

# p-Block metallocenes: the other side of the coin

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Although transition metal metallocenes (such as ferrocene,  $[(C_5H_5)_2Fe]$ ) have been a cornerstone in the development of modern organometallic chemistry and continue to be a focus for chemical and structural studies, in comparison the chemistry of the main group metal counterparts has remained relatively undeveloped. The recent resurgence of interest in p-block (Groups 13–15) metallocenes in particular has given fresh insights into the structural preferences, bonding requirements and reactivity of these under-publicised species, which in many ways represent ‘the other side of the coin’. The more varied (ionic and covalent) character of the metal–ligand bonds and the less restricted electronic requirements of p-block metals leads to greater structural diversity and radically different reactivity than is found for the transition metal relatives. This short review focuses on the remarkable range of p-block complexes that has so far been uncovered and attempts to unravel some of the electronic and structural trends in these species.

## 1 A difference in understanding

Since they were first synthesised in the mid to late 1950s transition metal metallocenes, containing cyclopentadienide and related ligands ( $C_5H_5^-$ , Cp)  $\pi$ -bonded to the metals, have played a central role in the development of modern organometallic chemistry.<sup>1,2</sup> The predominantly covalent metal–ligand

bonding in these species can be explained in simple terms as resulting from the high electronegativity of transition metals. However, more detailed examination shows that the metal–ligand interactions in these species involve a complicated covalent bonding situation resulting from a combination of donation of electron density from the ligand to the metal and ‘back-donation’ from the metal to the ligand. This bonding pattern is qualitatively similar to that occurring in transition metal carbonyl compounds, such as  $[Fe(CO)_5]$ , and is dependent on the key involvement of the metal d orbitals. The importance of covalency in these species and of the involvement of the metal d orbitals is stressed by the rigid electronic requirements of simple metallocenes such as ferrocene  $[Cp_2Fe]$  (Fig. 1) in which a total of eighteen electrons (5e from each Cp ligand, 8e from Fe) corresponds to the filling of the nine bonding molecular orbitals available and promotes greatest electronic stability (the so-called ‘18 electron rule’). The chemistry of transition metal metallocenes is a mature area in which the reactivity and bonding is well-understood.<sup>1,2</sup>

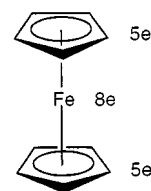


Fig. 1 Structure of Ferrocene

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Dominic S. Wright

Although main group metallocenes have been known for as long as their transition metal counterparts, studies to date have largely focused on the structures adopted by the neutral species in the solid state and comparatively few investigations have focused on the chemistry of these compounds in their own right.<sup>3</sup> In contrast to the transition metal compounds, only limited theoretical studies have so far been undertaken on the main group species. The more varied (generally more ionic) character of the metal–ligand bonding and the minimal involvement of higher energy metal d orbitals leads to less restricted electronic demands of the metals and to greater structural diversity than is found in the transition metal counterparts.<sup>3</sup> These bonding characteristics have made general structural trends difficult to discern and in many cases reduce ideas of electron counting to little more than formalisms. In particular, where ionic bonding is dominant, such as in metallocenes formed by the majority of s-block elements (Group 1, Li–Cs; Group 2, Mg–Ba), the relationship between hapticity of the cyclopentadienide ligand and the number of electrons supplied to the metal [e.g.  $\eta^3\text{-Cp}$  (3e),  $\eta^5\text{-Cp}$  (5e) (Fig. 2)] should not always be taken literally. Rather, in main group metallocenes the coordination of  $\pi$ -bonded Cp ligands is electronically flexible and generally weak.

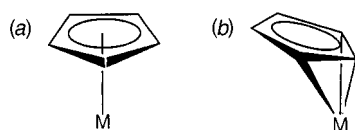


Fig. 2 Bonding of Cp to a metal (M) in (a)  $\eta^5$ -mode, and (b) an  $\eta^3$ -mode

As a consequence of the contraction in atomic radii across the d-block, the p-block metals which follow have similar electronegativities to transition metals and there is, as a result, a significantly higher percentage of covalent character in the metal–Cp bonding than is present in s-block metallocenes. This greater covalency has a profound impact on the structural and bonding patterns adopted. The character of p-block metallocenes (Group 13, Al–Tl; Group Ge–Pb; Group 15, As–Bi) can in many ways be seen to combine the distinctive structural features found in the s-block with those typical of d-block compounds.

This review focuses on the major structural classes of p-block metallocenes, on the nature of the bonding in these species and on the ways by which structural and chemical modification can be achieved. The principal aims are to highlight the fundamental characteristics of these species and to make some sense of the diverse range of structures observed.

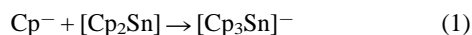
## 2 Reactivity patterns

Metallocenes of p-block elements exhibit very different reactivity to the transition metal analogues.<sup>3</sup> In contrast to the transition metal metallocenes, both the Cp ligands and the metal centres in main group complexes prove to be highly reactive and ligand exchange reactions and reactions involving a change in the oxidation state of the metal centres are particularly characteristic. The most marked difference with transition metal metallocenes is the far greater lability of the Cp rings, resulting from weaker metal–ligand interactions and the greater polarity of the metal–Cp bond.

### 2.1 Reactions at the metals

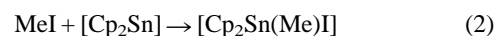
#### 2.1.1 Nucleophilic addition reactions

These can occur where weak nucleophiles are added to p-block metallocenes.<sup>4</sup> An example of this type is the reaction of  $\text{Cp}_2\text{Mg}$  with stannocene ( $\text{Cp}_2\text{Sn}$ ), resulting in the coordination of the  $\text{Cp}^-$  anion to the  $\text{Sn}^{\text{II}}$  centre [eqn. (1)]. This reaction is discussed in detail in section 3.2.

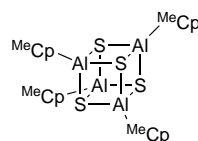


#### 2.1.2 Oxidative addition reactions

These are common in transition metal complexes of various types, particularly within catalytic cycles.<sup>2</sup> As the name suggests, these reactions involve an increase in the oxidation state and coordination number of the metal. This type of reaction is highly dependent on the relative stabilities of the oxidation states involved. For p-block elements there are two potentially stable oxidation states, corresponding to the use of the valence s and p electrons (the ' $n$  oxidation state') or the use of only the p electrons and with the retention of a non-bonding lone pair (the ' $n - 2$  oxidation state'). Elements at the top of a p-block group prefer the  $n$  oxidation state whereas those at the bottom prefer the  $n - 2$  (commonly known as the 'inert-pair effect'). This situation is largely the result of the increased stabilisation of the s orbitals as one descends the group, the main reason for which is a complex quantum mechanical effect which occurs in atoms with large nuclei (so-called 'relativistic effects').<sup>5</sup> The reaction between  $\text{Cp}_2\text{Sn}$  and  $\text{MeI}$  is an example of oxidative addition, in which the  $\text{Sn}^{\text{II}}$  centre is oxidised to  $\text{Sn}^{\text{IV}}$  with an increase in the coordination number of the metal [eqn. (2)].<sup>6</sup> This outcome can be compared to the same reaction with  $\text{Cp}_2\text{Pb}$  in which the  $\text{Pb}^{\text{II}}$  centre is retained as a result of the greater stability of the lower oxidation state [eqn. (3)].

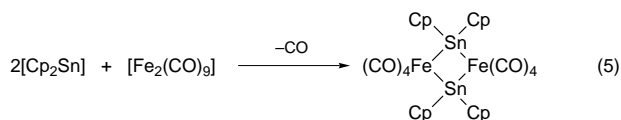


Recently, the metallocenes  $[\text{MeCpGa}]^7$  and  $[\text{MeCpAl}]^8$  ( $\text{MeCp} = \text{C}_5\text{Me}_5$ ) have been prepared. Owing to the much greater stability of the higher +3 oxidation state at the top of Group 13 these species are exceptionally reactive. Oxidative addition reactions with elements such as sulfur, selenium and phosphorus and reactions with transition metal–metal bonds are known,<sup>8</sup> e.g. eqn. (4).



#### 2.1.3 Lewis base characteristics

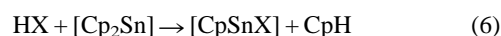
Lewis base characteristics of the metal lone pair in the  $n - 2$  oxidation state metallocenes tend to be limited as a result of the stabilisation of the non-bonding pair of electrons which is buried in the atomic structure of the metals and not particularly accessible. The lone pair can, however, be donated to transition metals, e.g. eqn. (5).



## 2.2 Ligand reactivity

### 2.2.1 Protolytic cleavage

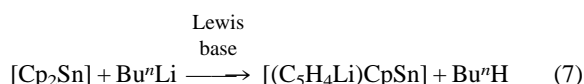
Protolytic cleavage of the Cp–metal bonds in p-block metallocenes results from acid–base reactions with stronger organic and inorganic acids,<sup>9</sup> e.g. eqn. (6).



This characteristic can be associated with the greater ionic character of the  $\text{metal}^{\delta+}\text{-Cp}^{\delta-}$  interactions in p-block metallocenes and is in marked contrast to the greater stability of transition metal–Cp bonding.

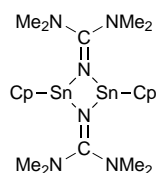
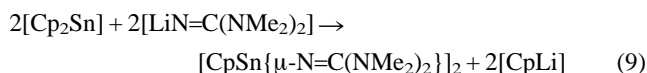
### 2.2.2 C–H Bond activation

C–H bond activation of the Cp ligand can be achieved by reactions with strong bases.<sup>10</sup> This mode of reaction is more common in transition metal metallocenes and can be used to functionalise metal-bonded Cp rings, *e.g.* eqn. (7).



### 2.2.3 Equilibration and nucleophilic substitution reactions

These are particularly common in p-block metallocenes. Equilibration involves facile ligand exchange between two complexes [eqn. (8)].<sup>11</sup> Nucleophilic substitution results from the interaction with stronger nucleophiles [eqn. (9)].<sup>12</sup>



## 3 Structural patterns

### 3.1 'Islands' of electronic stability

In view of the relatively high degree of covalent character of the p-block metallocenes compared to those of the s-block one might expect that, like transition metal complexes, the total number of metal and ligand electrons will become important in the filling of bonding molecular orbitals and that certain electronic configurations may be particularly favoured on the grounds of electronic stability. A further similarity with transition metal complexes is that  $\pi$ -bonding of the Cp ligands only normally occurs where the oxidation state of the p-block element is low. For p-block elements this is the 'lone-pair' oxidation state, involving only the use of p electrons and retention of a non-bonding lone pair. However, unlike transition metals the Cp–metal interactions do not involve d orbitals and adherence to the 18 electron rule should not be expected.<sup>3</sup>

Although formally adhering to the octet rule, the electronic structure of monomeric CpIn (occurring in the gas phase) is best understood by a molecular orbital (MO) description in which the eight electrons (formally 5e from Cp, 3e from In) are accommodated within four molecular orbitals arising from the overlap of the two lowest lying  $\pi$  MOs of the Cp ring [in phase ( $\psi_1$ ) and out of phase ( $\psi_2$ )] with two sp and two p orbitals of In.<sup>3</sup> This arrangement gives three filled bonding MOs and one non-bonding MO, in which the metal lone pair resides (Fig. 3). The unusual 'bent' (or angular) sandwich structure of Cp<sub>2</sub>Sn in the gas phase underlines the importance of the MO treatment in rationalising the behaviour of Group 14 metallocenes.<sup>13</sup> In a linear arrangement, only six bonding MOs result from the combination of the metal s and p orbitals with  $\psi_1$  and  $\psi_2$ , with the lone pair residing in an antibonding MO. The accommodation of all fourteen electrons is achieved by mixing the metal s orbital with the  $p_x$  atomic orbital, lowering the energy of the lone pair (Fig. 4). The tendency towards a more linear ('ferrocene-like') arrangement going from Cp<sub>2</sub>Sn to <sup>Me</sup>Cp<sub>2</sub>Sn and <sup>Ph</sup>Cp<sub>2</sub>Sn (<sup>Ph</sup>Cp = C<sub>5</sub>Ph<sub>5</sub>) is partly accounted for by steric congestion but also results from the higher energy of the lone pair orbitals in <sup>Me</sup>Cp<sub>2</sub>Sn and <sup>Ph</sup>Cp<sub>2</sub>Sn, which are not sufficiently stabilised by s/ $p_x$  orbital mixing to strongly favour the bent arrangement.<sup>3</sup>

Unfortunately, the level of theory for the Group 15 metallocenes (Cp<sub>3</sub>E; E = As–Bi) is not anywhere near as

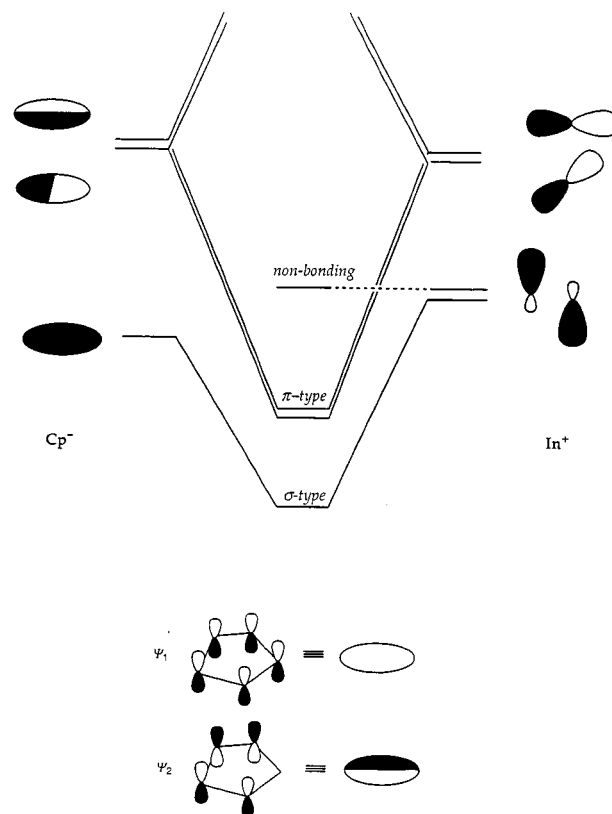


Fig. 3 MO diagram for [CpIn] monomer

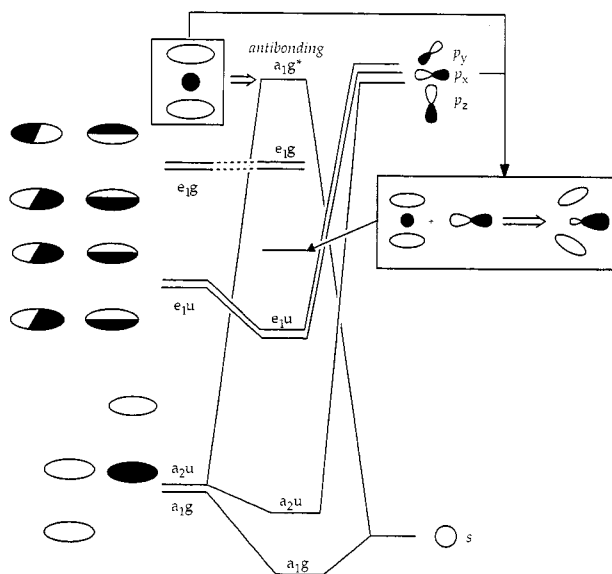


Fig. 4 MO diagram for linear [Cp<sub>2</sub>M] and the effect of  $p_x$ -lone-pair mixing

advanced as for the Group 13 and 14 complexes. However, in the neutral Group 15 complexes the tendency for Cp ligands to  $\pi$ -bond appears to be significantly less than for elements of Groups 13 and 14,<sup>3</sup> possibly as a result of the higher electronegativity of these elements and their consequently lower metallic character. It is noteworthy in this respect that as Group 15 is descended (the elements becoming more metallic) there is an increased ability to  $\pi$ -bond. Spectroscopic studies of Cp<sub>3</sub>As suggest that the Cp rings are  $\sigma$ -bonded (giving an 8e octet), whereas rapid interconversion between an 8e  $\sigma$ -bonded structure and a 20e  $\pi$ -bonded arrangement occurs for Cp<sub>3</sub>Sb in

solution. Two modifications of  $\text{Cp}_3\text{Bi}$ , an 8e  $\sigma$ -structure and a 20e  $\pi$ -structure, have been identified.

From the point of view of understanding the range of metallocenes which can be prepared, it is of value to regard the formal electron counts of the neutral ('parent')  $\pi$ -bonded complexes of Groups 13 [ $\text{CpE}$  (8e)], 14 [ $\text{Cp}_2\text{E}$  (14e)] and 15 [ $\text{Cp}_3\text{E}$  (20e)] as representing 'islands' of electronic stability.<sup>14</sup> A range of mononuclear cationic and anionic  $\pi$  complexes can be derived from the parent metallocenes by the formal addition or removal of  $\text{Cp}^-$  ligands, generating charged complexes which are isoelectronic with a parent complex of a neighbouring Group (8e, 14e or 20e) (Fig. 5). It should be noted that this simple relationship does not define all known metallocene derivatives and other complexes whose formal electron counts do not adhere to this scheme are known (e.g.  $\text{CpSnCl}$ , 10e).

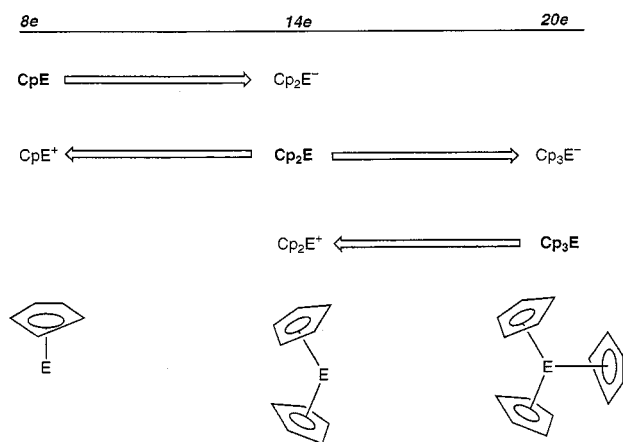


Fig. 5 Isoelectronic relationships of some anionic and cationic metallocenes

### 3.2 Isoelectronic cations and anions

The isoelectronic guidelines depicted in Fig. 5 give various targets for chemical study. In the case of anionic complexes the idea of the addition of  $\text{Cp}^-$  to a parent metallocene is not simply a formalism but works in practice. The reaction of  $\text{Cp}_2\text{Mg}$  with  $\text{CpTi}$  in the presence of the Lewis base donor PMDETA [ $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$ ] produces  $[\text{CpMg}\cdot\text{PMDETA}]^+[\text{Cp}_2\text{Ti}]^-$ ,<sup>14</sup> containing a thalocene anion which is isoelectronic with 14e  $\text{Cp}_2\text{Sn}$  (Fig. 6). Like  $\text{Cp}_2\text{Sn}$ , a bent sandwich arrangement is found in the thalocene anion. However, theoretical investigations of the stability of the bent versus the linear geometry reveal that the energy difference between these conformers is very small. The reason for this is most easily appreciated by the view of the electron density 'surface' of the  $[\text{Cp}_2\text{Ti}]^-$  anion in which an essential spherical lone pair orbital is localised on the Ti atom. Clearly, there is insufficient  $s/p_x$  mixing to make the bent arrangement significantly favoured and the lone pair orbital therefore has largely  $s$  character. This finding has a broader significance to the electronic structures and stabilities of all 14e systems of this type. As one descends a Group in the p-block the valence  $s$  orbital becomes increasingly stabilised with respect to the  $p$  as a result of relativistic effects. This factor is apparent in the electronic structure and arrangement of  $[\text{Cp}_2\text{Ti}]^-$ , since the low energy of the  $s$  orbital makes  $s/p_x$  mixing less favourable. Some hint of the general nature of this observation is given by the more angular arrangement of  $\text{Cp}_2\text{Sn}$  ( $125^\circ$ ) than  $\text{Cp}_2\text{Pb}$  ( $143^\circ$ )<sup>3</sup> in the gas phase and this is confirmed by theoretical calculations of  $\text{Cp}_2\text{E}$  ( $\text{E} = \text{Ge-Pb}$ ) which show that the lone-pair orbital becomes progressively less stable and the difference in energy between the bent and linear conformations becomes almost insignificant as Group 14 is descended.<sup>4</sup>

A further feature of the  $[\text{Cp}_2\text{Ti}]^-$  anion is the asymmetry of the bonding of the two Cp rings, seen in the noticeable constriction of the electron density linking one of these ligands

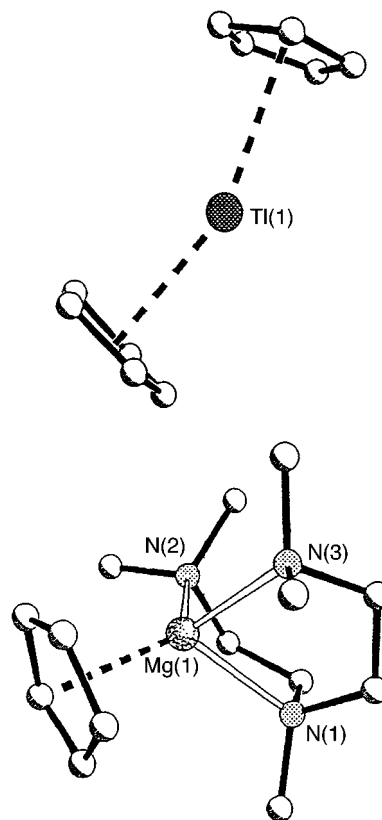


Fig. 6 Structure of  $[\text{CpMg}\cdot\text{PMDETA}]^+[\text{Cp}_2\text{Ti}]^-$

to Ti. This suggests that in electronic terms the anion can be described as a 'close-contact' complex between  $\text{Cp}^-$  and  $\text{CpTi}$  ( $[\text{CpTi}\cdot\text{Cp}]^-$ ). In fact the character of this and related systems is highly dependent on the situation and coordination of the cation. In  $[\text{CpTi}(\mu\text{-Cp})\text{Li}\cdot\text{PMDETA}]$  (Fig. 7), the presence of an ion-contact between the  $\text{Li}^+$  cation (which competes for the electron density of the bridging  $\mu\text{-Cp}$  ligand) weakens the  $\text{Ti}-(\mu\text{-Cp})$  interaction and has a profound effect on the charge distribution of the  $[\text{Cp}_2\text{Ti}]^-$  unit (now best regarded as a 'loose-contact' complex between  $\text{CpTi}$  and  $\text{CpLi}$ ).<sup>14</sup>

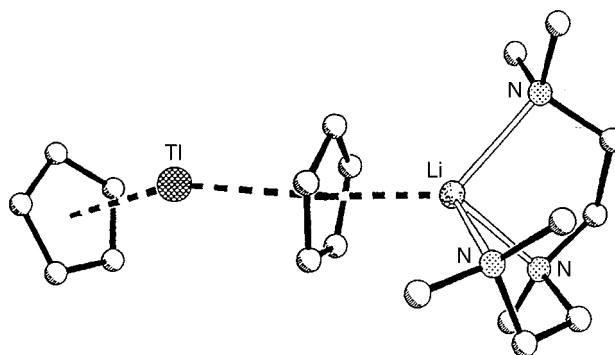


Fig. 7 Structure of  $[\text{CpTi}(\mu\text{-Cp})\text{Li}\cdot\text{PMDETA}]$

The same general features seen in the  $[\text{Cp}_2\text{Ti}]^-$  system are also apparent in formally 20e complexes containing  $[\text{Cp}_3\text{E}]^-$  ( $\text{E} = \text{Sn, Pb}$ ) anions. The reactions of  $\text{Cp}_2\text{E}$  with  $\text{CpNa}$  or  $\text{Cp}_2\text{Mg}$  give ion-separated or ion-paired complexes depending on the cation and the extent of its Lewis base solvation.<sup>4</sup> In  $[\text{Mg}(\text{thf})_6]^{2+}[\text{Cp}_3\text{E}^-]_2$  and  $[\text{Cp}_2\text{E}(\mu\text{-Cp})\text{Na}\cdot\text{PMDETA}]$   $\pi$ -bonded, 'paddle-wheel' arrangements of the three Cp ligands surrounding the Group 14 metals result in almost trigonal planar metal geometries (Fig. 8). This arrangement is extremely unusual for stannate or plumbate anions,  $\sigma$ -bonded organometallic anions of this type (such as 8e  $[\text{Ph}_3\text{E}]^-$ ) conforming to

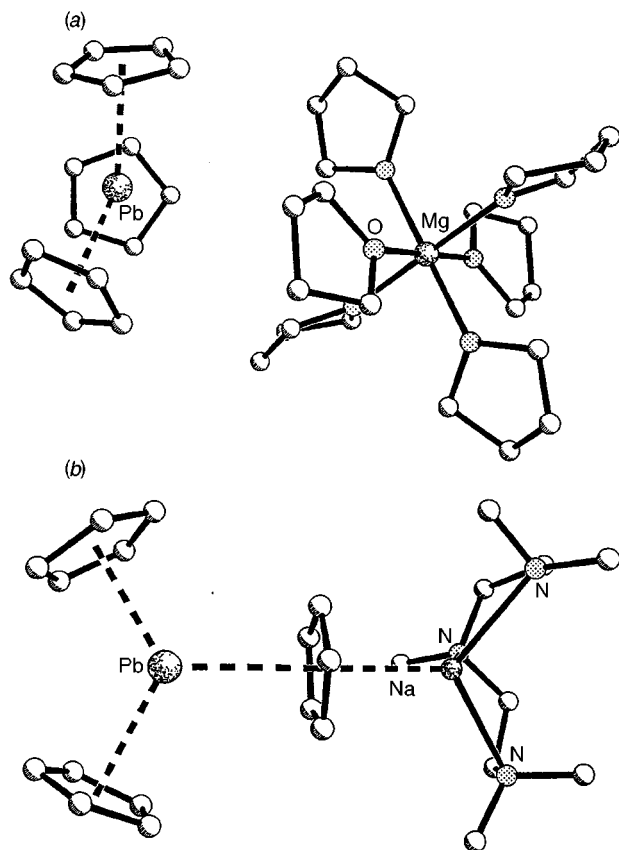


Fig. 8 (a) Structure of  $[\text{Mg}(\text{thf})_6]^{2+}[\text{Cp}_3\text{E}^-]_2$  and (b)  $[\text{Cp}_2\text{E}(\mu\text{-Cp})\text{Na}\cdot\text{PMDETA}]$

the VSEPR model and having pyramidal metal geometries. The  $\pi$ -bonding of Cp to the  $\text{Sn}^{\text{II}}$  and  $\text{Pb}^{\text{II}}$  centres in  $[\text{Cp}_3\text{E}]^-$  clearly overwhelms conventional octet considerations and their effects on structure. However, the switch from an  $\eta^5$ -Cp bonding mode in  $[\text{Cp}_2\text{E}(\mu\text{-Cp})\text{Na}\cdot\text{PMDETA}]$  to an  $\eta^3$ -mode in  $[\text{Mg}(\text{thf})_6]^{2+}[\text{Cp}_3\text{E}^-]_2$  and the less planar geometry of the Group 14 metal centres in the ion-separated  $[\text{Cp}_3\text{E}]^-$  anions can be viewed as resulting from a shift towards partial  $\text{sp}^3$  hybridisation.<sup>4</sup> As with complexes containing  $[\text{Cp}_2\text{Tl}]^-$  anions, the nature of  $[\text{Cp}_3\text{E}]^-$  anions is highly dependent on potential competition with cations and spectroscopic and theoretical studies illustrate that the Sn environment in  $[\text{Cp}_2\text{Sn}(\mu\text{-Cp})\text{Na}\cdot\text{PMDETA}]$  is electronically similar to that in  $\text{Cp}_2\text{Sn}$ . This complex is therefore best considered as a 'loose-contact' type complex between  $\text{Cp}_2\text{Sn}$  and  $\text{CpNa}\cdot\text{PMDETA}$ .<sup>4</sup>

Cationic complexes were the earliest examples which portrayed an underlying isoelectronic relationship in p-block metallocenes. Perhaps the most well known example is the 8e  $[(^{\text{Me}}\text{Cp})\text{Sn}]^+$  cation (Fig. 9), isoelectronic with the neutral Group 13 metallocene units of  $\text{CpTl}$  or  $\text{CpIn}$ .<sup>3</sup> This cation is the product of the reaction of  $(^{\text{Me}}\text{Cp})_2\text{Sn}$  with the acid  $\text{HBF}_4$ , resulting in the formal loss of  $\text{Cp}^-$  as  $\text{CpH}$ . The formation of adducts of this cation with various Lewis base donors is also known.<sup>3</sup> A second representative of this class is the 14e  $[(^{\text{Me}}\text{Cp})_2\text{As}]^+$  cation (Fig. 10), generated by the reaction of  $[(^{\text{Me}}\text{Cp})_2\text{AsF}]$  with  $\text{SbF}_5$ .<sup>3</sup> Like the isoelectronic neutral metallocene units of Group 14 in the gas phase, a bent sandwich arrangement occurs for the  $[(^{\text{Me}}\text{Cp})_2\text{As}]^+$  cation in the solid state. The use of the more sterically demanding  $^{\text{Me}}\text{Cp}$  ligand in these cationic species is required for their stabilisation.

A more recent development is illustrated by the synthesis and structure of the 12e  $[(^{\text{Me}}\text{Cp})_2\text{Al}]^+$  cation (Fig. 11).<sup>8</sup> This species is prepared by the disproportionation reaction of the Al<sup>II</sup> complex  $[(^{\text{Me}}\text{Cp})\text{Al}]$  with  $\text{AlCl}_3$ , and is formally isoelectronic with s-block metallocenes such as  $\text{Cp}_2\text{Mg}$  and  $[\text{Cp}_2\text{Li}]^-$ .<sup>3,16</sup>

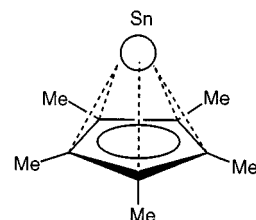


Fig. 9 Structure of the  $[(^{\text{Me}}\text{Cp})\text{Sn}]^+$  cation

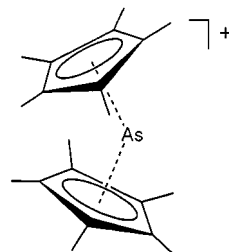


Fig. 10 Structure of the  $[(^{\text{Me}}\text{Cp})_2\text{As}]^+$  cation

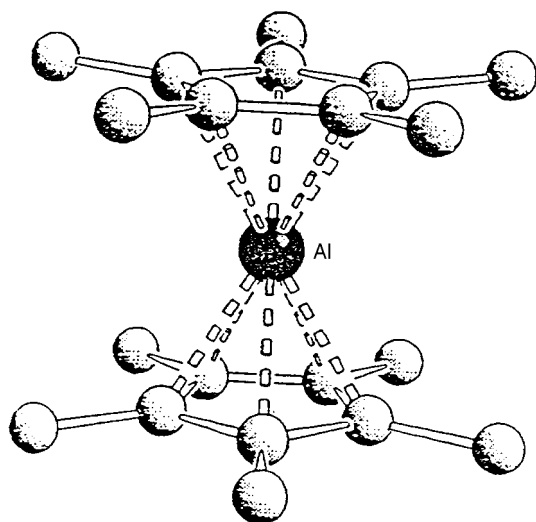


Fig. 11 Structure of the  $[(^{\text{Me}}\text{Cp})_2\text{Al}]^+$  cation

Like these complexes a linear ('ferrocene-like') sandwich structure is found for the  $[(^{\text{Me}}\text{Cp})_2\text{Al}]^+$  cation in the solid state; the reasons for which can be seen by returning to the MO diagram for  $\text{Cp}_2\text{Sn}$  shown in Fig. 4. Unlike the 14e Group 14 metallocenes, deformation of the structure into a bent conformation is not necessary in a 12e system since an additional bonding orbital is not required. The considerable interest in Al cations of this type has been generated by the discovery that the less sterically shielded  $[(^{\text{Me}}\text{Cp})_2\text{Al}]^+$  cation is effective in alkene polymerisation.<sup>17</sup>

### 3.3 Fragmentation and control of the metallocene lattice

So far the discussion of the structures formed by p-block metallocenes has been confined to the consideration of isoelectronic relationships in simple mononuclear complexes. However, although all the known neutral metallocene complexes are monomeric in the gas phase many are in fact associated into polymeric or molecular arrangements in the solid state.<sup>3</sup> The simplest metallocenes, containing unsubstituted Cp ligands, often form polymeric strand structures in which the molecular units are linked by metal-( $\mu\text{-Cp}$ )-metal interactions. The structures of  $\text{CpTl}$  and  $\text{CpIn}$  [Fig. 12(a)] and of the orthorhombic form of  $\text{Cp}_2\text{Pb}$  [Fig. 12(b)] adopt this structural pattern.<sup>3</sup> The tendency for  $\text{Cp}_2\text{Pb}$  to polymerise in this manner is unique in Group 14 and probably stems from the more

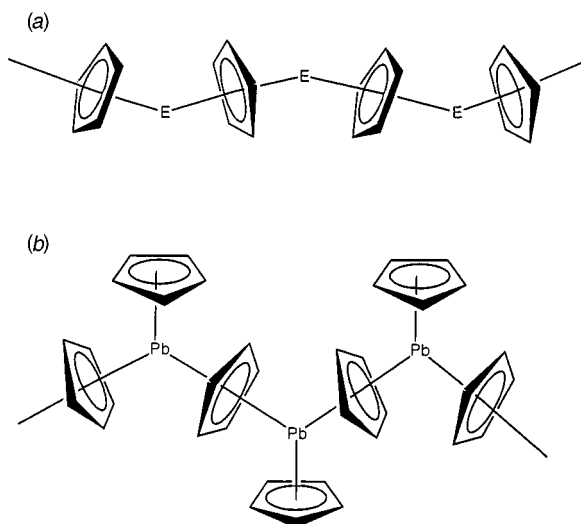


Fig. 12 Structures of (a)  $[\text{CpE}]$  ( $E = \text{In, Tl}$ ), and (b)  $[\text{Cp}_2\text{Pb}]$

electropositive nature of Pb. This arrangement can be compared to the structure of  $\text{Cp}_2\text{Sn}$ ,<sup>3</sup> which retains its monomeric nature in the solid state. As is illustrated by the dissociation of these polymeric structures into monomers in the gas phase and in solution, the association of the molecular units is weak. What is surprising is that such association should occur at all in these species, bearing in mind the presence of metal lone pairs which would normally suggest donor rather than acceptor character. The reasons for the weak acceptor properties arise from the low energy of the lone pair orbitals which have considerable s-character and are buried in the atomic structure of the metals.

Using the formal electron count of the metals as a basis for the interpretation of structural trends is of far less value in these polymeric systems. However, one observation is that the metal environments within the strand structures of  $\text{CpE}$  ( $E = \text{In, Tl}$ ) and  $\text{Cp}_2\text{Pb}$  resemble those present in mononuclear  $[\text{Cp}_2\text{Tl}]^-$ <sup>14</sup> and  $[\text{Cp}_3\text{Pb}]^-$ <sup>4</sup> anions (Figs. 7 and 8, respectively), which can be regarded as representing discrete fragments of the polymeric lattices of the neutral metallocenes. It is of interest to imagine whether 'extended' anions can be prepared, corresponding to larger segments of these polymeric arrangements. The syntheses of such species is in fact accomplished very easily by reacting  $\text{CpTl}$  or  $\text{Cp}_2\text{Pb}$  with alkali metal cyclopentadienides in the presence of cyclic polyethers (so-called crown ethers). These Lewis base ligands contain molecular cavities which are highly specific for the complexation of alkali metal cations of a particular size [e.g. 12-crown-4 and 15-crown-5 (Fig. 13)]. The

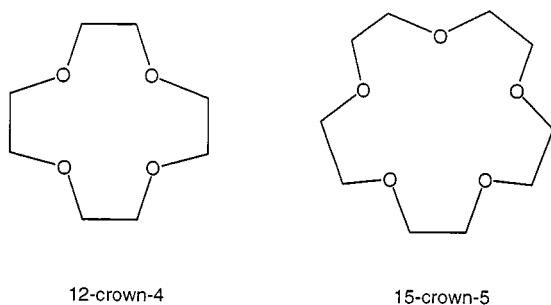


Fig. 13 Structures of 12-crown-4 and 15-crown-5

sandwich cations  $[\text{Li}(12\text{-crown-4})_2]^+$  and  $[\text{K}(15\text{-crown-5})_2]^+$  are particularly stable<sup>18</sup> and the effect of their formation in these reactions is to separate the alkali metal cation and the metallocene anion, thus preventing competition for Cp electron density and encouraging the growth of larger anion chains. The structures of  $[\text{Li}(12\text{-crown-4})_2]^+ \cdot [\text{Cp}_3\text{Tl}_2]^-$ <sup>14</sup> and  $[\text{K}(15\text{-crown-5})_2]^+ \cdot [\text{Cp}_5\text{Pb}_2]^-$ <sup>19</sup> contain the dinuclear, triple-

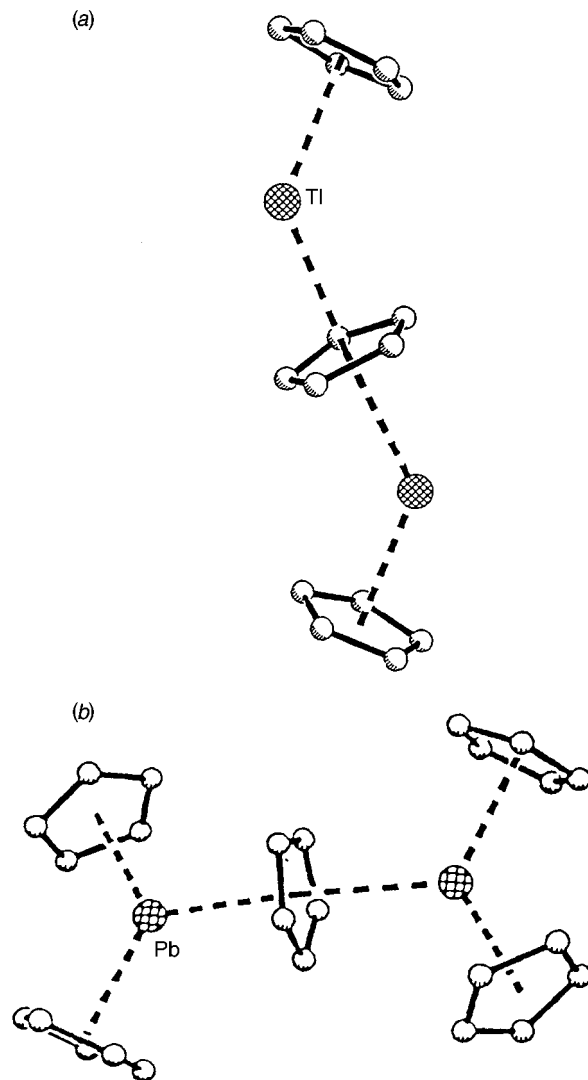


Fig. 14 Structures of (a)  $[\text{Cp}_3\text{Tl}_2]^-$  and (b)  $[\text{Cp}_5\text{Pb}_2]^-$

decker sandwich anions shown in Fig. 14. These species are the next homologues of the mononuclear  $[\text{Cp}_2\text{Tl}]^-$  and  $[\text{Cp}_3\text{Pb}]^-$  anions discussed previously.

The inherent weakness of the association of the metallocene units means that lattice energy considerations dominate the choice of extended anions which are formed. This subtle influence is best seen in  $[\text{Li}(12\text{-crown-4})_2]^+ \cdot [\text{Cp}_5\text{Pb}_2]^- \cdot [\text{Cp}_9\text{Pb}_4]^-$  (Fig. 15) in which the formation of two

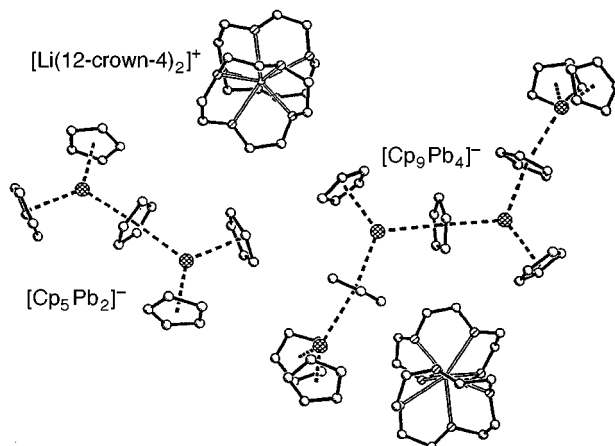


Fig. 15 Structure of  $[\text{Li}(12\text{-crown-4})_2]^+ \cdot [\text{Cp}_5\text{Pb}_2]^- \cdot [\text{Cp}_9\text{Pb}_4]^-$

different homologous anions (as opposed, for example, to the isomeric alternative of two identical  $[\text{Cp}_7\text{Pb}_3]^-$  anions) is probably due to effective packing in the crystalline lattice.<sup>14</sup>

Chemical fragmentation of the extended lattice of a p-block metallocene is one way by which modification of these systems can be achieved. However, there are some more obvious expressions of the weakness in the association of the molecular units in these species. In particular, dramatic changes in the structural pattern found in the Group 13 complexes occur upon increasing the substitution of the Cp rings. In contrast to the polymeric arrangement found for  $\text{CpIn}$  in the solid state, the structures of  $^{\text{Me}}\text{CpIn}$ <sup>20</sup> and  $^{\text{Me}}\text{CpGa}$ <sup>7</sup> are composed of discrete metal octahedra in which the metal centres are linked by weak interactions [Fig. 16(a)]. Such metal...metal interactions are reasonably common in compounds of  $\text{Tl}^{\text{I}}$  and  $\text{In}^{\text{I}}$  in general and are present within the structures of  $\text{CpIn}$  and  $\text{CpTl}$ , linking the polymeric stands together. Increasing the steric bulk of the substituents present on the Cp rings tends to drive the structures towards smaller molecular arrangements, an example of which is  $[\text{B}^z\text{CpIn}]$  [ $\text{B}^z\text{Cp}=\text{C}_5(\text{CH}_2\text{Ph})_5$ ] in which extensive metal...metal interactions are precluded by the steric demands and metal shielding of the ligand. The structure is that of a loosely

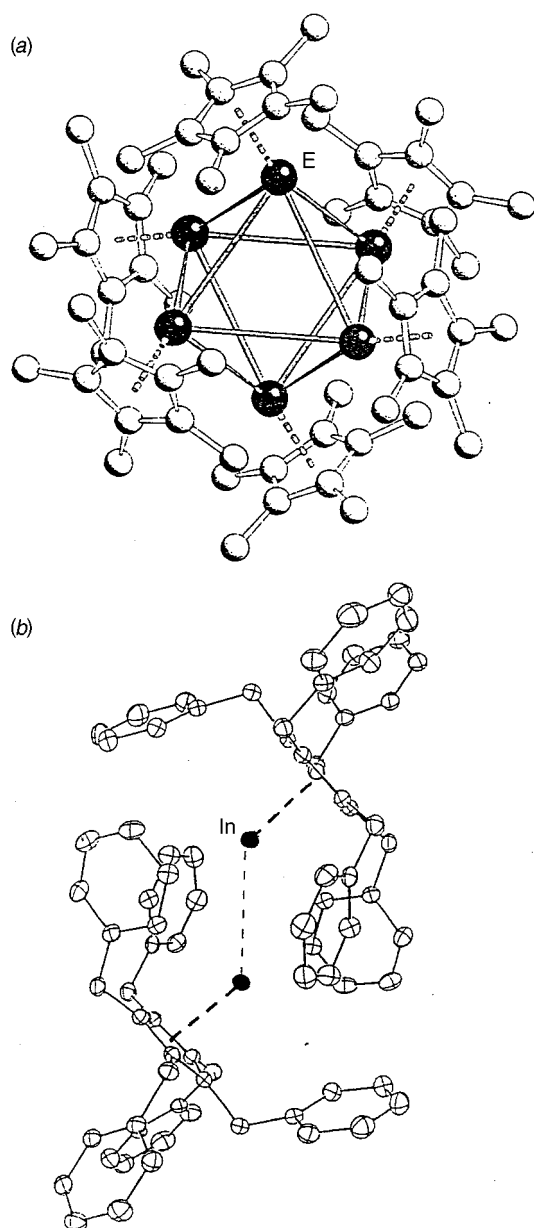


Fig. 16 Structures of (a)  $[\text{MeCpE}]$  ( $\text{E}=\text{In}, \text{Ga}$ ) and (b)  $[\text{B}^z\text{CpIn}]$

linked dimer in which two molecular units are joined by only one  $\text{In}\cdots\text{In}$  interaction [Fig. 16(b)].<sup>21</sup>

Although  $\text{In}^{\text{I}}$  and  $\text{Tl}^{\text{I}}$  complexes have been known for many years, the synthesis of stable organometallic complexes of  $\text{Ga}^{\text{I}}$  and  $\text{Al}^{\text{I}}$  has only been made possible recently. Previously,  $\text{Al}^{\text{I}}\text{Cl}$  was thought to occur only in the gas phase at low pressure. However, careful experimental work revealed that this low-oxidation state salt, which is the key starting material for organo- $\text{Al}^{\text{I}}$  compounds, can be isolated in a metastable form.<sup>8</sup> The structure of  $[\text{MeCpAl}]$  is particularly intriguing, being composed of an  $\text{Al}-\text{Al}$  bonded  $\text{Al}_4$  tetrahedron (Fig. 17).<sup>8</sup> Like

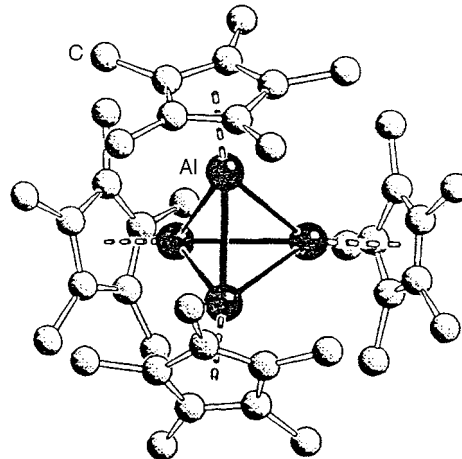


Fig. 17 Structures of  $[\text{MeCpAl}]_4$

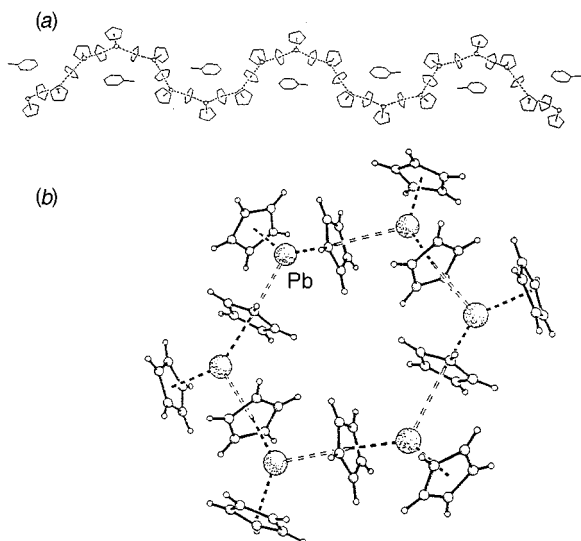
other +1 oxidation state complexes discussed above, these metal-metal interactions appear to defy simple bonding interpretations. They are commonly described as 'closed-shell', dispersive interactions and can only really be explained by detailed quantum mechanical treatments.<sup>22</sup> Quantum mechanical calculations and spectroscopic studies of  $[\text{MeCpAl}]_4$  give good agreement of about  $150 \text{ kJ mol}^{-1}$  for the association energy of the cluster (*i.e.* very weakly associated).

A more recent development has been the realisation that the choice of solvent from which the metallocene is crystallised may affect the structure adopted.<sup>23</sup> If crystals of  $\text{Cp}_2\text{Pb}$  are grown by sublimation from the vapour then the orthorhombic form is obtained, which has the polymeric zig-zag structure shown in Fig. 12(b). If the orthorhombic form is crystallised from toluene then the major product is the inclusion compound  $[\{\text{Cp}_2\text{Pb}\}_3\text{toluene}]_\infty$ , having a similar structure to the orthorhombic form but now with an undulating, sinusoidal arrangement of the polymer chain [Fig. 18(a)]. The minor product of recrystallisation is a new hexagonal phase of plumbocene in which six  $\text{Cp}_2\text{Pb}$  units are linked together into a cyclic doughnut [Fig. 18(b)]. A similar structural pattern has been found for the  $\text{Tl}^{\text{I}}$  complex  $[(1,3\text{-Me}_3\text{Si})_2\text{CpTl}]_6$  in the solid state.<sup>24</sup>

#### 4 Perspectives on the future and closing remarks

The amazing structural diversity of main group metallocenes and the variety of bonding patterns they adopt make their study extremely exciting. There is still great scope for novel chemical and structural investigations of these systems and, in particular, for more extensive theoretical calculations probing the factors responsible for electronic and thermodynamic stabilisation. This review has used simple chemical concepts of design and structural modification in an attempt to provide a broader picture of the underlying trends in these species. These concepts are obviously far from complete and as new species emerge one important area will be the further refinement of existing structural models and the development of new structural concepts.

New synthetic challenges are already apparent in the investigation of unusual, highly reactive low-oxidation state  $\pi$



**Fig. 18** Structures of (a)  $[(Cp_2Pb)_3 \cdot toluene]$  and (b) the hexagonal form of  $[Cp_2Pb]$

complexes, such as  $[MeCpAl]$ . There will undoubtedly be increased activity in this area in future. In addition, engineering the crystal lattices of metallocene complexes and the preparation of new cationic and anionic multi-decker sandwich and cage arrangements provide a large area of interest, which is still under development.

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