123.5–136.5°). Is there a structural conformity between the heavy anionic alkali metallocenes and alkaline-earth metallocenes? The latter metallocenes are typified by their bent structures which violate VSEPR-rules and simple electrostatic bonding models [75,76,156–158]. It is believed that packing effects and intermolecular interactions do not play a significant role in the solid state structures of Cp^*_2Ca and Cp^*_2Ba and, in particular, are not responsible for the bending (Cp–Ca–Cp = 146.3° and Cp–Ba–Cp = 131.0°) [155]. This argument is enforced by structural analyses of these metallocenes in the gas phase which likewise indicate bent structures [159,160]. Arguments advanced as explanations for the bending (attractive van der Waals forces between the Cp rings, induced polarization of the metal centre by the ligands and involvement of d-orbitals) could to a certain extent similarly be applied to the heavier anionic alkali metallocenes. High-level ab initio calculations indeed show that bent structures play a role in the coordination chemistry of the Cs cation: the minimal energy structure of $Cs^+(H_2O)_2$ is a bent structure with a $O-Cs^+-O$ angle of 113.3° [cf. the angle of 109.6° in $Ba^{2+}(H_2O)_2$] [161]. However, the extremely small linearization energy of only 0.26 kcal/mol shows the potential surface to be very shallow [cf. the linearization energy for bent $Ba^{2+}(H_2O)_2$ is 1.03 kcal/mol]. The energy involved with the intermolecular contacts in the solid state structure of [$Cp_3Cs_2^-$][Ph_4P^+] is much larger. The bent structure as a typical energy minimum for sandwich cesocene complexes can therefore not be confirmed by our experimental data. The use of bulky substituted Cp ligands could probably yield anionic rubidocene or cesocene sandwich complexes in which intermolecular Cp^--M^+ interactions are negligible. The structural identification of such compounds will reveal more about their similarity with the bent structures of the heavier alkaline-earth metallocenes. However, as has been indicated by the calculations [161], the energy difference between linear and bent sandwich complexes is probably extremely small. Therefore anionic sandwich complexes of the heavier alkalimetals (Rb and Cs) are better described as very floppy molecules which can adopt structures with a variety of bending angles.

4.6. Nomenclature for anionic alkalimetallocene sandwich complexes

A possible systematic IUPAC name for 'the lithocene anion' appears to be 'di-2,4-cyclopentadien-1-yllithate(1 −)' [162], a name which is not only long and complicated but also gives a wrong picture of the bonding in the [Cp_2Li^-] molecule. In general, Cp_2M sandwich complexes are known by common names (like ferrocene), a situation which is also highly desired in the chemistry of the Group I metallocene sandwich complexes. However, according to the metallocene nomenclature [163] the name ending '-ocene' should be confined to molecules having the structure bis(η^5-cyclopentadienyl)metal in which the rings are essentially coplanar and the metal belongs to the d-block series (names like 'barocene' and 'titanocenedichloride' are not official). Nevertheless, common names for anionic alkalimetallocene sandwich complexes were introduced. It was found that naming these new species is not self-evident.

The original version of our manuscript described the [Cp_2Li^-] species as 'the lith*io*cene anion', however, this name was changed by the editors of the magazine in 'the lith*o*cene anion' (in analogy to existing common names: *magnes*-ium → *magnes*-ocene and therefore *lith*-ium → *lith*-ocene). Thus, the following anionic sandwich complex in the series, the [Cp_2Na^-] species, was described by us as 'the sod*o*cene anion'. However, the editors of another magazine questioned this name and proposed that 'sod*io*cene' sounds more reasonable (in anology with the fact that phenylsodium is sometimes described as 'sod*io*-benzene').

Is there any system in the naming of the sandwiched metal compounds? It should be noted that the first sandwich complex 'ferrocene' stems from the Latin element name 'ferrum': *ferr*-um → *ferr*-ocene and therefore *lithi*-um → *lithi*-ocene seems to be allowed. Apart from the *o*cene–*io*cene controversy, naming of the alkalimetallocene anions leads to other problems. For example it is not always clear which Latin name should be used in the prefix: the Latin word for sodium is 'natrium' but medieval Latin uses the word 'sodanum' (headache remedy) [164]. In a report on an anionic sodium sandwich complex, the [Cp_2Na^-] unit was named '*sod*ocene anion' in the English version of the paper (after the Latin 'sodanum' or the English 'sodium'?), but surprisingly the german version used the name '*Natr*o-cen Anion' (after the Latin or the German 'natrium'?) [124,125]. At least the use of one Latin prefix for different languages would be highly desired. It should be noted that the anion [$Cp_3Cs_2^-$] was described by us as '*ce*socene' in the English version and 'C*ae*socen' in the German version of the publication. However, the prefix 'c*ae*s', derived from the Latin 'caesius', should be preferred in both languages. Despite our recommendation [165] it has been published in the English version of the original paper as '*ce*socene' [127,128] with the argumentation that this conforms more with the English spelling. In this respect it should be mentioned that 'cesium' represents the American spelling whereas the British word for Cs is 'caesium'.

New IUPAC nomenclature rules for all sandwich compounds not belonging to the d-block metal compounds is higly desirable. In this work, the names for the anionic sandwich complexes have been adapted to the first common name used for a [Cp_2M^-] species, the lithocene anion [122,123], and to the names used in the original publications of our contributions.

5. Summary and outlook

This work summarizes selected structural data of all Cp-alkalimetal compounds published up to September 1997 including own unpublished results (the indenyl, fluorenyl and higher delocalized systems have been excluded deliberately and are only occasionally mentioned for comparison). An overview has been given of all different structural types encountered in the chemistry of the Cp-alkalimetal compounds: one-dimensional linear polymers, two-dimensional sheet-like polymers, three-dimensional polymers, solvated linear polymers, solvated monomers, oligomeric chain or ring structures, inverse sandwich cations and sandwich anions.

The rapidly developing interest for Cp-alkalimetal compounds with one (or more) intramolecular coordinating group(s) will likely result in new structural types. Also, the fully unknown chemistry of mixed alkalimetal systems, CpM/CpM′, or mixed anion systems, CpM/RM, could show surprisingly new bonding types. The new field of alkalimetallocene anions is still largely unexplored. The structures of some simple $[Cp_2M^-]$ anions are known, however, not much information is available on the consequences of substituting the Cp rings. Further research in the field of alkyl or silyl substituted alkalimetallocene anions is needed. For the larger metal cations (Rb^+, Cs^+) even species like $[Cp_3M^{2-}]$ or $[Cp_5M_2^{3-}]$ are predicted.

6. General remarks

Some of the work described in this review article originates from unpublished results from our own laboratory. All of these experiments described, have been performed under argon with the use of freshly dryed and destilled solvents and Schlenk/syringe techniques. Calculations have been done with the *GAUSSIAN94* program [166] using the standard designated methods and basis sets [MP2 refers to MP2(fc)]. All geometrical calculations and graphical work on the X-ray structures has been performed with the *EUCLID* package [167].

Acknowledgements

This review article represents the larger part of my ‘Habilitationsarbeit’ at the University of Konstanz (Germany) and is born out of the interaction I had with people from different research groups. Apart from all these people I am especially grateful to the co-authors of our relevant contributions (Dr M.H. Prosenc and Dr U. Rief) and to the Professors Hans-Herbert Brintzinger and Gerhard Müller for fruitful discussions and laboratory facilities. I also thank the Professors H.J.T. Bos (Utrecht, The Netherlands), J. McCleverty (Bristol, UK) and A. Salzer (Aachen, Germany) for helpful discussions on the nomenclature problem. Dr R.E Dinnebier (Bayreuth, Germany), Prof. H. Schnöckel (Karlsruhe, Germany) and Prof. Wai-Kwok Wong (Hong Kong) are kindly acknowledged for sending me the atom coordinates of their X-ray contributions. Finally, I thank the Alexander von Humboldt Stiftung and the European Community for financial support of the work in Konstanz.

References

[1] T.J. Kealy, P.L. Pauson, Nature 168 (1951) 1039.

[2] G. Wilkinson, M. Rosenblum, M.C. Whiting, R.B. Woodward, J. Am. Chem. Soc. 74 (1952) 2125.
[3] V. Grignard, C. Courtot, Chem. Zentr. II (1914) 397.
[4] H.E. Roscoe, J. Liebigs, Ann. Chem. 232 (1886) 352.
[5] G. Kraemer, A. Spilker, Ber. Dtsch. Chem. Ges. 29 (1896) 552.
[6] Étard, Lambert, Compt. Rend., 112, 945.
[7] J. Thiele, Ber. Dtsch. Chem. Ges. 33 (1900) 666.
[8] J. Thiele, Ber. Dtsch. Chem. Ges. 34 (1901) 68.
[9] F. Runge, Organometall Verbindungen, Stuttgart (Germany) 1944, pp. 8–11.
[10] H.P. Fritz, R. Schneider, Chem. Ber. 93 (1960) 1171.
[11] H.P. Fritz, L. Schäfer, Chem. Ber. 97 (1964) 1829.
[12] R.H. Cox, H.W. Terry, Jr., L.W. Harrison, J. Am. Chem. Soc. 93 (1971) 3297.
[13] W.T. Ford, J. Organomet. Chem. 32 (1971) 27.
[14] P. Fischer, J. Stadelhofer, J. Weidlein, J. Organomet. Chem. 116 (1976) 65.
[15] T. Aoyagi, H.M.M. Shearer, K. Wade, G. Whitehead, J. Chem. Soc. Chem. Comm. (1976) 164.
[16] T. Aoyagi, H.M.M. Shearer, K. Wade, G. Whitehead, J. Organomet. Chem. 175 (1979) 21.
[17] P. Jutzi, E. Schlüter, C. Krüger, S. Pohl, Angew. Chem. 95 (1983) 1015.
[18] P. Jutzi, E. Schlüter, C. Krüger, S. Pohl, Angew. Chem., Int. Ed. Engl. 22 (1983) 994.
[19] P. Jutzi, E. Schlüter, S. Pohl, W. Saak, Chem. Ber. 118 (1985) 1959.
[20] M.F. Lappert, A. Singh, L.M. Engelhardt, A.H. White, J. Organomet. Chem. 262 (1984) 271.
[21] P. Jutzi, Adv. Organomet. Chem. 26 (1986) 217.
[22] P. Jutzi, Pure Appl. Chem. 61 (1989) 1731.
[23] P. Jutzi, Pure Appl. Chem. 62 (1990) 1035.
[24] P. Jutzi, J. Organomet. Chem. 400 (1990) 1.
[25] E. Weiss, Angew. Chem. 105 (1993) 1565.
[26] E. Weiss, Angew. Chem., Int. Ed. Engl. 32 (1993) 1501.
[27] D. Stalke, Angew. Chem. 106 (1994) 2256.
[28] D. Stalke, Angew. Chem., Int. Ed. Engl. 33 (1994) 2168.
[29] E. Hückel, Z. Physik 70 (1931) 204.
[30] S. Harder, unpublished results (University of Konstanz).
[31] C. Lambert, P. von R. Schleyer, Angew. Chem. 106 (1994) 1187.
[32] C. Lambert, P. von R. Schleyer, Angew. Chem., Int. Ed. Engl. 33 (1994) 1129.
[33] S. Harder, PhD. Thesis, University of Utrecht, The Netherlands, 1990, p. 2.
[34] J.B. Collins, A. Streitwieser, J. Comput. Chem. 1 (1980) 81.
[35] R.F.W. Bader, P.J. MacDougall, J. Am. Chem. Soc. 107 (1985) 6788.
[36] A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83 (1985) 735.
[37] J.P. Ritchie, S.M. Bachrach, J. Am. Chem. Soc. 109 (1987) 5909.
[38] H. Horn, R. Ahlrichs, J. Am. Chem. Soc. 112 (1990) 2121.
[39] E.D. Jemmis, P. von R. Schleyer, J. Am. Chem. Soc. 104 (1982) 4781.
[40] E.D. Jemmis, S. Alexandratos, P. von R. Schleyer, A. Streitwieser, Jr., H.F. Schaefer III, J. Am. Chem. Soc. 100 (1978) 5695.
[41] J.B. Collins, P. von R. Schleyer, Inorg. Chem. 152 (1977) 16.
[42] S. Alexandratos, A. Streitwieser, H.F. Schaefer III, J. Am. Chem. Soc. 98 (1976) 7959.
[43] E.D. Jemmis, S. Alexandratos, P. von R. Schleyer, A. Streitwieser, Jr., H.F. Schaefer III, J. Am. Chem. Soc. 100 (1978) 5695.
[44] K.C. Waterman, A. Streitwieser, Jr., J. Am. Chem. Soc. 106 (1984) 3138.
[45] W. Bauer, T. Clark, P. von R. Schleyer, J. Am. Chem. Soc 109 (1987) 970.
[46] W. Bauer, M. Feigel, G. Müller, P. von R. Schleyer, J. Am. Chem. Soc. 110 (1988) 6033.
[47] W. Bauer, P.A.A. Klusener, S. Harder, et al., Organometallics 7 (1988) 552.
[48] W.N. Setzer, P. von R. Schleyer, Adv. Organomet. Chem. 24 (1985) 353.
[49] G. Corongiu, E. Clementi, E. Pretsch, W. Simon, J. Chem. Phys. 72 (1980) 3096.
[50] E. Kaufmann, B. Tidor, P. von R. Schleyer, J. Comput. Chem. 7 (1986) 334.
[51] H. Chen, P. Jutzi, W. Leffers, M.M. Olmstead, P.P. Power, Organometallics 10 (1991) 1282.
[52] R.E. Dinnebier, U. Behrens, F. Olbrich, Organometallics 16 (1997) 3855.

[53] R.E. Dinnebier, F. Olbrich, S. van Smaalen, P.W. Stephens, Acta Cryst. B53 (1997) 153.
[54] W.J. Evans, T.J. Boyle, J.W. Ziller, Organometallics 11 (1992) 3903.
[55] P. Jutzi, W. Leffers, B. Hampel, S. Pohl, W. Saak, Angew. Chem. 99 (1987) 563.
[56] P. Jutzi, W. Leffers, B. Hampel, S. Pohl, W. Saak, Angew. Chem., Int. Ed. Engl. 26 (1987) 583.
[57] S. Zhang, J. Liu, G. Wei, G. Lin, W. Chen, Polyhedron 12 (1993) 2771.
[58] B. Zhang, J. Zhongsheng, W. Yuling, W. Gecheng, C. Wenqi, Chem. Res. Chin. Univ. 8 (1992) 15.
[59] G.E. Herberich, A. Fischer, Organometallics 15 (1996) 58.
[60] W.P. Schaefer, W.D. Cotter, J.E. Bercaw, Acta Cryst. C49 (1993) 1489.
[61] G. Rabe, H.W. Roesky, D. Stalke, F. Pauer, G.M. Sheldrick, J. Organomet. Chem. 403 (1991) 11.
[62] V. Jordan, U. Behrens, F. Olbrich, E. Weiss, J. Organomet. Chem. 517 (1996) 81.
[63] F.H. Allen, O. Kennard, Chem. Des. Automatic News 8 (1993) 31.
[64] P. Jutzi, W. Leffers, S. Pohl, W. Saak, Chem. Ber. 122 (1989) 1449.
[65] A. Sekiguchi, Y. Sugai, K. Ebata, C. Kabuto, H. Sakurai, J. Am. Chem. Soc. 115 (1993) 1144.
[66] J.J. Stezowski, H. Hoier, D. Wilhelm, T. Clark, P. von R. Schleyer, J. Chem. Soc. Chem. Comm. (1985) 1263.
[67] F. Zaegel, J.C. Gallucci, P. Meunier, B. Gautheron, M.R. Sivik, L.A. Paquette, J. Am. Chem. Soc. 116 (1994) 6466.
[68] A. Hammel, W. Schwarz, J. Weidlein, Acta Cryst. C46 (1990) 2337.
[69] J. Hiermeier, F.H. Köhler, G. Müller, Organometallics 10 (1991) 1787.
[70] H. Chen, P. Jutzi, W. Leffers, M.M. Olmstead, P.P. Power, Organometallics 10 (1991) 1282.
[71] C. Näther, T. Hauck, H. Bock, Acta Cryst. C52 (1996) 570.
[72] J. Lorberth, S.-H. Shin, S. Wocadlo, W. Massa, Angew. Chem. 101 (1989) 793.
[73] J. Lorberth, S.-H. Shin, S. Wocadlo, W. Massa, Angew. Chem., Int. Ed. Engl. 28 (1989) 735.
[74] C. Schade, P. von R. Schleyer, Adv. Organomet. Chem. 27 (1987) 169.
[75] T.P. Hanusa, Chem. Rev. 93 (1993) 1023.
[76] D.J. Burkey, T.P. Hanusa, Common Inorg. Chem. 17 (1995) 41.
[77] R. Blom, K. Faegri, Jr., T. Midtgaard, J. Am. Chem. Soc. 113 (1991) 3230.
[78] R.D. Moulton, R. Farid, A.J. Bard, J. Electroanal. Chem. 256 (1988) 309.
[79] T. Kinoshita, N. Murata, R. Fujita, Y. Yanagi, K. Takeuchi, J. Organomet. Chem. 471 (1994) 19.
[80] P. Jutzi, Common Inorg. Chem. 6 (1987) 123.
[81] P.J. Barker, A.G. Davies, R. Henriquez, J.-Y. Nedelec, J. Chem. Soc. Perkin Trans. II (1982) 745.
[82] J.-M. Lehn, G. Wipff, J. Am. Chem. Soc. 98 (1976) 7498.
[83] W. Thatcher Borden, E.R. Davidson, N.H. Andersen, A.D. Denniston, N.D. Epiotis, J. Am. Chem. Soc. 100 (1978) 1604.
[84] P.v.R. Schleyer, T. Clark, A.J. Kos, et al., J. Am. Chem. Soc. 106 (1984) 6467.
[85] Q. Lin, W.-T. Wong, Polyhedron 13 (1994) 3027.
[86] C. Dohmeier, E. Baum, A. Ecker, R. Köppe, H. Schnöckel, Organometallics 15 (1996) 4702.
[87] M. Könemann, G. Erker, M. Grehl, R. Fröhlich, E.-U. Würthwein, J. Am. Chem. Soc. 117 (1995) 11215.
[88] R. Amstutz, T. Laube, W.B. Schweizer, D. Seebach, J.D. Dunitz, Helv. Chim. Acta 67 (1984) 224.
[89] S. Harder, J. Boersma, L. Brandsma, et al., Organometallics 8 (1989) 1688.
[90] S. Corbelin, J. Kopf, E. Weiss, Chem. Ber. 124 (1991) 2417.
[91] S. Harvey, C.L. Raston, B.W. Skelton, A.H. White, M.F. Lappert, G. Srivastava, J. Organomet. Chem. 328 (1987) C1.
[92] M.G. Davidson, D. Stalke, D.S. Wright, Angew. Chem. 104 (1992) 1265.
[93] M.G. Davidson, D. Stalke, D.S. Wright, Angew. Chem., Int. Ed. Engl. 31 (1992) 1226.
[94] M.A. Paver, C.A. Russell, D. Stalke, D.S. Wright, J. Chem. Soc. Chem. Commun. (1993) 1349.
[95] D.R. Armstrong, R. Herbst-Irmer, A. Kuhn, et al., Angew. Chem. 105 (1993) 1807.
[96] D.R. Armstrong, R. Herbst-Irmer, A. Kuhn, et al., Angew. Chem., Int. Ed. Engl. 32 (1993) 1774.
[97] M.A. Power, C.A. Russell, D.S. Wright, Angew. Chem. 107 (1995) 1679.
[98] M.A. Power, C.A. Russell, D.S. Wright, Angew. Chem., Int. Ed. Engl. 34 (1995) 1545.
[99] P. Jutzi, A. Seufert, J. Organomet. Chem. 161 (1978) C5.
[100] C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, Angew. Chem. 105 (1993) 1714.

[101] C. Dohmier, H. Schnöckel, C. Robl, U. Schneider, H. Ahlrichs, Angew. Chem., Int. Ed. Engl. 32 (1993) 1655.
[102] P. Jutzi, T. Wippermann, C. Krüger, H.-J. Kraus, Angew. Chem. 95 (1983) 244.
[103] P. Jutzi, T. Wippermann, C. Krüger, H.-J. Kraus, Angew. Chem., Int. Ed. Engl. 22 (1983) 250.
[104] P. Jutzi, D. Kanne, C. Krüger, Angew. Chem. 98 (1986) 163.
[105] P. Jutzi, D. Kanne, C. Krüger, Angew. Chem., Int. Ed. Engl. 25 (1986) 164.
[106] P. Jutzi, U. Holtmann, D. Kanne, et al., Chem. Ber. 122 (1989) 1629.
[107] P. Jutzi, F. Kohl, P. Hofmann, C. Krüger, Y.-H. Tsay, Chem. Ber. 113 (1980) 757.
[108] J.L. Atwood, W.E. Hunter, A.H. Cowley, R.A. Jones, C.A. Stewart, J. Chem. Soc. Chem. Comm. (1981) 925.
[109] W. Strohmeier, H. Lansfeld, F. Gernert, Z. Elektrochem. 66 (1962) 823.
[110] R. den Besten, S. Harder, L. Brandsma, J. Organomet. Chem. 385 (1990) 153.
[111] S.D. Stults, R.A. Andersen, A. Zalkin, J. Am. Chem. Soc. 111 (1989) 4507.
[112] W.J. Evans, M.S. Sollberger, J.L. Shreeve, J.M. Olofson, J.H. Hain, Jr., J.W. Ziller, Inorg. Chem. 31 (1992) 2492.
[113] J.C. Berthet, C. Villiers, J.F. Le Maréchal, et al., J. Organomet. Chem. 440 (1992) 53.
[114] L.A. Paquette, W. Bauer, M.R. Sivik, M. Bühl, M. Feigel, P. von R. Schleyer, J. Am. Chem. Soc. 112 (1990) 8776.
[115] M. Eiermann, K. Hafner, J. Am. Chem. Soc. 114 (1992) 135.
[116] C. Mink, K. Hafner, Tetrahedron Lett. 35 (1994) 4087.
[117] A. Ayalon, A. Sygula, P.-C. Cheng, M. Rabinovitz, P.W. Rabideau, L.T. Scott, Science 265 (1994) 1065.
[118] D. Malaba, L. Chen, C.A. Tessier, W.J. Youngs, Organometallics 11 (1992) 1007.
[119] M. Pilz, J. Allwohn, P. Willershausen, W. Massa, A. Berndt, Angew. Chem. 102 (1990) 1085.
[120] M. Pilz, J. Allwohn, P. Willershauser, W. Massa, A. Berndt, Angew. Chem., Int. Ed. Engl. 29 (1990) 1030.
[121] H.-D. Hausen, J. Tödtmann, J. Weidlein, J. Organomet. Chem. 466 (1994) C1.
[122] S. Harder, M.H. Prosenc, Angew. Chem. 106 (1994) 1830.
[123] S. Harder, M.H. Prosenc, Angew. Chem., Int. Ed. Engl. 33 (1994) 1744.
[124] J. Wessel, U. Behrens, E. Lork, R. Mews, Angew. Chem. 107 (1995) 516.
[125] J. Wessel, U. Behrens, E. Lork, R. Mews, Angew. Chem., Int. Ed. Engl. 34 (1995) 443.
[126] S. Harder, M.H. Prosenc, U. Rief, Organometallics 15 (1996) 118.
[127] S. Harder, M.H. Prosenc, Angew. Chem. 108 (1996) 101.
[128] S. Harder, M.H. Prosenc, Angew. Chem., Int. Ed. Engl. 35 (1996) 97.
[129] F. Zaegel, J.C. Gallucci, P. Meunier, B. Gautheron, M.R. Sivik, L.A. Paquette, J. Am. Chem. Soc. 116 (1994) 6466.
[130] W.-K. Wong, L. Zhang, W.-T. Wong, F. Xue, T.C.W. Mak, Polyhedron 15 (1996) 4593.
[131] W. Bünder, E. Weiss, J. Organomet. Chem. 92 (1975) 1.
[132] E. Weiss, E.O. Fischer, Z. Anorg. Allg. Chem. 284 (1956) 69.
[133] J.D. Dunitz, L.E. Orgel, A. Rich, Acta Crystallogr. 9 (1956) 373.
[134] W. Bünder, E. Weiss, J. Organomet. Chem. 92 (1975) 65.
[135] P. Seiler, J.D. Dunitz, Acta Crystallogr. B36 (1980) 2255.
[136] D.R. Armstrong, A.J. Edwards, D. Moncrieff et al., J. Chem. Soc. Chem. Commun. (1995) 927.
[137] O. Zhou, J.E. Fischer, N. Coustel, et al., Nature 351 (1991) 462.
[138] S. Harder, M. Lutz, S. Obert, Manuscript in Preparation.
[139] S. Harder, M. Lutz, A.W.G. Straub, Organometallics 16 (1997) 107.
[140] H. Schwemlein, H.-H. Brintzinger, J. Organomet. Chem. 254 (1983) 69.
[141] M. Rieckoff, U. Pieper, D. Stalke, F.T. Edelmann, Angew. Chem. 105 (1993) 1102.
[142] M. Rieckoff, U. Pieper, D. Stakle, P.T. Edelmann, Angew. Chem., Int. Ed. Engl. 32 (1993) 1079.
[143] D. Seyferth, H.P. Withers, Jr., Organometallics 1 (1982) 1275.
[144] H.P. Withers, Jr., D. Seyferth, J.D. Fellmann, P.E. Garrou, S. Martin, Organometallics 1 (1982) 1283.
[145] I. Manners, Adv. Organomet. Chem. 37 (1995) 131.

[146] J.J. Brooks, W. Rhine, G.D. Stucky, J. Am. Chem. Soc. 94 (1972) 7339.
[147] D. Hoffmann, F. Hampel, P.v.R. Schleyer, J. Organomet. Chem. 456 (1993) 13.
[148] S. Corbelin, J. Kopf, E. Weiss, Chem. Ber. 124 (1991) 2417.
[149] J.W. Johnson, P.M. Treichel, J. Am. Chem. Soc. 99 (1977) 1427.
[150] C. Kowala, J.A. Wunderlich, Acta Crystallogr. B32 (1976) 820.
[151] M. Bochmann, S.J. Lancaster, M.B. Hursthouse, M. Mazid, Organometallics 12 (1993) 4718.
[152] H. Viebrock, D. Abeln, E. Weiss, Z. Naturforsch. B49 (1994) 89.
[153] K.W. Nugent, J.K. Beattie, T.W. Hambley, M.R. Snow, Aust. J. Chem. 37 (1984) 1601.
[154] R. Zerger, G. Stucky, J. Organomet. Chem. 80 (1974) 7.
[155] R.A. Williams, T.P. Hanusa, J.C. Huffman, Organometallics 9 (1990) 1128.
[156] P. Jutzi, J. Organomet. Chem. 400 (1990) 1.
[157] D.J. Burkey, T.P. Hanusa, Common Inorg. Chem. 17 (1995) 41.
[158] T.V. Timofeeva, J.-H. Lii, N.L. Allinger, J. Am. Chem. Soc. 117 (1995) 7452.
[159] R.A. Andersen, J.M. Boncella, C.J. Burns, R. Blom, A. Haaland, H.V. Volden, J. Organomet. Chem. 312 (1986) C49.
[160] R.A. Andersen, R. Blom, C.J. Burns, H.V. Volden, J. Chem. Soc. Chem. Commun. (1987) 768.
[161] M. Kaupp, P.v.R. Schleyer, M. Dolg, H. Stoll, J. Am. Chem. Soc. 114 (1992) 8202.
[162] M. Kaupp, P.v.R. Schleyer, M. Dolg, H. Stoll, Chem. Abstr. 123 (1995) 143950d.
[163] Private Communication with Prof. A. Salzer.
[164] Handbook of Chemistry and Physics, CRC Press, Florida, 1980, p. B-21.
[165] Personal Communication with the Editorial Board of Angewandte Chemie.
[166] M.J. Frisch, G.W. Trucks, H.B. Schlegel et al., *GAUSSIAN 94*, Revision C.3. Gaussian, Pittsburgh, Pennsylvania, USA, 1995.
[167] A.L. Spek, The EUCLID package, Computational Crystallography, D. Sayre (Ed.), Clarendon Press, Oxford, 1982.