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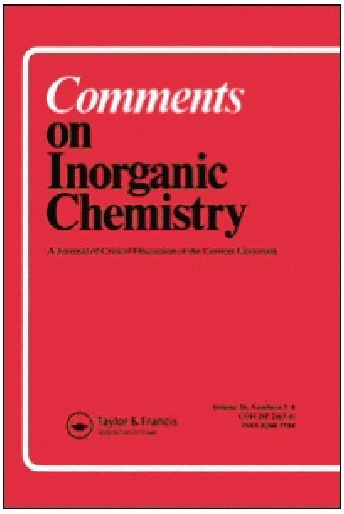

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Publication details, including instructions for authors and subscription information:
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The Versatility of the Pentamethylcyclopentadienyl Ligand in Main-Group Chemistry

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To cite this Article Jutzi, Peter(1987) 'The Versatility of the Pentamethylcyclopentadienyl Ligand in Main-Group Chemistry', Comments on Inorganic Chemistry, 6: 3, 123 — 144

To link to this Article: DOI: 10.1080/02603598708072286

URL: http://dx.doi.org/10.1080/02603598708072286

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The Versatility of the Pentamethylcyclopentadienyl Ligand in Main-Group Chemistry

Examples from different fields have been collected to demonstrate the unique properties of the pentamethylcyclopentadienyl (cp*) ligand in main-group chemistry. First, compounds with σ-bonded cp* ligands are thermally very stable and, therefore, allow detailed investigations of their temperature-dependent dynamic behavior. Drastic differences in the rates of 1,5-sigmatropic rearrangements are observed; the comparison of experimental results with theoretical calculations is very useful in understanding basic principles of fluxionality. Second, the polyhapto-bonded cp* ligand stabilizes π-complexes with main-group elements as central atoms. Using isolobal and isoelectronic relationships, these π-complexes can be organized in four structurally different classes. Furthermore, the cp* ligand is sterically demanding in boron, silicon, phosphorus, and sulfur compounds, leading to kinetically stabilized species and rendering nucleophilic substitution reactions more difficult. Finally, the cp* ligand is a good leaving group; cp*-element bonds can be split by nucleophilic, electrophilic and reducing agents, thus allowing an interesting substitution chemistry.

It is rather unusual to describe the chemistry of compounds or classes of compounds with special emphasis on a common ligand instead of a common element. Nevertheless, I will choose this approach and present a very unique ligand, whose properties allowed the discovery and the further development of some interesting fields in main-group chemistry. The species in question is the pentamethylcyclopentadienyl ligand.[1] Several advantages of the cp* ligand have to be addressed.

First, the permethylation raises the thermal stability of compounds with a σ-bonded cyclopentadienyl ligand. Consequently,

Comments Inorg. Chem.
1987, Vol. 6, No. 3, pp. 123–144
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detailed investigations concerning the fluxional behavior are possible, even at higher temperatures.

Second, π-complexes with permethylated cyclopentadienyl ligands are also comparatively more stable thermally. This allows the synthesis and characterization of new π-complexes with main-group elements as central atom.

Third, the σ-bonded cp* ligand has to be regarded as very bulky and, therefore, can stabilize unusual bonding situations. Furthermore, the chemistry of some cp* compounds is that expected for sterically overcrowded molecules.

Finally, the σ- or π-bonded cp* ligand is a good leaving group, thus allowing substitution reactions under element–carbon bond cleavage in many situations.

In the following sections some representative examples showing the versatility of the cp* ligand in main-group chemistry are given.

1. FLUXIONAL MONOHAPTO-PENTAMETHYLCYCLOPENTADIENYL COMPOUNDS

One of the most interesting features in monohapto cyclopentadienyl compounds is their fluxionality due to sigmatropic rearrangements. No other class of fluxional molecules has been investigated so intensively. The comparison of experimental results with theoretical calculations has turned out to be especially useful in understanding basic principles of dynamic behavior.[2]

In cyclopentadienyl compounds of the type C_5H_5El, two different rearrangement processes are possible (see Fig. 1). First, a nondegenerate 1,2-hydrogen shift may occur, producing isomers with the main-group element in an allylic or vinylic position of the cyclopentadiene system. Second, a degenerate 1,2-shift of the element fragment may take place, producing only identical compounds with the element in an allylic position.

In pentamethylcyclopentadienyl compounds, Me_5C_5El, nondegenerate methyl migrations, which can complicate the analysis of element migration processes, are not observed in the usual NMR temperature range. Furthermore, these compounds are thermally much more stable, thus allowing the observation of fluxionality by NMR spectroscopy even at elevated temperatures. Hence, pen-

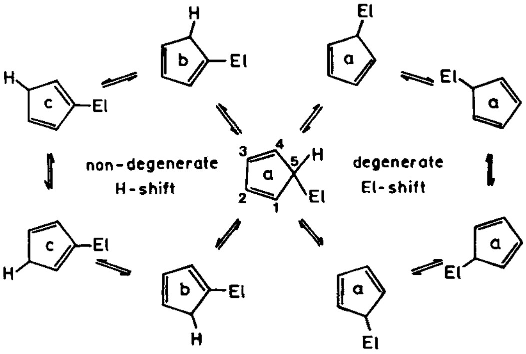


FIGURE 1 Fluxional behavior of cyclopentadienyl compounds.

tamethylcyclopentadienyl compounds are most suitable for the investigation of the dynamics of element migrations.

Recent developments have revealed drastic differences in the fluxional behavior among the pentamethylcyclopentadienyl compounds of main-group elements.[2] Rates for sigmatropic rearrangements vary over a wide range. Typical examples of compounds with main-group III, IV, and V elements are collected in Table I. Activation energies of these processes depend (i) on the nature of the main-group element itself, and (ii) on the further ligands bonded to the relevant main-group element.

Provided that the substituents are the same, the heavier elements in each main-group encounter lower activation barriers toward migration. The bond strength between the cyclopentadienyl carbon atom and the main-group element decreases in the monohapto ground-state structure (type A, Fig. 2) going to the heavier congeners, whereas it increases in the transition state structures (type B) in the same direction owing to better overlap. The result is an overall lowering of the relevant activation energies for the heavier homologues. An energy profile for degenerate sigmatropic rearrangements in cyclopentadienyl compounds is given in Fig. 2.

Pentamethylcyclopentadienyl compounds of aluminum(III), gallium(III), indium(III), thallium(III), tin(IV), lead(IV), antimony(III) and bismuth(III) are generally so highly fluxional (E_A-values lower than 5 kcal mol^{-1}) that it is impossible to ascertain the mechanism for the rearrangements with low-temperature NMR.[2]

TABLE I

Activation energies for 1,2-element shifts in pentamethylcyclopentadienyl compounds of some main-group elements (Ref. 2)

Compound	E_A (kcal mol^{-1})	Compound	E_A (kcal mol^{-1})
$Me_5C_5BMe_2$[3]	<5	$Me_5C_5P{=}C(SiMe_3)_2$[9]	<8
BCl_2[3]	<5	$P{=}PC_5Me_5$[10]	<8
BF_2[3]	12.4 ± 2.2		
$B(OMe)_2$[3]	13.7 ± 0.5	PBr_2[8]	5.2 ± 2.3
$B(NMe_2)_2$[3]	20.6 ± 1.2	PCl_2[8]	12.0 ± 1.6
$BCl_2 \cdot py$[3]	>25	$P(CN)_2$[8]	16.4 ± 0.3
		PF_2[8]	16.7 ± 0.7
$Me_5C_5CMe_3$	>40[a]	$P(SMe)_2$[8]	17.5 ± 1.3
$SiMe_3$[5]	15.3 ± 0.2	$P(C_6F_5)_2$[8]	17.2 ± 3.2
$GeMe_3$[6]	11.4 ± 1.3	$P(NMe_2)_2$[8]	19.0 ± 1.2
$SnMe_3$[6]	<5	PMe_2[8]	23.0 ± 0.5
		$P(C_6H_5)_2$[8]	24.3 ± 1.0
$Me_5C_5NMe_2$[7]	>25	PH_2[8]	31.3 ± 1.8
PMe_2[8]	23.0 ± 0.5		
$AsMe_2$[6]	17.1 ± 0.4	$PMe_3^+I^-$[11]	>35
$SbMe_2$[6]	11.3 ± 1.4	$P(S)R_2$[11]	>35
		$PR_2 \cdot Cr(CO)_5$[11]	>35

[a] Estimated value relative to $C_5H_4Me_2$.[4]

By analogy with the dynamic behavior of the lighter elements, a 1,2-shift can be anticipated, but other mechanisms are also possible; η^1, η^2 and η^5 structures are very close in energy and might represent ground or transition states in rearrangement processes.

Pentamethylcyclopentadienyl compounds of phosphorus display most clearly the influence of the further substituents on the main-

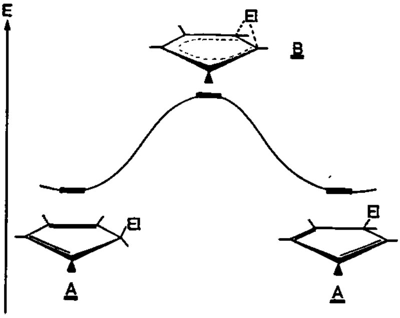


FIGURE 2 Energy profile for degenerate sigmatropic rearrangements.

group element on the rate of sigmatropic rearrangements.[8,9,10,11] Surprisingly large differences in fluxionality are observed, as documented for some typical examples in Table I. Activation energies lie between <5 and >35 kcal mol^{-1}, i.e., the molecular structures have to be classified over a wide range from highly fluxional to rigid. The dynamic behavior of these compounds depends on the coordination number (c.n.) of phosphorus. Whereas molecules with c.n. 2 are highly fluxional, those with c.n. 4 are rigid on the NMR time scale. Conspicuous changes in fluxionality are observed for compounds with three-coordinated phosphorus.

The dynamic behavior of cp* phosphorus compounds has also been treated theoretically by extended Hückel and MNDO calculations.[12] To explain substituent effects in the phosphorus compounds of Table I, it is important to regard the MO representations of the relevant dihapto transition states, portrayed in Fig. 3. The very low activation energies in compounds with divalent phosphorus are caused by a pronounced stabilization of the transition state **B1** by interaction of the cyclopentadienyl π-system with the π^*-orbital at phosphorus. The energy of the transition state **B2** for pentamethylcyclopentadienyl phosphanes (c.n. 3 in the ground state) is mainly influenced by the pseudo-allylic PX_2 fragment, the energy of which varies drastically depending on the electronic effects of the substituent X.

As a result, great differences in activation energies are expected. Finally, no marked stabilization is expected for the transition state **B3** in compounds with tetravalent phosphorus; these species are rigid on the NMR time scale.

Similar dramatic substituent effects on the fluxionality were observed for cp* compounds of boron,[2,3] but not for compounds of the group IV element silicon.[2] Mesomeric effects—mainly re-

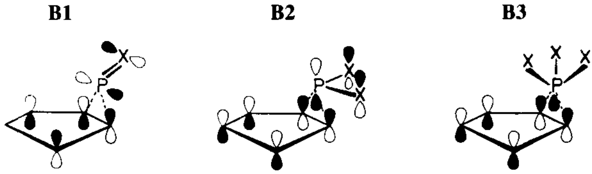


FIGURE 3 Frontier orbital interaction in the transition states for sigmatropic rearrangements in cyclopentadienyl compounds with two-, three-, and four-coordinated phosphorus.

sponsible for differences in the dynamic behavior—cannot occur in compounds with tetra or higher coordinated silicon. Hence, a pronounced influence of substituents is not expected, as documented by many examples in the literature.

The dynamic behavior of the pentamethylcyclopentadienyl compounds with main-group elements is described in the recent literature in detail; the results[2] can also be used as a basis for the discussion of fluxionality in other systems where sigmatropic processes are observed.

2. PENTAMETHYLCYCLOPENTADIENYL π-COMPLEXES WITH MAIN-GROUP ELEMENTS AS CENTRAL ATOMS

Many mainly recent examples document that polyhapto bonding of organic π-systems is not restricted to transition elements; main-group elements can also serve as central atoms.[13] In this class of compounds, the pentamethylcyclopentadienyl ligand plays a dominant role. Pentamethylcyclopentadienyl complexes are generally much more stable than the corresponding cyclopentadienyl species due to kinetic and/or thermodynamic effects. These π-complexes can be organized into four structurally different classes of compounds, as portrayed in Fig. 4. In each class, compounds possess comparable structures due to the presence of isolobal and isoelectronic main-group element fragments.

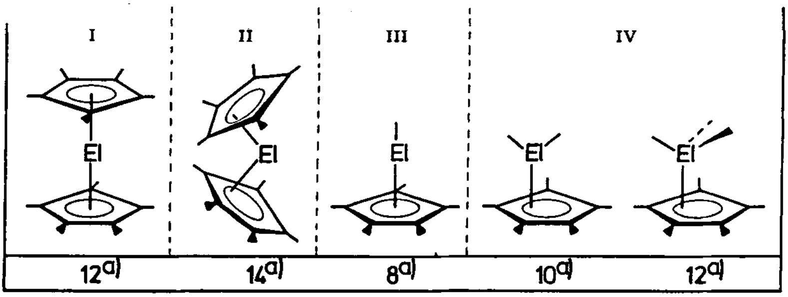
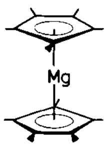


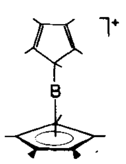
FIGURE 4 Classification of cp*-complexes in main-group chemistry. a) number of total electrons [from the cp*π-system and the main-group element fragment].

Class I Complexes

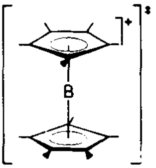
During the development of metallocene chemistry in the groups of E. O. Fischer[14] and G. Wilkinson,[15] the first π-complex of magnesium, Cp_2Mg, was also synthesized. The permethylated derivative, Cp_2^*Mg (Ia), was described many years later.[16] It is the only representative of class I complexes known so far. Its ferrocene-like structure was concluded from spectroscopic data. The ^{25}Mg-NMR suggests that mainly covalent interactions determine the bonding in magnesocene and its derivatives.[17] Following the octet rule for main-group elements, four electrons from the cp units have to remain in nonbonding orbitals (total electron count: 12).



Ia



Ib



Ib‡

Isoelectronic to Cp_2^*Mg is the boron cation $[Cp_2^*B]^+$ (Ib), which was verified in a compound with BF_4^- as counterion.[18] Interestingly, a magnesocene-type structure is not realized in this π-complex. Whereas one cp* ring is π-bonded, the other is σ-bonded and responsible for the fluxionality observed for this species. At higher temperature, rapid sigmatropic rearrangements of the boryl fragment finally lead to a situation where the σ-bonded cyclopentadienyl ligand becomes π-bonded and vice versa. The transition state for such a σ/π-interchange can be represented by a symmetrical sandwich structure (Ib‡). It is of interest to compare the bonding in $[Cp_2^*B]^+$ with that in berrylocene, Cp_2Be, which is still a subject of debate.

Class II Complexes

The whole series of permethylated metallocenes with group IV elements as central atoms is known. Decamethylsilicocene, published in 1986,[19] is the first silicon(II) compound stable at ambient temperature; its successful synthesis is a further example for the utility of the cp* ligand in main-group chemistry. The decamethylmetallocenes of germanium,[20] tin,[21] and lead[21] are more stable than the parent compounds. In the solid state all metallocenes show a bent sandwich structure with a stereochemically active lone pair and asymmetrically pentahapto-bonded cyclopentadienyl rings (see Table II). The distorted η^5-attachment of the cp* rings is not reflected in the low temperature ^1H or ^{13}C NMR spectra; therefore, the barrier for rotation must be very low ($\leq$5 kcal mol^{-1}). Surprisingly, in the crystal structure of Cp_2^*Si, two different molecules are observed, the one with the expected bent structure, the other with cp* rings in a parallel orientation. According to PES data,[13,22] the energies of the HOMO's in the group IV metallocenes are nearly the same, thus independent of the central atom and indicating the nonbonding character of these orbitals [see Table II].

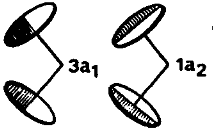
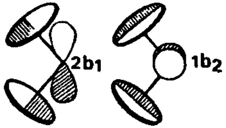
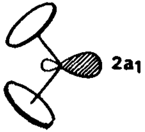
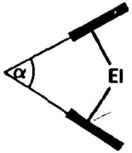
Isoelectronic with the group IV metallocenes are cationic species of the type $Cp_2^*El^+$ containing group V elements. They can be prepared by halide-ion abstraction from neutral bis(η^1-pentamethylcyclopentadienyl)element halides. The complex $[Cp_2^*P]^+$ BCl_4^- is thermally unstable; its structure was concluded from NMR spectroscopic data.[23] However, the bis(pentamethylcyclopentadienyl)arsenium and stibenium tetrafluoroborates, $[Cp_2^*El]^+$ BF_4^-, are stable at ambient temperature.[24] An x-ray crystal structure analysis of the arsenic compound shows the molecule to possess the expected bent sandwich structure; the metal-ring bonding is distorted in the direction of dihapto bonding to the one and trihapto bonding to the other cp* ring (see Fig. 5). In solution these cationic π-complexes are highly fluxional. A low nucleophilicity of the counter anion is important for their stabilization.

Class III Complexes

Compounds belonging to this class can also be regarded as nidoclusters with a pentagonal pyramidal structure. Using isolobal and isoelectronic main-group fragments, as indicated in Fig. 6, a basis for the understanding of the bonding in these complexes is given. Once more, it was the cp* ligand which allowed the first synthesis of interesting π-complexes.

Pentamethylcyclopentadienyl borinium cations, $[Cp^*BR]^+$, are

TABLE II Decamethylmetallocenes of silicon, germanium, tin, and lead; PES and structure data

	$(Me_5C_5)_2Si$	$(Me_5C_5)_2Ge$	$(Me_5C_5)_2Sn$	$(Me_5C_5)_2Pb$
	6.70 eV 6.96	6.60 eV 6.75	6.60 eV 6.60	6.33 eV 6.88
	8.06 8.30	7.91 8.05	7.64 7.64	7.38 7.38
	7.5	8.36	8.40	8.93
 α(°)	0$^{a)}$; 25.3$^{d)}$	22±2$^{b)}$	36.4$^{a,c)}$ 35.4	37.1$^{a)}$
Range of El-C Distances (Å)	2.42 2.32-2.54		2.58-2.77	2.69-2.90
Avarage El-C Distances (Å)	2.42 2.42	2.52	2.64	2.79

[a] X-ray; [b] GED; [c] two independent molecules; [d] two conformers in the unit cell

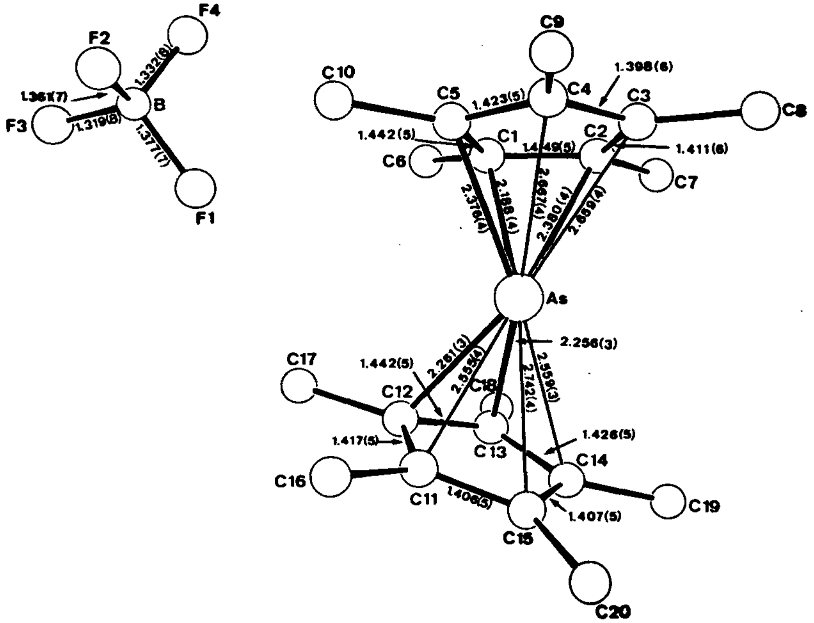


FIGURE 5 Structure of $[\mathrm{Cp_2^*As}]^+\mathrm{BF_4^-}$ in the crystal.

prepared by halide-ion abstraction from neutral cp* boron halides, by protonation of a cp* diaminoborane, or by substitution reactions, as indicated in the Eqs. (1), (2), (3), and (4).[25,26]

$$\mathrm{Cp^*B(R)Hal} \xrightarrow{\mathrm{ElHal_3}} [\mathrm{Cp^*BR}]^+\mathrm{ElHal_4^-} \tag{1}$$

$$\mathrm{R = Cl, Br, I, Cp^*, CMe_3, C_6H_2Me;} \quad \mathrm{Hal = Cl, Br, I}$$

$$\mathrm{Cp^*B(NMe_2)_2} \xrightarrow[-[\mathrm{H_2NMe_2}]^+\mathrm{BF_4^-}]{\mathrm{2HBF_4}} [\mathrm{Cp^*BNMe_2}]^+\mathrm{BF_4^-} \tag{2}$$

$$\mathrm{Cp_2^*BF} \xrightarrow[-\mathrm{Cp^*H}]{\mathrm{F_3CSO_3H}} [\mathrm{Cp^*BF}]^+\mathrm{F_3CSO_3^-} \tag{3}$$

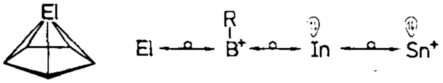


FIGURE 6 Main-group fragments for nido-clusters with a pentagonal pyramidal structure.

$$[Cp^*BI]^+BI_4^- \xrightarrow[-LiI]{LiMe} [Cp^*BMe]^+BI_4^- \qquad (4)$$

The structure of these complexes was determined by ^{11}B, ^1H, and ^{13}C NMR spectroscopy. The ^{11}B resonances for the π-complexed boron atoms are found at rather high field (−40 to −50 ppm, $BF_3 \cdot OEt_2$ as ref.), indicating charge transfer—mainly from the cp* system—to the boron.

Further representatives of class III complexes are ionic species of the type $[Cp^*El]^+X^-$, where a cp* ligand is pentahapto-bonded to an isolated germanium or tin atom. Reaction of decamethylgermanocene or -stannocene with electrophiles proceeds by attack at the cp*π-system, followed by abstraction of a cyclopentadiene and formation of ionic species, as indicated in Eq. (5).[20] In an alternative procedure, a chloride anion is abstracted from cp* germanium or tin chloride according to Eq. (6).[27]

$$Cp_2^*El + EX \xrightarrow[-Cp^*E]{} [Cp^*El]^+X^- \qquad (5)$$

$$El = Ge, Sn;\ E = H, Me;\ X = BF_4, C_5(COOMe)_5, F_3CSO_3$$

$$Cp^*El\text{-}Cl + AlCl_3 \longrightarrow [Cp^*El]^+AlCl_4^- \qquad (6)$$

The x-ray crystal structure of $[Cp^*Sn]^+BF_4^-$ confirms the presence of isolated cations and anions in the solid state (see Fig. 7). The cp* ligand is symmetrically pentahapto-bonded to the tin atom. The tin ring-centroid distance is considerably shorter than in decamethylstannocene, Cp_2^*Sn.[20]

The chemistry of species of the type Cp^*El^+ is determined by the attack of nucleophiles at the group IV element, by the attack of electrophiles at the cp* ring, and by oxidative addition reactions.

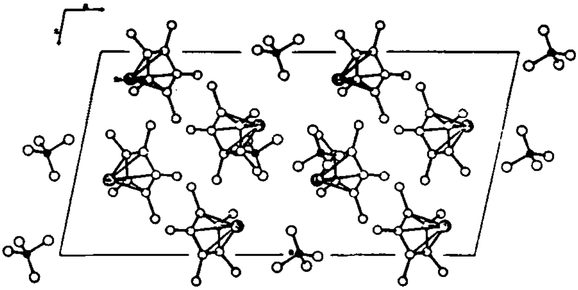


FIGURE 7 Structure of $[Cp^{*}Sn]^{+}BF_4^{-}$ in the crystal.

Very interesting properties are introduced by the cp* ligand in indium(I) chemistry. Whereas cyclopentadienylindium, H_5C_5In, is polymeric in the solid state and tris(trimethylsilyl) cyclopentadienylindium, $(Me_3Si)_3H_2C_5In$, monomeric, the Cp*In crystallizes as a hexamer, in which the indium atoms occupy the vertices of a distorted octahedron.[28] Indium–indium distances are in the range of 3.94 to 3.96 Å. The volatility of Cp*In suggests that the octahedral cluster has only marginal stability. The golden-yellow color of solid Cp*In is unique in the cyclopentadienyl chemistry of main-group elements. This complex is synthesized by the reaction of indium(I)chloride with Cp*lithium[28] or by reduction of bis(pentamethylcyclopentadienyl)indium(III)chloride.[29] The corresponding thallium compound, Cp*Tl, is quite normal in its behavior.[30,44] It forms a polymeric zig-zag chain structure similar to that of H_5C_5Tl, but with much shorter Tl–Tl distances, which is indicative of a higher degree of covalent bonding.[44]

Class IV Complexes

In this class of compounds the cp* ring is not pentahapto-bonded to a main-group element, but has slipped sideways in the direction of di- or trihapto-bonding, as portrayed in Fig. 8. According to MO calculations, di-, tri-, or pentahapto configurations are all very similar in energy. As a consequence, di- or trihapto-bonding is observed only in the solid state; in solution these complexes are highly fluxional. The main-group fragments once more are char-

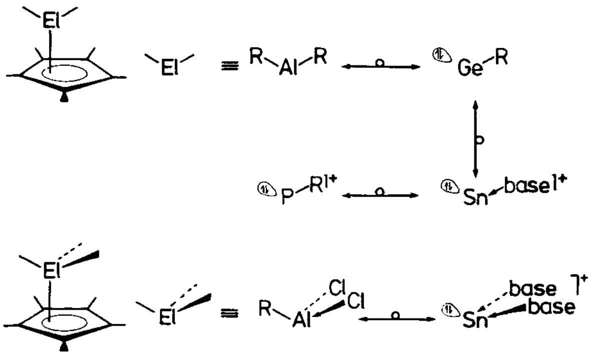


FIGURE 8 Di- or trihapto pentamethylcyclopentadienyl compounds.

acterized by the number of valence electrons and by comparable frontier orbitals. As described in Figs. 4 and 8, two different bonding situations are observed, which correspond to an overall electron-count of 10 and 12. For the latter group of compounds (number of total electrons = 12), a reasonable distinction between the preference of a σ- or a π-type structure is not possible using this simplified description of bonding. For example, all compounds known so far belonging to the types $Cp^*El_{IV}R_3$, $Cp^*El_VR_2$ or $[Cp^*El_VR_3]^+$ are σ-bonded to the cp* ring.[2]

The aluminum complex Cp*Al(Me)Cl was synthesized by the reaction of Cp*magnesium chloride with $[Me_2AlCl]_2$.[31] The x-ray crystal structure reveals a dimeric unit, in which each aluminum atom is trihapto-bonded to the cp* ring (see Fig. 9).

In the reaction of the cationic Cp*tin unit with pyridine, pyrazine, and 2,2′-bipyridyl, adducts are formed in which the cp* ring is di- or trihapto-bonded to the tin atom, as portrayed in Fig. 9.[32]

The orange-red color of the bipyridyl complex is caused by charge transfer from the tin lone-pair to the π*-orbital of the heteroaromatic system.

The introduction of the cp* ligand allowed a kinetic and thermodynamic stabilization of compounds with divalent germanium. Cp* germanium chloride, Cp*GeCl, is prepared by the reaction of Cp* lithium with germanium dichloride[33]; further substitution reactions with bis(trimethylsilyl)methyllithium or lithium amides

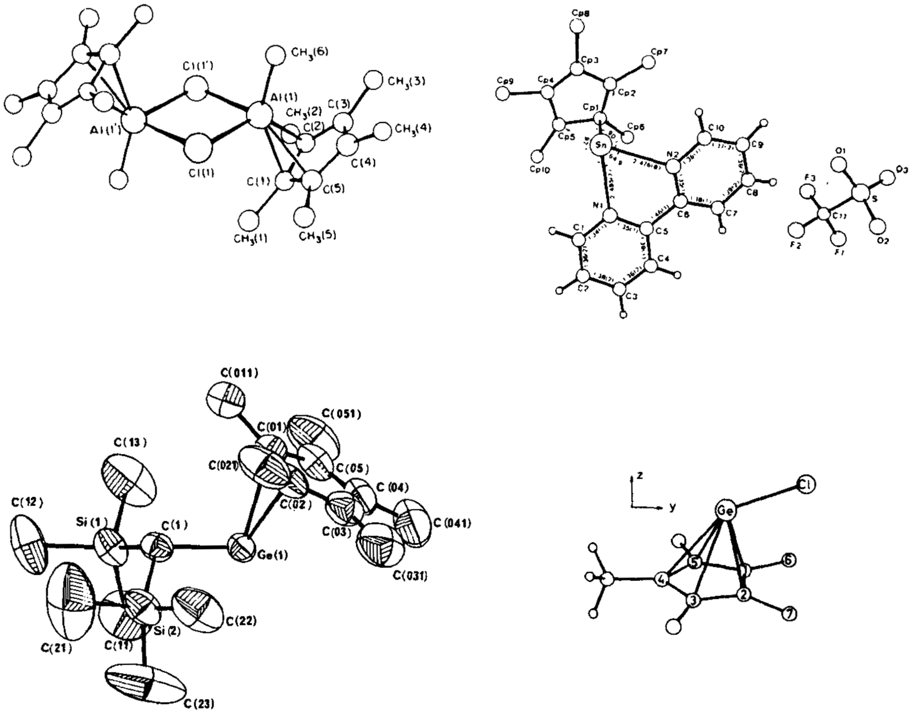
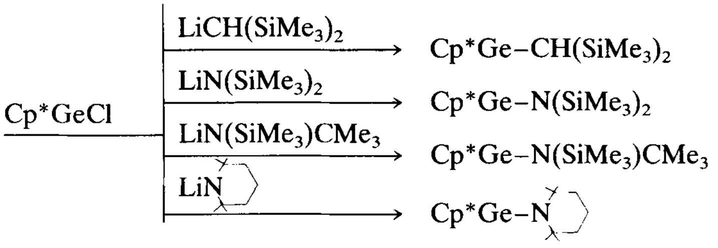


FIGURE 9 Structural data of the complexes $[Cp^*Al(Me)Cl]_2$,[a)] $[Cp^*Sn{\cdot}bipy]^+CF_3SO_3^-$,[a)] $Cp^*GeCH(SiMe_3)_2$,[a)] and Cp^*GeCl[b)]. a) x-ray crystal structure; b) electron diffraction study.

lead to alkyl or amino substituted germylenes,[34] as described in Eq. (7).



(7)

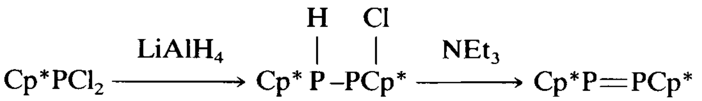
Complexes of the type Cp*GeR are monomeric in the solid state, in solution, and in the gas phase. Structural data for $Cp^*GeCH(SiMe_3)_2$[34] and Cp*GeCl[35] are presented in Fig. 9.

Finally, two compounds from phosphenium and arsenium ion chemistry demonstrate the utility of the cp* ligand to stabilize interesting bonding situations by π-complex formation. Halide-ion abstraction from neutral cp*halogeno(amino)phosphanes leads to ionic species of the type $[Cp^*PNR_2]^+ X^-$.[36] Similarly, the first clear-cut example of an arsenium ion was produced by chloride abstraction from $Cp^*(Me_2N)AsCl$.[37] So far, no crystal structure data are available for these complexes. MNDO calculations reveal a dihapto structure as a global minimum and a very low barrier to circumannular migration of the ElR-moiety. A low nucleophilicity of the counter-anion is also important for the stabilization of these cationic π-complexes.

3. STERIC DEMANDS OF THE PENTAMETHYLCYCLOPENTADIENYL GROUP

Kinetic stabilization of reactive species is a key topic in modern chemistry. Using bulky ligands, it is possible to stabilize nonclassical (p-p)π systems (B≡N, Si═C, Si═Si, P═C, P═N, P═P, Si═P, etc.), electron-deficient compounds in monomeric form and, therefore, in unusual hybridization (BeR_2, GeR_2, SnR_2) and hitherto unknown cationic species (BR_2^+, PR_2^+). In this context, the space-demanding qualities of the σ-bonded pentamethylcyclopentadienyl ligand are of interest.

Very recently the cp* ligand was successfully used in diphosphene chemistry. Bis(pentamethylcyclopentadienyl)diphosphene could be synthesized in a reaction sequence described in Eq. (8).[10]



$$\mathrm{Cp^*PCl_2} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{Cp^*}\overset{\mathrm{H}}{\overset{|}{\mathrm{P}}}-\overset{\mathrm{Cl}}{\overset{|}{\mathrm{P}}}\mathrm{Cp^*} \xrightarrow{\mathrm{NEt_3}} \mathrm{Cp^*P{=}PCp^*} \tag{8}$$

The cp* substituted diphosphene exhibits long-term stability at ambient temperature, thus demonstrating a sufficient kinetic stabilization by the cp* ligand. An x-ray diffraction analysis showed the *trans* orientation of the σ-bonded cp* ligand and a normal P=P bond length, as portrayed in Fig. 10.

A further indication of the bulkiness of the cp* group stems from organosilicon chemistry. Chlorosilanes with one or two cp* ligands show a reduced reactivity against nucleophiles. For example, the air-stable bis(pentamethylcyclopentadienyl)dichlorosilane is not attacked by water or other protic nucleophiles. An x-ray crystal structure was undertaken to elucidate the environment of the silicon atom in this compound.[38] As portrayed in Fig. 11, strong deviation from tetrahedral arrangement at silicon is observed. Whereas the CSiC angle is widened to 122°, the ClSiCl angle is diminished to 101°. Similar distortions are also observed in the crystal structure of other bis(pentamethylcyclopentadienyl) substituted compounds (see Fig. 11). Thus, in bis(pentamethyl-

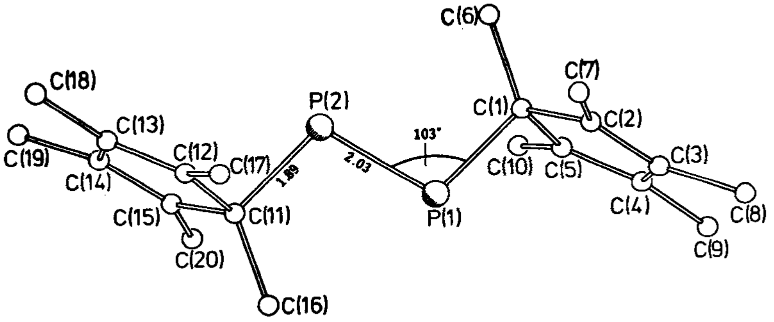


FIGURE 10 Structure of Cp*P=PCp* in the crystal.

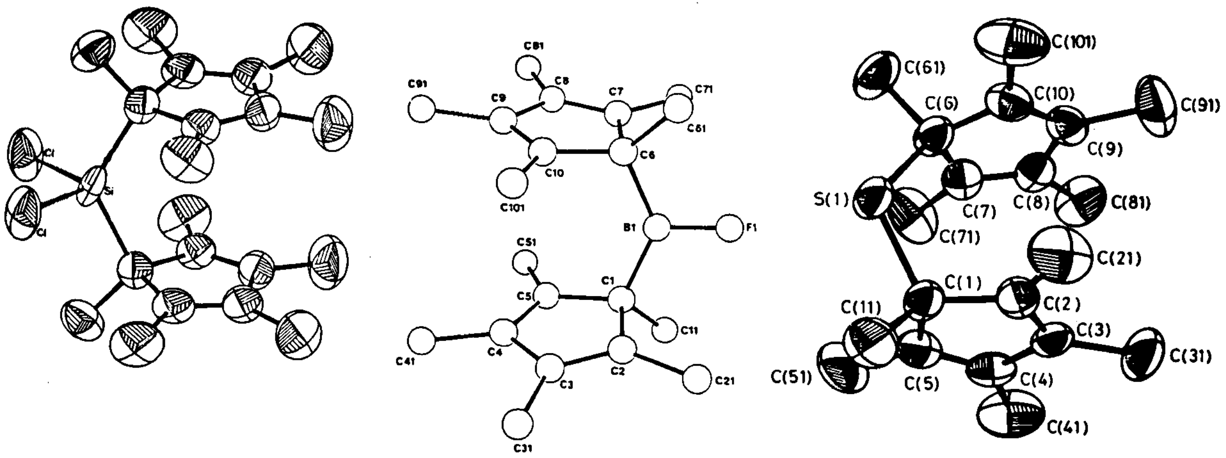


FIGURE 11 Structure of $Cp_2^*SiCl_2$, Cp_2^*BF, and Cp_2^*S in the crystal.

cyclopentadienyl)sulfide, the CSC angle is widened to 111.7°, compared to an angle of about 104° in other diorganylsulphides.[39] In bis(pentamethylcyclopentadienyl)fluoroborane the CBC angle is widened to 131°.[3]

Cp* ligands render nucleophilic substitutions more difficult not only in silicon, but also in boron and phosphorus chemistry. Thus, the compounds Cp_2^*BCl and Cp_2^*PCl react with organolithium species as nucleophiles only under more drastic conditions.

As shown in this section, boron, silicon, phosphorus, and sulfur compounds containing two cp* ligands can be regarded as sterically overcrowded molecules.

4. SPLITTING OF Cp*-ELEMENT BONDS

A further great advantage of the cp* ligand merits brief discussion. According to our experience, the σ- or π-bond between the cp* ligand and a main-group element can be readily broken. Carbon-element cleavage is performed in the reaction with either nucleophiles or electrophiles or with reducing agents. This will be illustrated by some typical examples.

Some cp* phosphorus compounds react with organolithium species as nucleophiles under P–C splitting. This was first observed[6] in the reaction of pentamethylcyclopentadienylphosphane, Cp^*PH_2, with butyllithium, as indicated in Eq. (9). Later on, this reaction principle was transferred to diphosphene chemistry and allowed for the first time substitution reactions at the P=P unit [Eq. (10)].

$$Cp^*PH_2 + BuLi \longrightarrow BuPH_2 + Cp^*Li \qquad (9)$$

$$Cp^*P{=}PCp^* \xrightarrow[-Cp^*Li]{RLi} RP{=}PCp^* \xrightarrow[-Cp^*Li]{RLi} RP{=}PR \qquad (10)$$

A cp* ligand as a nucleofugal leaving group was also observed in tin chemistry. As an example, in the reaction of decamethylstannocene with bis(trimethylsilyl)methyllithium, the bis[bis(trimethylsilyl)methyl]stannylene is formed [Eq. (11)].[40]

$$\begin{gathered} Cp_2^*Sn + 2\ RLi \longrightarrow 2\ Cp^*Li + R_2Sn \\ R = CH(SiMe_3)_2 \end{gathered} \qquad (11)$$

Some examples from boron and tin chemistry demonstrate the easy El–Cp* bond cleavage with electrophiles. Thus, in the reaction of bis(η^1-pentamethylcyclopentadienyl)fluoroborane with trifluoromethyl sulfonic acid, the cp* system is protonated and eliminated as the neutral hydrocarbon; an ionic species containing the Cp*BF$^+$ cation is formed [Eq. (12)].[26] Decamethylstannocene reacts with protic agents in a similar fashion [Eqs. (13) and (14)].[20,41]

$$\mathrm{Cp_2^*BF} \xrightarrow[-\mathrm{Cp^*H}]{\mathrm{F_3CSO_3H}} [\mathrm{Cp^*BF}]^+\mathrm{F_3CSO_3^-} \qquad (12)$$

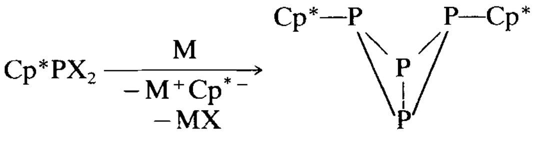
$$\mathrm{Cp_2^*Sn} \xrightarrow[-2\ \mathrm{Cp^*H}]{2\ \mathrm{HX}} \mathrm{SnX_2} \qquad (13)$$

$$\mathrm{Cp_2^*Sn} \xrightarrow[-\mathrm{Cp^*H}]{\mathrm{HBF_4}} [\mathrm{Cp^*Sn}]^+\mathrm{BF_4^-} \qquad (14)$$

Finally, three examples for the reaction of Cp*-element compounds with reducing agents are described. Addition of alkali metals to the group IV metallocenes leads to the group IV metals in their zeroth oxidation state and to the formation of pentamethylcyclopentadienide alkali metal compounds [Eq. (15)].[42] In the reaction of pentamethylcyclopentadienyldihalogenophosphanes with alkali metals or magnesium, reduction to the butterfly species Cp$_2^*$P$_4$ and formation of the corresponding metal cyclopentadienides is observed [Eq. (16)].[43] In indium chemistry, the bis(pentamethylcyclopentadienylindium(III)chloride is reduced with alkali metal naphthalenides to pentamethylcyclopentadienylindium(I) [Eq. (17)].[29]

$$\mathrm{Cp_2^*El} \xrightarrow[-2\ \mathrm{M^+Cp^{*-}}]{2\ \mathrm{M}} \mathrm{El} \qquad (15)$$

El = Si, Ge, Sn; M = alkali metal



(16)

$$\mathrm{Cp_2^*InCl} \xrightarrow[\substack{-\mathrm{M^+Cp^{*-}} \\ -\mathrm{MCl}}]{\mathrm{M}} \mathrm{Cp^*In} \qquad (17)$$

Summarizing all these observations in substitution chemistry, the cp* ligand must also be regarded as a many-sided functional group in main-group chemistry.

CONCLUDING REMARKS

It has been the aim of this Comment to draw the readers' attention to the versatility of the pentamethylcyclopentadienyl ligand in main-group chemistry. Several examples from different fields have been chosen to demonstrate the interesting properties of this rather unique ligand. The starting material generally used to introduce the ligand is pentamethylcyclopentadiene, $\mathrm{Me_5C_5H}$, which can be readily synthesized following two different procedures.[45,46] Finally, it is hoped that this Comment will stimulate further application of the pentamethylcyclopentadienyl ligand in main-group chemistry.

Acknowledgments

The work of the author's group described here was done by a team of active and skillful co-workers, whose names are given in the references and to whom I wish to express my gratitude. Generous support for our studies by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged as well. I am thankful to Mrs. C. Drexhage for preparing the manuscript for publication.

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References

1. In the subsequent discussion this ligand will be abbreviated cp*.
2. P. Jutzi, Chem. Rev. **86**, 983 (1986).

3. P. Jutzi and B. Krato, Chem. Ber. (in press).
4. S. McLean and D. M. Findlay, Can. J. Chem. **48**, 3107 (1970).
5. P. Jutzi, H. Saleske, D. Bühl and H. Grohe, J. Organomet. Chem. **252**, 29 (1983).
6. P. Jutzi, B. Hielscher and H. Saleske (unpublished).
7. G. Boche (unpublished).
8. P. Jutzi and H. Saleske, Chem. Ber. **114**, 222 (1984).
9. D. Gudat, E. Niecke, B. Krebs and M. Dartmann, Chimia **39**, 277 (1985).
10. P. Jutzi, U. Meyer, B. Krelos and M. Dartmann, Angew. Chem. **98**, 894 (1986).
11. P. Jutzi, H. Saleske, D. Nadler, J. Organomet. Chem. **118**, C8 (1978).
12. W. W. Schoeller, Z. Naturforsch. **38b**, 1636 (1983).
13. P. Jutzi, Adv. Organomet. Chem. **26**, 217 (1986).
14. E. O. Fischer and W. Hafner, Z. Naturforsch. **B9**, 503 (1954).
15. F. A. Cotton and G. Wilkinson, Chem. Ind. 307 (1954).
16. J. L. Robbins, N. Edelstein, B. Spencer and J. C. Smart, J. Am. Chem. Soc. **104**, 1882 (1982).
17. R. Benn, H. Lehmkuhl, K. Mehler and A. Rufinska, Angew. Chem. **96**, 521 (1984).
18. P. Jutzi and A. Seufert, J. Organomet. Chem. **161**, C5 (1978).
19. P. Jutzi and D. Kanne, Angew. Chem. **98**, 163 (1986).
20. P. Jutzi, F. X. Kohl, C. Krüger and Y. H. Tsay, Chem. Ber. **113**, 757 (1980).
21. J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones and C. A. Stewart, J. Chem. Soc. Chem. Commun. 925 (1981).
22. R. Gleiter (unpublished).
23. P. Jutzi and H. Saleske, IX. Int. Conf. Organomet. Chem., Dijon, Abstr. A 38 (1979).
24. P. Jutzi, Th. Wippermann, C. Krüger and H. J. Kraus, Angew. Chem. **95**, 244 (1983).
25. P. Jutzi, A. Seufert and W. Buchner, Chem. Ber. **112**, 2488 (1979).
26. P. Jutzi and B. Krato (in preparation).
27. P. Jutzi and B. Hampel, Organometallics **5**, 730 (1986).
28. O. T. Beachley, Jr., M. R. Churchill, J. C. Fettinger, J. C. Pazik and L. Victoriano, J. Am. Chem. Soc. **108**, 4666 (1985).
29. P. Jutzi and W. Leffers (unpublished).
30. G. A. Ruprecht, L. W. Messerle, J. D. Fellmann and R. R. Schrock, J. Am. Chem. Soc. **102**, 6236 (1980).
31. P. R. Schonberg, R. T. Paine and C. F. Campana, J. Am. Chem. Soc. **101**, 7726 (1979).
32. F. X. Kohl, E. Schlüter, P. Jutzi, C. Krüger, G. Wolmershäuser, P. Hofmann and P. Stauffert, Chem. Ber. **117**, 1178 (1984).
33. F. X. Kohl and P. Jutzi, J. Organomet. Chem. **243**, 31 (1983).
34. P. Jutzi, B. Hampel, M. B. Hursthouse and A. J. Howes, Organometallics **5**, 1944 (1986).
35. L. Fernholt, A. Haaland, P. Jutzi, F. X. Kohl and R. Seip, Acta Chem. Scand. **A38**, 211 (1984).
36. S. G. Baxter, A. H. Cowley and S. K. Mehrotra, J. Am. Chem. Soc. **103**, 5572 (1981).
37. A. H. Cowley and S. K. Mehrotra, J. Am. Chem. Soc. **105**, 2074 (1983).
38. P. Jutzi and D. Kanne (unpublished).
39. A. J. Bard, A. H. Cowley, J. K. Leland, G. J. N. Thomas, N. C. Norman, P. Jutzi, Ch. P. Morley and E. Schlüter, J. Chem. Soc. Dalton Trans. 1303 (1985).
40. P. Jutzi and B. Hielscher, Organometallics **5**, 2511 (1986).

41. P. Jutzi, F. X. Kohl, E. Schlüter, M. B. Hursthouse and N. P. Walker, J. Organomet. Chem. **271**, 393 (1984).
42. P. Jutzi and B. Hielscher, Organometallics **5**, 1201 (1986).
43. P. Jutzi and Th. Wippermann, J. Organomet. Chem. **287**, C5 (1985).
44. H. Werner, H. Otto and H. J. Kraus, J. Organomet. Chem. **315**, C57 (1986).
45. R. S. Threlkel and J. E. Bercaw, J. Organomet. Chem. **136**, 1 (1977).
46. F. X. Kohl and P. Jutzi, *Organomet. Synth.*, Vol. 3, eds. R. B. King and J. J. Eisch (Elsevier, Amsterdam, 1986).