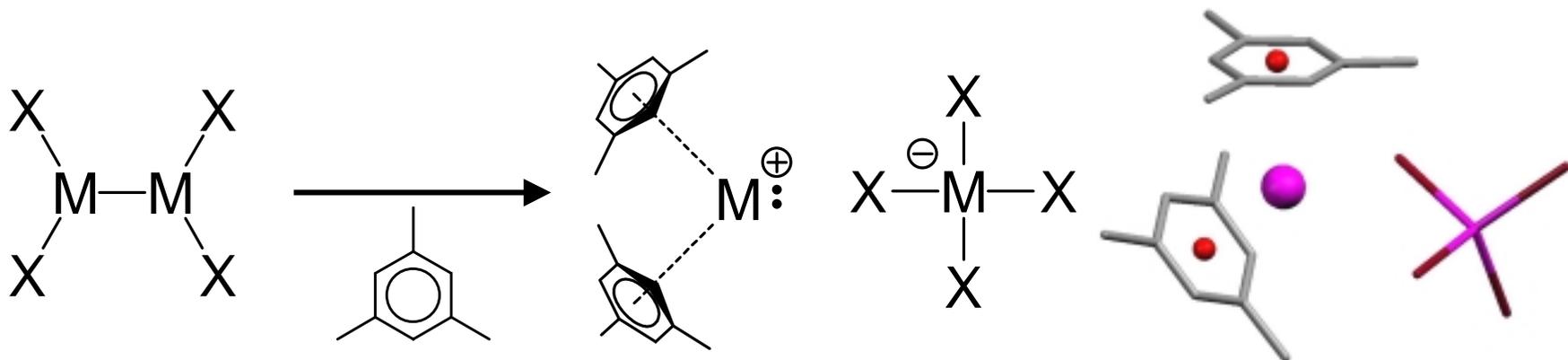




A strict definition of “metalloene” insists that such compounds must contain a metal that is sandwiched between two cyclopentadienyl (C_5H_5 , Cp) groups, however I will use the term to describe any compounds containing a “metal” that is bonded to the π -cloud of a cyclopentadienyl (or similar) substituent. I will use the term for convenience because:

- (a) some of the important p-block elements are not metals
 - (b) many of the main group compounds are necessarily sandwiched between two Cp substituents
 - (c) other substituents analogous to Cp are also of interest
-

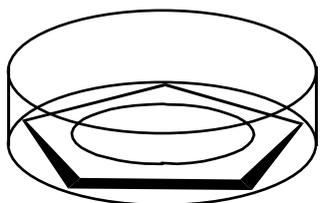


M = Ga, In, Tl; X = Cl, Br (See: Schmidbaur, *Angew. Chem. Int. Ed.*, 1985, 24, 893).

Chem 59-651 Cyclopentadienyl Ligand Basics

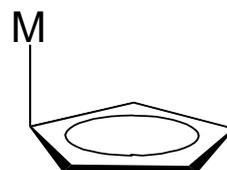
The structural features and bonding interactions between cyclopentadienyl groups and metal atoms shows considerable variation and is described using a few different conventions (See Jutzi and Burford, *Chem. Rev.*, 1999, 99, 969 and references therein). In most main group metallocenes, even those that are σ -bonded in the solid state, the rings rotate rapidly through a series of 1,2-shifts.

A Cp group can be considered to be p-bonded to an element if the element sits inside the cylinder defined by the 5 carbon atoms of the Cp ligand. The center of mass of the 5 C atoms is known as the *centroid*.

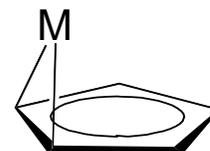


A σ -bonded Cp can be identified by the angle at the *ipso* carbon and bond lengths should indicate single bonds to the *ipso* carbon and a localized diene structure for the α and β carbon fragment.

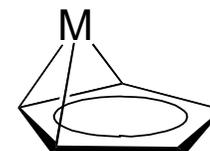
Hapticity:



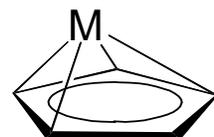
η^1 -Cp



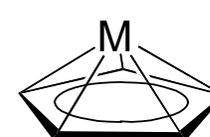
η^2 -Cp



η^3 -Cp

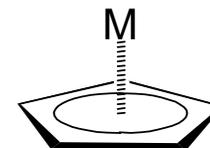


η^4 -Cp

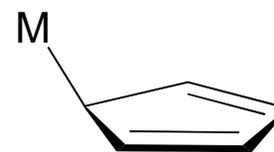


η^5 -Cp

\equiv



η^5 -Cp



σ -Cp

Chem 59-651 Cyclopentadienyl Ligand Basics

To understand the nature of the covalent bonding between a cyclopentadienyl ligand and an element, one must examine the important molecular orbitals of the ligand. Note that the orbital interactions are generally more important for the elements in the p-block (and d-block) because the elements of the s-block are almost purely ionic.

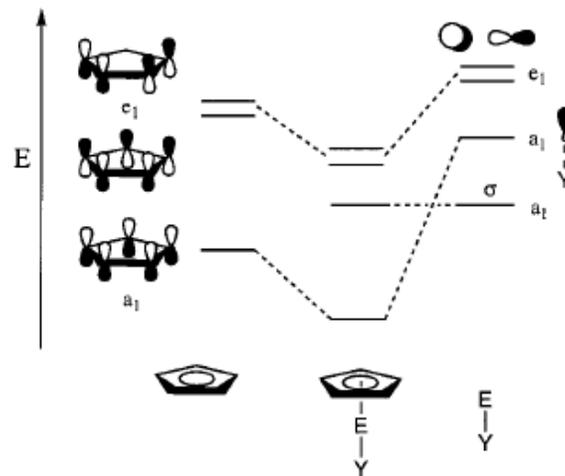
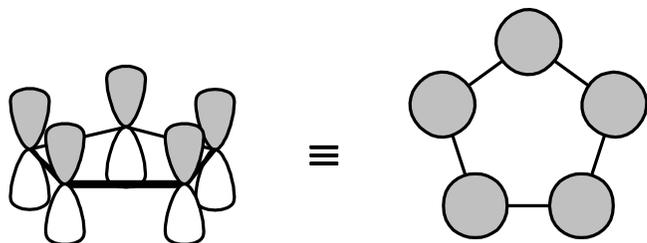
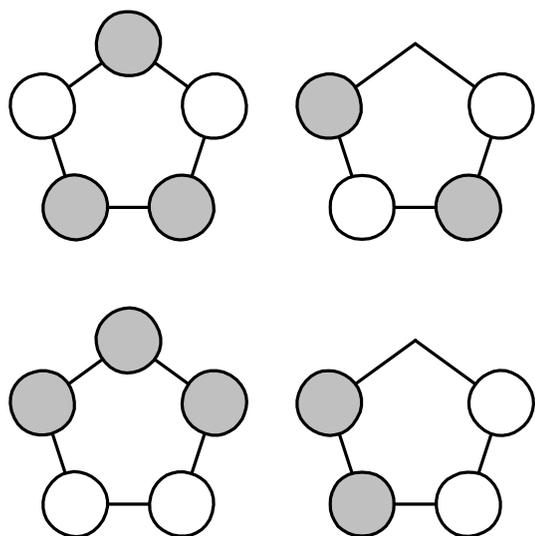


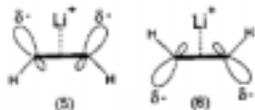
Figure 1. General molecular orbital diagram for Cp–main group element interactions of local C_{5v} symmetry, showing only occupied orbitals.

The SALCs of the Cp ligand can interact with appropriate AOs on the metal.

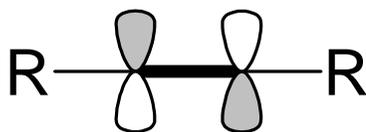
Chem 59-651 Cyclopentadienyl Ligand Basics

The metrical parameters of the Cp substituent can also provide significant information about the nature of the Cp-E interaction. In particular, the groups attached to the carbon atoms of the Cp ring often bend out of the plane of the ring and the amount and direction of the bending can be used to determine whether the interaction is predominantly covalent or ionic.

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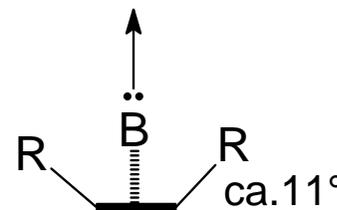
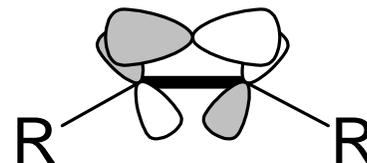
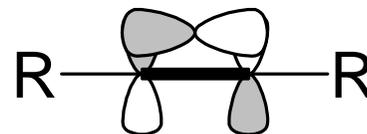
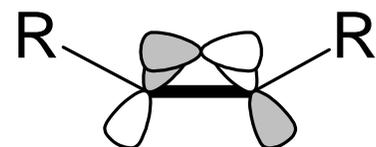
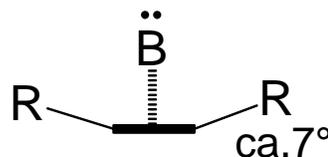


For ionic compounds, the substituents bend away from the metal because this increases the amount of negative charge on the face of the ring adjacent to the cation. Similar bending is observed if a positive charge is used instead of a cation in computational investigations.



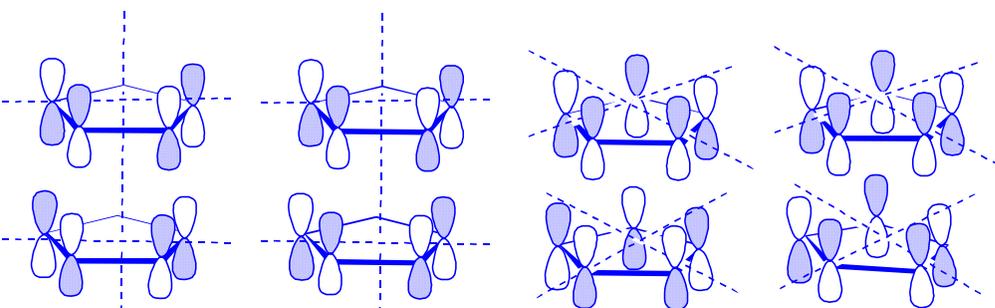
For covalent compounds, the direction of the bending is variable and depends on the size of the p orbitals on the metal. The π orbitals on the Cp ring distort to create the most effective overlap.

The nature of the bending can prove the nature of the Cp-E bonding ([Macdonald, JACS, 1999, 121, 12113, and refs.](#)).

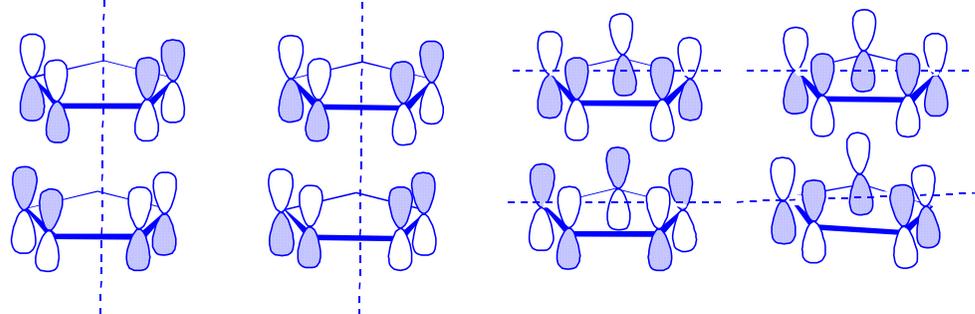




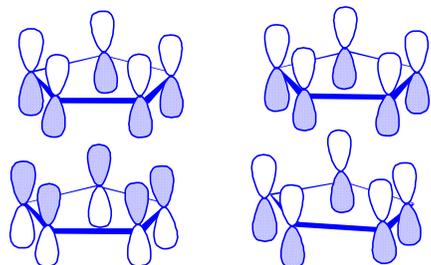
For sandwich-type compounds, the SALCs can be obtained by considering the interactions between the orbitals on both rings. Remember that interactions will only be possible between MOs of the same symmetry - this means all you have to do is consider the nodal properties of the combinations. I.e. you can only obtain valid combinations from orbitals that have the same nodal planes.



2 node combinations



1 node combinations



0 node combinations

Chem 59-651 Cyclopentadienyl Ligand Basics

Many of the sandwich compounds in the main group do not have “linear” (centroid-E-centroid) structures with the Cp rings parallel to one another (i.e. D_{5h} or D_{5d} symmetry); the Cp SALCs for the bent geometries interact with the AOs on the central element in a different manner. The orbital that is most stabilized by bending is the p orbital that corresponds to a lone-pair for metallocenes in group 14 and 15 thus bent geometries are generally observed for such compounds.

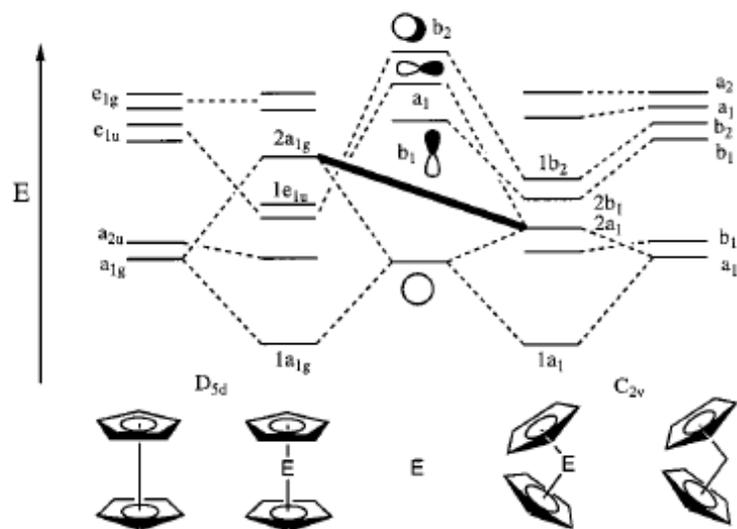
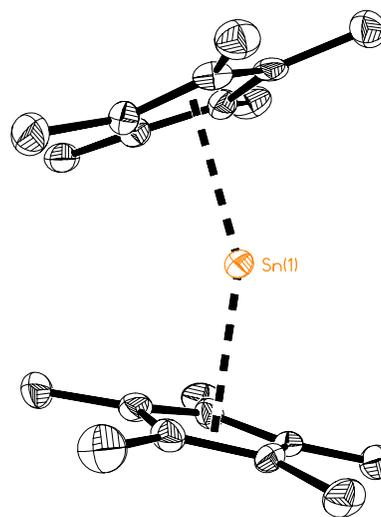


Figure 2. General molecular orbital diagrams for 14 electron bis(cyclopentadienyl)main group element complexes with parallel (D_{5d}) and bent (C_{2v}) structures, showing only occupied orbitals.



The bent structure of Cp^*_2Sn



The metallocenes of groups 1 and 2 are primarily ionic compounds and these are valuable reagents for the synthesis of cyclopentadienyl compounds for the rest of the elements in the periodic table. Despite their simple molecular formulae, the alkali metal metallocenes exhibit interesting and informative structural chemistry (See Harder, *Coord. Chem. Rev.*, 1998, 176, 17 and references therein). Note that CpNa and CpK were first synthesized in 1900 and were the first cyclopentadienyl metal compounds. These predate ferrocene by almost 50 years but the structures of these compounds were not investigated or understood until the late 1950's.



Fig. 5. 'Side-on' $\text{Cp}^- \cdots \text{Li}^+$ coordination in comparison to 'face-on' $\text{Cp}^- \cdots \text{Li}^+$ 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).

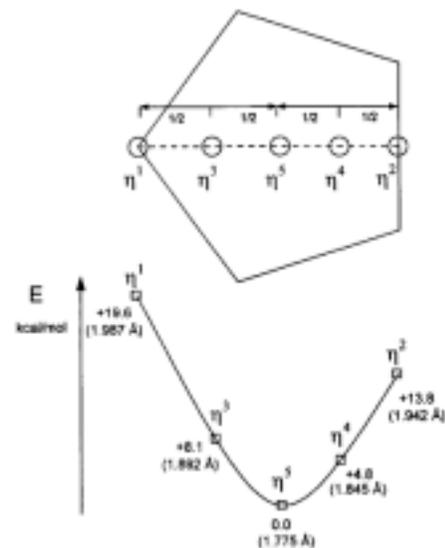


Fig. 3. A haptotropic search on CpLi (MP2/6-31+G*) (Li is shifted over the Cp plane from left to right). The energy as well as the Cp(plane)-Li distance (given in parentheses) increase with decreasing hapticity.



Because of the charge distribution on the anion, the alkali metal compounds have either linear “super sandwich” structures or zig-zag structures. The actual arrangement depends on the size of the cation, the substituents on the Cp' ligand, and the presence or absence of donor molecules.

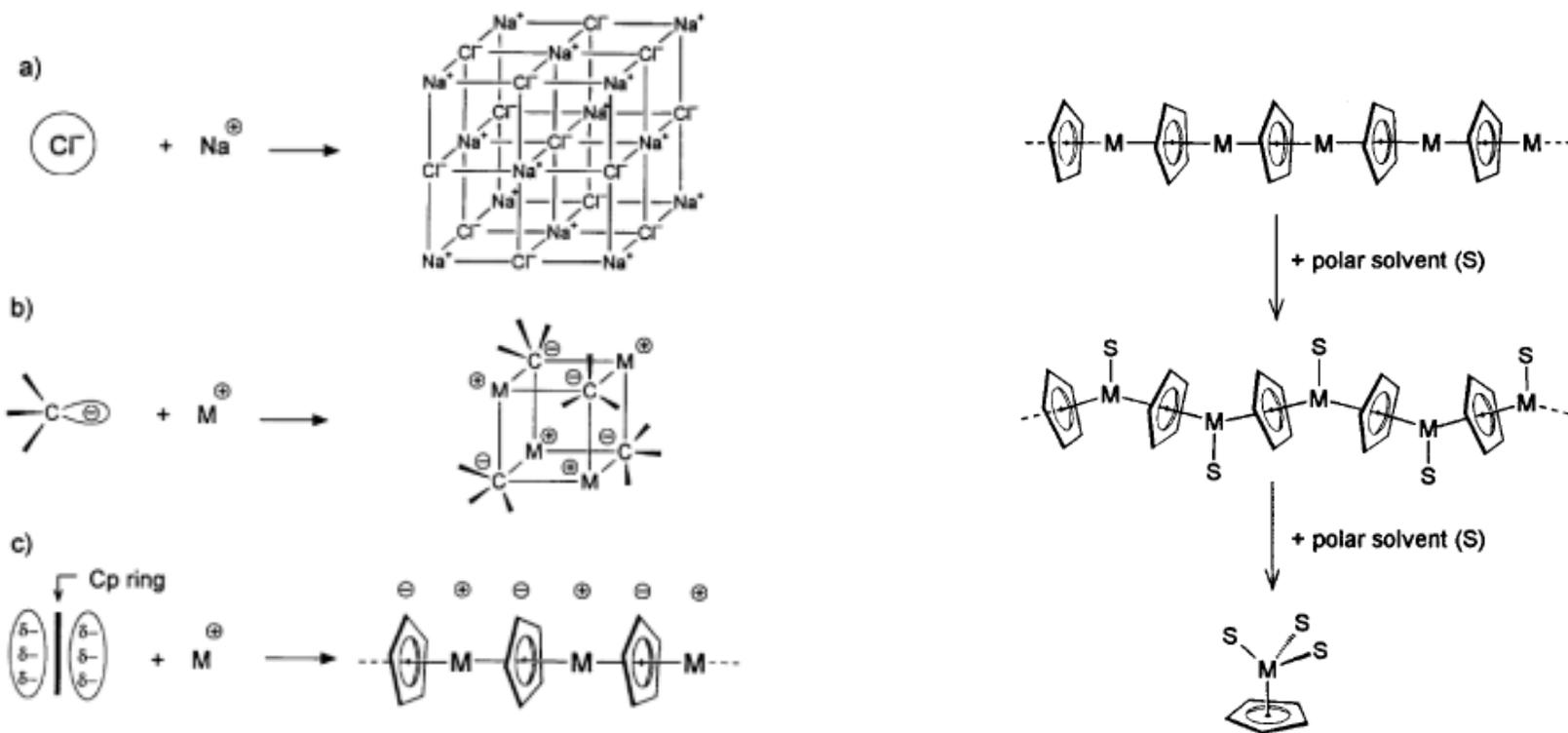


Fig. 6. The relationship between the structure of the anion and the structure of the aggregate.

Note: Cp' indicates a cyclopentadienyl group with various substituents.



CpLi and CpNa both have nearly perfectly linear “super sandwich” structures that were solved by X-ray powder diffraction (XRD). The heavier analogues adopt zig-zag structures to fill their larger coordination spheres.

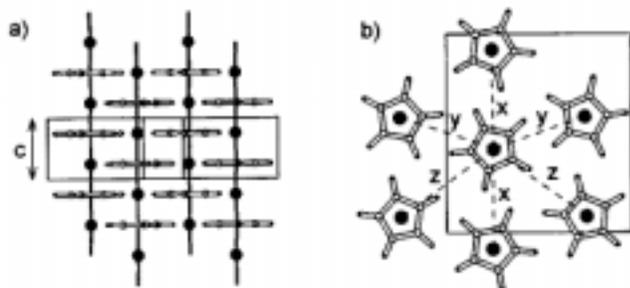


Fig. 7. (a) View perpendicular on the linear chains of CpM ($M = \text{Li}$ or Na). (b) View along the linear chains of CpM (the distances between neighbouring chains are designated with x , y and z ; for $M = \text{Li}$: $x = 5.565 \text{ \AA}$, $y = 5.557 \text{ \AA}$ and $z = 6.260 \text{ \AA}$; for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

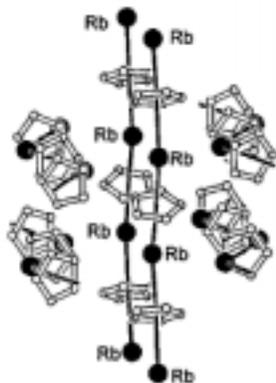


Fig. 9. CpRb (phase I) shows layers of parallel chains. Subsequent layers possess a mutually perpendicular orientation. ‘Side-on’ $\text{Cp}^- \cdots \text{Rb}^+$ bonding proceeds within the layers and between the layers.

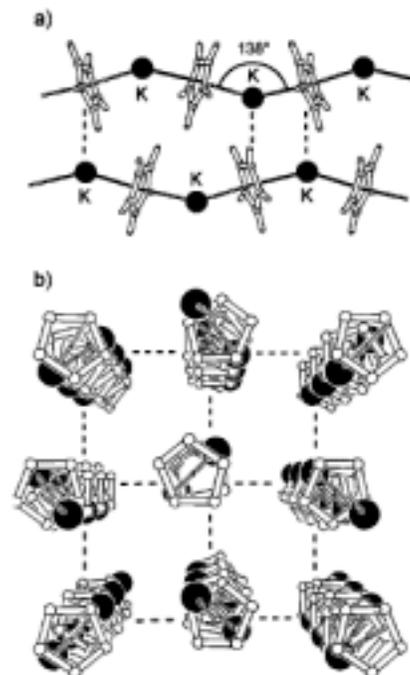


Fig. 8. (a) Two neighbouring ‘zig-zag’ chains of CpK units. (b) Perspective view along the interacting chains in the structure of CpK; hydrogen atoms are omitted for clarity.



Monomeric or various zig-zag structures can also be obtained by introducing donor molecules into the system. Again, the actual structure adopted depends on the size of the Cp' ligand and the size of the cation.

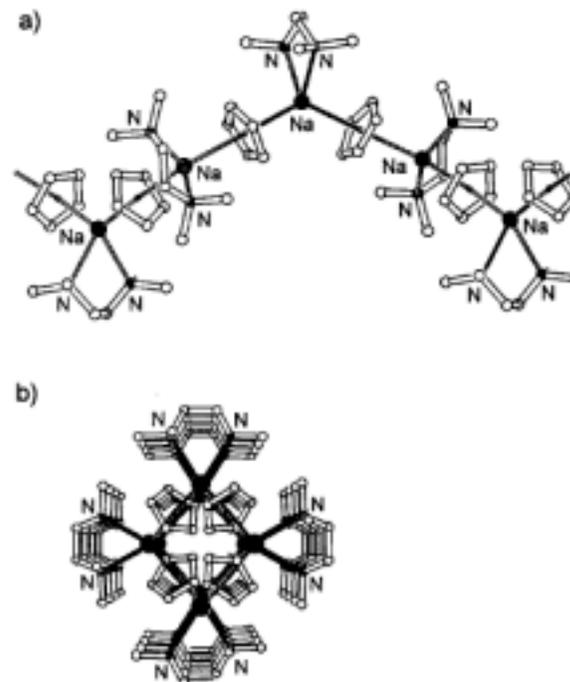
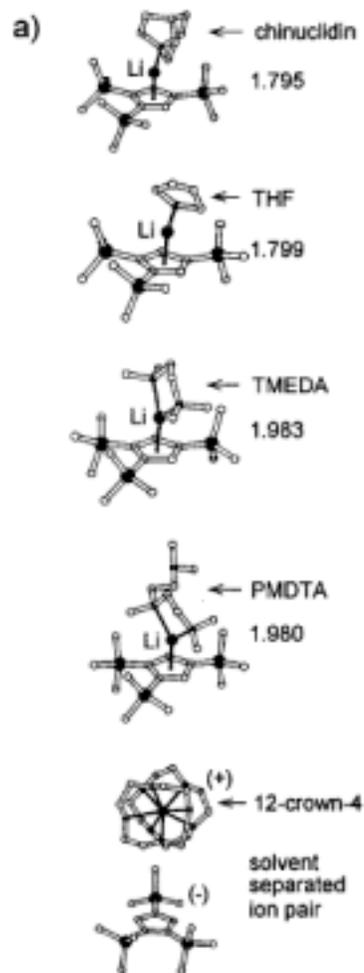


Fig. 14. The spiral chain structure of $\text{CpNa} \cdot \text{TMEDA}$. (a) View perpendicular on the chain. (b) View along the spiral chain.

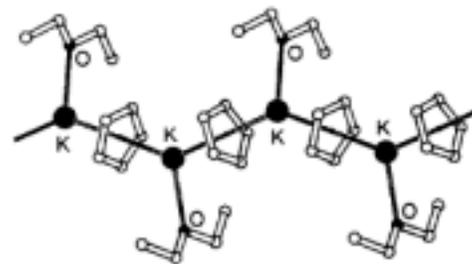


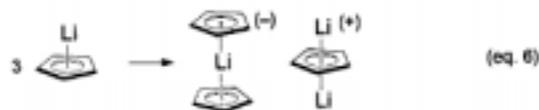
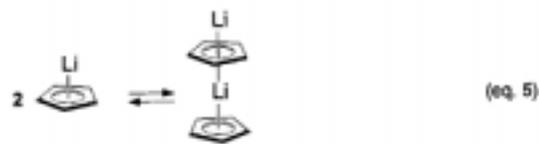
Fig. 13. The crystal structure of $\text{CpK} \cdot \text{Et}_2\text{O}$: a 'zig-zag' chain typical for the structures of solvated polymeric Cp-alkalimetal complexes.



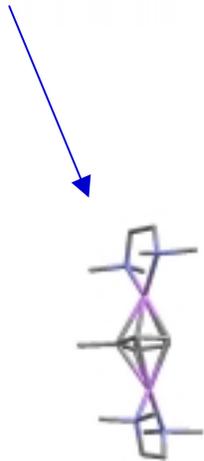
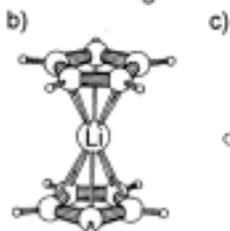
In solution, the alkali metal Cp compounds can adopt a variety of forms that can be considered as pieces of the supersandwich structure.

Dissociation/association reactions such as those indicated below have been confirmed by conductivity measurements, molecular weight determinations and through the synthesis/trapping of related species.

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2 CpM
+ [PPh₄]Cl



[LiCpLi(TMEDA)₂]

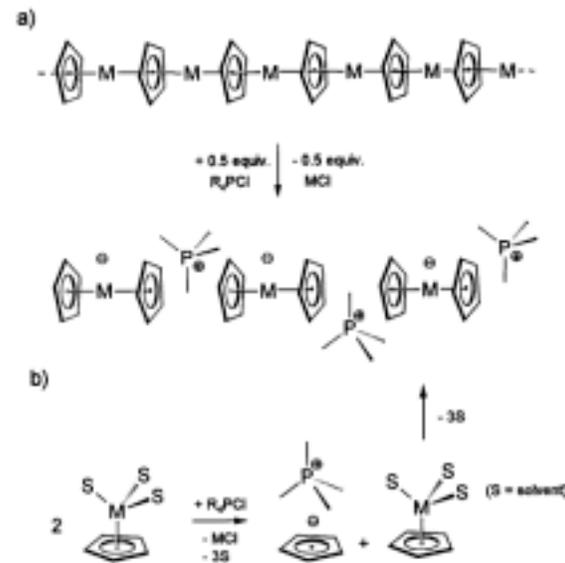
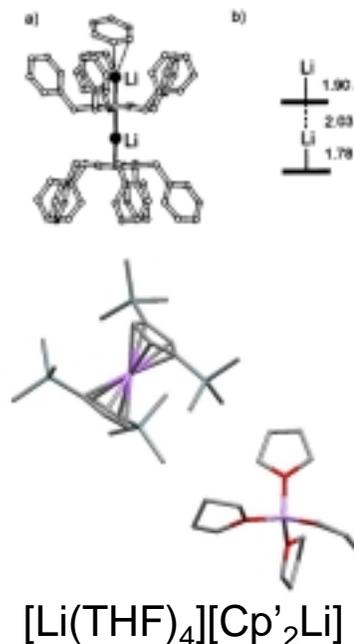
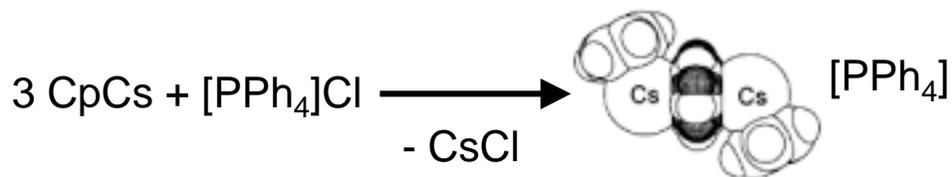
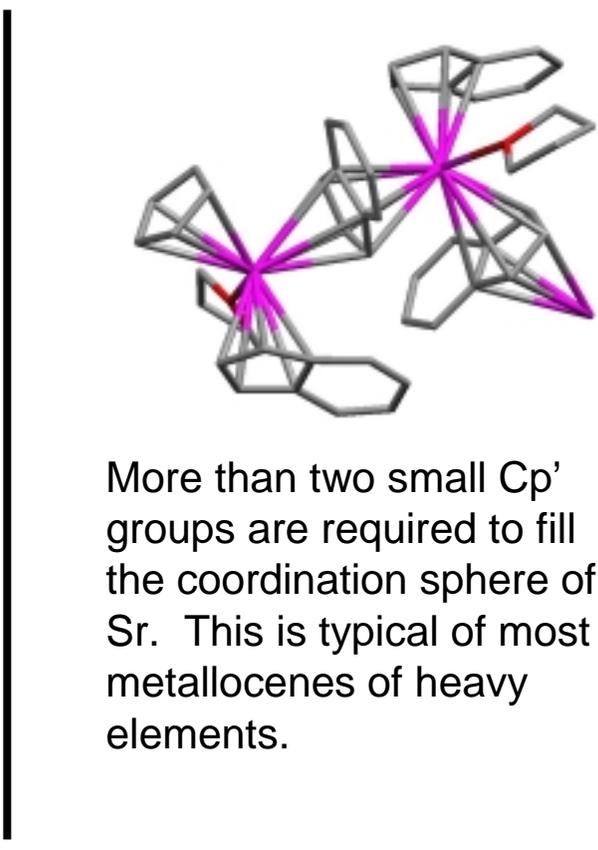
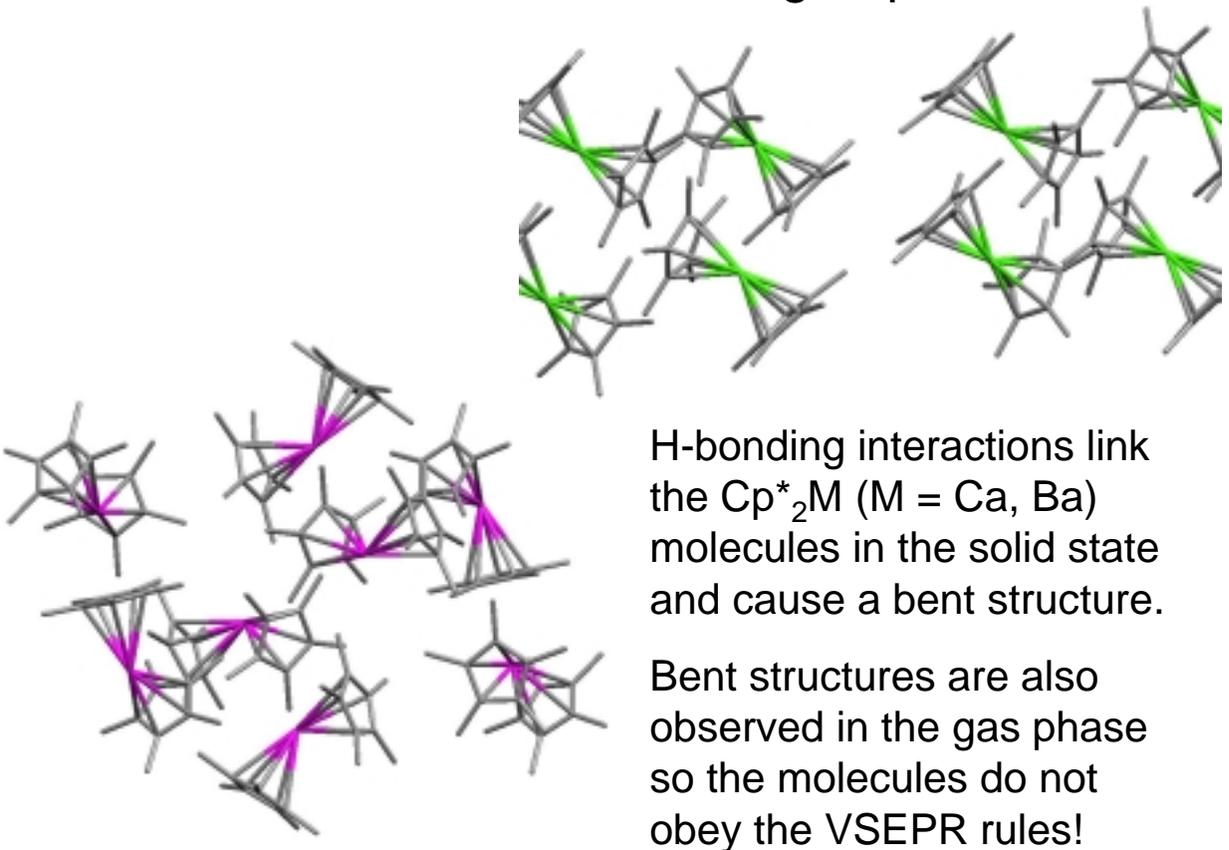


Fig. 24. Approach for the synthesis of anionic metallocene sandwich complexes.



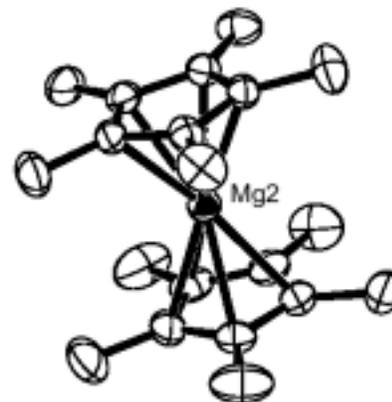
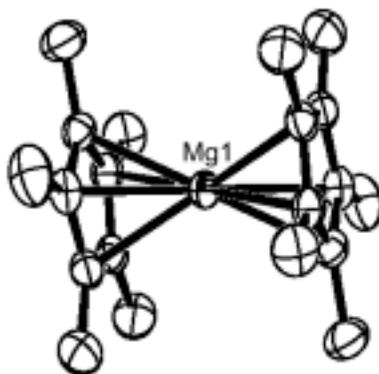
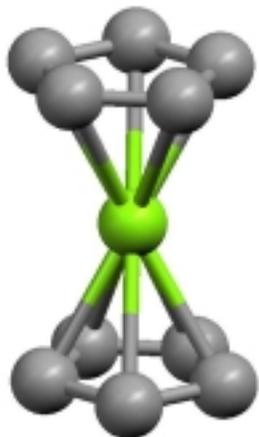


The alkali metal metallocenes are useful metathesis reagents for making other metallocenes. Similarly, the alkaline earth metallocenes are useful reagents for the synthesis of other metallocenes however the structural properties of some of the group 2 compounds are quite different than those of the group 1 metallocenes. The heavier analogues are highly ionic and contain large cations, thus they can also form polymeric structures similar to those found for the heavier group 1 metallocenes.

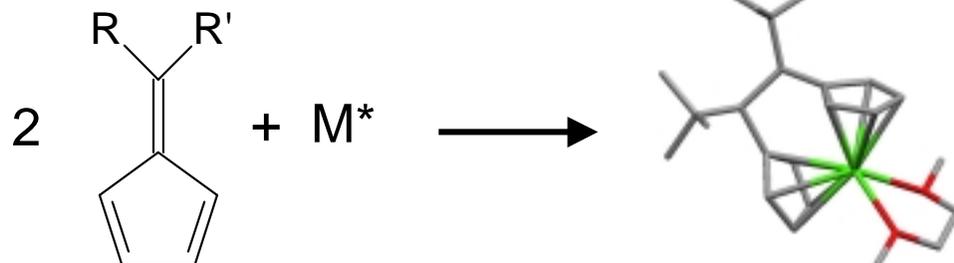




If the cations are relatively small or the bulk of the steric bulk of the substituents on the Cp' ligand are large enough, the structures of the group 2 metallocenes have parallel ring D_{5d} or D_{5h} structures similar to those of the first row transition metal metallocenes.

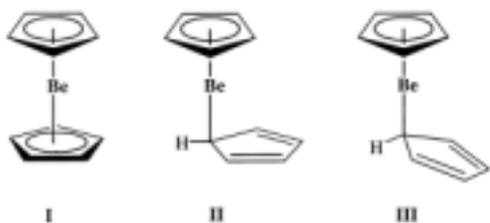


Ansa-metallocenes contain a bridge that connects two Cp' groups. Such ligands enforce a bent geometry and are useful for many types of transition metal catalysts. Some types of these ligands can be made from the reaction of fulvenes with metal atoms:

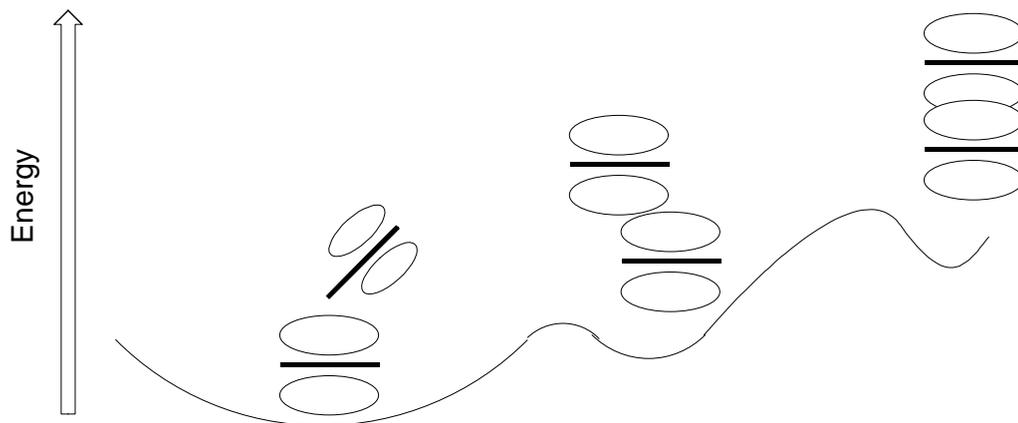
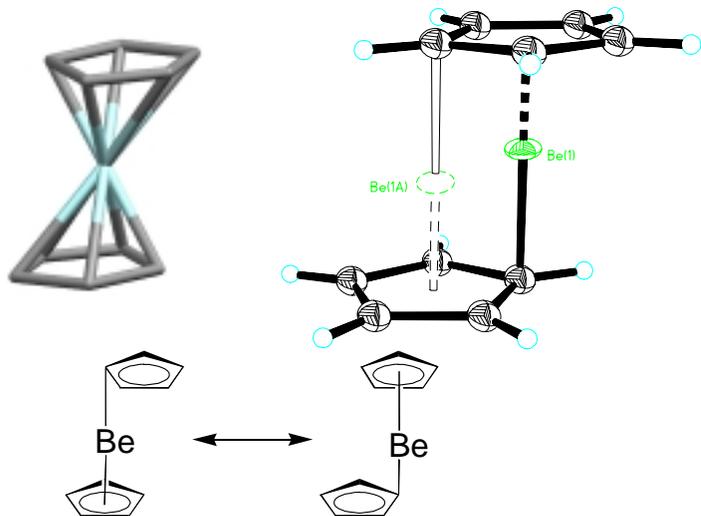




Beryllocenes have some of the most bizarre structural features of any of the metallocenes in the periodic table (at least at first glance). The primary reason for this is the very small size of the Be^{+2} ion. The parent beryllocene, Cp_2Be , has a structure unlike that of any other main group metallocene.



The “slipped-sandwich” structure is also observed in solution (proven by dipole moment measurements) and in the gas phase (electron diffraction).

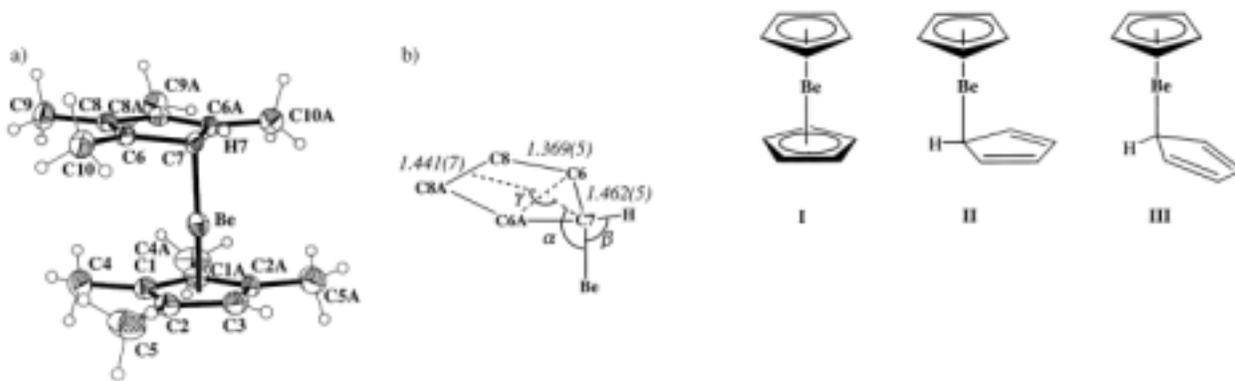


The rings are offset to avoid repulsion between the p-clouds of the Cp rings. The small size of Be^{+2} would require an inter-ring distance of around 3.0 \AA in a $D_{5d/h}$ structure, which is smaller than the 3.35 \AA inter-plane distance in graphite.

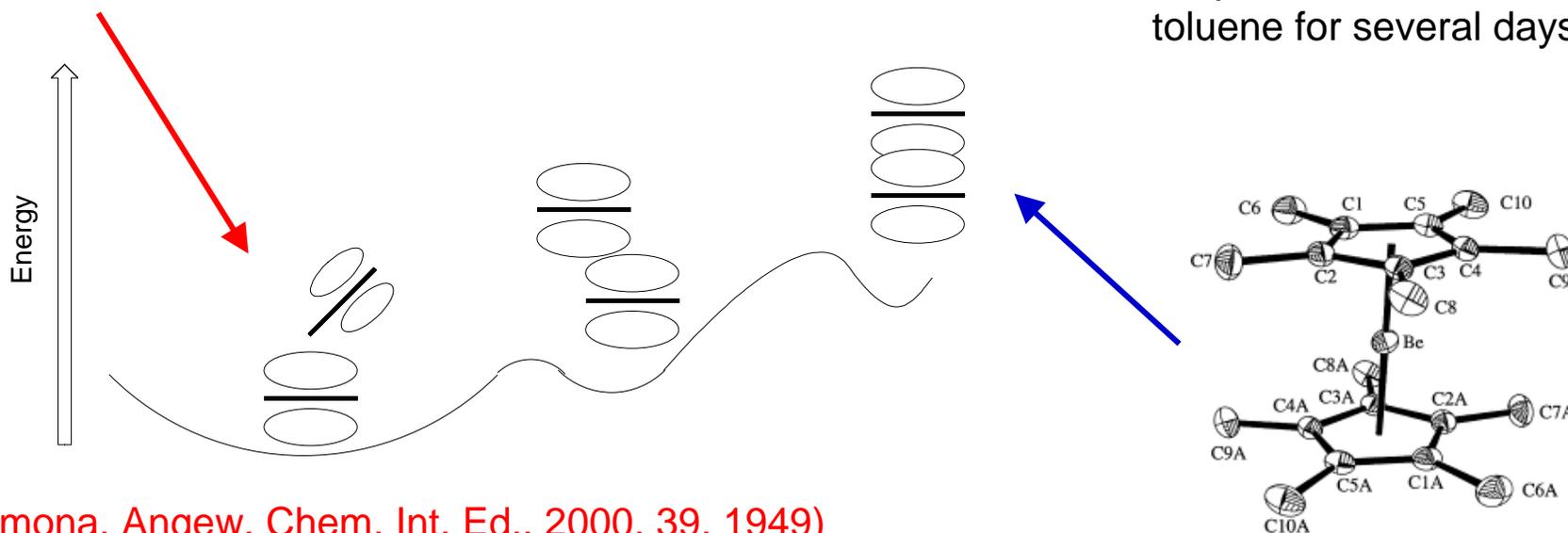
(See: Wong, *Acta. Cryst. Sect. B.*, 1972, 28, 1662;
Nugent, *Aust. J. Chem.*, 1984, 37, 1601,
Haaland, *J. Chem. Phys.* 1964, 40, 3434 and many
more papers listed in Jutzi's review)



Because of the shallow potential energy surface for beryllocenes, changes in the steric requirements of the Cp' ligands cause changes in the observed geometries.



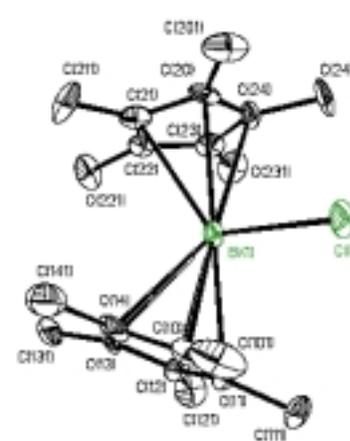
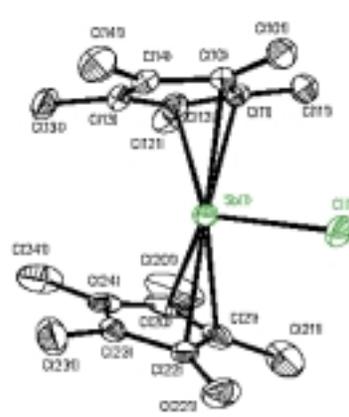
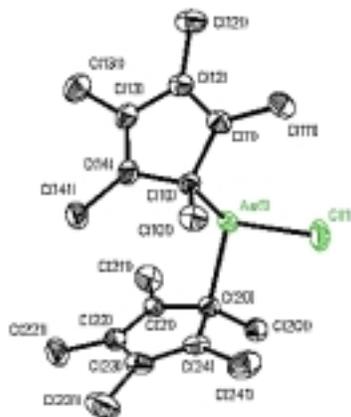
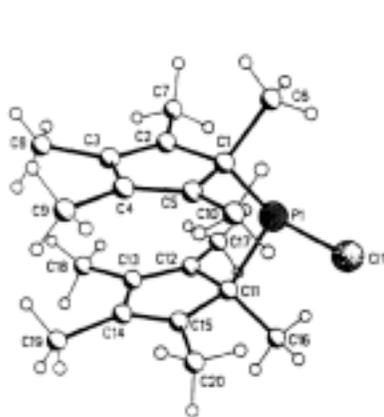
Ligand-ligand repulsion and the gear-like shape of the C₅Me₅ group forces a near D_{5d} structure for Cp*₂Be. One must use extreme conditions to force both rings onto the Be atom: 2 Cp*K and reflux in toluene for several days.





In contrast to the s-block cyclopentadienyl compounds, those of the p-block have a greater amount of covalent bonding. This is exemplified by the metallocenes of group 15 (Jutzi, *Angew. Chem., Int. Ed.*, 1983, 22, 250; Niecke, *Bull. Soc. Chim. Fr.*, 1997, 134, 1039; Cowley, *Can. J. Chem.*, 2002, 80, 1518).

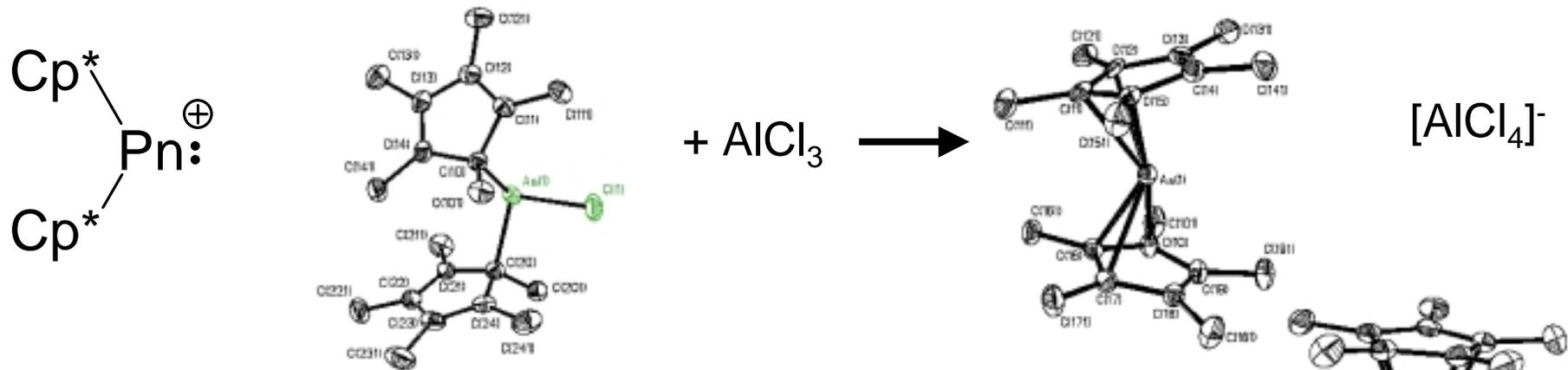
The neutral compounds have σ -bonded Cp* rings in the solid state for P and As, however only one signal is observed in the ^1H NMR spectrum for As in solution because of rapid 1,2-migrations.



In contrast, the Sb and Bi analogues have π -bonded Cp* rings in the solid state. Again, this is a consequence of the size of the larger atoms and their larger coordination spheres.

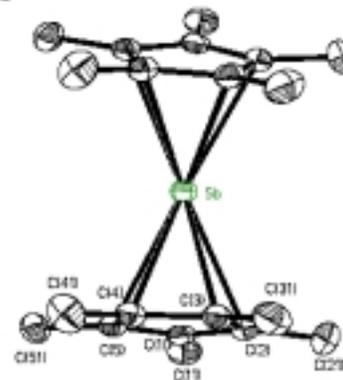
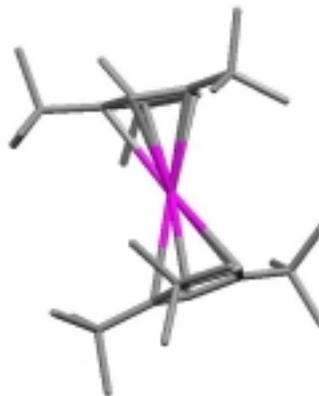
Chem 59-651 **P-block Cyclopentadienyl Compounds**

For As, Sb and Bi, the cationic metallocenes are readily made by halide abstraction using a strong Lewis acid or by metathesis reactions.



Note that these hydrocarbon substituted pnicogen ions are stable because of the combined σ - and π - donor properties of the η -bonded Cp' ligand.

For Sb and Bi, if the substituents on the ring are large enough, the rings become almost parallel. This is a manifestation of the “inert s-pair” effect.

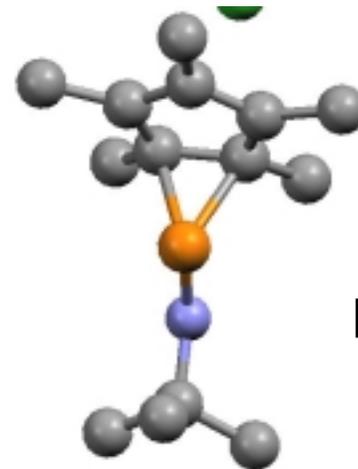
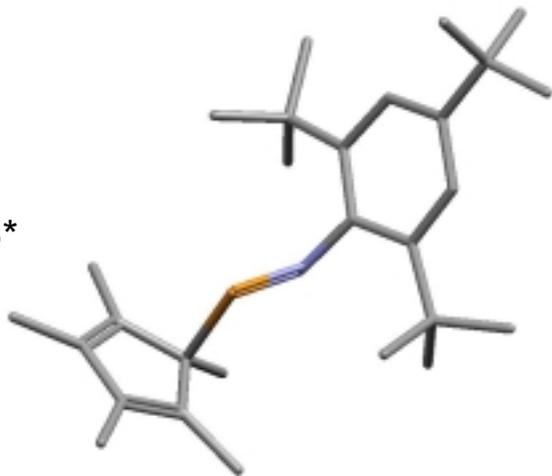


To date, no nitrenium or phosphenium cations of this type have been synthesized.



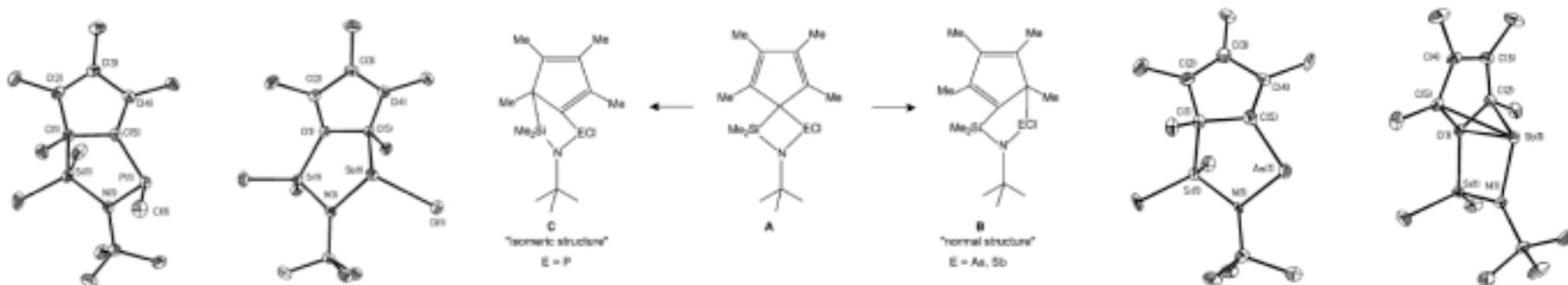
In fact, there are only a couple of examples with π -bonded Cp' groups to P atoms and they are both Cp* ligands (Niecke, JACS, 1992, 114, 8857; Niecke, JCS, Dalton Trans, 1989, 693).

Mes*N=PCp*



[tBu(H)N-PCp*]⁺

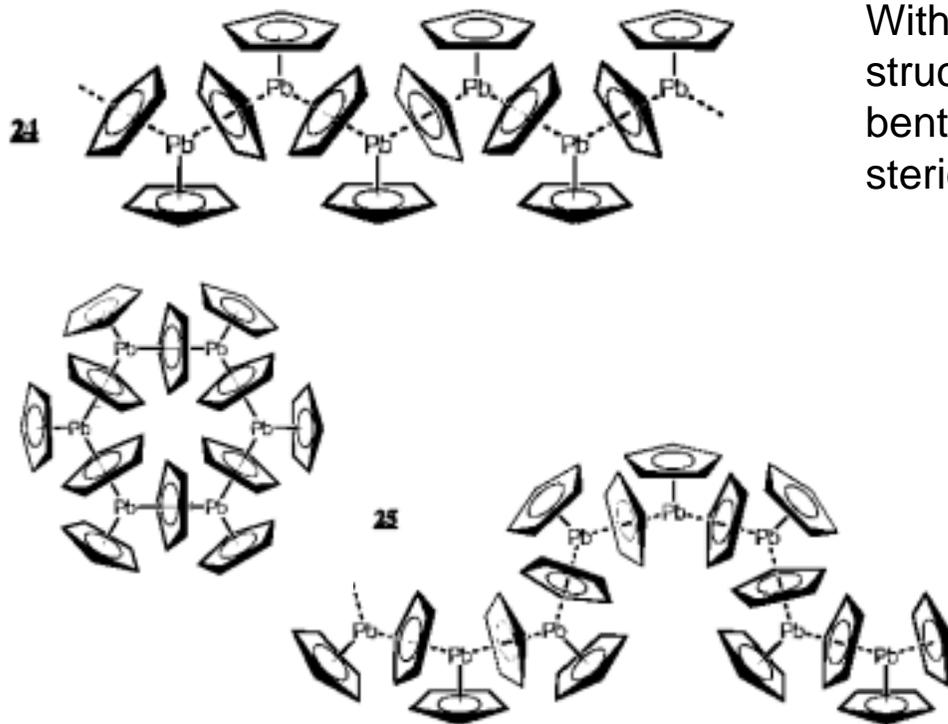
Some recently reported results suggest that π -bonding from Cp groups to P atoms is actually unfavourable and is only stable if possible rearrangement pathways are blocked (Cowley, Chem. Comm., 2003, 430).



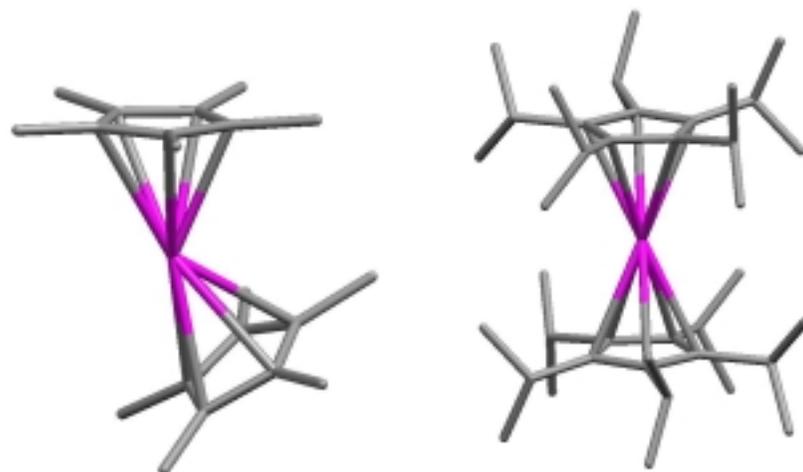


The metallocenes from group 14 have been studied extensively. If the group 14 element is in a high oxidation state, the compounds are generally sigma bonded (and the elements often act as a bridge connecting two Cp' groups). The compounds containing low oxidation state group 14 elements have a greater tendency to have π -bonded Cp' groups.

The Pb compounds are often polymeric or oligomeric in the solid state because of the large size and low electronegativity of the atom, as we saw for the heavy s-block compounds.

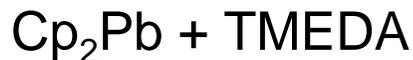


With substituted Cp' groups, monomeric structures are obtained. These can have either bent or parallel ring structures depending on the steric demands of the ligand.

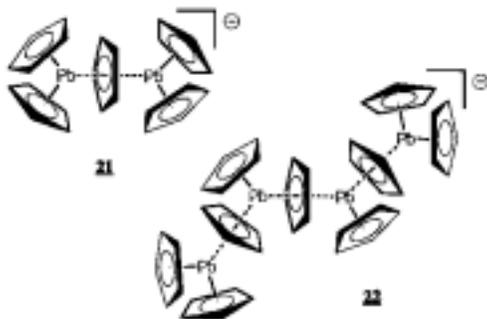




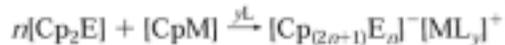
For the plumbocenes with just Cp groups, monomeric species can be obtained by adding Lewis bases. This perhaps surprising observation is another manifestation of the “inert s-pair” on the heavy atom.



This concept can be used to isolate oligomeric anions of Pb and Sn. The Lewis bases in these cases are just more Cp anions ([Wright, Organometallics, 1999, 18, 1148](#)).



These results illustrate the importance of non-coordinating cations and the need for complementary anion and cation sizes.



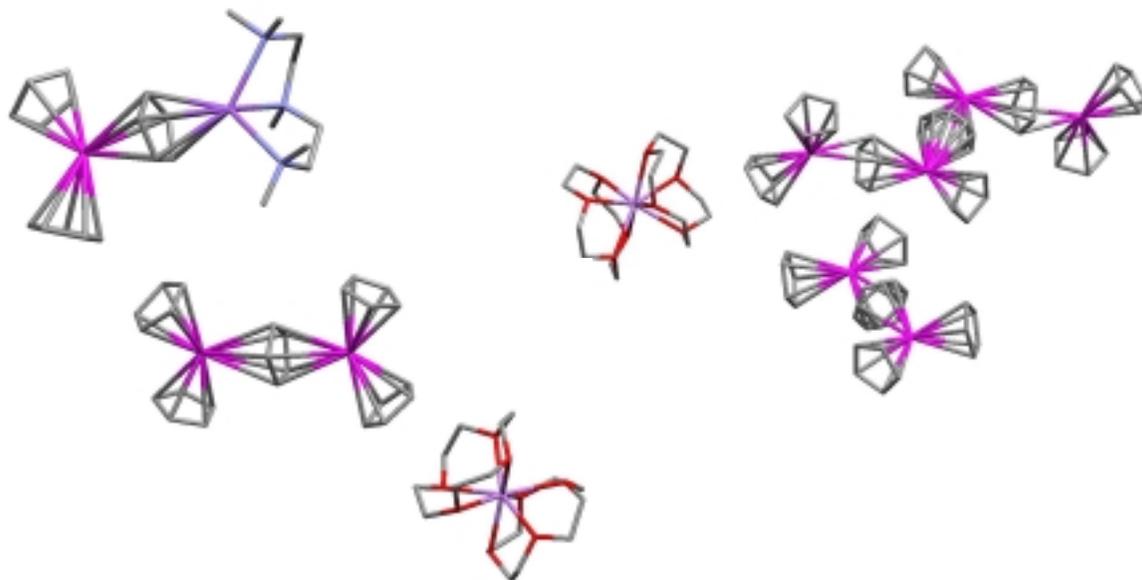
E = Pb ($n = 3$), M = Li, L = 12-crown-4 ($y = 2$) (1)^a

E = Sn ($n = 1$), M = Li, L = 12-crown-4 ($y = 2$) (2)

E = Pb ($n = 1$), M = Na, L = 15-crown-5 ($y = 1$) (3)

E = Pb ($n = 2$), M = K, L = 2,2,2-crypt ($y = 1$) (4)

E = Pb ($n = 2$), M = Cs, L = 18-crown-6 ($y = 1$) (5)

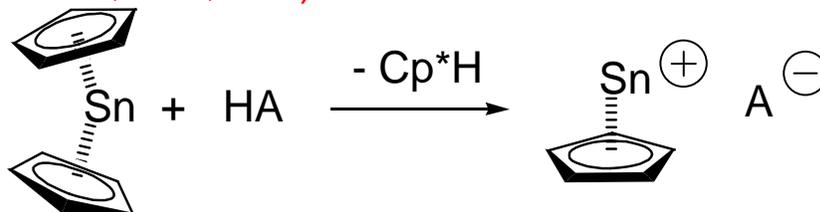


^a The empirical formula of 1, $[\text{Cp}_3\text{Pb}][\text{Li}(12\text{-crown-4})]$, suggests the presence of the $[\text{Cp}_3\text{Pb}]^-$ anion. However, the structural formula is $[\text{Cp}_2\text{Pb}]_2[\text{Cp}_3\text{Pb}][\text{Li}(12\text{-crown-4})]_2$.



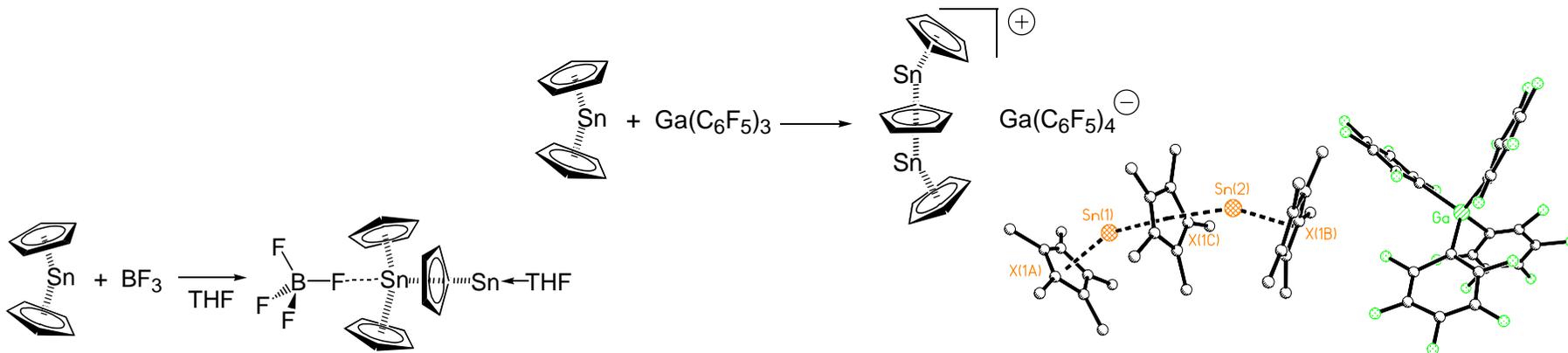
Tin analogues do not display the same tendency to oligomerize and shows the same kind of Lewis acidity as the Pb compounds. One of the more prevalent kinds of reactions that works for dicyclopentadienyl Pb, Sn and Ge compounds is acidolysis of a Cp ligand to form half-sandwich cations

(E.g. Jutzi, *Chem. Ber.*, 1980, 113, 757).



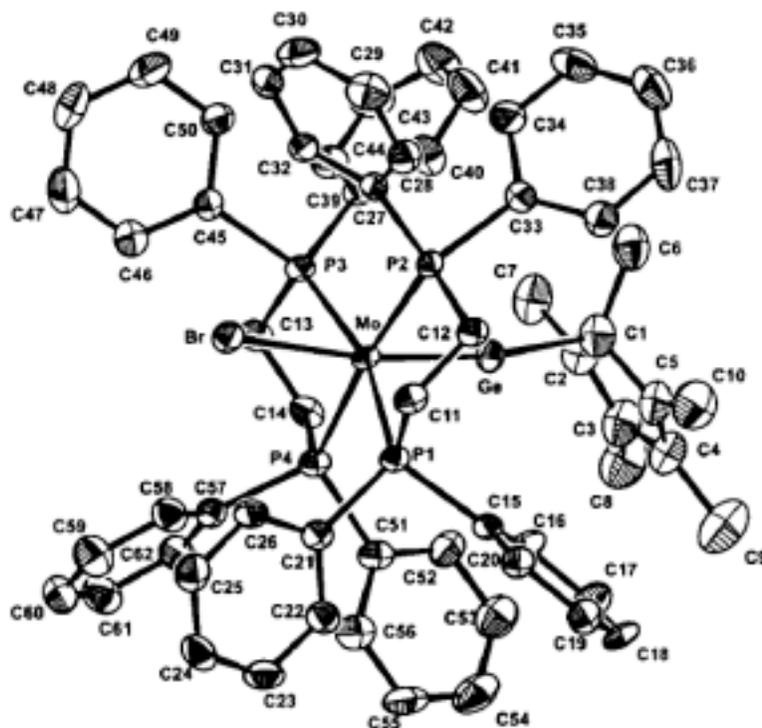
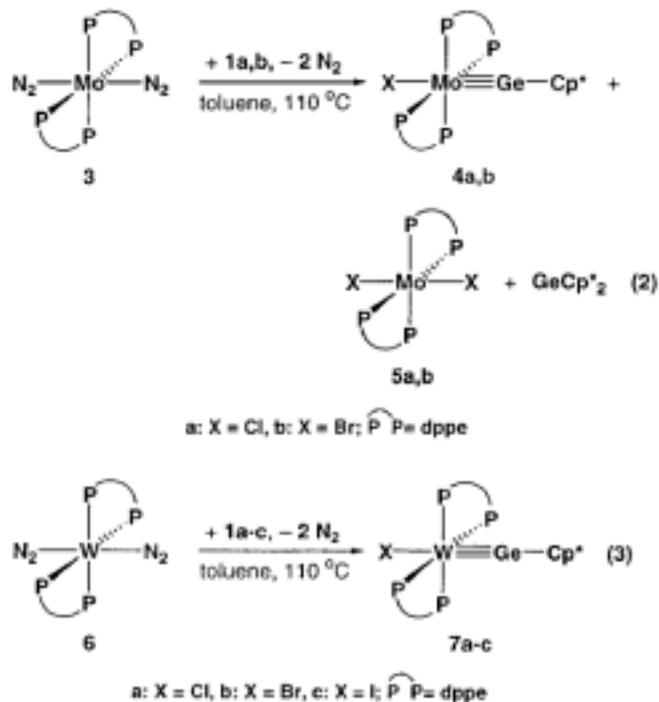
This is a very useful reaction that also illustrates a significant difference between many of the main group metallocenes and those of the transition metals: the HOMO in most of the main group metallocenes is based on the ligand and not on the metal.

Such reactions can be used to build cationic multi-decker sandwich compounds (Cowley, *Chem. Comm.*, 2001, 175) if appropriate anions are used.





Analogous half-sandwich germanium cations, generated by “oxidative addition” reactions to transition metal fragments were used to make rare transition metal≡Ge triple bonds (Filippou, *Angew. Chem., Int. Ed.*, 2000, 39, 2778; Filippou, *Organometallics*, 2002, 21, 653).

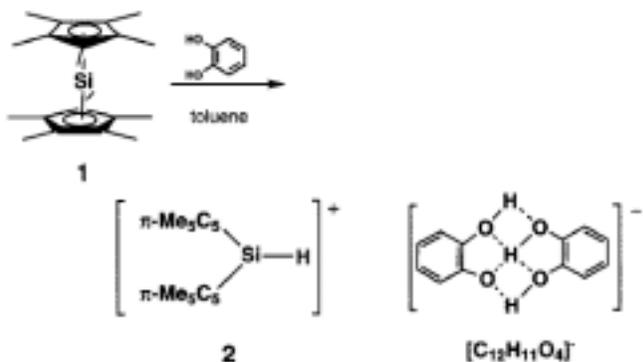
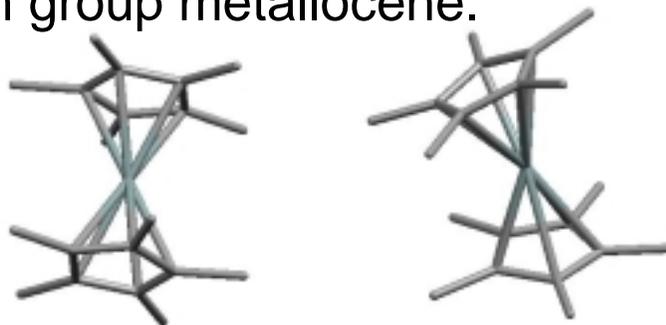


The Cp* ring is clearly σ -bonded to the Ge atom and the geometrical parameters around the Ge atom are consistent with the formulation of these compounds as having triple bonds. These results are in stark contrast to the Group 13 analogues.

Chem 59-651 P-block Cyclopentadienyl Compounds

The only π -bonded metallocene for silicon is Cp^*_2Si (Jutzi, *Angew. Chem., Int. Ed.*, 1986, 25, 164) and it is an odd main group metallocene.

Cp^*_2Si has both bent and ring-parallel forms in the same crystal structure. In this case, the parallel ring structure is not because of an "inert s-pair" and must be caused by the small size of Si.



In contrast to the heavier analogues, Cp^*_2Si can be protonated at Si to make rare silylium cations.

Cp^*_2Si , related Cp^*Si compounds and the Ge analogues can be used as sources for Si and Ge films and materials using CVD and other deposition/decomposition methods (see: Jutzi, *Chem. Vap. Dep.*, 2000, 6, 63; *JOMC*, 2001, 620, 20).

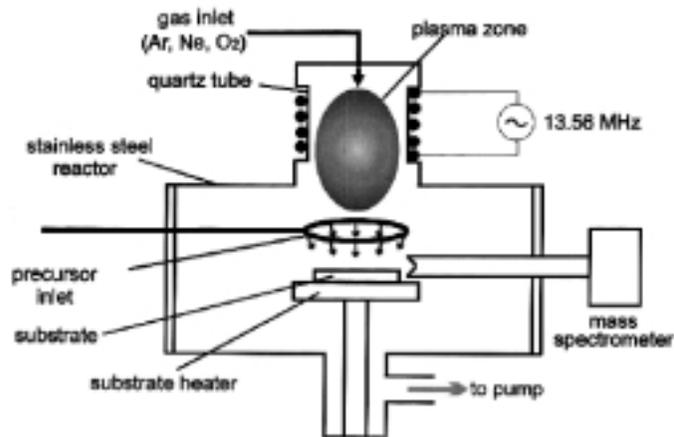
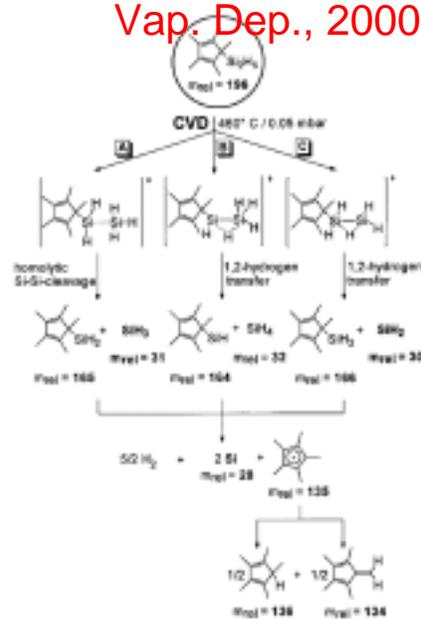
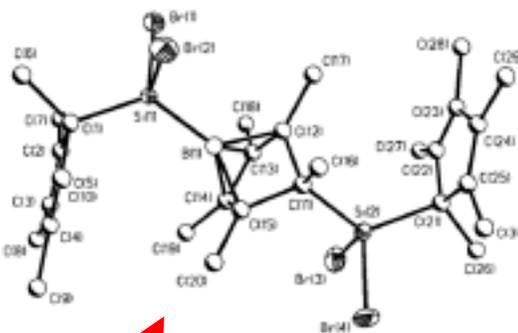
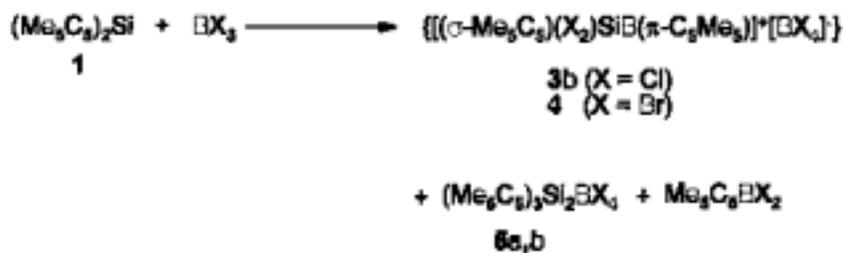
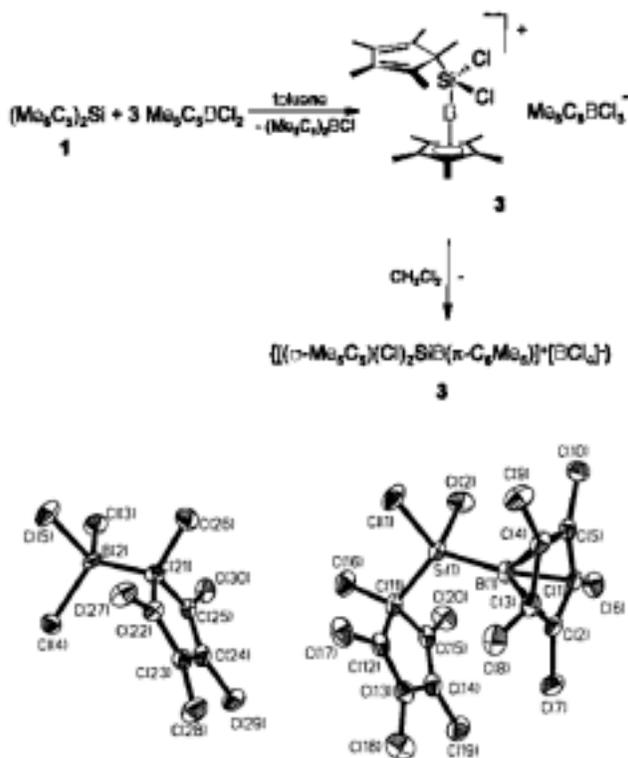


Fig. 3. Remote plasma-enhanced MOCVD reactor.

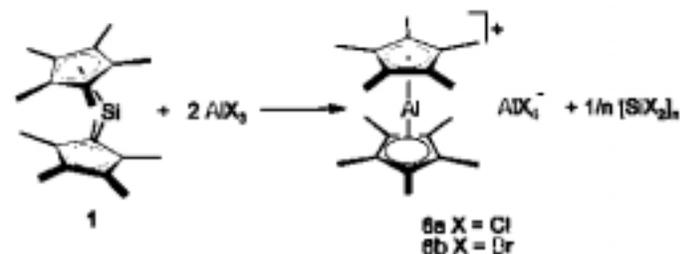


Cp^*_2Si is a very reactive metallocene and has a rich insertion and oxidation chemistry with main group and transition metal compounds. In almost every case, the reactions are driven by the need for the Si (II) to become oxidized to Si (IV). Here are some examples with group 13 compounds (Jutzi, *Organometallics*, 1999, 18, 5531):

Scheme 1

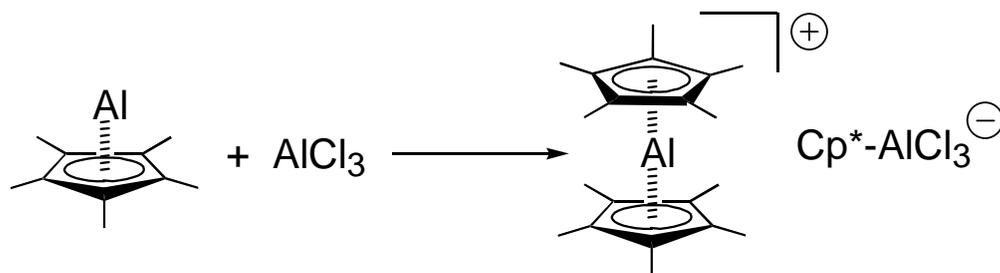


An odd $\eta^4\text{-Cp}^*$





The metallocenes from group 13 are some of the most useful metallocenes in the p-block and have an incredible diversity in the types of structures they adopt. The oxidation state of the group 13 element plays an important role in determining the structure and reactivity of the molecules. There are only a few M (III) compounds, but each of the analogues is remarkably different.



(Schnöckel et al. *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1655; Shapiro, *Organometallics*, 2000, 19, 3361)

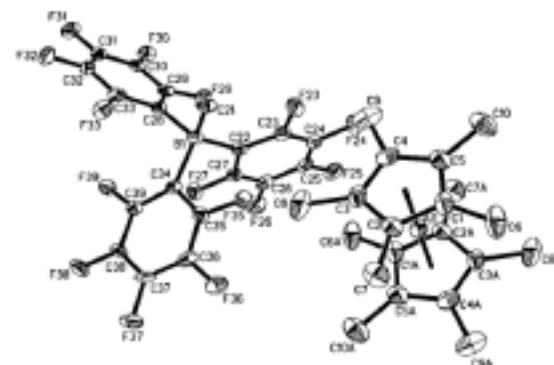
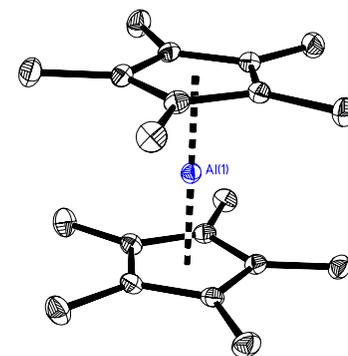
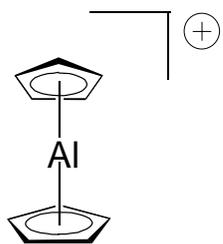


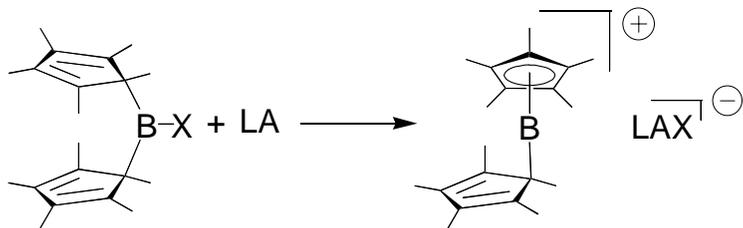
Figure 4. ORTEP drawing of the molecular structure of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Al}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$. Thermal ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity.



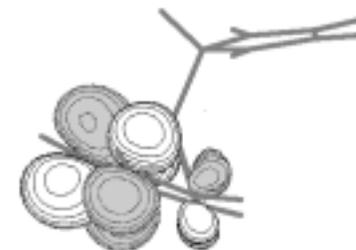
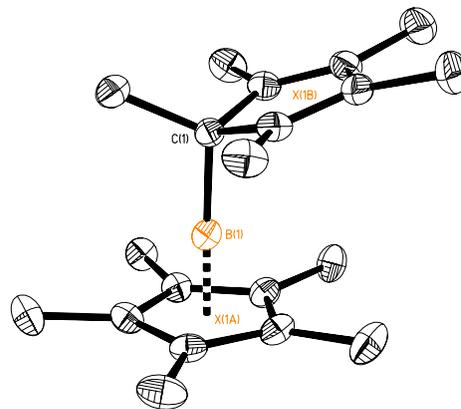
Bochmann found that the parent aluminocenium cation is an effective initiator for olefin polymerization (*Angew. Chem. Int. Ed. Engl.* 1996, 35, 2226) but it is only stable at low temperatures.



The B analogue was characterized by NMR (Jutzi, JOMC, 1978, 161, C5) and crystallography (Cowley, Chem. Comm., 2000, 911) and was the first metallocene to show the σ -Cp, π -Cp structure that had been predicted for beryllocene.

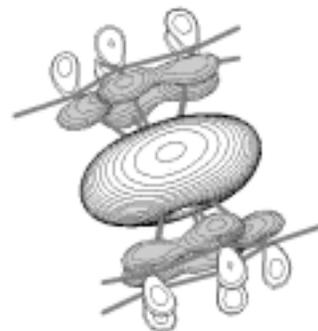
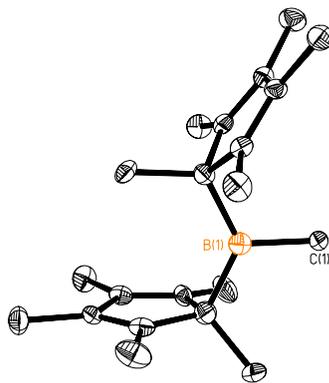
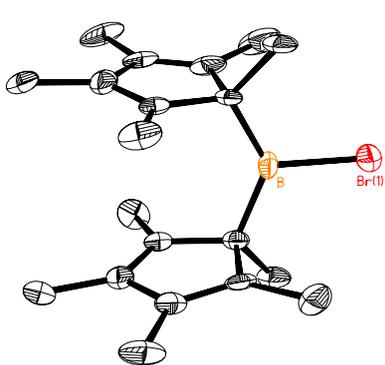


X = Cl	LA = AlCl ₃ , GaCl ₃	LAX = AlCl ₄ ⁻ , GaCl ₄ ⁻
X = Cl, Br	LA = LiB(C ₆ F ₅) ₄	LAX = B(C ₆ F ₅) ₄ ⁻
X = Me	LA = B(C ₆ F ₅) ₃ Ga(C ₆ F ₅) ₃	LAX = MeB(C ₆ F ₅) ₃ ⁻ MeGa(C ₆ F ₅) ₃ ⁻



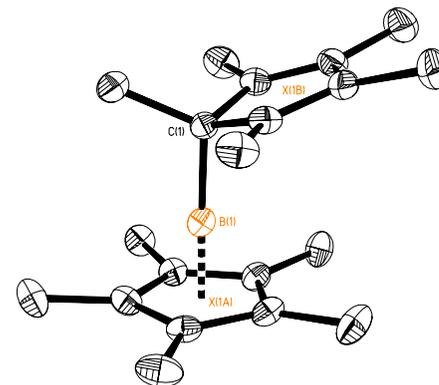
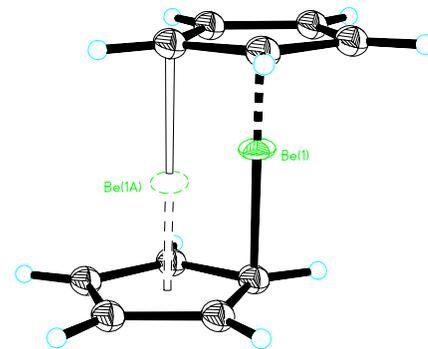
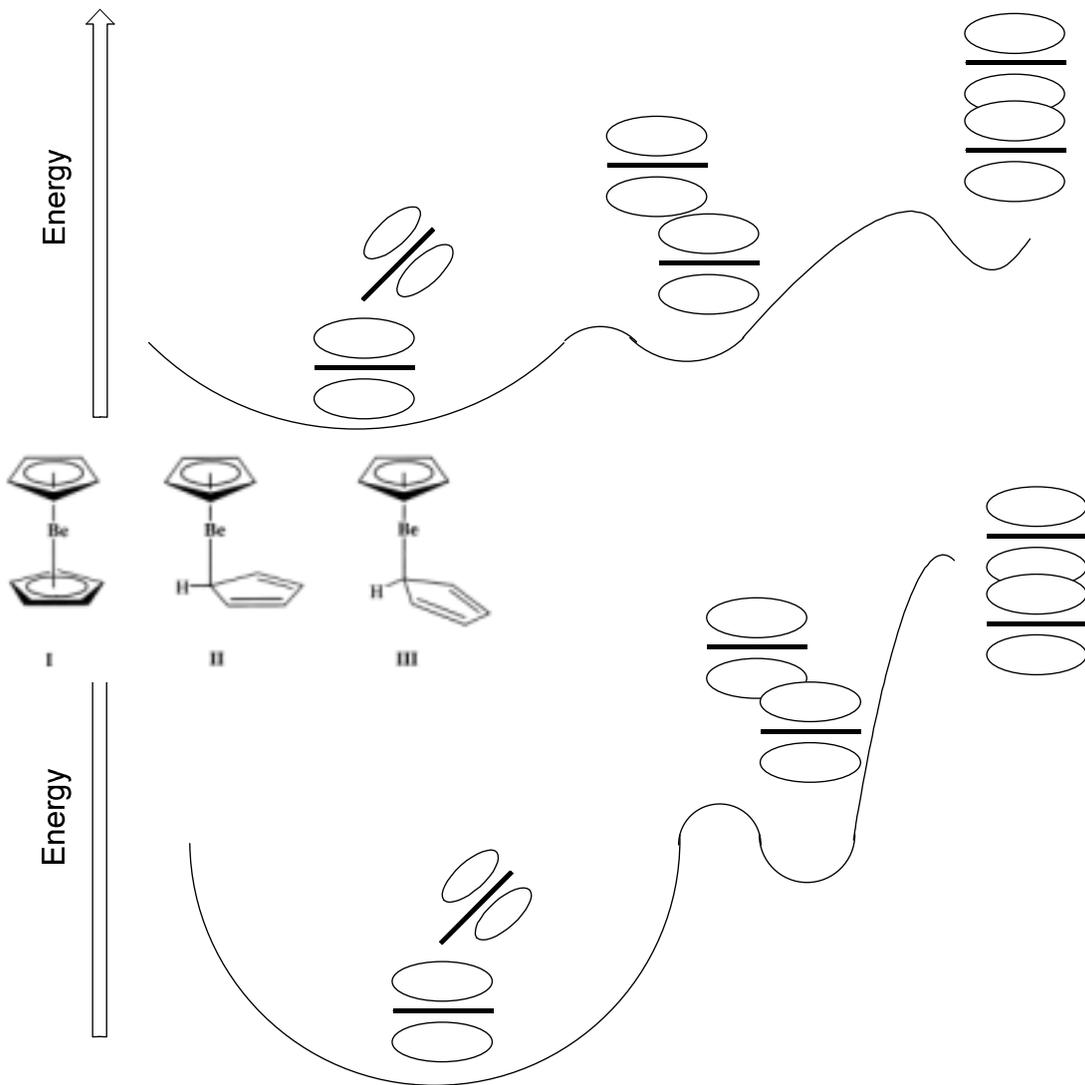
LUMO

This metallocene has the smallest ring-ring distance of any bis Cp' compound in the periodic table and it is not an effective initiator of olefin polymerization.

Cp₂Al⁺ LUMO

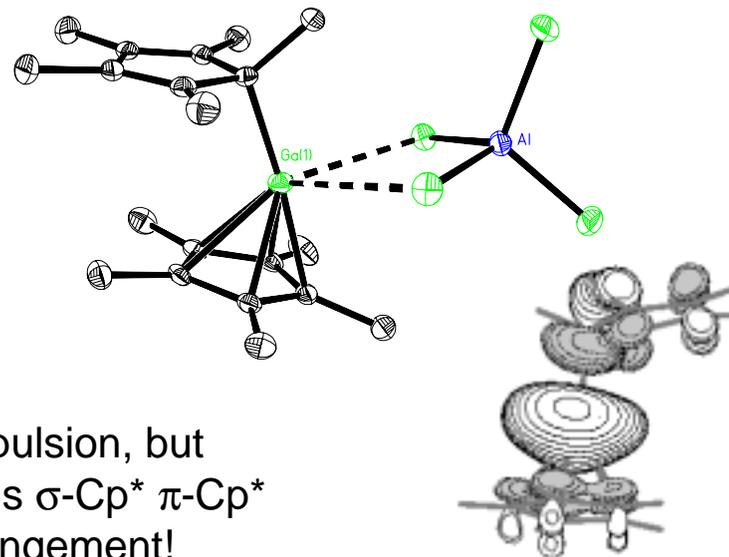
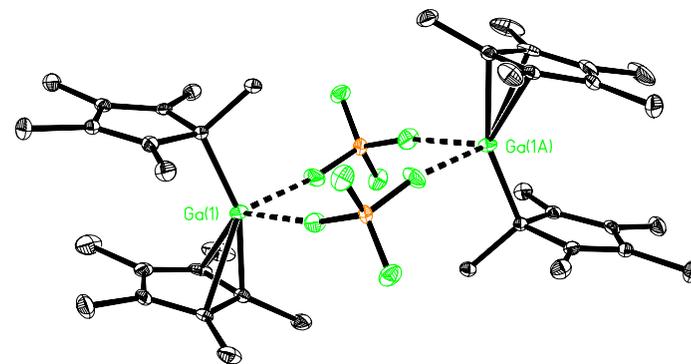
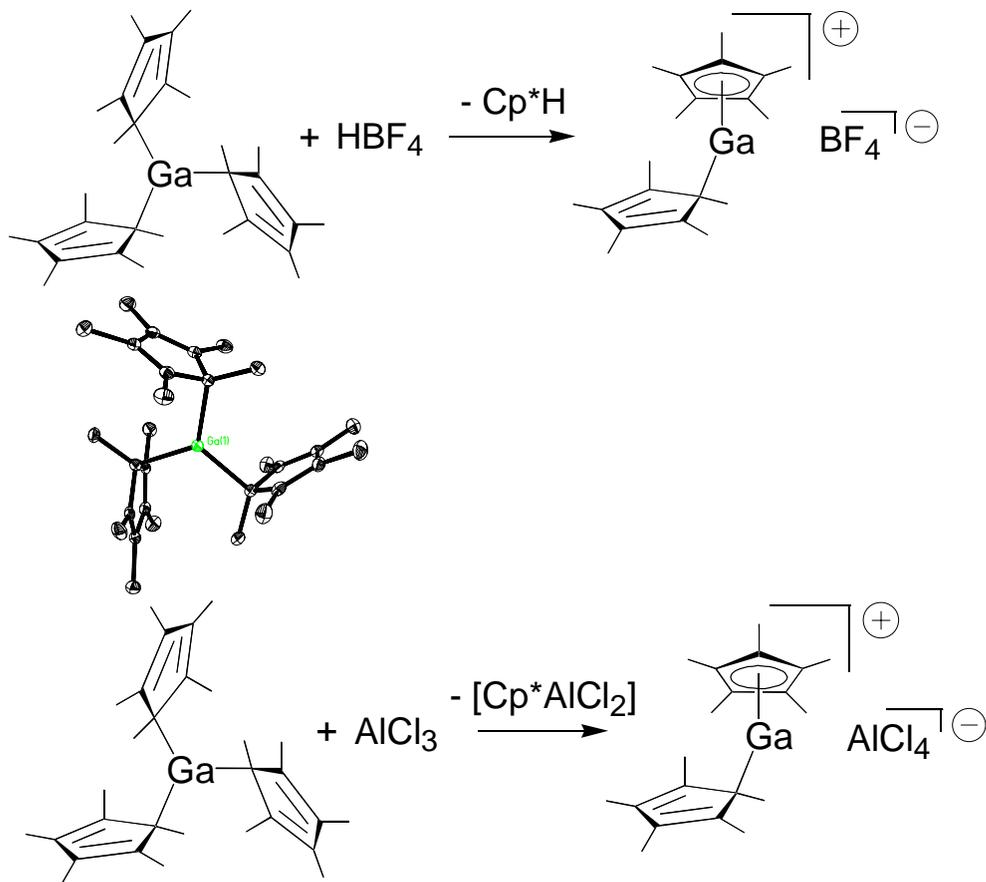


The higher effective nuclear charge and smaller size of B^{+3} vs. Be^{+2} makes for a steeper potential energy surface and requires the σ -Cp, π -Cp structure.





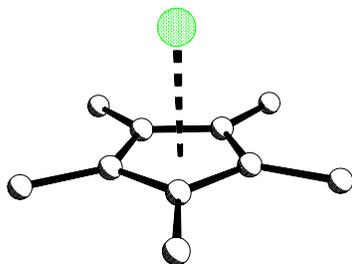
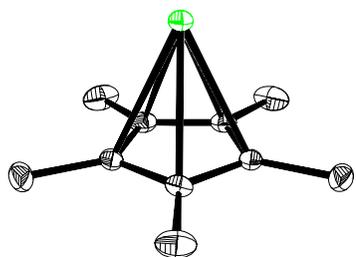
Cp* acidolysis with protic or Lewis acids works to give the desired salts. Surprisingly, the gallocenium cation also has a σ -Cp, π -Cp structure instead of the D_{5d} type structure of $Cp^*_2Al^+$ (Macdonald, JACS, 2000, 122, 11725).



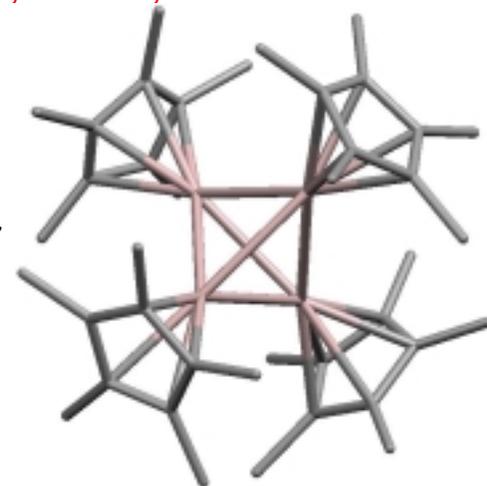
Cp^*_2Ga has this structure NOT because of inter-ring repulsion, but because it is more electronegative than Al. In effect, this σ -Cp* π -Cp* bonding is the covalent alternative to the bis- η^5Cp^* arrangement!



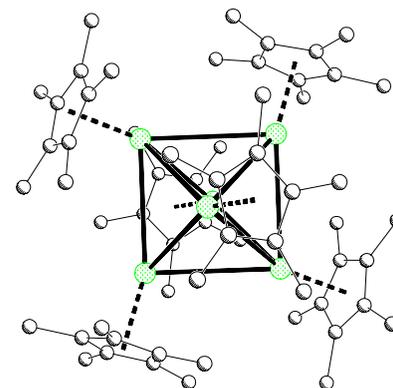
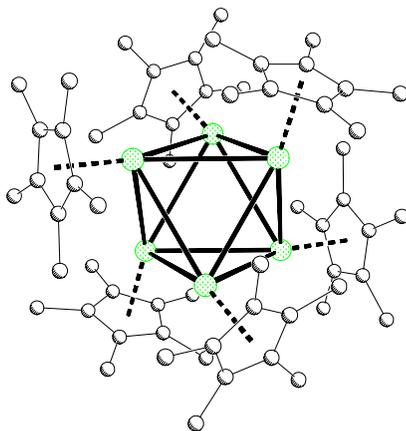
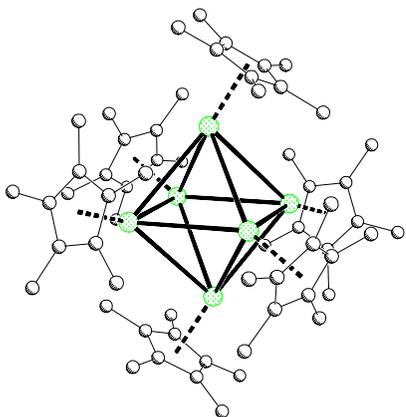
One of the most heavily investigated groups of main group cyclopentadienyl compounds are those of the group 13 elements in the +1 oxidation state. These compounds have the general formula Cp^*M and all of them are stable compounds except for boron (See: Macdonald, JACS, 1999, 121, 12113, and references therein).



Cp^*Al forms a tetrameric cluster in the solid state.



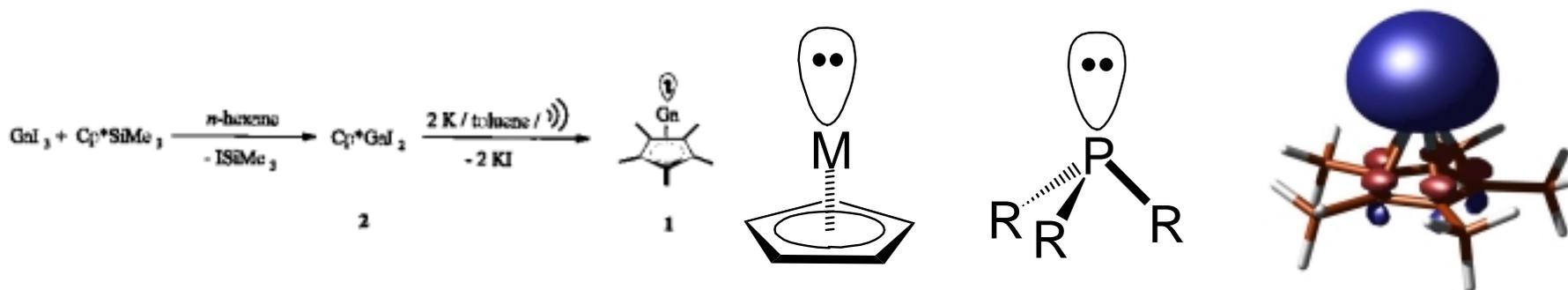
In the gas phase or solution the compounds are generally monomeric.



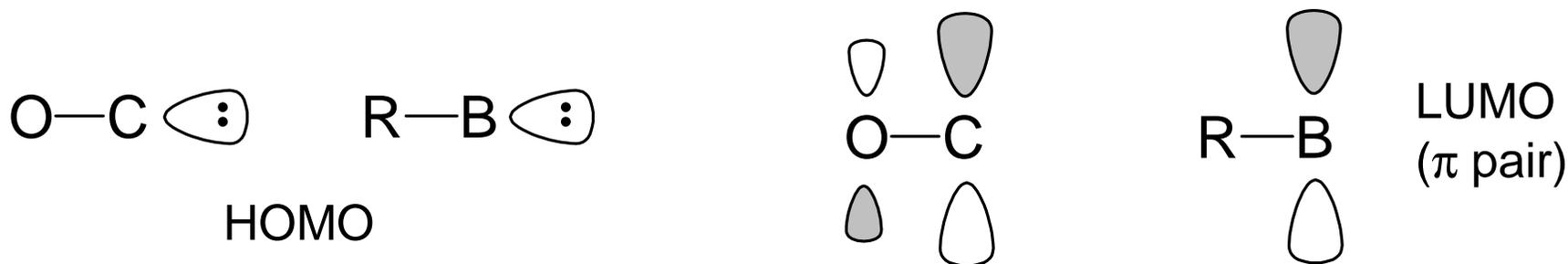
Cp^*Ga and Cp^*In form *isostructural* hexameric clusters with S_6 symmetry in the solid state - the structures are determined by the close packing of the ligands. Note that these clusters do not conform to Wade's rules that you would use for boranes.



The electronic structure of these half sandwich compounds provides a lone pair of electrons on the group 13 element - this means that the group 13 element can act as a donor (similar to phosphines) to Lewis acids. Note that this is a complete reversal of the usual group 13 reactivity and it is made possible by the stabilizing characteristics of the Cp* ligand.

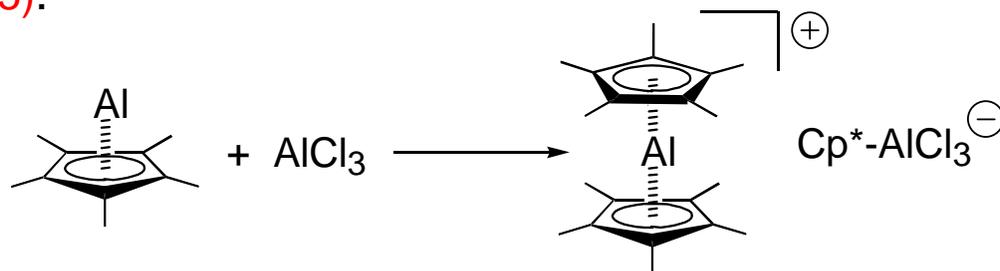


Furthermore, the HOMOs and LUMOs for ligands of the general form R-M are, in theory, analogous to those of CO ligands (the most common organometallic ligand) (Baerends, *Chem. Eur. J.*, 1998, 4, 210). Because of this similarity, the coordination chemistry of such compounds has been investigated in detail both experimentally and theoretically.

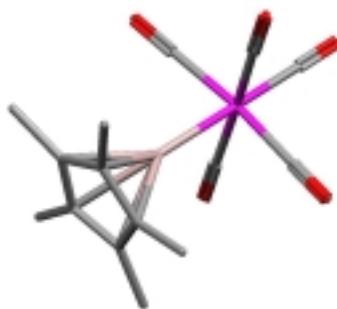
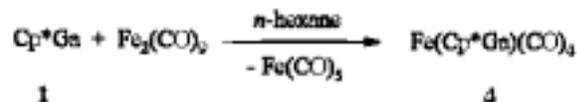
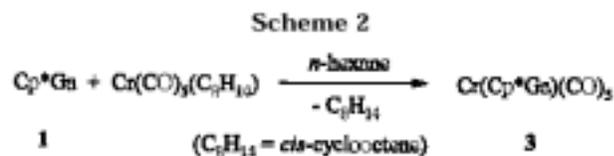




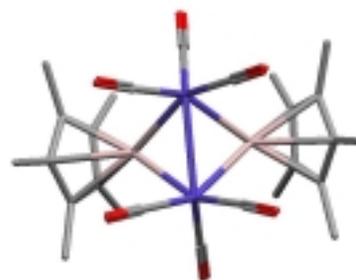
The first attempt to make a simple main group Lewis acid-base complex resulted in the oxidation of the univalent group 13 element (Schnöckel et al. *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1655).



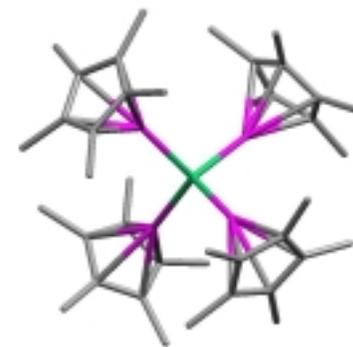
The first successful examples of coordination complexes with such ligands were obtained with transition metal fragments (Fischer and Weiß, *Angew. Chem. Int. Ed. Engl.* 1999, 38, 1655). Like CO groups, the R-M ligands can bond to the metals in either terminal or bridging modes. Numerous transition metal carbonyl complexes of Cp*M ligands have been isolated.



Cp*Al-Cr(CO)₅



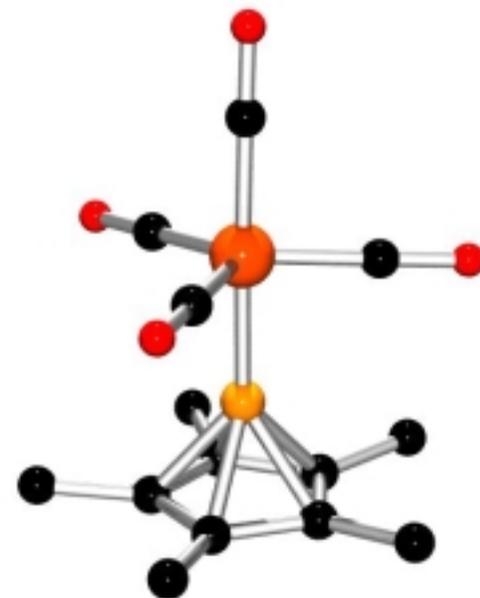
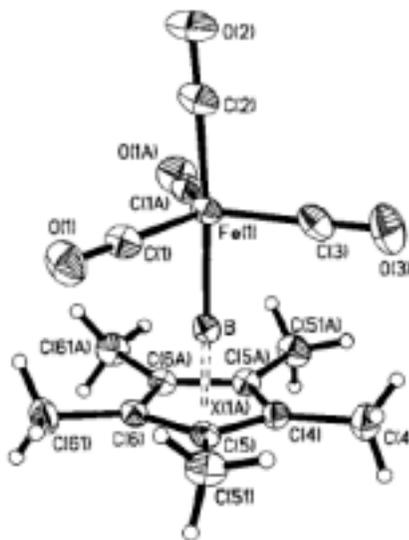
(Cp*Al)₂[Co(CO)₃]₂



Ni(AlCp*)₄



Generally unstable or inisolable molecules can often be obtained in the coordination sphere of a suitable transition metal. Using this strategy, Cowley prepared the first example of a univalent Cp'B fragment (Cowley, *JACS*, 1998, 120, 6401) by way of an *in situ* reduction of Cp*BCl₂.



Similar reactions have been used to make transition metal borylene complexes with various other types of substituents on the B atom, in particular, numerous R₂NB-TM complexes have been prepared (See: Braunschweig, *Coord. Chem. Rev.*, 2001, 223, 1).

Chem 59-651 P-block Cyclopentadienyl Compounds

The nature of the group 13 - transition metal bond has been debated intensively since Robinson's report of the first "ferrogallyne", which he proposed to have a Ga=Fe triple bond (Robinson, *Organometallics*, 1997, 16, 4511).

A number of Cp*Ga-TML_n complexes were subsequently synthesized (e.g. Jutzi, *Organometallics*, 1998, 17, 1305) that did not seem to be consistent with a Ga-TM triple bond.

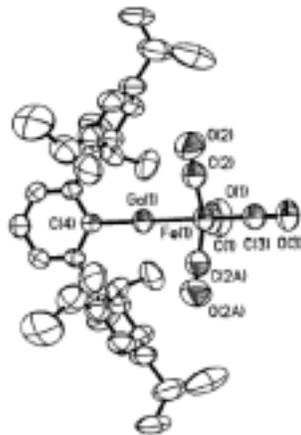
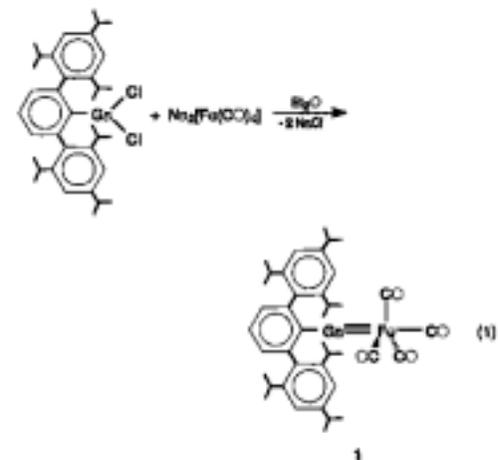


Figure 2. Molecular structure of Cr(Cp*Ga)(CO)₃, 3.

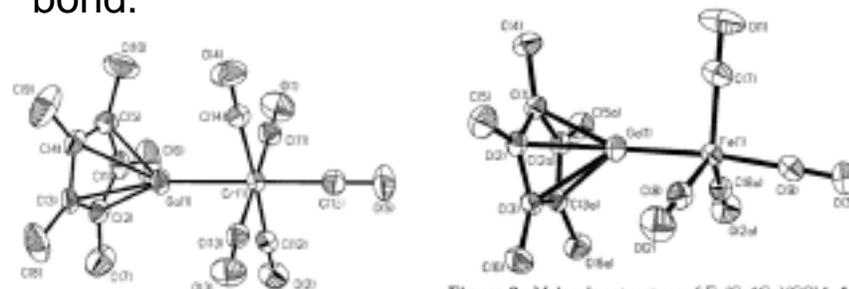


Figure 3. Molecular structure of Fe(Cp*Ga)(CO)₄, 4.

A triple bond in these cases would be composed of a σ -bond from the Ga to the Fe and two π -"back bonds" from the Fe to the empty p-orbitals on Ga (this is the Dewar-Chatt-Duncanson model of donor-acceptor interactions).



When R is Cp', the cyclopentadienyl group has already populated the vacant p orbitals on Ga and has thus raised the energy of the vacant orbitals. Because of this, the only bond between the Ga and the metals is the σ -bond from the Ga to the Fe.



The actual bonding is primarily ionic and depends strongly on all the ligands attached to the transition metal (See: Frenking, *Organometallics*, 2000, 19, 571).



Unlike the relatively inert Cp' groups in transition metal metallocenes, the Cp* groups attached to the group 13 elements are readily transferred to a metal to which they will make a stronger bond (e.g. Jutzi, *Organometallics*, 2000, 19, 1445).

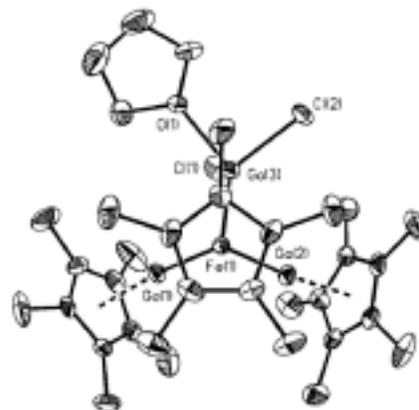
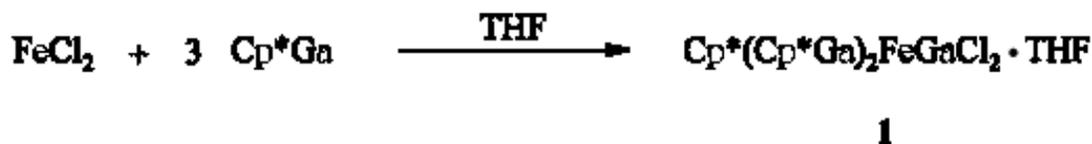


Figure 1. Molecular structure of Cp*(Cp*Ga)₂FeGaCl₂·THF (1).

Furthermore, because the group 13 element is in a low oxidation state, the Cp*M ligands can insert themselves into bonds. Such reactions are analogous to oxidative addition reactions that are common for low oxidation state transition metal organometallic species.

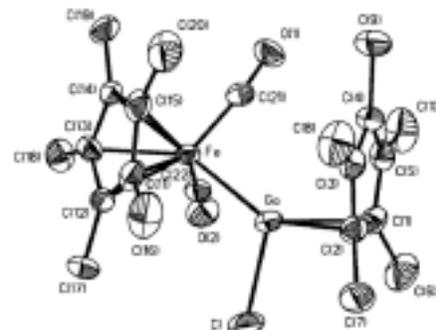
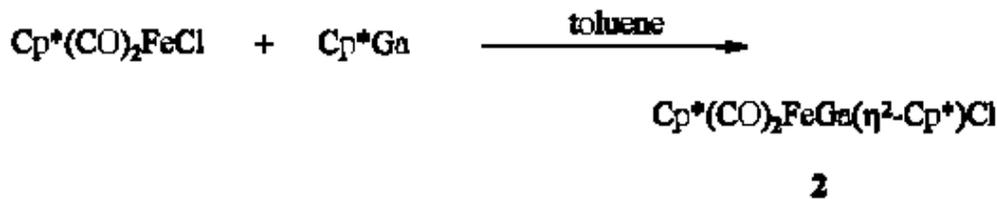
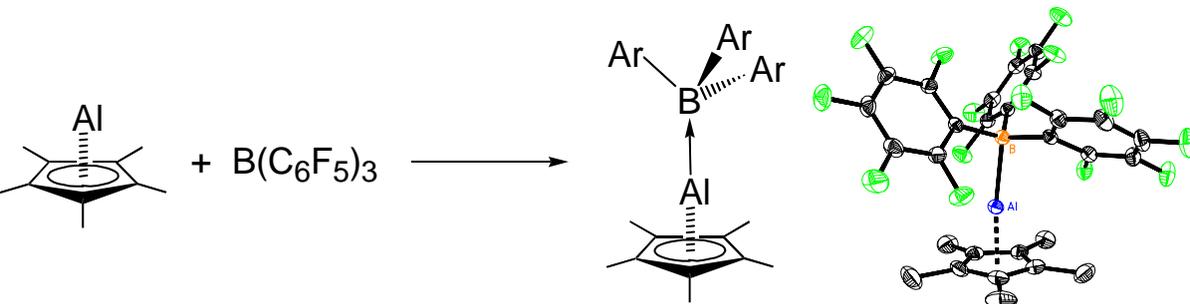


Figure 2. Molecular structure of Cp*(CO)₂FeGa(η²-Cp*)Cl (2).



Main group Lewis acids can also be used to complex Cp*M fragments in certain circumstances. The first example of such a complex was made with Cp*Al and the strong Lewis acid B(C₆F₅)₃ (Cowley, JACS, 2000, 122, 950).

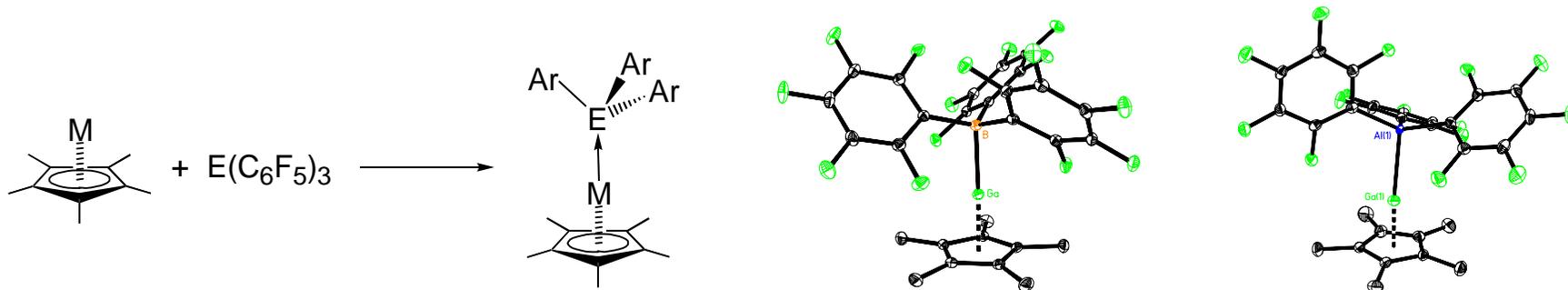


Sum of C-B-C angles: 339.8(6)^o

Ph₃P-B(C₆F₅)₃ Σ(C-B-C): 339.9(4)^o

(Erker, Organometallics 2000, 19, 3361).

Similarly, most of the other simple adducts of the form Cp*M-E(C₆F₅)₃ are accessible using similar reactions for M = Al and Ga.



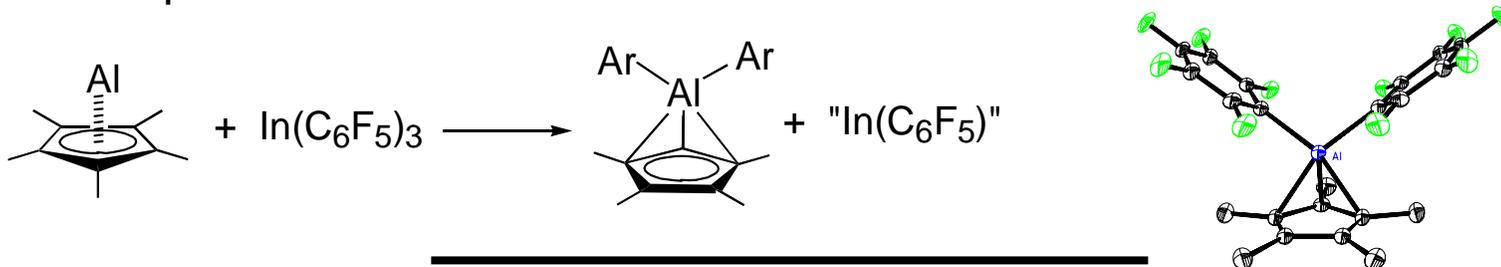
M = Al, Ga, In

E = B, Al, Ga, In

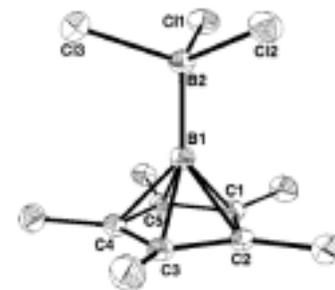
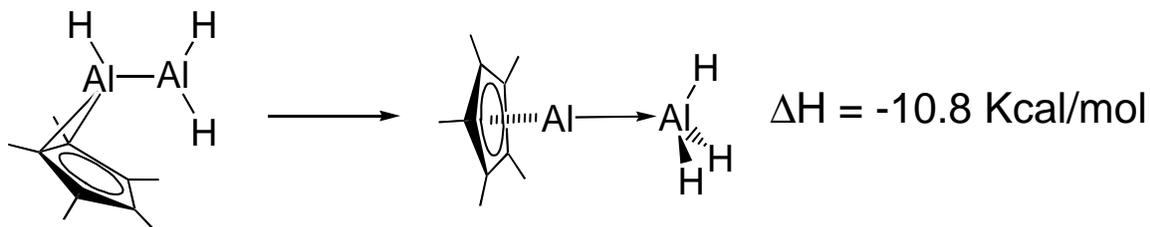
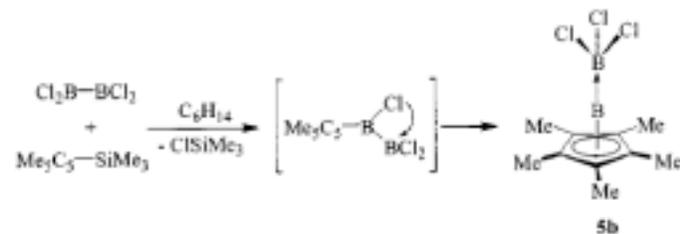
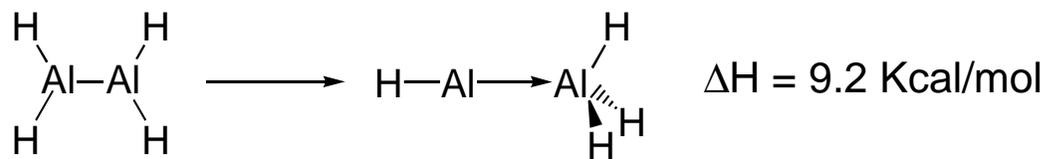
The results indicate that Cp*Al is a better donor than Cp*Ga, as one would predict.



One of the important observations regarding such compounds is that the relative stability of the oxidation states of the group 13 elements is important in determining the stability of the complex (Cowley, JACS, 2000, 122, 950). Since the stability of the +1 oxidation state increases down the group, it is only possible to make Cp*M-E(C₆F₅)₃ complexes if nM ≥ nE; otherwise, the complex will “disproportionate” to give compounds with a more stable distribution of oxidation states.



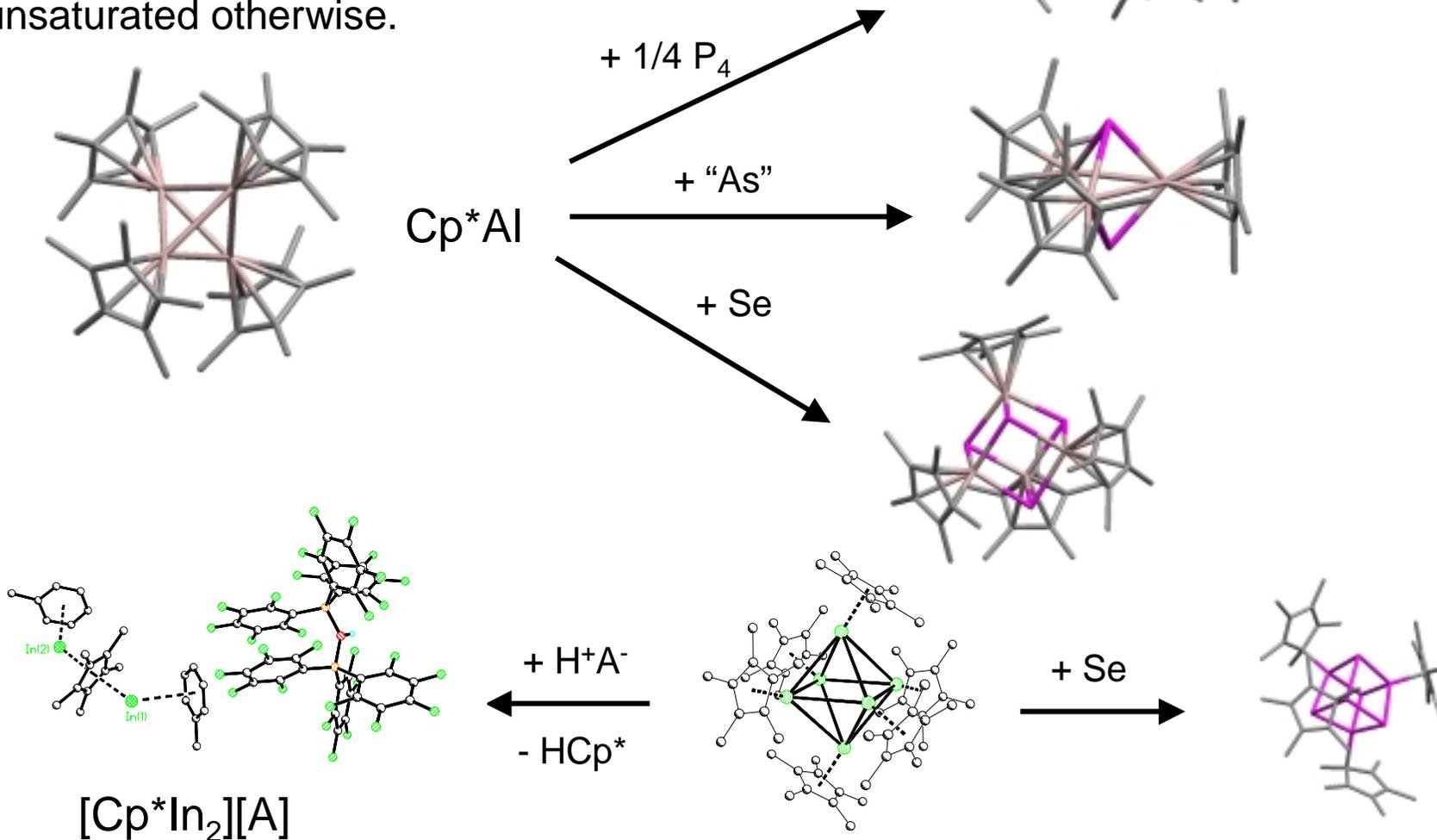
An important observation derived from these compounds is that the presence of Cp' groups actually changes the thermodynamic preferences of many chemical systems.



(Macdonald, Chem. Comm., 2001, 75; Frenking, JACS, 2002, 124, 7240; Jutzi, Eur. J. Inorg. Chem., 2000, 1927)

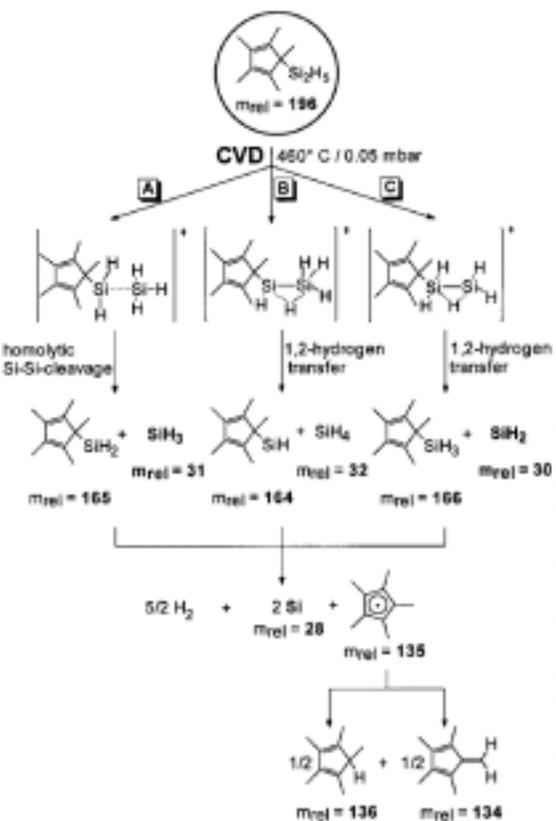


Low oxidation state main group Cp' compounds tend to form clusters. This trend is also evident in many of the compounds that they form when they become oxidized - especially if the compound would be unsaturated otherwise.



The ready cleavage of the Cp'-M bonds makes such compounds, and their main group or transition metal complexes, ideal reagents for MOCVD preparation of materials and films, as illustrated by the results in the review by Fischer (*Angew. Chem. Int. Ed. Engl.* 1999, 38, 1655). The complexed compounds can be considered "single source precursors" - these are compounds that contain the components of the desired material bonded together in a single compound.

As I indicated before, related Cp'Si compounds and the Ge analogues can be used as sources for Si and Ge films and materials using CVD and other deposition/decomposition methods (see: Jutzi, *Chem. Vap. Dep.*, 2000, 6, 63; JOMC, 2001, 620, 20). Similar results are also obtained for Al and Ga precursors (see: Jutzi, *Organometallics*, 2000, 19, 1292).



Scheme 1. Fragmentation pathways of $\text{Me}_2\text{C}(\text{SiH}_2)_2$.

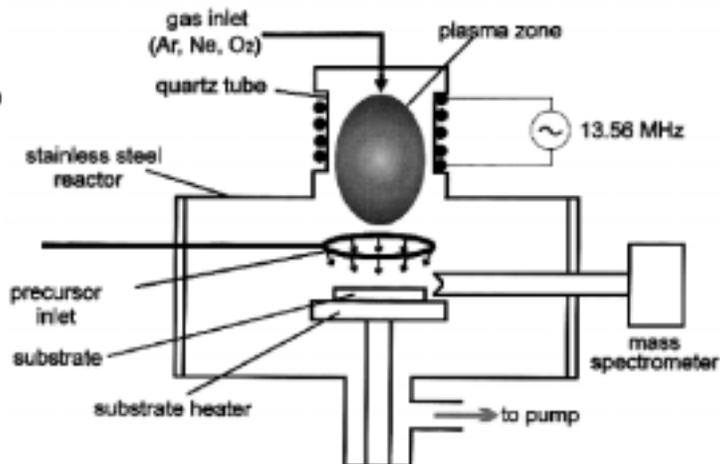
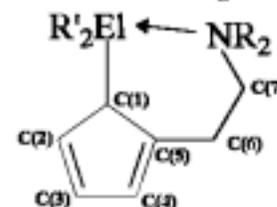
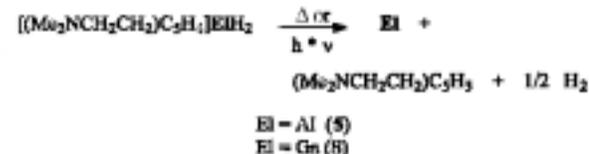


Fig. 3. Remote plasma-enhanced MOCVD reactor.

Scheme 3. Numbering Pattern



Scheme 4. Decomposition of 5 and 8 by MOCVD and Irradiation





Cp' metal compounds and related compounds can also be used for the "solvothermal" formation of nano-scale (particles and tubes) and bulk materials. Recent examples of such work has been described for In nanoparticles, nanotubes and In_3Sn nanowires (Chaudret, *Angew. Chem. Int. Ed. Engl.* 2001, 40, 448; *Angew. Chem. Int. Ed. Engl.* 2001, 40, 2984). The structure of the materials obtained depend on the experimental conditions and the templating agent that was used.

PVP = polyvinylpyrrolidone
 TOPO = trioctylphosphine oxide
 HDA = hexadecylamine

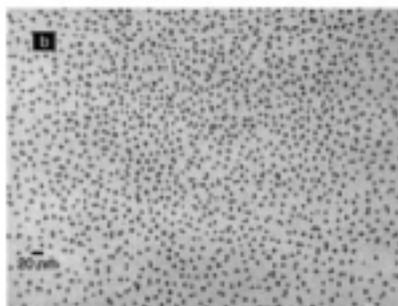
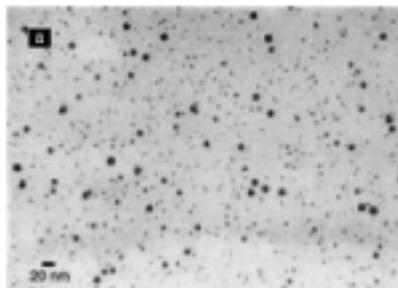


Figure 1. Transmission electron micrographs of indium particles in PVP a) in the absence of water (colloid 1), b) in the presence of traces of water (colloid 2).

Both are particles embedded in PVP polymer.

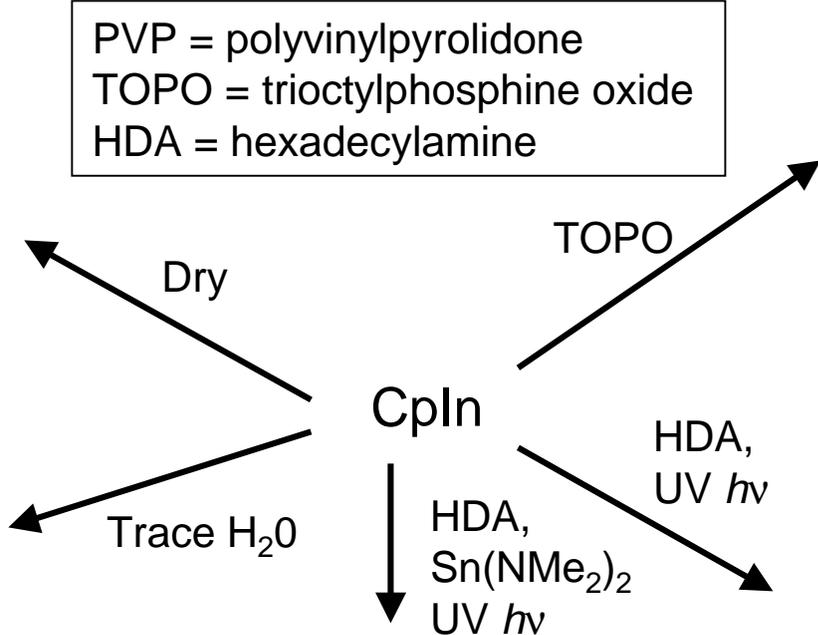


Figure 3. TEM micrograph of In_3Sn nanowires prepared in the presence of HDA.

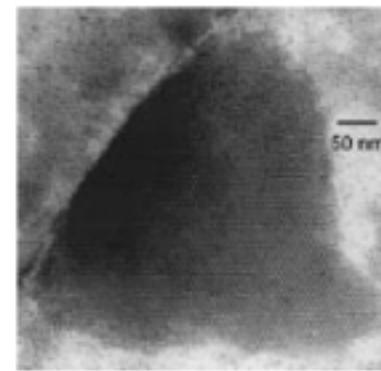


Figure 4. Ordered arrays of colloid 3.

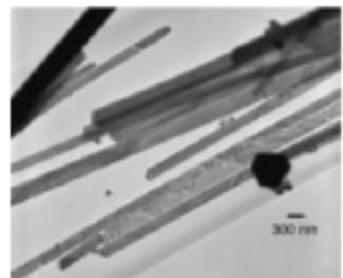
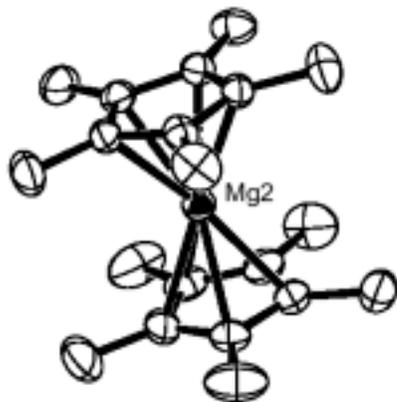


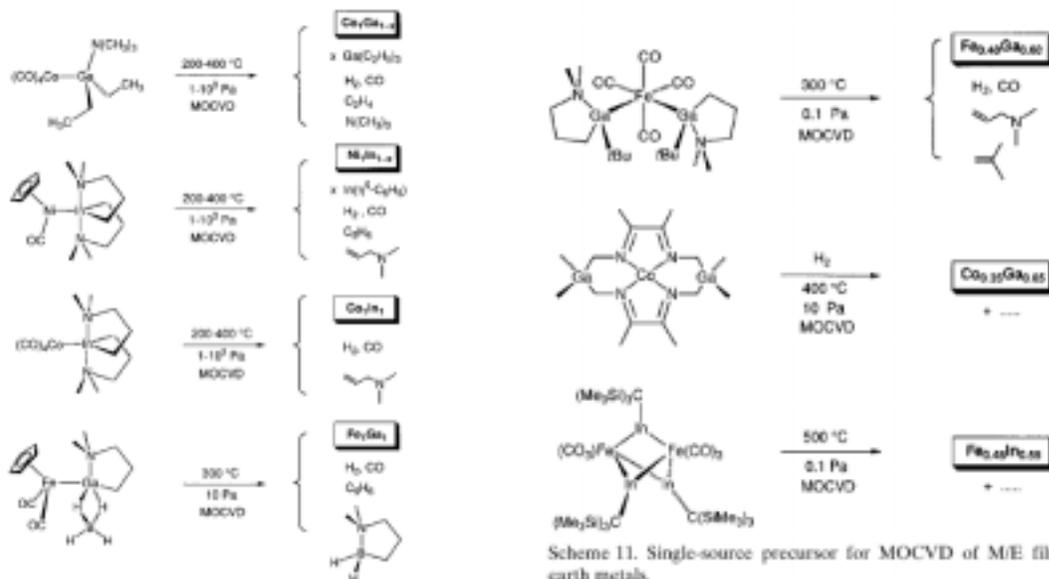
Figure 5. TEM micrograph of indium nanowires prepared in the presence of HDA (0.5 equiv).

Clusters and Materials Precursors

Note that many other types of ligands are also suitable for materials precursors. Important qualities for a precursor include: relative stability, volatility (for CVD), suitable decomposition pathways, a minimum of significant contaminant-forming decomposition pathways (such as carbides). Because of the ready cleavage of Cp'-element bonds for main group compounds, and the volatility of many of these species, main group metallocenes are often ideal precursors for the synthesis of many interesting materials. Furthermore, they are often used to introduce dopants during the formation of other materials.



For example, Cp*₂Mg is sold by Strem in 99.999% purity because it is generally used as a high-purity source for Mg as a p-type dopant for semi-conductors.



Scheme 10. Ligand control of the film composition for the MOCVD of MIE films using precursors of the type K.

Scheme 11. Single-source precursor for MOCVD of MIE films rich in earth metals.

The types of materials that can be made using such methods is likely limited only by the imagination of the researchers.



Cluster formed by the thermolysis, photolysis or reaction of main group Cp' and other low oxidation state compounds can provide us with insight into the formation of materials from such precursors. In effect such clusters can be considered as various steps along the pathway to the appropriate materials. Furthermore, such species may themselves be used as precursors for the formation of new materials.

Some results of Wiberg et al. demonstrate both reactivity and materials formation. Note that the compounds on the right-hand side are steps along the way to the deposition of In metal. (*Angew. Chem. Int. Ed.*, 1999, 38, 839 and 2563; *Eur. J. Inorg. Chem.*, 2002, 341)

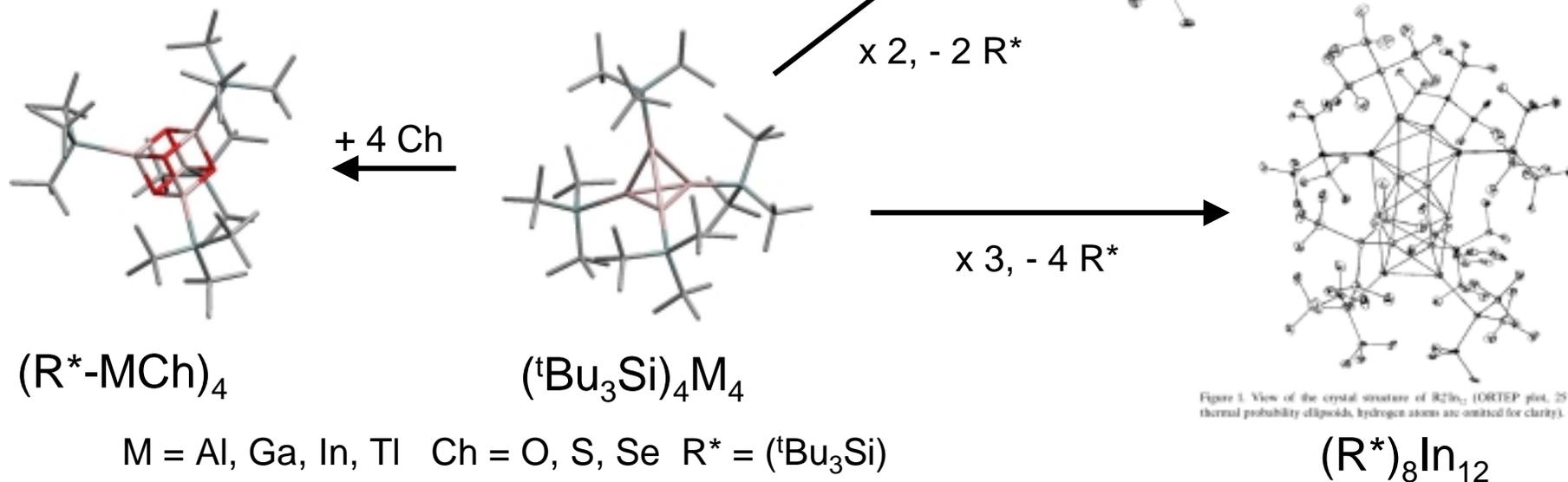


Figure 3. View of the crystal structure of R_2In_2 (ORTEP plot, 25% thermal probability ellipsoids, hydrogen atoms are omitted for clarity).



A series of studies by Schnöeckel provides insight into the formation of Al metal from Al(+1) starting materials. These studies resulted in the isolation of clusters containing 7 Al atoms (*Angew. Chem. Int. Ed.*, 1999, 38, 2926), 12 Al atoms (*Chem. Comm.*, 1999, 1933), and 14 Al atoms (*Angew. Chem. Int. Ed.*, 2000, 39, 799). Each of these clusters contains an Al core that may be derived from the structure of bulk aluminum. Because of this, the clusters (at least the larger ones) can be considered fragments of metal with an organic coating.

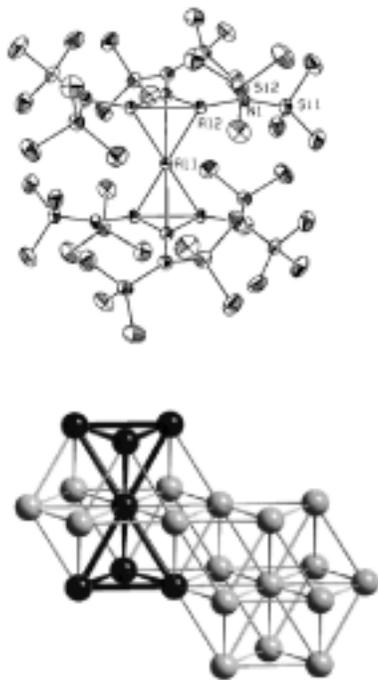


Figure 1. Section of the solid-state structure of aluminum (ccp). The Al₇ fragment is shaded darkly.

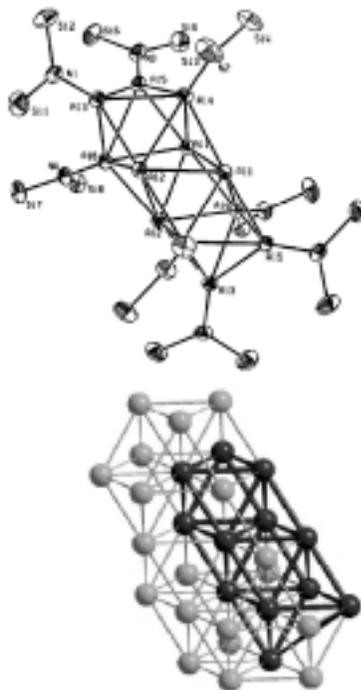
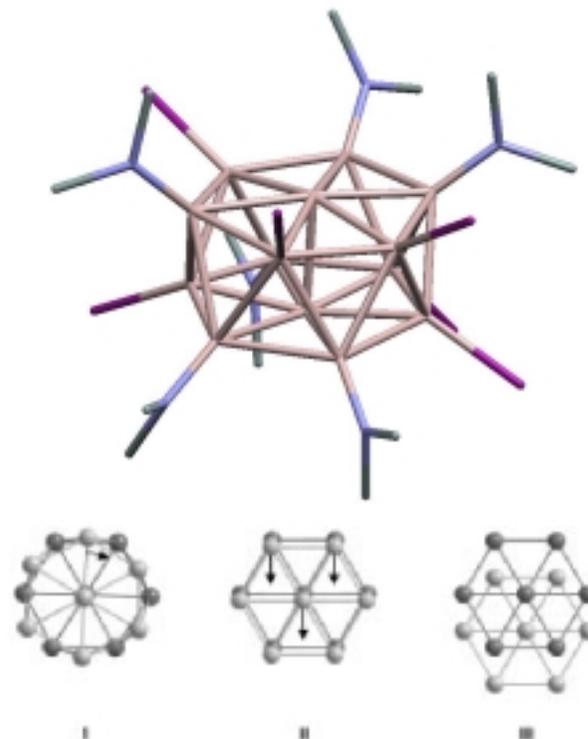


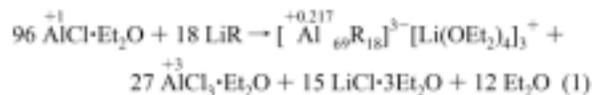
Fig. 2 Section of the aluminum metal lattice (ccp); an Al₁₂ unit is accentuated.



The only difference in the syntheses of these clusters is the temperature at which the solution was kept and the length of time of the crystallization process.



The largest of the characterized particles yet are those of Schnöeckel (*Nature*, 1997, 387, 379; *Inorg. Chem.*, 2001, 40, 4830). These are anionic clusters containing 69 and 77 Al atoms, respectively. Since the compounds crystallize, the molecular structure can be studied and appreciated - this is in contrast with most other types of nanoparticles and allows for a much better understanding of the bonding within the clusters.

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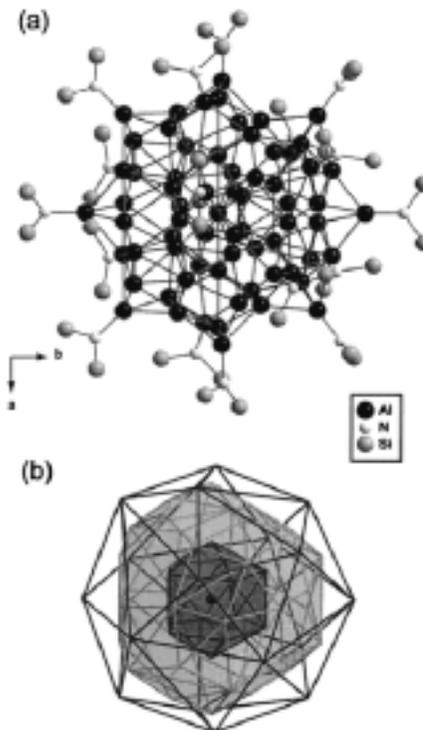


Figure 1. (a) Molecular structure of the anion of 1 (methyl groups excluded). (b) Shell-like Al frame of 1 (from central atom to the exterior): 1st shell, 12 Al atoms; 2nd shell, 38 Al atoms; 3rd shell, 18 Al atoms.

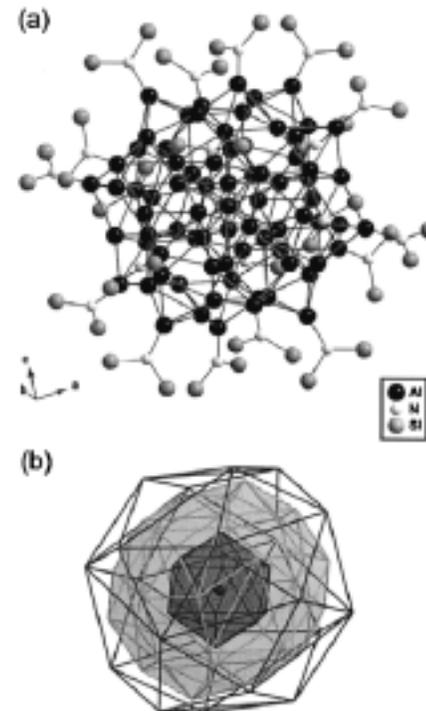
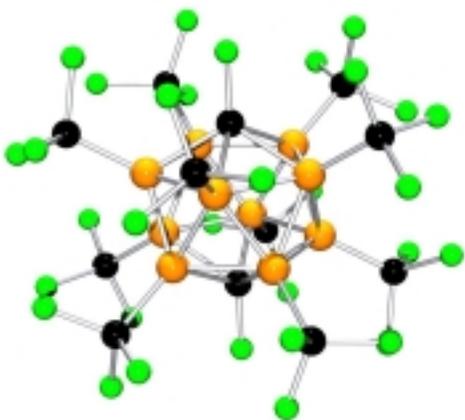


Figure 2. (a) Molecular structure of the anion of 2 (methyl groups excluded). (b) Shell-like Al skeleton of 2 (from central atom to exterior): 1st shell, 12 Al atoms; 2nd shell, 44 Al atoms; 3rd shell, 20 Al atoms.

Main Group Clusters

Unfortunately, we did not have enough time to talk about the rational syntheses of many classes of main group clusters (boranes, carboranes, Zintl ions, heterocubanes, SN compounds, alumoxanes, and many others). Those of you who wish to learn more about such compounds may want to start with the book “Clusters Molecules of the p-Block Elements” by Catherine Housecroft.

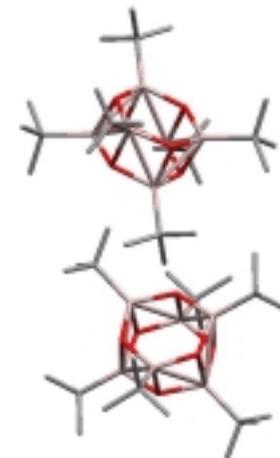
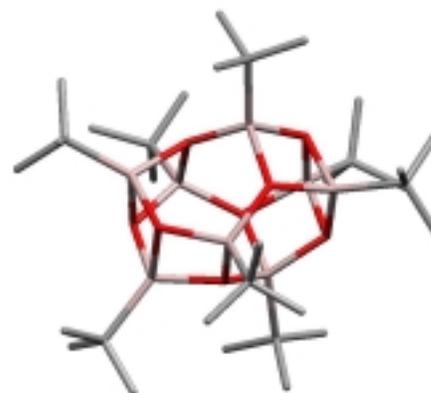
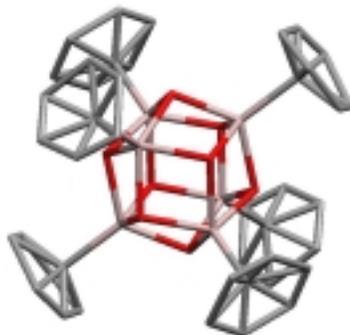
Zintl ions: Sn_9^{-3} and Ge_{27}^{-6}



A perfluorinated carborane



Some ^tBu alumoxanes:



Conclusion

I hope that you have gained some insight into at least a few of the types of molecules and systems that are of interest to Main Group chemists.

Probably the most important lessons to take from this class are:

The the “rules” for structure, bonding and reactivity that have been derived from Organic chemistry are a special case of the rules that govern the chemistry of the rest of the elements in the periodic table.

The d-orbitals that form the basis of transition metal chemistry are unimportant for the compounds of the main group.

The seemingly bizarre chemistry of the main group elements can often be understood on the basis of periodic trends - in particular, electronegativity, effective nuclear charge and the size of atoms (and orbitals), however...

We do not understand how everything works! Chemists must continue to investigate systems (using both synthetic and theoretical methods) to improve our understanding of the “rules” that determine the possible.