Journal of Organometallic Chemistry, 400 (1990) 1–17
Elsevier Sequoia S.A., Lausanne
JOM 21178

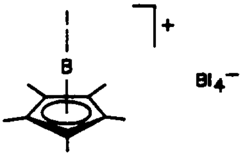
Cyclopentadienyl complexes with main-group elements as central atoms—a decade of research

P. Jutzi
Faculty of Chemistry, University of Bielefeld, W-4800 Bielefeld (Germany)

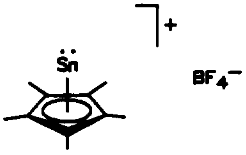
(Received June 8th, 1990)

Introduction

During the 1970's we examined in detail the dynamic behaviour of sigma-bonded cyclopentadienyl compounds of main-group elements. As a result, we now think we understand the reasons for the large differences in fluxionality of these species [1]. In the context of this research project, we were also interested in, among other things, fluxional cyclopentadienyl boron compounds. When we tried to synthesize diiodo(pentamethylcyclopentadienyl)borane by the reaction of trimethyl(pentamethylcyclopentadienyl)germane with triiodoborane, we observed the formation of the ionic species **1**, having a π-bonded boron atom in the *nido*-cluster cation [2]. Later we were able to synthesize the ionic compound **2**, with a π-bonded tin atom in the cation, starting from the π-complex decamethylstannocene and tetrafluoroboric acid [3]. This was the beginning of our intensive and systematic work in the field of π-coordination to main-group elements from the *p*- as well as from the *s*-block.



1



2

A review article with all the information so far available on π-coordination to main-group elements was published a few years ago [4] and some progress reports have been given [5,6]. This review is concentrated mainly on π-complexes involving cyclopentadienyl ligands, and discusses general principles of structure, bonding, and reactivity. Furthermore, some very recent results in the field, predominantly from our group in Bielefeld, are described.

Structure and bonding: a classification

If some simplifications are made, it is possible to classify all cyclopentadienyl π-complexes in terms of typical structure and bonding features. Firstly, we have to

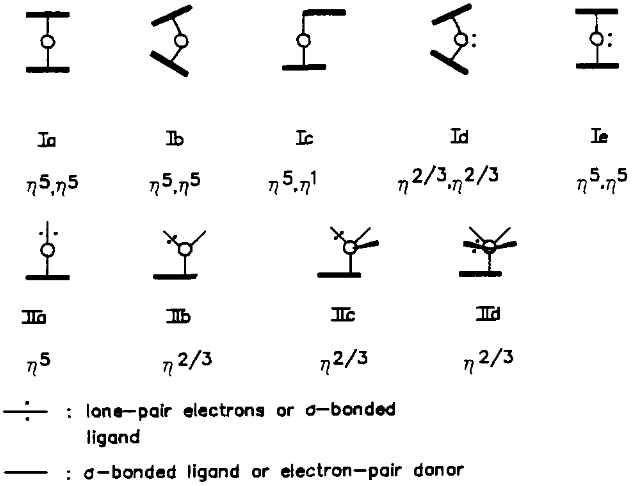


Fig. 1. Structure types for sandwich and half-sandwich compounds with predominantly covalent cp-element bonding.

differentiate between compounds in which the cyclopentadienyl–element bonding is predominantly covalent and those in which it is predominantly ionic. A high degree of ionic character can be assumed for all the alkali metal and heavier earth alkali metal (Ca, Sr, Ba) compounds. The environment of the corresponding cations is governed by the steric requirements of the cyclopentadienide anions and additional coordinating species. Electron-counting rules do not define the structures of these compounds. Borderline bonding situations presumably are found in magnesium(II), indium(I), thallium(I), lead(II), and bismuth(III) complexes. Unfortunately, clear-cut information on the cyclopentadienyl–metal bonding modes in these compounds, for example from IR and Raman investigations, is not available so far. Qualitative assignments rely on NMR and structural parameters. In the complexes of all the other compounds, the bonding between the main-group element and the cyclopentadienyl-ligand is regarded as predominantly covalent.

In Fig. 1, typical sandwich and half-sandwich structures observed for compounds with covalent cp-element bonding are presented schematically, together with the notation of the hapticity of the cp ligand.

Regular sandwich structures (**Ia**) are observed for all magnesocenes [4] with the exception of hexakis(trimethylsilyl)magnesocene [7], for which a bent sandwich structure (**Ib**), which minimizes the repulsive interactions of the trimethylsilyl groups, has been found. The structure of beryllocene [4] is controversial, and is represented here by **Ic**: In the solid state one cp ring is η^5-bonded and the other η^1-bonded to the beryllium atom, and in the gas phase the structure is similar. Interestingly, a comparable structure has been found for the bis(pentamethylcyclopentadienyl)boronium cation [4]. Bent sandwich structures of type **Id** are expected, and are in fact found for the metallocenes of silicon [8], germanium, tin, and lead [4], and also for the isoelectronic bis(pentamethylcyclopentadienyl)phosphonium, arsonium, and stibonium cations [4]. These complexes are highly fluxional in solution; their η^2- or η^3-bonding has been demonstrated by X-ray and electron diffraction studies. In the case of steric overcrowding by five bulky substituents on the cyclopentadienyl ring, the highly unusual regular sandwich structures **Ie** are observed. This situation is found in one of the two conformers of decamethylsilicocene [8] and in decaphenylstannocene [9]. "*Where are the lone pair electrons in these π-complexes and in other subvalent fourth-group compounds?*" is an interesting question that was asked by the late J.J. Zuckerman [10]. In the above complexes the lone-pair possesses pure *s*-character; the electrons occupy an antibonding molecular orbital.

Four different types of half-sandwich structures have to be considered for monocyclopentadienyl π-complexes with predominant covalent cp-element bonding. These are also schematically represented in Fig. 1. Highly symmetrical half-sandwich complexes of type **IIa** are known for many main-group elements. They can be regarded as *nido*-clusters with a pentagonal-pyramidal structure. The cations of the previous mentioned compounds **1** and **2** belong to this class, as do other cyclopentadienyl complexes with the following main-group element fragments, which are isoelectronic and isolobal with $B{-}R^+$ or $Sn:^+$:Be–R [4], In: (gas phase [4,11]), Tl: (gas phase [4,12] and solid state [13]), $C{-}R^{2+}$ [4], $Ge:^+$ [4], and $Pb:^+$ [14]. Even more common are complexes of type **IIb**, in which there is asymmetrical π-bonding to a cyclopentadienyl ligand in a η^2- or η^3-fashion. Compounds with the following isolobal and isoelectronic element fragments belong to this series: AlR_2, GaR_2, InR_2, CR_2^+, RGe:, RSn:, RPb:, donor → $Ge:^+$, donor → Sn^+, $RP:^+$, and $RAs:^+$ [4]. Similar bonding situations are found for complexes belonging to the structure types **IIc** and **IId**, in which the number of ligands at the main-group element is further increased; simultaneously, the bonding to the cyclopentadienyl ligand is weakened. In some very few situations, weak coordination of further ligands does not change the η^5-bonding of the cyclopentadienyl ligand; the solid-state structure of the dimeric $Me_5C_5PbBF_4$ [14] is portrayed as an example in Fig. 2. Complexes of type **IIb–d** are highly fluxional in solution; the η^2- or η^3-bonding has so far been established only by X-ray or electron diffraction studies. Generally, higher coordinated π-complexes of type IId are found only for the heavier elements. It must be emphasized that structural alternatives for **IIb** and **IIc** with η^1-bonded cyclopentadienyl ligands may be energetically favoured, especially for cp compounds with the lighter elements, e.g. B, Si, Ge, P, As [1].

Structure types observed for non-donor-stabilized cyclopentadienyl complexes with predominantly ionic cp-element bonding are depicted schematically in Fig. 3. Several interesting structural features have been revealed by solid state as well as gas

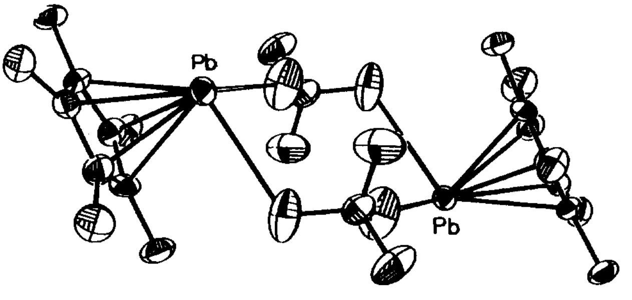


Fig. 2. Solid-state structure of $Me_5C_5PbBF_4$.

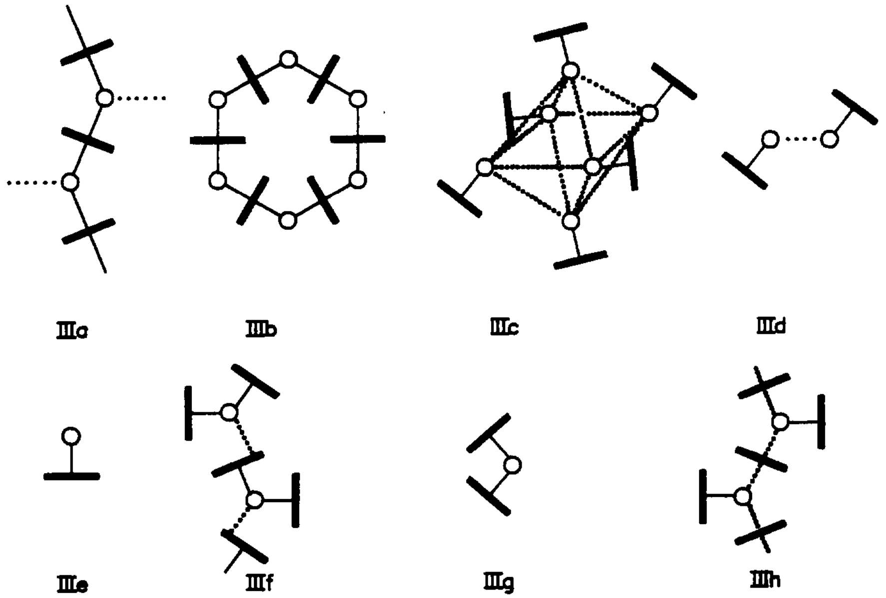


Fig. 3. Structure types for non-donor-stabilized cyclopentadienyl complexes with predominantly ionic cp–element bonding.

phase investigations for this class of compounds. Some of the results have been published only recently, and reflect the degree of current interest in this topic.

The complex potassium-trimethylsilylcyclopentadienide still represents the only structurally characterized base-free alkali metal cyclopentadienide [15]. This compound crystallizes in a polymeric zig-zag chain structure of type **IIIa**. Each potassium atom is centrally positioned between two bridging cyclopentadienyl rings, and interacts with a further cyclopentadienyl ring of a neighbouring chain [5,15]. Similar polymeric chain structures are found for several cyclopentadienylindium and -thallium compounds [4,16–19]. In all these cases, weak interactions with relevant metals of adjacent chains are presumably structure determining [11]. When the hydrogen atoms of the cyclopentadienyl ring are substituted by more bulky groups, the coordination pattern changes drastically. Thus, hexameric solid-state structures are found for bis(trimethylsilyl)cyclopentadienylthallium [19] (type **IIIb**) and pentamethylcyclopentadienylindium [11] (type **IIIc**), whereas dimeric units are present in solid pentabenzylcyclopentadienylindium [20] and -thallium [21] (type **IIId**). The latter two structure types are currently of special interest in the context of the controversial discussion of nonclassical metal–metal interactions in indium(I) and thallium(I) chemistry [22]. As described earlier, the cyclopentadienyl and pentamethylcyclopentadienyl compounds of indium and thallium form monomeric half sandwich units (type **IIa**, covalent model, or type **IIIe**, ionic model) in the gas phase [4,11,12], and in one case also in the solid state [13].

Little is known about the solid-state structures of the base-free cyclopentadienyl compounds of the heavier alkaline earth metals. The only structure described to date is that of calcocene, $Ca(C_5H_5)_2$: This compound crystallizes as a polymer, with each calcium atom attached to four bridging cyclopentadienyl rings in a complicated η^5-, η^3-, η^3-, η^1-fashion [4]. The solid state structure of barium-bis(penta-

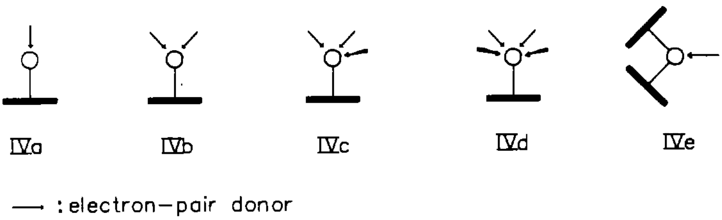
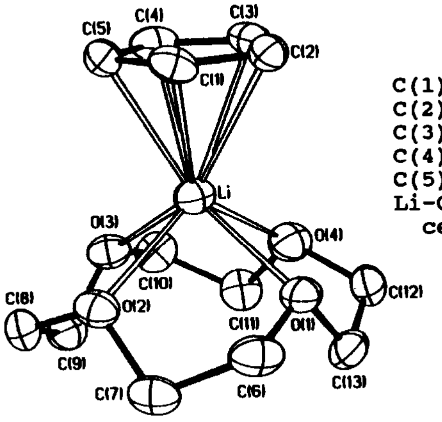


Fig. 4. Structure types for donor-stabilized cyclopentadienyl complexes with ionic cp–metal bonding.

methylcyclopentadienide) has been determined only very recently. It shows a bent metallocene in a polymeric chain built up by weak barium-cyclopentadienyl interactions [23] (type **IIIf**). Surprisingly, bent metallocene-type structures **IIIg** are present in the gas phase for calcium-, strontium-, and barium-bis(pentamethylcyclopentadienide), as shown by recent GED studies [24,25]. The bent structures can be rationalized in terms of a polarized ion model [26]. As already argued for the bent metallocene structures of divalent *f*-block elements and for some heavy alkaline earth metal dihalides, a bent structure may optimize the polarization of a large cation by two anions and may give better total electrostatic bonding for the two rings. Compared with **IIIf**, a more symmetrical structure **IIIh** is observed for the polymeric plumbocene, $Pb(C_5H_5)_2$; interestingly, a monomeric structure (type **Id** or **IIIg**) has been found for the permethylated derivative [4].

Several ionic cyclopentadienyl complexes of *s*-block metals in which one or more additional donor species are coordinated to the metal centre have been structurally characterized. Relevant structure types are shown schematically in Fig. 4. In all these compounds the metal is η^5-bonded to the cyclopentadienyl ring. In comparable series of complexes, the metal–cyclopentadienyl bond distance decreases with the decreasing number of coordinated donor functions [5].

Type **IVa**-complexes have so far only been observed for lithium compounds with several bulky substituents on the cyclopentadienyl ring. Thus, lithium-tris(trimethylsilyl)cyclopentadienide forms 1 : 1 adducts with many monodentate donor molecules [4,27]. The most usual coordination pattern, at least for lithium and sodium



C(1) - C(2) = 1.385(4) Å
C(2) - C(3) = 1.399(3) Å
C(3) - C(4) = 1.402(4) Å
C(4) - C(5) = 1.398(3) Å
C(5) - C(1) = 1.390(3) Å
Li-Cp(ring centroid) = 2.063 Å

Fig. 5. Crystal structure of $H_5C_5Li(12\text{-crown-}4)$.

cyclopentadienyl compounds, is represented in complexes of type **IVb** [4,27]. The "pianostool" geometry **IVc** is found for the tetrahydrofuran complex of potassium-pentabenzylcyclopentadienide [28], the "normal-chair" geometry **IVd** in the [12-crown-4] complex of lithium-cyclopentadienide [29] (Fig. 5). A segment from the polymeric structure of barium-bis(pentamethylcyclopentadienide) (**IIIe**) is present in the crystal structure of THF-adducts of calcium- and strontium-bis[bis(trimethylsilyl)cyclopentadienide] [30,31] (type **IVe**), once more indicating the preference of the heavier group 2 metallocenes for bent structures.

Substituted cyclopentadienyl systems and their preferential application

The permethylated cyclopentadienyl ligand has so far played a very important role in our chemistry. Use of this ligand has allowed the synthesis of interesting π-complexes, whose cyclopentadienyl analogues are too unstable to be isolated under ordinary conditions. The triply-trimethylsilylated cyclopentadienyl system has also been shown to be very useful in some important cases. Currently, some otherwise substituted cyclopentadienyl systems are being explored with great success, and not only in our group. In the following section the most widely used ligands are considered in respect of their influence on π-complex properties, and suggestions are offered for the preferential application of these ligands.

The pentamethylcyclopentadienyl ligand

There are many advantages of the pentamethylcyclopentadienyl ligand: first, the absence of hydrogen substituents precludes interference from prototropic rearrangements and metallation processes in σ-bonded precursor molecules; second, the steric demand of this ligand can be used for kinetic stabilization and to induce pronounced structural changes; third, the electronic effect of five methyl substituents has implications for the reactivity. Finally, the pentamethylcyclopentadienyl ligand provides better solubility and crystallinity.

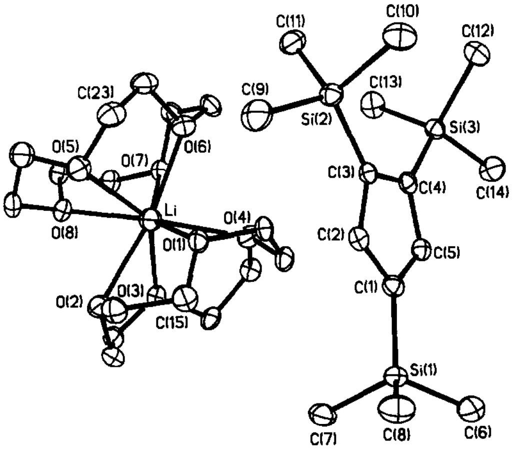
Sigma-bonded cyclopentadienyl compounds are often precursors in the synthesis of π-complexes. In these situations it is absolutely necessary to have the relevant allylic isomer present; otherwise, monohapto–polyhapto rearrangements cannot take place. Thus, prototropic processes [1] must be avoided. Per-alkylation or -arylation of the cyclopentadienyl ring is essential; permethylation is the more easily achieved. Instructive examples arise in boron and phosphorous chemistry [4]. In another synthetic strategy, π-complexes are prepared from higher valent precursors by reduction with alkali metals or their equivalents. Once again, permethylation is indicated, in this case to avoid metallation at the cyclopentadiene system. The most impressive example of this strategy is found in silicon chemistry [8].

Kinetic stabilization by permethylation of the cyclopentadienyl ligand is often used in the π-complex chemistry not only of *p*-block, but also of *d*- and *f*-block elements. It allows the synthesis of otherwise highly unstable species. Furthermore, the steric demand of a pentamethylcyclopentadienyl ring prevents oligo- or polymerisation; dramatic changes in structure can result. This becomes evident by comparison of the structures of the parent and the permethylated calcocene, plumbocene, and cyclopentadienylindium.

Permethylation of the cyclopentadienyl ring also has electronic implications. There is not enough information available to demonstrate this by comparing chemical properties, but it can be readily seen from relevant PES data. For example, vertical ionizations from orbitals with cyclopentadienyl character are about 1 eV lower in energy for the permethylated compounds in the magnesocene, stannocene, and pumbocene series [4]. The same feature is revealed by calculations on many metallocenes [4], cyclopentadienyl(chloro)germylene [4], and cyclopentadienylindium compounds [11]. It is generally accepted that the electron density in the valence region and at the metal is increased by permethylation of the cyclopentadienyl ring. It is assumed that the covalent character of the cyclopentadienyl–metal bond increases at the same time.

Trimethylsilylated cyclopentadienyl ligands

Up to three trimethylsilyl groups can be introduced into the cyclopentadienyl system. It is a general effect that silylation of substrates increases the lipophilicity and volatility of the resulting compounds. Increasing trimethylsilyl substitution can be expected to result in increased kinetic stability of reactive species. The mono- and bis-(trimethylsilyl)substituted cyclopentadienyl ligands already play a distinctive role in organometallic chemistry, especially in the π-complex chemistry of *f*-block elements [32]. Therefore it is not surprising that silylated cyclopentadienyl ligands show interesting effects when combined with those main-group elements in cases where predominantly ionic bonding is assumed for the parent compounds. They have been successfully used in lithium [27], sodium [33], potassium [15], calcium [30,31], strontium [31], indium [33], and thallium [4,19] chemistry. Changes in physical and structural properties are striking. In the case of the volatile tris(trimethylsilyl)cyclopentadienylthallium we have suggested that there is a higher degree of covalency in the cyclopentadienyl–thallium bond. For comparison with other more or less ionic silylated cyclopentadienyl compounds, we have synthesized and structurally characterized the crown-ether complex $(Me_3Si)_3H_2C_5^-$ (12-crown-4)$_2$Li$^+$, which contains a bare cyclopentadienide ligand [33] (Fig. 6). In the series of the trimethylsilylated metallocenes of germanium, tin, and lead, the stability against oxidation and thermal decay increases with increase in the number of silyl sub-



C(1) - C(2) = 1.414(3) Å
C(2) - C(3) = 1.413(3) Å
C(3) - C(4) = 1.446(3) Å
C(4) - C(5) = 1.414(3) Å
C(5) - C(1) = 1.414(3) Å
C(1) - Si(1) = 1.836(2) Å
C(3) - Si(2) = 1.836(2) Å
C(4) - Si(3) = 1.842(2) Å

Fig. 6. Crystal structure of $(Me_3Si)_3H_2C_5^-$ (12-crown-4)$_2$Li$^+$.

stituents [4,34]. In hexakis(trimethylsilyl)magnesocene, the steric repulsion between the bulky silyl groups results in a bent-metallocene structure [7].

These electronic and steric effects can at present be discussed only in very qualitative terms, since precise data are not yet available.

The pentaphenyl- and the pentabenzylcyclopentadienyl ligand

Obviously, cyclopentadienyl ligands with five phenyl or benzyl substituents are sterically highly demanding, and unusual structural and electronic features can be expected. There is much current interest in using these systems in the π-complex chemistry of main-group elements. The first complex containing the pentaphenylcyclopentadienyl ligand was decaphenylstannocene [9], which has a fascinating structure (type **Ie**, see above). The tin atom lies on an inversion centre between symmetry-related cyclopentadienyl rings. The attached phenyl groups are canted to each cyclopentadienyl ring in an opposed paddle wheel fashion, and the molecule falls into the very rare S_{10} symmetry class. Germanium, lead, and other tin derivatives [35], as well as a thallium complex [36], containing this ligand are also known.

Even more extensively used is the pentabenzylcyclopentadienyl ligand. Complexes with germanium, tin, and lead [37,38], as well as with indium [20], thallium [13,21] and potassium [28] as central atoms have been synthesized and characterized by X-ray diffraction studies. Most of the above mentioned complexes are air-stable and have interesting molecular structures (see above chapter). The enhanced stability can be attributed to a shielding effect of the phenyl groups on the reactive metal centres. In the solid state structures, two or three of the benzyl groups of a pentabenzylcyclopentadienyl ligand are bent towards the relevant centre in such a way that bonding interactions are feasible.

The deprotonated dimethylsilanediyl-bis(tetramethylcyclopentadiene) as ligand

Similar bonding interactions are observed in complexes of germanium(II) and tin(II) with the above π-ligand. Crystal structure investigations confirm metallocenophane-like structures, in which the central atom is η^5-bonded to the cyclopentadienyl ring and also weakly η^2-bonded to one of the double bonds of the cyclopentadiene ligand [39], as portrayed in Fig. 7. These complexes possess model character for the interaction of a cyclopentadienyl–element unit with unsaturated hydrocarbons.

The 1,3-di-t-butylcyclopentadienyl ligand

In the sandwich and half-sandwich chemistry of germanium, tin, and lead, the introduction of two t-butyl substituents in 1,3-position of the cyclopentadienyl ligand is of great advantage [40]. Compared with the parent complexes, the substituted derivatives are more thermally stable, more soluble in non-polar solvents, and less air sensitive. This is the result of substantial kinetic stabilization and effective shielding of the metal centres. Major structural influences are observed in the case of the half-sandwich complex $(^t\mathrm{Bu})_2\mathrm{C}_5\mathrm{H}_3\mathrm{PbBF}_4$ [40].

The 1,3,7,9-tetra-t-butylfulvalene ligand

From both the experimental and the theoretical point of view there is current interest in non-classical attractive metal–metal interactions between molecular units

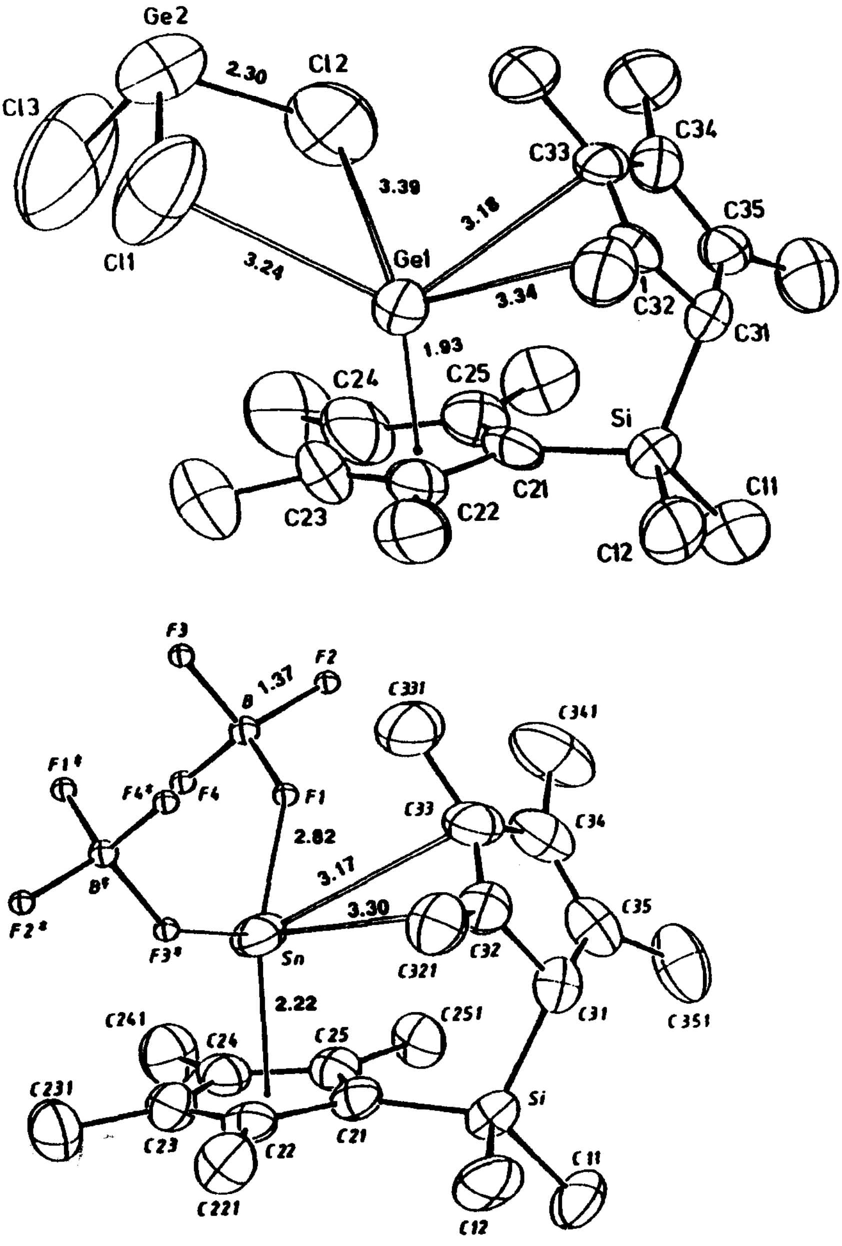
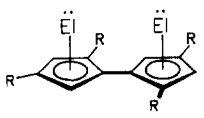


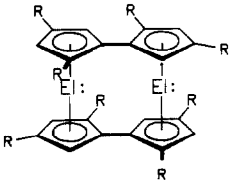
Fig. 7. Crystal structure of a Ge^{II}- and a Sn^{II}-cyclopentadienyl complex with additional metal–olefin interaction.

that possess already closed subshells ($d^{10}s^2$) and therefore should not form further bonds. In the case of the cyclopentadienyl complexes this phenomenon has given rise to controversy in indium(I) and thallium(I) chemistry. In contributions in this area, we have used the 1,3,7,9-tetra-t-butylfulvalene as a π-ligand [41], and synthesized half-sandwich complexes of type **V** with the elements indium and thallium [42] and sandwich complexes of type **VI** with the elements germanium and tin [43]. These compounds seem to us best suited for non-classical metal–metal interactions. Assessment of the solid state structures is under investigation.



V

El=In,Tl R=^{t}Bu



VI

El=Ge,Sn

Cyclopentadienyl and carbollyl ligands: a comparison

At a first approximation, the isolobal principle highlights the relationship between cyclopentadienide, the open face of some carbollide, and certain hydroborate ligands, as portrayed in Fig. 8. These anionic systems also are isoelectronic, with negative charges ranging from -1 to -4. The flexibility in the ligand charge has already allowed the synthesis of many interesting π-complexes [4]. Advances in the chemistry of carbollide complexes with group 13 and 14 elements have been reviewed recently [44].

A *closo* species of the type $R_2C_2B_nH_nEl$ represents an interesting electronic system because of the unusual configuration involving a "bare" metal atom incorporated in a polyhedron with its unshared electron pair directed away from the polyhedral surface. In cyclopentadienyl chemistry a similar situation is found in compounds of type **IIa** (see above). The failure of the above compounds to form adducts with Lewis acids is in keeping with the nearly symmetrical electron distribution, as indicated by MO calculations [45]. In tin chemistry, similarities between *closo*-stannacarboranes and the pentamethylcyclopentadienyltin cation became apparent. Given the Lewis acidity of the latter [4], it was expected that stannacarboranes would behave similarly. This possibility was explored by treating $Me_2C_2B_9H_9Sn$ with mono- and bi-dentate Lewis bases [46], and later also by investigations involving smaller stannacarboranes [44,47]. The major structural effect of base complexation was the slippage of the apical tin atom from a nearly η^5-bonding to an η^3-triboraallyl-type bonding in the adducts. The question of the origin of the observed structural distortions has also been treated theoretically [48–50]: the displacement of the tin atom towards the unique boron on the B_3C_2 open face leads to primarily σ-bonding to the tin atom due to rehybridization of the relevant atoms. This contrasts with the predominant π-interactions of a cyclopentadienyl ligand.

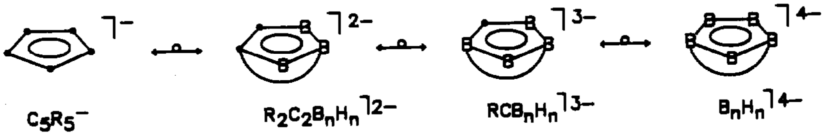


Fig. 8. Isolobal and isoelectronic anionic π-ligands.

Table 1

^{119}Sn NMR data of tin(II) compounds

Compound	δ^{119}Sn	Lit.	Compound	δ^{119}Sn	Lit.
$[(Me_3Si)_2N]_2Sn$	+776	51	$Me_2C_2B_9H_9Sn$	−379	53
$[(Me_2C_2B_9H_9)_2Sn]^{2-}$	+449	53	$(Me_5C_5)_2Sn$	−2129	4
$[Me_2C_2B_9H_9SnCl]^-$	+224	53	$[Me_5C_5Sn]^+$	−2247	4

Differences between the π-bonding of cyclopentadienyl and carbollyl ligands to a tin center can also be detected from the ^{119}Sn NMR data for comparable compounds. The large range of ^{119}Sn chemical shifts indicates that this parameter is extremely sensitive towards changes in the surroundings of a tin atom [51]. In general, organometallic tin(II) compounds are of special interest in the context of the theory of nuclear shielding. Whereas monomeric tin(II) amides give signals at the low-field end for all known ^{119}Sn resonances, the cyclopentadienyl complexes of tin(II) are found at the other extreme, at very high field; an explanation has been given in terms of different contributions of the paramagnetic term as part of the nuclear screaning constant [51]. An intermediate shift region is observed for tin(II) dicarbollide complexes. A list of relevant ^{119}Sn NMR data is given in Table 1. A high coordination number of the tin atom is related to high shielding. Thus, a dicarbollide ligand seems to be less strongly coordinating and less electron-donating than a cyclopentadienyl ligand in comparable bonding situations.

Our main interest in this area of π-complex chemistry is concentrated on compounds with the $Me_2C_2B_9H_9^{2-}$ ligand [4,46,52]. Currently we are trying to complete a series of complexes whose analogues in cycloptenadienyl chemistry are already known and have been structurally characterized. Examples with elements from groups 13, 14, and 15 as central atoms are given in Table 2. π-Complex structures for these compounds have been deduced from NMR investigations, and in the case of $Me_2C_2B_9H_9Tl_2$ [53] (Fig. 9) and $Me_2C_2B_9AsCl$ [53] (Fig. 10) also from X-ray crystal structure analyses.

Interestingly, the high oxidation states of main-group elements can be stabilized by π-complexation with dicarbollide ligands. Recent examples have arisen from aluminum [54], gallium [55], silicon [56,57], and germanium [58] chemistry. Sandwich-type structures have been established by X-ray crystallography. The number of interstitial bonding electrons in these compounds is the same as that in the cyclopentadienyl complex magnesocene (12 electrons, type **Ia** in the structure and bonding section above). In the gallium compound, the central atom is significantly

Table 2

Comparable cyclopentadienyl and dicarbollyl compounds [a]

$(Me_5C_5)_2El$	[4]	Me_5C_5ElCl	[4]
$[(Me_2C_2B_9H_9)_2El]^{2-}$	[53]	$[Me_2C_2B_9H_9ElCl]^-$	[53]
$[Me_5C_5El]^+$	[4]	Me_5C_5Tl	[4]
$Me_2C_2B_9H_9El$	[4,53]	$Me_2C_2B_9H_9Tl^-$	[53]
$Me_5C_5PNH^tBu$	[64]		
$Me_2C_2B_9H_9AsCl$	[53]		

[a] El = Ge, Sn.

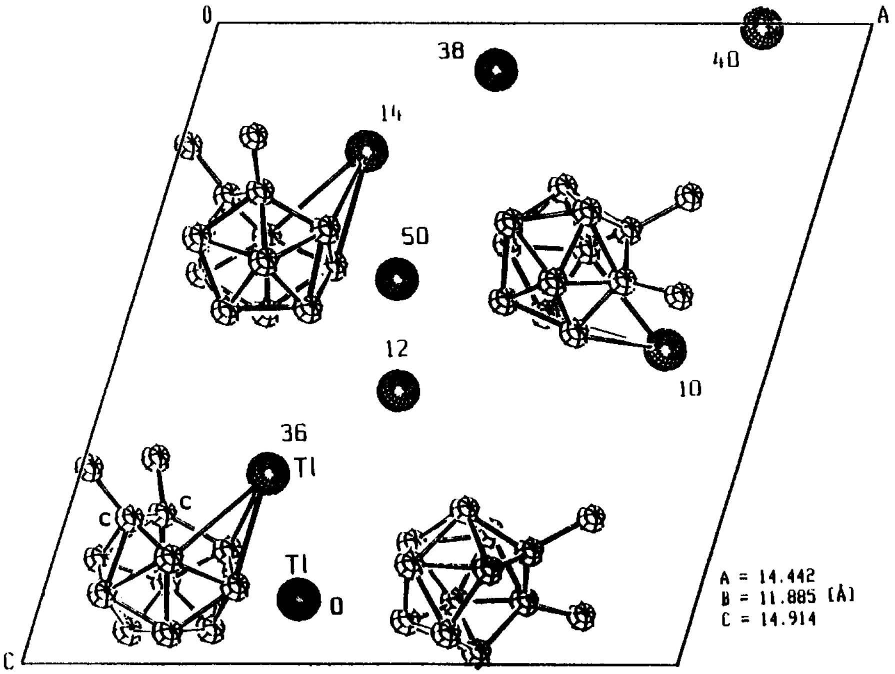
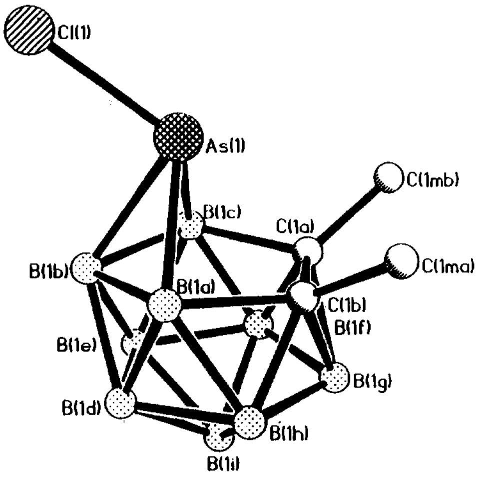


Fig. 9. Crystal structure of $Me_2C_2B_9H_9Tl_2$ (lower half of the unit cell, space group $P2_1/c$).

slipped toward the three boron atoms in each of the B_3C_2 faces; formally, the carbollide ligands donate 4 electrons each, resulting in a total of 8 electrons in the valence shell of a gallium(III) center [55]. A half-sandwich structure has been deduced for the tin(IV) complex $Me_2C_2B_9H_9SnMe_2$ from its ^{119}Sn and ^{11}B NMR data [52]. In view of these very recent results, the π-complex chemistry of high-valent *p*-block elements involving carbollide ligands seems to be very promising.



As(1) - Cl(1) = 2.216(6) Å
As(1) - B(1a) = 2.239(21) Å
As(1) - B(1b) = 2.154(19) Å
As(1) - B(1c) = 2.234(20) Å
∢ B(1a), B(1b), B(1c)-
B(1a), C(1b), C(1a),
B(1c) = 9.1°

Fig. 10. Crystal structure of $Me_2C_2B_9H_9AsCl$.

The chemistry of cyclopentadienyl complexes: some general principles

The chemistry of many classes of cyclopentadienyl complexes has not so far been investigated in detail, but recent results are starting to provide a basis for developing general principles of reactivity. The chemistry is determined by the acceptor qualities of the relevant central atom, by the role of the lone-pair electrons if present, and by the functionality of the cyclopentadienyl and the further ligands. In this section, emphasis is placed on the functionality of the cyclopentadienyl ligand, with the aid of some typical examples.

The cyclopentadienyl ligand as leaving group

Reactions with electrophiles

The most widely used reaction principle in main-group cyclopentadienyl chemistry involves cyclopentadienyl transfer to other elements from the *p*, *d*, and *f* block, according to the general equation:

$$R_5C_5M + ElX \longrightarrow R_5C_5El + MX \qquad (1)$$

Cyclopentadienyl compounds of the alkali metals, of magnesium, and of thallium(I) are most often used for cyclopentadienyl transfer. Owing to the differing nucleophilicity and tendency for redox processes, the choice of the best transfer agent depends on the electronic requirements at the electrophilic centre El. In some situations use of cyclopentadienyl transfer agents with low nucleophilicity is indicated. For example, the pentamethylcyclopentadienyltin cation has been successfully used in cyclopentadienyl transfer to a boron centre (eq. 2) [59]; with stronger nucleophiles further attack at boron cannot be avoided.

$$Me_5C_5Sn^+CF_3SO_3^- + BI_3 \longrightarrow Me_5C_5BI^+CF_3SO_3^- + SnI_2 \qquad (2)$$

In the metallocene chemistry of germanium, tin, and lead, Cp–El bond cleavage by electrophiles EX has opened up an interesting route to half-sandwich complexes (eq. 3) [4,14,39]. Oxidative addition and reductive elimination reactions may be involved in these processes. The use of the pentamethylcyclopentadienyl ligand as leaving group in the reaction of [tris(trimethylsilyl)methyl] (pentamethylcyclopentadienyl)germylene with hydrogen chloride has led to the synthesis of the highly reactive [tris(trimethylsilyl)methyl](chloro)germylene; the corresponding oxidative addition product has been shown to be a reaction intermediate (eq. 4) [60].

$$\begin{tikzcd}
(R_5C_5)El \arrow[r, "+EX", "-R_5C_5E"'] & R_5C_5ElX \arrow[d, shift left] & (3) \\
(El = Ge, Sn, Pb) & {[R_5C_5El]^+X^-} \arrow[u, shift left] &
\end{tikzcd}$$

$$\begin{tikzcd}
(Me_3Si)_3CGeC_5Me_5 \arrow[r, "HCl"] & (Me_3Si)_3CGe(H)(Cl)C_5Me_5 \arrow[d, "-Me_5C_5H"] & (4) \\
& (Me_3Si)_3CGeCl &
\end{tikzcd}$$

Reaction with nucleophiles

The reaction of cyclopentadienyl π-complexes with strong anionic nucleophiles results in an overall nucleophilic substitution with the cyclopentadienide ligand as the leaving group:

$$R_5C_5El + Nu^- \longrightarrow NuEl + R_5C_5^- \qquad (5)$$

This behaviour will be illustrated with some examples from tin and germanium chemistry. Decamethylstannocene reacts with [bis(trimethylsilyl)methyl]lithium to give bis[bis(trimethylsilyl]stannylene and lithium pentamethylcyclopentadienide (eq. 6) [61]. In the reaction with methyllithium, the initial formation of a short-lived [bis(pentamethylcyclopentadienyl)methyltin]lithium species has been demonstrated by trapping experiments (eq. 7) [61]; thus, oxidative addition-reductive elimination processes have generally to be taken in account.

$$(Me_5C_5)_2Sn + 2(Me_3Si)_2CHLi \longrightarrow \left[(Me_3Si)_2CH\right]_2Sn + 2Me_5C_5Li \qquad (6)$$

$$(Me_5C_5)_2Sn + MeLi \longrightarrow (Me_5C_5)_2Sn(Me)Li \xrightarrow[-LiX]{+RX} (Me_5C_5)_2Sn(Me)R \qquad (7)$$

$$(Me_3Si)_2CHGeC_5Me_5 + LiC(SiMe_3)_3 \longrightarrow (Me_3Si)_2CHGeC(SiMe_3)_3 + Me_5C_5Li \qquad (8)$$

In the case of pentamethylcyclopentadienyl-substituted alkylgermylenes, nucleophilic substitution with bulky alkyllithiums leads to dialkylgermylenes; a concrete example is shown in eq. 8 [60]. Thus, displacement of a cyclopentadienyl ligand leads to structures with open coordination positions, i.e. with high reactivity and limited stability. It is evident, that the nucleophilic substitution of cyclopentadienide ligands represents a very promising synthetic tool in the chemistry of low-valent p-block elements.

Single-electron-transfer reactions

Different from the bonding in most of the cyclopentadienyl complexes of d-block elements, the HOMO's and LUMO's in complexes of p-block elements are concentrated mainly on the π-ligands and not on the metal. Thus, in single-electron reduction or oxidation processes the attack takes place at a cyclopentadienyl ligand. Owing to the stability of a cyclopentadienyl radical or anion, cyclopentadienyl–element bond cleavage follows, as shown in a general form in eq. 9.

$$R_5C_5El \left\{ \begin{array}{l} \xrightarrow{+e^-} R_5C_5^- + El \\ \xrightarrow{-e^-} R_5C_5^{\cdot} + El^+ \end{array} \right. \qquad (9)$$

In consequence, it has not been possible to detect stable radical cations or anions in cyclovoltammetric studies of sandwich and half-sandwich compounds; under mass-spectrometric conditions, the relevant molecular ions readily fragmentate with loss of a cyclopentadienyl moiety [8].

In chemical experiments, treatment of cyclopentadienyl complexes with single-electron oxidizing or reducing agents leads to decomposition. For example, the group 14 metallocenes react with arene radical anions to give the cyclopentadienide anion and the corresponding group 14 element in its zero oxidation state (eq. 10) [8,62].

$$(R_5C_5)_2El \xrightarrow{+2e^-} 2R_5C_5^- + El \qquad (10)$$

(El = Si, Ge, Sn, Pb)

$$(Me_5C_5)_2ElHal_2 \xrightarrow[-2Hal^-]{+2e^-} (Me_5C_5)_2El \qquad (11)$$

(El = Si, Ge, Sn)

$$(Me_5C_5)_2InCl \xrightarrow[-Cl^-,\ -Me_5C_5^-]{+2e^-} Me_5C_5In \qquad (12)$$

In view of these findings, difficulties are to be expected in those strategies for the synthesis of main-group cyclopentadienyl complexes, that are based on reduction processes. Appropriate conditions have to be chosen to avoid further reduction of the desired compounds. As shown in eq. 11 and 12, the decamethylmetallocenes of silicon, germanium, and tin, as well as pentamethylcyclopentadienylindium, have been synthesized starting from higher valent precursors [8,62]. Interestingly, one of the cyclopentadienyl units is also displaced in the synthesis of the indium compound, once more demonstrating the functionality of this ligand [63].

Conclusion

There is no doubt that the greatest impact on the π-complex chemistry of main group elements to date has been made by compounds with π-bonded cyclopentadienyl ligands. This review has dealt with general principles of structure and bonding in such complexes; and the functionality of the cyclopentadienyl ligand has also been briefly described.

In the past investigations have concentrated mainly on the synthesis, the structure, and the bonding of cyclopentadienyl complexes; this area now is at a very exciting stage of development. In the future, research efforts presumably will focus to a much greater extent on the chemistry of π-complexes. Recent results in this field are very promising.

Acknowledgments

The work of the author's group described above was carried out by a team of active and skillful co-workers, whose names are given in the references and to whom I express my appreciation. Generous financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is also gratefully acknowledged.

References

1 P. Jutzi, Chem. Rev., 86 (1986) 894.
2 P. Jutzi, A. Seufert, Angew. Chem., 89 (1977) 339; Angew. Chem. Int. Ed. Engl., 16 (1977) 330.
3 P. Jutzi, F.X. Kohl, C. Krüger, Angew. Chem., 91 (1979) 81; Angew. Chem., Int. Ed. Engl., 18 (1979) 59.
4 P. Jutzi, Adv. Organomet. Chem., 26 (1986) 217.
5 P. Jutzi, Pure Appl. Chem., 61 (1989) 1731.

6 P. Jutzi, Pure Appl. Chem., 62 (1990) 1035.
7 C. Morley, P. Jutzi, C. Krüger, Organometallics, 6 (1987) 1084.
8 P. Jutzi, U. Holtmann, D. Kanne, C. Krüger, R. Blom, R. Gleiter, I. Hyla-Kryspin, Chem. Ber., 122 (1989) 1629.
9 M.J. Heeg, C. Janiak, J.J. Zuckerman, J. Am. Chem. Soc., 106 (1984) 4259.
10 S.N. Ng, J.J. Zuckerman, Adv. Inorg. Chem. Radiochem., 29 (1985) 297.
11 O.T. Beachley, Jr., R. Blom, M.R. Churchill, K. Faegri, Jr., J.C. Fettinger, J.C. Pazik, L. Victoriano, Organometallics, 8 (1989) 346.
12 R. Blom, H. Werner, J. Wolf, J. Organomet. Chem., 354 (1988) 293.
13 H. Schumann, C. Janiak, M.A. Khan, J.J. Zuckerman, J. Organomet. Chem., 354 (1988) 7.
14 P. Jutzi, R. Dickbreder, H. Nöth, Chem. Ber., 122 (1989) 865.
15 P. Jutzi, W. Leffers, B. Hampel, S. Pohl, W. Saak, Angew. Chem., 99 (1987) 563; Angew. Chem., Int. Ed. Engl., 26 (1987) 583.
16 O.T. Beachley, Jr., J.C. Pazik, T.E. Glassmann, M.R. Churchill, J.C. Fettinger, R. Blom, Organometallics, 7 (1988) 1051.
17 H. Werner, H. Otto, H.J. Kvans, J. Organomet. Chem., 315 (1986) C57.
18 P. Jutzi, W. Leffers, G. Müller, J. Organomet. Chem., 334 (1987) C24.
19 S. Harvey, C.L. Raston, B.W. Shelton, A.H. White, M.F. Lappert, G. Srivastava, J. Organomet. Chem., 328 (1987) C1.
20 H. Schumann, C. Janiak, F. Gürlitz, J. Loebel, A. Dietrich, J. Organomet. Chem., 363 (1989) 243.
21 H. Schumann, C. Janiak, J. Pickardt, U. Börner, Angew. Chem., 99 (1987) 788; Angew. Chem., Int. Ed. Engl., 26 (1987) 789.
22 C. Janiak, R. Hoffmann, Angew. Chem., 101 (1989) 1706; Angew. Chem., Int. Ed. Engl., 28 (1989) 1688; idem, J. Am. Chem. Soc., 112 (1990) 5924.
23 R.A. Williams, T.P. Hanusa, J.C. Huffmann, J. Chem. Soc., Chem. Commun., (1988) 1045; see also: T.P. Hanusa, Polyhedron, 9 (1990) 1345.
24 R.A. Anderson, R. Blom, J.M. Boncella, C.J. Burns, H.H. Volden, Acta Chem. Scand., A 41 (1987) 24.
25 R. Blom, K. Faegri, Jr., H.H. Volden, Organometallics, 9 (1990) 372.
26 M. Guido, G. Gigli, J. Chem. Phys., 65 (1976) 1397.
27 P. Jutzi, W. Leffers, S. Pohl, W. Saak, Chem. Ber., 122 (1989) 1449.
28 J. Lorberth, S.H. Shin, S. Wocadlo, W. Massa, Angew. Chem., 101 (1989) 793; Angew. Chem., Int. Ed. Engl., 28 (1989) 735.
29 P. Jutzi, W. Leffers, P. Power, M. Olmstead, unpublished.
30 P. Jutzi, W. Leffers, G. Müller, B. Huber, Chem. Ber., 122 (1989) 879.
31 L.M. Engelhardt, P.C. Junk, C.L. Raston, A.H. White, J. Chem. Soc., Chem. Commun., (1988) 1500.
32 M.F. Lappert, P.J.E. Yarrow, J.L. Atwood, R. Shakir, J. Halton, J. Chem. Soc., Chem. Commun., (1980) 987.
33 P. Jutzi, W. Leffers, Ph.P. Power and H. Olmstead, unpublished.
34 P. Jutzi, E. Schlüter, M.B. Hursthouse, A.M. Arif, R.L. Short, J. Organomet. Chem., 299 (1986) 285.
35 C. Janiak, H. Schumann, C. Stauder, B. Wrackmeyer, J.J. Zuckerman, Chem. Ber., 121 (1988) 1745.
36 H. Schumann, C. Janiak, H. Khani, J. Organomet. Chem., 330 (1987) 347.
37 H. Schumann, C. Janiak, E. Hahn, J. Loebel, J.J. Zuckerman, Angew. Chem., 97 (1985) 765; Angew. Chem., Int. Ed. Engl., 24 (1985) 773.
38 H. Schumann, C. Janiak, E. Hahn, C. Kolax, J. Loebel, M.D. Rausch, J.J. Zuckerman, M.J. Heeg, Chem. Ber., 119 (1986) 2656.
39 F.X. Kohl, R. Dickbreder, P. Jutzi, G. Müller, B. Huber, Chem. Ber., 122 (1989) 871.
40 P. Jutzi, R. Dickbreder, J. Organomet. Chem., 373 (1989) 301.
41 P. Jutzi, J. Schnittger, Chem. Ber., 122 (1989) 629.
42 P. Jutzi, J. Schnittger, M.B. Hursthouse, Chem. Ber., in press.
43 P. Jutzi, A. Becker, J. Schnittger, in preparation.
44 N.S. Hosmane, J.A. Maguire in J.L. Liebman, A. Greenberg, R.E. Williams (Eds.), Advances in Boron and the Boranes, VCH Publishers, 1988.
45 J.A. Maguire, G.P. Ford, N.S. Hosmane, Inorg. Chem., 27 (1988) 3354.
46 P. Jutzi, P. Galow, S. Abu-Orabi, A.M. Arif, A.H. Cowley, N.C. Norman, Organometallics, 6 (1987) 1024.
47 U. Siriwardane, J.A. Maguire, J.J. Baniwicz, N.S. Hosmane, Organometallics, 8 (1988) 2792.

48 R.D. Barreto, T.P. Fehlner, N.S. Hosmane, Inorg. Chem., 27 (1988) 453.
49 J.A. Maguire, G.P. Ford, N.S. Hosmane, Inorg. Chem., 27 (1988) 3354.
50 D.A. Brown, M.O. Fanning, N. Fitzpatrick, Inorg. Chem., 17 (1978) 1620.
51 B. Wrackmeyer, J. Magn. Reson., 61 (1985) 536; Ann. Rep. on NMR Spectroscopy, 16 (1985) 73.
52 P. Jutzi, P. Galow, J. Organomet. Chem., 319 (1987) 139.
53 P. Jutzi, D. Wegener, M.B. Hursthouse, unpublished.
54 W.S. Rees, Jr., D.M. Schubert, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc., 108 (1986) 5367.
55 M.A. Bandman, C.B. Knobler, M.F. Hawthorne, Inorg. Chem., 28 (1989) 1204.
56 W.S. Rees, Jr., D.M. Schubert, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc., 108 (1986) 5369.
57 N.S. Hosmane, P. de Meester, U. Siriwardane, M.S. Islam, S.C. Chu, J. Chem. Soc., Chem. Commun., (1986) 1421; U. Siriwardane, M.S. Islam, T.H. West, N.S. Hosmane, J.A. Maguire, A.H. Cowley, J. Am. Chem. Soc., 109 (1987) 4600.
58 N.S. Hosmane, P. de Meester, U. Siriwardane, M.S. Islam, S.C. Chu, J. Am. Chem. Soc., 108 (1986) 6050.
59 F.X. Kohl, P. Jutzi, Angew. Chem., 95 (1983) 55; Angew. Chem., Int. Ed. Engl., 22 (1983) 56.
60 P. Jutzi, A. Becker, unpublished.
61 P. Jutzi, B. Hielscher, Organometallics, 5 (1986) 2511.
62 P. Jutzi, B. Hielscher, Organometallics, 5 (1986) 1201.
63 P. Jutzi, W. Leffers, unpublished.
64 D. Gudat, M. Nieger, E. Niecke, J. Chem. Soc., Dalton Trans., (1989) 693.