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Beryllocene and related slip-sandwich structures

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Abstract

The structures of main group metal cyclopentadienyl complexes range from centrally bonded ferrocene analogues to peripherally bonded cyclopentadiene analogues. It is proposed that the wide variety of structures arises from two opposing forces. One is the delocalisation energy of the cyclopentadienyl ligand which favours central bonding. The other is the metal–carbon σ-bond energy which favours peripheral bonding. Unusual structures such as the slip-sandwich geometry of beryllocene result when neither of these forces is dominant. This continuum model rationalises the available structural data and provides an explanation for some of the spectroscopic features of main group metal cyclopentadienyl compounds.

Introduction

In transition metal compounds the cyclopentadienyl group (Cp) has two main structural roles. In some compounds the Cp group can be considered to act as a two-electron donor, to form a single localised covalent bond between one carbon atom (C(5)) and the metal atom. The bonding is analogous to that in corresponding metal alkyl derivatives and the Cp group has a structure similar to that of cyclopentadiene. This is described as monohapto (η^1) or peripheral [1] coordination (Fig. 1(a)). Alternatively, the ring can act as a six electron donor with strong π-bonding interactions with the metal atom, as in ferrocene and numerous other transition metal Cp derivatives. This is described as pentahapto (η^5) or central coordination (Fig. 1(b). These two structural roles suffice to describe the structures of most transition metal cyclopentadienyl compounds.

Among the main group elements, however, there are some unusual structures which do not fit into this simple classification scheme. The variety of structures of the main group metal cyclopentadienyl compounds is the consequence of the polarity of the metal–carbon bond. The structures depend on the electronegativity of the metal in the compound, the presence or absence of metal orbitals suitable for π bonding with the Cp ring, and on the number of coordination positions available for bonding with the cyclopentadienyl group.

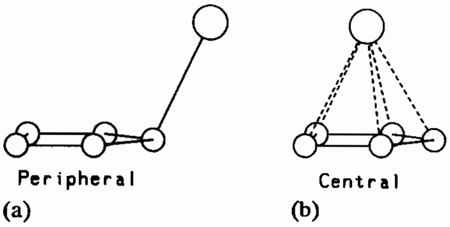

Fig. 1. The two main structural roles of the Cp group: (a) peripheral or η^1; (b) central or η^5.

Some of the compounds for which the structures are known could be described as trihapto. In cases where only one metal orbital is available for bonding with the ring, however, there are no essential features of the bonding in these compounds which differ from the bonding in monohapto compounds in anything other than degree. Hence the term peripheral can be used to encompass both mono- and trihapto types of structures.

Structure of bis(cyclopentadienyl)beryllium

One of the examples of unusual modes of coordination of the Cp group to metal atoms is the structure of bis(cyclopentadienyl)beryllium, $BeCp_2$. Several possible structures for bis(cyclopentadienyl)beryllium have been proposed. The compound is polar in solution [2], which rules out the possibility of a symmetrical sandwich structure, Fig. 2(a), similar to that of its heavier homologue, magnesocene [3, 4], or the more familiar ferrocene.

Half-sandwich compounds of beryllium, however, are well known [5–10]. These have the beryllium atom symmetrically coordinated to one Cp ring, which donates six electrons. The eight electron shell is completed by bonding to a two-electron σ donor such as chloride or the methyl group. The proposed σ–π structure for

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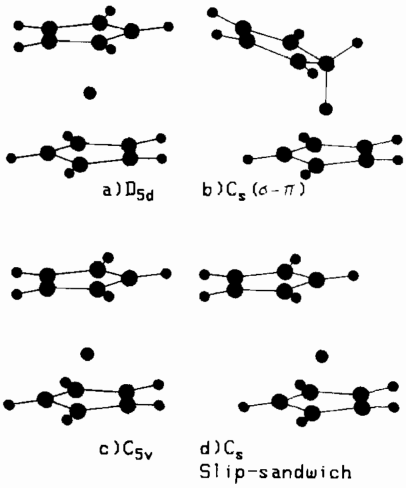

Fig. 2. Proposed structures for biscyclopentadienylberyllium.

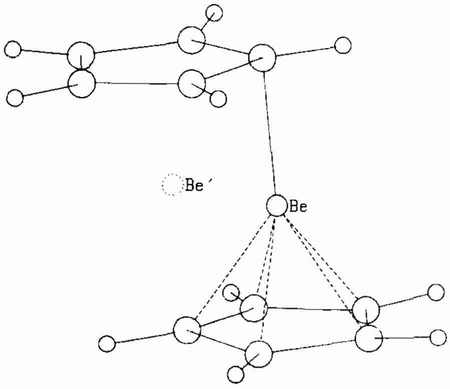

Fig. 3. The structure of biscyclopentadienylberyllium determined by X-ray diffraction.

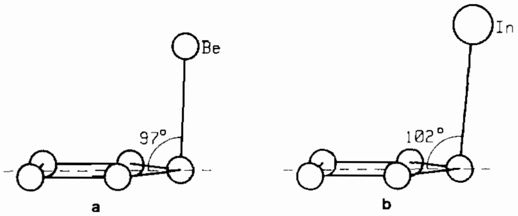

Fig. 4. Peripherally bonded cyclopentadienyl groups in $BeCp_2$ (a) and $InCp_3$ (b).

$BeCp_2$, Fig. 2(b), is similar to these compounds, with the monohapto cyclopentadienyl ring fulfilling the role of the chloride or methyl group. This structure satisfies the requirement of a strict eight valence electron shell for beryllium, and has been observed by NMR for the isoelectronic bis(pentamethylcyclopentadienyl)boron cation [11]. A number of theoretical studies have suggested that this is the minimum energy structure for the compound [12–15].

Two other structures have been proposed from experimental evidence. The unsymmetrical sandwich structure, Fig. 2(c), was used to fit gas phase electron diffraction data in the first reported structural study of this compound [16]. The slip-sandwich structure, Fig. 2(d), was then observed by low temperature X-ray diffraction [17–19]. A subsequent gas phase electron diffraction study indicated that the slip-sandwich structure is also consistent with the electron diffraction data [20].

The vibrational spectra of the compound show little difference among the solid, liquid and solution states [21, 22], which indicates that the solid state structure persists in all phases.

The unusual slip-sandwich structure type was first observed for bis(cyclopentadienyl)beryllium. The two rings in $BeCp_2$ are parallel and crystallographically indistinguishable due to disorder of the beryllium atom between the two sites Be and Be′, shown in Fig. 3. The two sites are separated by 1.303 Å. The beryllium atom is above the centre of one ring, and almost directly below one carbon atom, C(5), of the other ring.

The accuracy of the determination of the carbon–carbon bond lengths in the more recent low temperature structure determination [19] is sufficient that some conclusions may be drawn about the bonding in the ring. The structure of the peripherally bonded ring in the absence of disorder may be estimated by assuming that the observed bond lengths are the average of those for the two rings and that the centrally bonded ring has equal C–C bond lengths of 1.41 Å. The C–C bond lengths calculated for the peripherally bonded ring show the pattern long, short, medium, which is the same pattern as observed in cyclopentadiene. In cyclopentadiene [24], the long bond length of 1.51 Å corresponds to a C–C single bond, and the short distance of 1.34 Å to a C–C double bond. In $BeCp_2$, the estimated long distance of 1.44 Å is significantly less than the full C–C single bond length, while the short bond length of 1.38 Å is longer than a C–C double bond. In the fully delocalised cyclopentadienyl group in magnesocene the C–C bond lengths are about 1.40 Å [3]. Thus, in bis(cyclopentadienyl)beryllium, the electronic structure of the peripheral ring is somewhat localised towards the cyclopentadiene structure, but not to the extent of alternating single and double bonds.

Peripherally bonded structures in $BeCp_2$ and related compounds

The most striking feature of the structure of bis(cyclopentadienyl)beryllium is that, although the rings are parallel, as in ferrocene, they are offset relative to each other with a 'slip' of 1.2 Å. This results in an unusual geometry about carbon atom C(5), as shown in Fig. 4(a). Carbon (5) is nearly coplanar with the neighbouring carbon atoms, C(1) and C(4), and the attached hydrogen atom, H(5). It has a trigonal pyramidal geometry with the beryllium, rather than the tetrahedral geometry expected for monohapto coordination. The Be–C bond makes an angle of 97° with the ring plane. If the geometry about this carbon atom were tetrahedral, the angle would be 125°. There is no evidence of any dynamic disorder at H(5), which might be expected if H(5) were significantly out of the plane of the peripherally bonded ring.

The gas phase structure of bis(pentamethylcyclopentadienyl)zinc recently determined by electron diffraction [23] is extraordinarily similar to that of $BeCp_2$. In this slip-sandwich structure the angle between the ring plane and the C(5)–Zn bond is 96°.

Examination of the published structures shows that most peripherally bonded main group cyclopentadienyl compounds display deviations from tetrahedral geometry at C(5) (Table 1). In cyclopentadiene this angle is 127°, but it is significantly less even in the σ-bonded silyl and germyl compounds. In none of the compounds listed can metal–ring π bonding contribute significantly to the resultant structure. Thus, for a single metal to ring σ interaction, this angle varies between 127 and 69°. The diminution of the angle might be ascribed to intermolecular forces in the crystal, but in the case of $BeCp_2$, there are no unusually close approaches between molecules in the crystal. Also, in the gas phase, H_3SiCp [32], H_3GeCp [30], $Zn(C_5Me_5)_2$ [23], and (possibly) $BeCp_2$ [20] have structures in which the angle is significantly below 125°. Therefore this appears to be a real property of the isolated molecules, and not due to crystal packing forces alone.

The ordering of the compounds by angle suggests that this angle is determined by the polarity of the metal–carbon bond. The effect of an increase in the electropositive character of the metal is to increase the ionic character of the bond and to decrease the angle.

The metal to C(5) bond lengths are also listed. These are compared with M–C bond lengths for methyl or phenyl carbon atoms in the same or related compounds. The comparison is expressed as the percentage increase of the metal–Cp distance compared with the metal–methyl distance. For example, in the half-sandwich compound methyl(cyclopentadienyl)beryllium, the Be–C(methyl) distance is 1.706 Å [10]. In $BeCp_2$, the corresponding Be–C distance is 1.826 Å, which is about 7% longer. Similarly, the In–C distance of 2.24 Å in $InCp_3$ is 7% longer than the In–C distances in trimethylindium, at 2.09 Å [41]. The errors involved in these comparisons are large, but there is a possible correlation between a longer metal–carbon bond and a smaller angle between the bond and the ring plane.

Bonding hypothesis

The large variety of observed M–C(5)–ring angles implies that the two structural roles described above, monohapto and pentahapto, are limiting structures for main group cyclopentadienyl compounds, with a continuous range of possible structures in between (Fig. 5). For structures at different positions along the curve from monohapto (A in Fig. 5) to pentahapto (C) there are a number of changes in bonding. The metal–carbon bond becomes longer and weaker, and the ionic character of the interaction increases. The increased delocalisation of the cyclopentadienyl ring causes the C–C bonds to approach equal lengths, and the geometry

TABLE 1. The angle between the M–C bond–ring plane and the M–C bond length for a number of peripherally bonded main group cyclopentadienyl compounds

Metal	Compound	Angle (°)	M–C distance (Å)	Elongation (%)	Reference
H	HCp	127	1.10	0	24, 28
Zn	$Zn(C_5H_4SiMe_3)_2$	127	2.07	9	23, 29
Ge	H_3GeCp	120	1.97	1	30, 31
Si	$Zn(C_5H_4SiMe_3)_2$	120	1.88	1	23, 33
Si	H_3SiCp (g)	117	1.88	1	32, 33
Ge	H_3GeCp (g)	116	1.97	1	30, 31
Hg	$[Me_2SC_5H_4HgI_2]_2$	115	2.20	5	34, 35
Sn	$SnCp_4$	115	2.27	6	37, 38
Pb	Ph_3PbCp	112	2.30	4	39
Hg	$[Ph_3PC_5H_4HgI_2]_2$	107	2.29	10	36, 35
Ga	$[GaCp_2(OEt)]_2$	106			27
In	$InCp_3$	102	2.24	7	25, 40
Ga	$GaCp_3$	101	2.05	4	26, 41
Be	$BeCp_2$	97	1.83	7	20, 10
Zn	$Zn(C_5Me_5)_2$	96	2.04	7	23, 29
Al	$[Al(Cl)(Me)C_5Me_5]_2$	69	2.10	9	42, 43

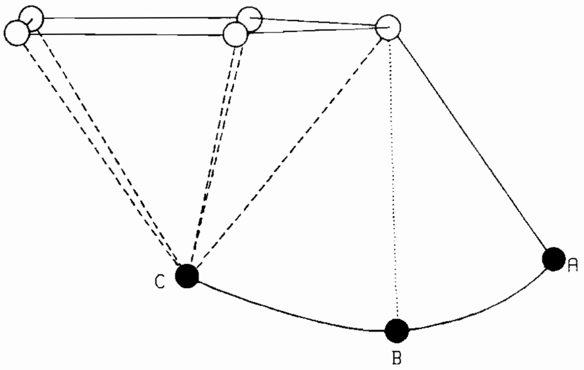

Fig. 5. The range of structures from monohapto (A) to pentahapto (B).

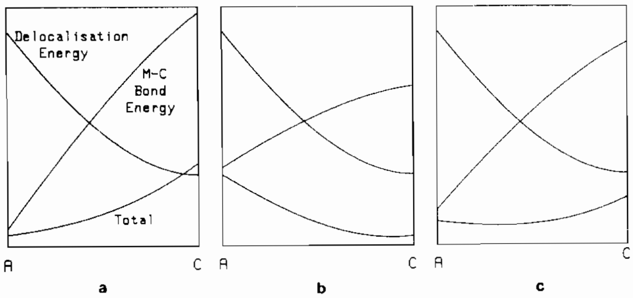

Fig. 6. An illustration of the division of the total energy of an MCp system into delocalisation and M–C bond energies for the cases of strong (a), weak (b) and intermediate (c) M–C bond strengths.

around C(5) changes from tetrahedral to trigonal. The C(5)–H(5) bond therefore moves into the plane of the ring and becomes stronger. The observed structure of the peripheral ring in bis(cyclopentadienyl)beryllium is indicated at position B in Fig. 5.

The energy of the M–Cp interaction may be considered in two parts. One part is the contribution of the metal–carbon bond to the stability of the compound. The other part is the delocalisation energy of the ring π system. The overall energy of the molecule in any conformation depends on the values of both of these components. The delocalisation energy is a minimum at position C, where the ring is fully delocalised. (The delocalisation energy for any fixed geometry is taken to be independent of the metal ion.) The metal–carbon bond is strongest for a structure at position A. The contribution of this bond to the stability of the system decreases as the position of the metal relative to the ring changes from A to C.

For an element which forms a strong bond to carbon, for example, silicon, the difference in M–C bond energy between A, where there is a strong localised M–C bond, and C, where the interaction is predominantly ionic, is large compared with the difference in delocalisation energy between these two structures. The total energy will show a minimum close to A (Fig. 6(a)). If the M–C bond heterolysis energy is small, as for the magnesium–carbon bond, the difference in the bond energy between A and C is small compared with the delocalisation energy. The contribution of the delocalisation energy dominates and the minimum in the total energy curve occurs at C (Fig. 6(b)). This results in a rather ionic centrally bonded derivative. For intermediate values of the bond heterolysis energy, e.g. for beryllium–, gallium– or indium–carbon bonds, neither contribution to the total energy dominates. The position of the minimum on the total energy curve depends on the particular shapes and magnitudes of the delocalisation energy and bond energy curves (Fig. 6(c).

The bond energy curve contains all of the contributions to the energy of the system which depend on M. This changes with the metal atom, and also with the other groups which are bonded to the metal atom. The vibrational spectra of cyclopentadienyldimethylaluminium, Me_2AlCp, and its diethyl etherate, $Me_2AlCp \cdot OEt_2$ [44], provide an example of the effect of a change in the environment of the metal atom. Aluminium is generally four coordinate in organometallic compounds. The unsolvated Me_2AlCp molecule has two available coordination positions at Al to be filled by the Cp group, which results in a form of peripherally bonded structure which has not yet been properly characterised. The etherate has one coordination position at Al available for bonding to the Cp group and might also have been expected to have a peripheral structure. The Raman spectrum shows, however, that the coordination of the Cp group is actually central. This is a clear example of the situation indicated by Fig. 6(b), where a group which does not π bond to the Cp ring has an ionic centrally coordinated structure. The difference in the structures can be interpreted as the result of the increase in electron density at the Al atom in the etherate, which strongly stabilises the cation in the ionic form (at C in Fig. 6(b)). This increase in electron density at Al reduces the tendency of the Al atom to attract electron density from the Cp group, i.e. the electronegativity of the Al atom is lower in this environment.

The shape and magnitude of the delocalisation energy curve is altered when the cyclopentadienyl group is substituted. Hückel theory calculations show that the stability due to π-electron delocalisation of the anions of indene and fluorene relative to the localised parent hydrocarbon is less than for cyclopentadiene. The acid dissociation constants reflect this difference. Cyclopentadiene is reasonably acidic, with a pK_a of 15. The pK_a of indene is 18.5, and that of fluorene 22.9 [45]. The difference in delocalisation energy between points A and C is therefore less for these groups than for the Cp group. This decrease in the contribution of the delocalisation energy causes the minimum in the total energy curve to shift towards A. The metal–carbon bond is predicted to be more localised in indenyl compounds than in the corresponding cyclopentadienyl compounds, and even more localised in the fluorenyl derivatives. For a given fragment M, therefore, the M–C bond should be at a greater angle relative to the ring plane in the fluorenyl compound than in the indenyl compound, and both should have a greater angle than the cyclopentadienyl compound.

Very few structures of peripherally bonded indenyl or fluorenyl derivatives of main group elements have been reported. In each example listed in Table 2 the angle is greater than in the cyclopentadienyl compound, although the differences are not necessarily significant. A further example is provided by the solid state structures of the magnesium compounds, where $MgCp_2$ has a symmetrical sandwich structure while $Mg(indenyl)_2$ has a complex bridged structure with more localised Mg–C interactions [49]. Thus the limited available information is compatible with the hypothesis that bonding in these systems is more localised than in the corresponding cyclopentadienyl compound.

Inductive substituent effects are expected to be similar, with electron withdrawing substituents stabilising the Cp anion, and thus increasing the tendency towards central bonding. More acidic substituted cyclopentadienes, though, have substituents with alternative bonding sites, e.g. –COR or –CN. Less acidic substituted cyclopentadienes, e.g. C_5Me_5H, should form compounds with more M–C bond localisation than in the unsubstituted cyclopentadiene analogue. Two zinc compounds show such a substituent effect [23]. The permethylated compound $Zn(C_5Me_5)_2$ has a slip-sandwich structure analogous to that of $BeCp_2$ (Fig. 2(d)), while $Zn(C_5H_4SiMe_3)_2$ has a σ–π structure similar to Fig. 2(b). This is the result expected if the silyl group has a strongly electron donating inductive effect, thus destabilising the anion form of the substituted cyclopentadienyl. A more localised form of metal–cyclopentadienyl bonding for the silyl compound compared with the methyl compound results in a much greater angle of the Zn–C bond to ring plane (Table 1).

Vibrational spectra

Vibrational spectroscopy can be used to distinguish between centrally and peripherally coordinated Cp rings. In the IR spectrum of a centrally bonded cyclopentadienyl ring there are only two allowed C–H stretching bands due to the high (C_{5v}) symmetry of the ring. Peripherally bonded rings have a much lower symmetry (C_s), and all of the C–H stretching frequencies are different, and all are allowed in the IR spectrum. Thus the complexity of the C–H stretching region of the IR spectrum allows the ring to be assigned as either centrally or peripherally coordinated. This method was used to assign a peripherally bonded structure to the cyclopentadienyl derivatives of mercury [50].

The localised cyclopentadienyl ring differs from the aromatic delocalised Cp group by possession of two carbon–carbon double bonds and an aliphatic sp^3 C–H bond. The double bonds have a stretching frequency at about 1600 cm^{-1}, and therefore should be easily identified. The C–H stretching vibrations for the vinyl C–H groups are observed around 3100 cm^{-1}, and the stretching frequency of the methylene C–H should be observed around 2900 cm^{-1}. A peripherally bonded ring should therefore be further identified by the presence of bands in the vibrational spectra at about 1600 and 2900 cm^{-1}. Inspection of the C–H stretching region for a number of compounds shows that the lowest energy C–H stretch is observed around 2900 cm^{-1} only for M=H [51, 52]. As H is replaced by less electronegative metals, the amount of delocalisation of the ring increases, as indicated by the value of the angle between the ring plane and the M–C bond. The frequency of the lowest energy C–H stretching band changes to 2932 cm^{-1} for Ge [53], to 2970 cm^{-1} for Sn [54] and Hg [50], and to 3013 cm^{-1} in

TABLE 2. Comparison of the M–C bond/ring plane angle for cyclopentadienyl and substituted cyclopentadienyl systems

Metal	Derivative	Angle (°)	Compound	Reference
Si	cyclopentadienyl	117	H_3SiCp	32
	fluorenyl	126–127	$Ph_2ClSi(Fluor)$ $(Me_3Si)_3Si(Fluor)$	46
Ge	cyclopentadienyl	120	H_3GeCp	30
	indenyl	122	$Ge(Ind)_4$	47
Sn	cyclopentadienyl	115	$SnCp_4$	36
	indenyl	117	$Sn(Ind)_4$	47
	fluorenyl	115	$Me_3Sn(Fluor)$	48

bis(cyclopentadienyl)beryllium [22]. The frequency of the lowest energy band in ionic centrally bonded cyclopentadienyl compounds, however, can be as low as 3027 cm^{-1} [55]. The presence or absence of an aliphatic sp^3 C–H stretching band obviously cannot be used as a diagnostic tool to decide between central and peripheral structures. The frequency does indicate the degree of delocalisation within the ring in compounds which are known to contain the peripherally bonded M–Cp group.

Bis(cyclopentadienyl)beryllium also lacks any bands in the 1500–1600 cm^{-1} region which can be assigned as carbon–carbon double bond stretching vibrations. The structure of the compound shows, though, that although the one ring is peripherally bonded, there are no full double bonds in the ring, and the hydrogen atom, H(5), is almost coplanar with the ring; the C–H bond therefore resembles those of centrally bonded derivatives.

Fluxional behavior

Peripherally bonded cyclopentadienyl rings are generally fluxional. That is, at some accessible temperature, the metal atom migrates around the ring at such a rate that all of the ring protons are equivalent in the NMR spectrum. If this process is fast at room temperature, only one signal is seen in the proton NMR spectrum. The spectrum therefore resembles that of a centrally bonded derivative where all of the protons are structurally equivalent. The fluxional motion may be slowed by lowering the temperature and in some cases the line broadens, then at still lower temperatures may split into the expected spectrum for a peripherally bonded ring. The rate of metallotropic rearrangement may be represented by the temperature at which this static spectrum is observed. This rate of motion is correlated with the degree of delocalisation of the ring, as represented by the angle defined earlier. For compounds where this angle is small (less than about 115°) the fluxional motion is sufficiently fast that even at temperatures of -80 °C (-135 °C for $BeCp_2$ [56]) the proton NMR signal is still a single sharp line.

The rearrangement can proceed by a series of 1,2 shifts in which the metal atom moves from one carbon atom to a neighbouring carbon atom. In a fully localised ring the π framework of the ring must rearrange, with double bonds becoming single bonds and vice versa. The difference in these bond lengths means that a 1,2 shift must be accompanied by a significant change in the structure of the ring. There must also be a change in the positions of the two hydrogen atoms on the carbon atoms involved, and movement of the position of the metal atom relative to the ring. These rearrangements contribute to the activation energy for this tautomerism. In a more delocalised compound the difference in structure between these two tautomers is much less, resulting in a lower activation energy and more rapid fluxional motion.

Main group metal cyclopentadienyl structures

The variety of structures observed for main group metal cyclopentadienyl compounds is summarised in Table 3. Four structural types have been observed. These are central, vinylic, peripheral and peripheral bridging structures. The occurrence of any of these types in a given compound can be rationalised in terms of the polarity of the M–C bond and the number of coordination positions on the metal atom available for bonding with the cyclopentadienyl ring.

Central bonding (η^5)

Central bonding of the metal atom to the cyclopentadienyl ring is expected for the electropositive metals of the alkali and alkaline earth series (excepting beryllium), where the low metal–carbon bond strength does not counteract the decrease in delocalisation energy in forming a peripherally bonded derivative. Central bonding is also expected when two π bonds can be formed between metal p or d orbitals and the degenerate *e* set of π orbitals of the cyclopentadienyl group (for example, in the compounds CpBeX and Cp^*BX^+), and in complexes where coordination of additional ligands leads to a reduction in the effective charge on the metal atom.

Centrally bonded structures are thus found in the more ionic cyclopentadienyls such as $Li[(CH_3)_3SiC_5H_4]\cdot$TMEDA [57], NaCp·TMEDA [58] and $MgCp_2$ [3, 4]. In solid $CaCp_2$ [59], central/central and central/peripheral bridging rings are observed. Central bonding also occurs in the compounds CpBeX [5–10, 17–19], where π bonding appears to be a major factor, with Cp^- taking three coordination positions.

Lower valent In [60, 61], Tl [61, 62], Si [63], Ge [64, 65], Sn [65–67] and Pb [67–69] also form centrally bonded cyclopentadienyl compounds. These are the only characterised organometallic compounds of these elements in the I or II oxidation states. The bis(pentamethyl)cyclopentadienyl cations of arsenic(III) and antimony(III), which are isoelectronic with the germanium(II) and tin(II) compounds, have also been prepared [70]. The structure of the arsenic compound is reported to be similar to the Group 14 metallocene structures, although with some distortion from a perfect di-pentahapto structure. The In, Tl and Pb compounds are polymeric with central/central bridging rings in the solid state.

TABLE 3. The distribution of types of metal cyclopentadienyl structures among the main group elements in their highest group oxidation state. There is a general trend towards peripheral, then vinyl structures towards the upper right hand corner

H peripheral HCp [24]				
Li central $LiC_5H_4SiMe_3$ TMEDA [57]	Be central CpBeCl [8] peripheral $BeCp_2$ [19]		B vinylic [71]	C vinylic [71]
Na central NaCp.TMEDA [58]	Mg central $MgCp_2$ [3]		Al central $Me_2AlCp.OEt_2$ [44] peripheral $[MeAl(C_5Me_5)Cl]_2$ [42] bridging Me_2AlCp [72]	Si vinylic Me_3SiCp [71] peripheral H_3SiCp [32]
K central KCp [50]	Ca central $CaCp_2$ [59]	Zn central CpZnMe(g) [29] peripheral $Zn(C_5Me_5)_2$ [23] bridging $ZnCp_2$ [73]	Ga peripheral $GaCp_3$ [26] bridging Me_2GaCp [41]	Ge vinylic Me_3GeCp [71] peripheral H_3GeCp [30]
Rb central RbCp [50]	Sr central $SrCp_2$ [50]	Cd	In peripheral $InCp_3$ bridging $InCp_3$ [25]	Sn peripheral $SnCp_4$ [37]
Cs central CsCp [50]	Ba central $BaCp_2$ [50]	Hg peripheral $HgCp_2$ [57]	Tl	Pb peripheral Ph_3PbCp [39]

Vinylic bonding

Vinylic structures are common for elements which bond strongly to carbon and which have electronegativities similar to or greater than that of hydrogen. The least electronegative substituent may be expected to be bonded to C(5) as this carbon atom can best accommodate a negative charge. The characterisation of these vinylic metal cyclopentadienyl compounds by NMR is discussed in ref. 71. For example, methylcyclopentadiene exists as a mixture of three isomers and boron cyclopentadienyls exist as mixtures of the two vinylic isomers. Vinylic/methylene (peripheral) equilibria are also observed for Si and Ge.

Peripheral bonding

Peripheral bonding is expected in compounds of less electropositive metals where there is only one coordination site available for bonding with the Cp group. Within this large class the reported structures vary among compounds with a consistent pattern as described above. As the angle between the metal–C(5) bond and the ring plane decreases for the more electropositive metals, the difference between the C–C bond lengths in the ring decreases. This indicates that the ring is becoming more delocalised. In none of these structures, however, do the C–C bond lengths suggest an allylic mode of bonding between the metal and ring.

The peripheral metal–cyclopentadienyl unit which results from a single M–C σ interaction can occur in structures which appear unrelated. The structure of tris(cyclopentadienyl)indium [25], for example, is naturally very different from that of bis(cyclopentadienyl)beryllium. Each indium atom is coordinated by four carbon atoms with two terminal and two bridging cyclopentadienyl groups. The two terminal rings are peripherally bonded to the indium atom and have the structure shown in Fig. 4(b). The angle between the In–C bond and the ring plane in this case is 102°, which is close to that of 97° found in the beryllium compound. Other compounds which have similar terminal peripherally bonded Cp rings are $GaCp_3$ (101°) [26] and $[GaCp_2(\mu\text{-}OEt)]_2$ (106°) [27].

Peripheral bridge bonding

In contrast with peripheral bonding, in which the C–C bond lengths of the Cp ring vary as in cyclopentadiene, in peripheral bridged structures (Fig. 7) the C–C bond lengths suggest that the cyclopentadienyl ring has allylic character. These are best characterised for the Group IIIB compounds Me_2AlCp [72], Me_2GaCp [41] and $InCp_3$ [25] (which has both terminal and bridging rings). An interesting compound of zinc, $Cp_3Zn_2N(SiMe_3)_2$ [74], is a dimer with a peripherally bridging cyclopentadienyl group, with both zinc atoms on the same side of the ring, while solid MeZnCp [75] and $ZnCp_2$ [73] have polymeric structures with the type of bridging rings shown in Fig. 7. Peripheral bridging cyclopentadienyl rings may be expected to be present in the solid state in compounds (particularly of Group IIIB metals) where the group bonded to the cyclopentadienyl ring has two vacant coordination sites, and no bridging group which will be preferred over the cyclopentadienyl group, in contrast to the bridging chlorine atom in $[Al(\mu\text{-}Cl)(R)C_5Me_5]_2$ [41]. In the gas phase compounds of the type R_2AlCp are monomeric, but electron diffraction data could not be unambiguously interpreted for the compound where R = methyl [55].

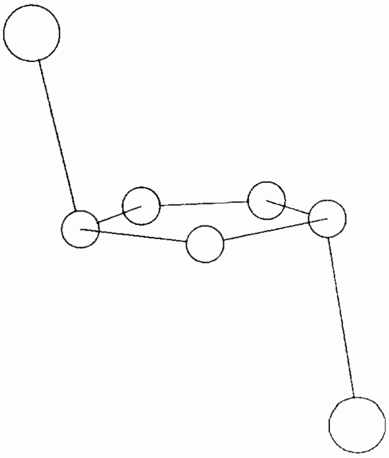

Fig. 7. The structure of a peripherally bridging Cp group.

Conclusions

The structural types of main group cyclopentadienyl compounds, R_nMCp, depend on the presence of suitable bonding orbitals on the R_nM group, on the available coordination sites and on the electronegativity of the coordinated metal atom. For the organometallic compounds of Groups III and IV the coordination number of the metal is generally four. Neutral compounds of the types R_2MCp and R_3MCp thus have two and one coordination positions, respectively, available for bonding to the Cp group, with the result that peripheral bridging is common for Group III, and only peripheral and vinylic bonding are known for group IV metals.

In the case where only a single bond can be formed between the metal atom and the cyclopentadienyl group, the M–Cp group may have a structure ranging between an ionic centrally bonded derivative and a fully localised cyclopentadiene-like structure. Generally the structure is intermediate between these two extremes. The partial negative charge on the ring is reflected in an increase in delocalisation of the π system of the ring due to hyperconjugation of the M–C bond with the ring π system. The partial delocalisation affects the structure of the M–Cp group. The most pronounced effect is the change in the geometry at C(5). Differences in M–C and C–C bond lengths compared with fully localised systems are expected and have been observed in some systems. The existence of this delocalisation can explain some of the more puzzling properties of these compounds, including the extremely fast metallotropic rearrangement in some compounds and the lack of such normal diagnostic features as carbon–carbon double bond stretching and methylene C–H stretching frequencies in the vibrational spectra.

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