

## Main-group metallocenes: Recent developments

Peter Jutzi

Faculty of Chemistry, University of Bielefeld, D 4800 Bielefeld, FRG

**Abstract**—Synthesis, structure, and chemistry of some trimethylsilylated and permethylated  $\pi$ -cyclopentadienyl compounds of s- and p-block elements are described. Bent-sandwich structures are found for the magnesium complex  $[(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2]_2\text{Mg}$ , for the calcium compound  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Ca}\cdot\text{THF}$  and for the metallocenes of germanium, tin and lead,  $(\text{Me}_5\text{C}_5)_2\text{El}$ . Half-sandwich structures could be proved for adducts of silylated cyclopentadienyllithium compounds with nitrogen- and oxygen- donors, for a new class of boron cations,  $\text{Me}_5\text{C}_5\text{BR}^+$ , and for the group 14 cations  $\text{Me}_5\text{C}_5\text{El}^+$  (El = Ge, Sn, Pb). - A bent-polydecker sandwich is the structural basis of the potassium compound  $(\text{Me}_3\text{Si})\text{C}_5\text{H}_4\text{K}$ . - Decamethylsilicocene,  $(\text{Me}_5\text{C}_5)_2\text{Si}$ , the first stable silicon(II) compound, could be synthesized from a silicon(IV) precursor,  $(\text{Me}_5\text{C}_5)_2\text{SiCl}_2$ . The properties of this  $\pi$ -complex are compared with those of the heavier homologues.

### INTRODUCTION

In recent years, there has been much progress in the  $\pi$ -complex chemistry of main-group elements (ref. 1). Cyclopentadienyl and isolobal five-membered ring systems as well as arene ligands (ref. 2) play an important role as  $\pi$ -electron donors to s- and p-block elements. In this report, recent developments in the cyclopentadienyl chemistry will be described. Special emphasis is given to partially trimethylsilylated and to permethylated cyclopentadienyl complexes with sandwich or half-sandwich structures.

### SILYLATED CYCLOPENTADIENYL COMPLEXES OF S-BLOCK ELEMENTS

The incorporation of trimethylsilyl groups into a cyclopentadienyl fragment has dramatic consequences concerning the structural and physico-chemical properties of alkali and earth-alkali metal cyclopentadienides. This is demonstrated by examples from lithium, potassium, magnesium, and calcium chemistry.

In contrast to lithium cyclopentadienide,  $\text{C}_5\text{H}_5\text{Li}$ , the tris(trimethylsilylated) compound  $(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2\text{Li}$  (**1**) is soluble in non-polar solvents, as expected for a species with an oligomeric or monomeric structure. On concentration of such solutions, an increase in viscosity is observed, presumably due to the formation of coordination polymers with bridging cyclopentadienyl groups (for comparison see structure of **4**).

With mono- and bidentate nitrogen or oxygen donors, compound **1** forms crystalline 1:1 adducts of type **2** or **3**, which are monomeric in the solid state, in solution and in the gas phase (Fig.1, ref. 3,4,5).

X-ray crystal structure data of **2a**, **2c** and **3a** show the presence of pentahapto-bonded cyclopentadienyl (Cp) rings and coordination patterns as portrayed in Fig. 1. The Cp centroid-lithium distances in **2a** and **2c** are very similar to the calculated ones of the hypothetical half-sandwich  $\text{C}_5\text{H}_5\text{Li}$  (ref. 6). Coordination of a second nitrogen donor leads to longer Cp centroid-lithium and lithium-nitrogen distances (compare **2a** and **3a**). Currently, there is no indication for covalent bonding between the Cp fragment and the lithium atom in the above complexes. This is in agreement with the findings for other  $\pi$ -complexes with a lithium center (ref. 7).

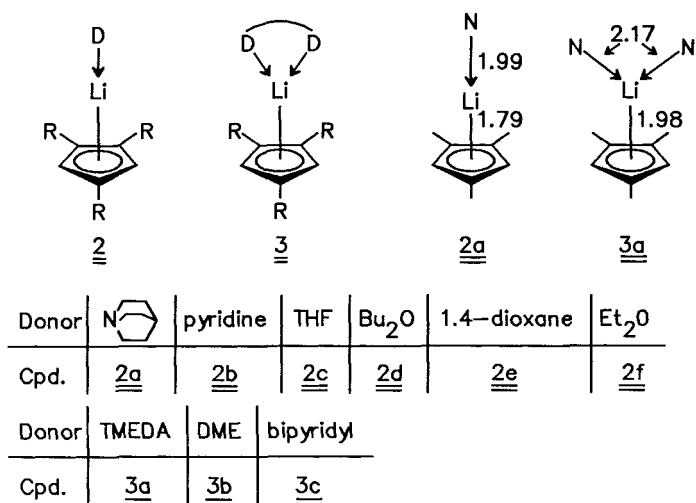


Fig. 1 Adducts of tris(trimethylsilyl)cyclopentadienyllithium.

Stimulated by the unusual behaviour of **1** in solution, we have tried to get solid-state information for base-free alkali metal cyclopentadienides. So far, we have found only one crystalline species, the potassium trimethylsilylcyclopentadienide,  $(\text{Me}_3\text{Si})\text{C}_5\text{H}_4\text{K}$  (**4**) (ref. 8). This extremely air-sensitive compound crystallizes in platelets, which can be shredded into very fine fibers. The macroscopic behaviour reflects a chain or layer structure, which could be proved by an X-ray structure analysis. Details of the structure of **4** are given in Fig. 2. The presence of a bent-polydecker sandwich is shown in Fig. 2a; the bending is caused by weak interactions between neighbouring chains. The organisation of these chains to double-layers and the structure-determining influence of the trimethylsilyl groups is indicated in Fig. 2b.

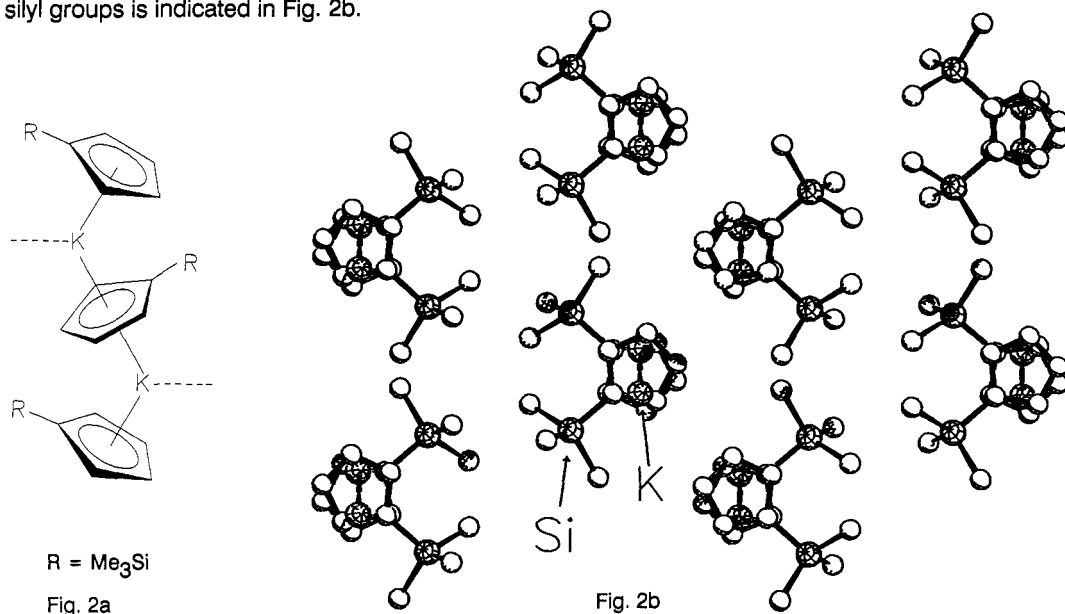


Fig. 2. Crystal structure of  $(\text{Me}_3\text{Si})\text{C}_5\text{H}_4\text{K}$  (**4**).

The steric influence of trimethylsilyl groups becomes evident also in the cyclopentadienyl chemistry of magnesium. Whereas magnesocene,  $(\text{C}_5\text{H}_5)_2\text{Mg}$ , possesses a ferrocene-like structure (ref. 9), the hexakis(trimethylsilyl)magnesocene,  $[(\text{Me}_3\text{Si})_3\text{C}_5\text{H}_2]_2\text{Mg}$  (**5**), crystallizes as a bent-sandwich molecule (angle Cp centroid-Mg-Cp centroid =  $171.1^\circ$ ) to minimize repulsive interactions between the silyl groups. Restricted rotation of the Cp rings is observed at low temperatures (ref. 10).

In calcium chemistry, X-ray studies of calcium dicyclopentadienide,  $(\text{C}_5\text{H}_5)_2\text{Ca}$  (calcocene) (ref. 11), and electron diffraction data of the amorphous permethylated compound  $(\text{C}_5\text{Me}_5)_2\text{Ca}$  (ref. 12) are known. Whereas the first one is an unusual coordination polymer with four cyclopentadienide

ligands attached to one calcium atom, the second one possesses an unexpected monomeric bent-sandwich structure. Silylation of calcocene leads to compounds which are better soluble in nonpolar solvents, but could not get crystallized so far. Molecular weight determinations show the presence of monomeric units in dilute solution. Crystalline adducts with oxygen donors are monomeric in solution and also in the solid state (ref. 13). The crystal structure analysis of the complex  $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Ca}\cdot\text{THF}$  (**6**) reveals the presence of bent-sandwich molecules (angle Cp centroid-Ca-Cp centroid =  $135.4^\circ$ ).

### PENTAMETHYLCYCLOPENTADIENYL COMPLEXES OF P-BLOCK ELEMENTS

For several reasons, the use of the pentamethylcyclopentadienyl (Pcp) instead of the cyclopentadienyl ligand is of great advantage in the  $\pi$ -complex chemistry of main-group elements. For example, a thermodynamic and/or kinetic stabilisation is observed in many situations. Furthermore, interesting structural changes are sometimes connected with this ligand exchange. Moreover, precursor molecules have become available which are rather unstable or exist in form of the wrong isomer (due to prototropic shifts) in the cyclopentadienyl case. Finally, synthetic routes are possible which cannot be used in the parent series.

#### $\pi$ -Complexes of Boron, Indium and Thallium

A new class of boronium salts is formed in a process, where a monohapto-pentahapto rearrangement of a cyclopentadienyl ligand takes place. Reaction of pentamethylcyclopentadienylboron halides with halide-acceptors yields the ionic species of type **Z** (equ.1 and Fig. 3). Other routes, using amino or Pcp ligands as leaving groups, also lead to the desired  $\pi$ -complexes (equ.2 and 3)(ref.14, 15).

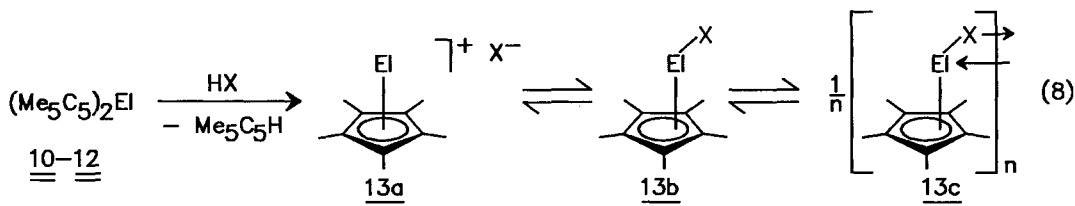
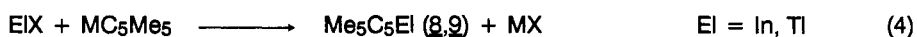


Fig. 3. Pentamethylcyclopentadienylboronium salts (equ.1).

The symmetrical  $\pi$ -structure has been concluded from  $^{11}\text{B}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  nmr- data. Complexes of this type can be regarded as nido-clusters, derived from the hypothetical  $\text{B}_6\text{H}_6^{4-}$  ion by substitution of five  $\text{BH}^-$  against five isoelectronic  $\text{CH}^+$ -units. The cation in **Zf** is isoelectronic with beryllocene and shows an interesting fluxional behaviour (ref. 16). In the reaction of the above compounds with nitrogen donors, borenium or boronium salts are formed, connected with a pentahapto-monohapto rearrangement of the Pcp ligand (ref. 17).

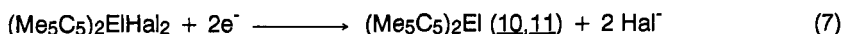
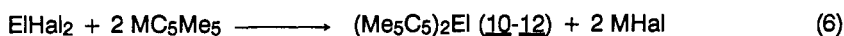
The pentamethylcyclopentadienylindium(I) and -thallium(I) complexes **8** and **9** have been synthesized only recently in salt-elimination reactions (equ. 4)(ref. 18, 19) or in a reduction process (equ. 5)(ref. 20).



Whereas the solid-state structure of **8** is as expected and comparable to that of  $\text{C}_5\text{H}_5\text{Tl}$  (ref. 19), the structure of **9** is very surprising: A hexameric species, based on a disturbed octahedron of indium atoms, has been found by X-ray structure analysis (ref. 18).

### Sandwich and Half-sandwich Compounds of Germanium, Tin and Lead

The decamethylmetallocenes **10-12** are synthesized by salt-elimination reactions (equ. 6)(ref. 21,22) and, in the case of **10** and **11**, also by reduction of the bis(pentamethylcyclopentadienyl)element dihalides (equ. 7)(ref. 23).

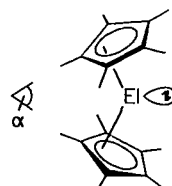


Ei	Ge	Sn	Pb
	<b>10</b>	<b>11</b>	<b>12</b>

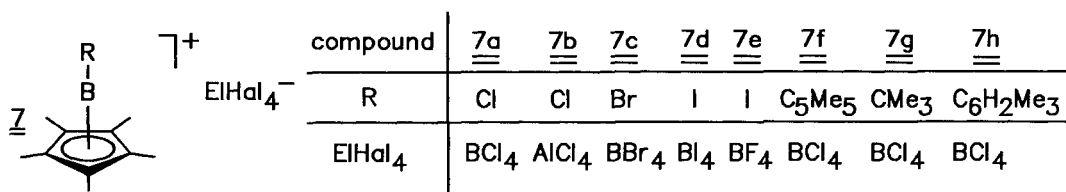
The complexes **10-12** possess a bent-sandwich structure. The Pcp rings are asymmetrically bonded to the group 14 element. The relevant angles between the Pcp planes as well as bonding distances are collected in Table 1. In solution, the compounds are highly fluxional; only averaged information is obtained from nmr investigations.

TABLE 1. Structure data of the metallocenes **10-12**

	<b>10</b>	<b>11</b>	<b>12</b>
$\alpha$ (°)	22±2 <sub>GED</sub>	36.4 35.4 <sub>x-ray</sub>	37.1 <sub>x-ray</sub>
aver. Ei-C	2.52	2.64	2.79
Ei-C (Å)		2.58-2.77	2.69-2.90



According to PES data and MO calculations, the HOMO's in these hypervalent molecules are non-bonding; Electron density is concentrated at the  $\pi$ -ligands. The lone-pair orbitals in **10-12** are of comparably lower energy. As a consequence of the MO sequence, the metallocenes are attacked by electrophiles at the  $\pi$ -system; this leads to the loss of a Pcp ligand and to the formation of half-sandwich complexes. For example, in the reaction of **10-12** with protic compounds, species of type **13** are formed (equ. 8)(ref. 21, 24).



The structure of these compounds depends on several factors (relevant group 14 element, nucleophilicity of X, solvent,...). Ionic species (**13a**) with the nido-cluster cation Me<sub>5</sub>C<sub>5</sub>Ei<sup>+</sup> and covalent molecules with different degrees of association (**13b,c**) have been observed. As an example, the solid-state structure of Me<sub>5</sub>C<sub>5</sub>PbBF<sub>4</sub> is portrayed in Fig. 4 (ref. 24).

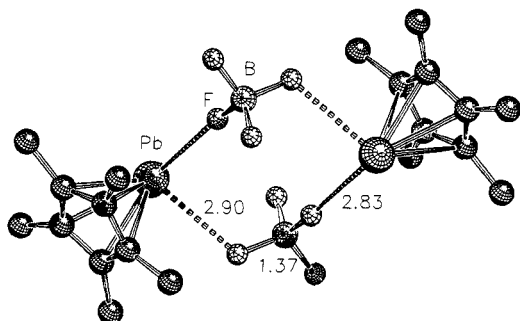
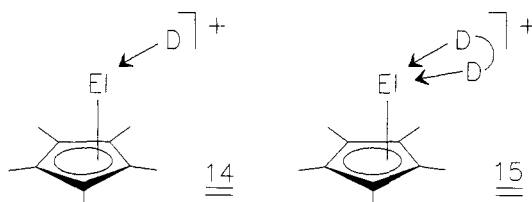


Fig. 4. Crystal structure of Me<sub>5</sub>C<sub>5</sub>PbBF<sub>4</sub>.



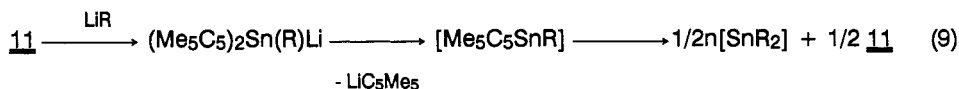
Ei=Ge,Sn,Pb; D= pyridine;

$\widehat{D} \widehat{D}$  = bipyridyl

Fig. 5.  $\pi$ -Complexes of type **14** and **15**.

Their electrophilic character determines the typical chemistry of this class of compounds. Covalent species  $\text{Me}_5\text{C}_5\text{EiR}$  are formed in the reaction with organometallic substrates MR, whereas 1:1 adducts of type 14 and 15 are the result of the reaction with mono- and bidentate  $\sigma$ -donor/ $\pi$ -acceptor molecules (Fig. 5). Due to Pcp ring slippage, the octet rule still holds for these cations.

An overall nucleophilic substitution takes place in the reaction of the metallocenes 10-12 with organolithium compounds. In the case of 11 it was demonstrated, that this reaction proceeds via an oxidative addition/reductive elimination process (equ. 9)(ref. 25).



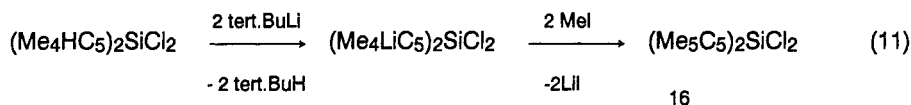
The metallocenes 10 and 11 can be reduced to the group 14 metals (equ. 10)(ref. 23). Thus, for the synthesis of 10 and 11 via the reduction process (equ.7), special care has to be taken in the choice of the appropriate reducing agent.



	EI	M
<u>10</u>	Ge	Li, Na, K, ( $\text{K}_2\text{C}_8\text{H}_8$ )
<u>11</u>	Sn	(Li), Na, K, ( $\text{Li}_2\text{C}_8\text{H}_8$ )

#### DECAMETHYLSILICOCENE - A STABLE SILICON(II) COMPOUND

The successful attempt to prepare the group 14 metallocenes 10 and 11 by a reduction process prompted us to try the synthesis of decamethylsilicocene (17) in a similar manner. The starting material, bis(pentamethylcyclopentadienyl)dichlorosilane (16), was prepared according to equ. 11 (ref. 26):



Treatment of 16 with alkali metal naphthalenides leads to 17, a colourless, air-sensitive, but thermally stable compound (equ. 12)(ref. 27):



An X-ray crystal structure analysis of 17 reveals the presence of two conformers in the unit cell: one with a ferrocene-like structure, the other with a bent-sandwich structure, as indicated in Fig. 6. An electron diffraction study (ref. 28) confirms a bent-sandwich structure for 17 in the gas phase.

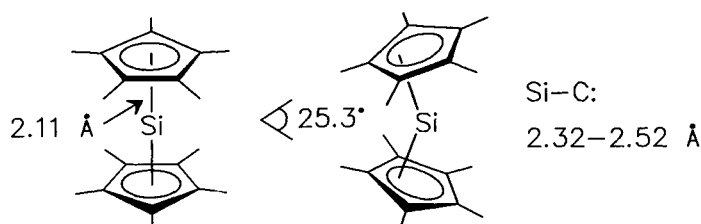


Fig. 6. Crystal structure of decamethylsilicocene (17)

According to the PE spectrum and to MO calculations (ref. 29), the HOMO in 17 still is represented by a ligand-centered, non-bonding orbital; but - in comparison to the situation in 10-12 - the lone-pair orbital is of higher energy. Consequently, electrophilic reagents can attack the silicocene molecule at the  $\pi$ -system or at the lone-pair. Attack at the lone-pair leads to insertion products or to highly reactive species with non-classical (p-p) $\pi$ -bonds. Attack at the  $\pi$ -system leads to loss of one Pcp ring and to the formation of highly reactive silicon(II) compounds. Some examples are collected in the equations of Fig. 7.

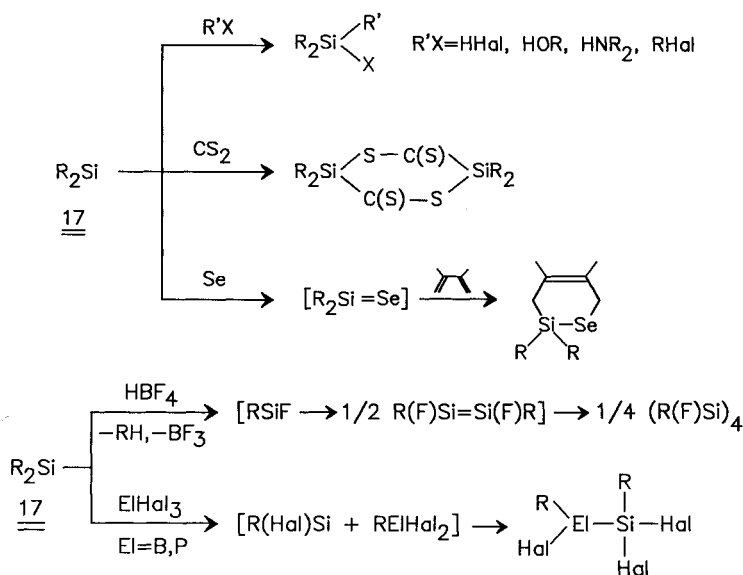


Fig. 7. Some reactions of decamethylsilicocene (17).

#### ACKNOWLEDGEMENTS

The support by the "Deutsche Forschungsgemeinschaft", the "Fonds der Chemischen Industrie", and the University of Bielefeld is gratefully acknowledged. Sincere thanks are extended to coworkers, past and present, who have taken part in this work.

#### REFERENCES

1. P. Jutzi, *Adv. Organometal. Chem.* **26**, 217 (1986).
2. H. Schmidbaur, *Angew. Chem.* **97**, 893 (1985).
3. P. Jutzi, E. Schlüter, S. Pohl and W. Saak, *Chem. Ber.* **118**, 1959 (1985).
4. W. Leffers, Dissertation Universität Bielefeld 1988.
5. M.F. Lappert, A. Singh, L.M. Engelhardt and A.H. White, *J. Organomet. Chem.* **262**, 271 (1984).
6. S. Alexandratos, A. Streitwieser, Jr. and H. Schaefer III, *J. Am. Chem. Soc.* **98**, 7959 (1976).
7. D. Seebach, R. Hässig and J. Gabriel, *Helv. Chim. Acta* **66**, 308 (1983).
8. P. Jutzi, W. Leffers, B. Hampel, S. Pohl and W. Saak, *Angew. Chem.* **99**, 563 (1987).
9. W. Bänder and E. Weiss, *J. Organomet. Chem.* **92**, 1 (1975).
10. C.P. Morley, P. Jutzi, C. Krüger and I.M. Wallis, *Organometallics* **6**, 1084 (1987).
11. R. Zerger and G. Stucky, *J. Organomet. Chem.* **80**, 7 (1974).
12. R.A. Anderson, R. Blom, I.M. Boncella, C.I. Burns and H.V. Volden, *Acta Chem. Scand.* **A41**, 24 (1987).
13. P. Jutzi, W. Leffers, G. Müller and B. Huber, *Chem. Ber.* in press.
14. P. Jutzi, A. Seufert and W. Buchner, *Chem. Ber.* **112**, 2488 (1979).
15. B. Krato, Dissertation Universität Bielefeld 1986.
16. P. Jutzi and A. Seufert, *J. Organomet. Chem.* **161**, C5 (1978).
17. P. Jutzi, B. Krato, M. Hursthouse and A.I. Howes, *Chem. Ber.* **120**, 1091 (1987).
18. O.T. Beachley, M.R. Churchill, I.C. Fettinger, I.C. Pazik and L. Vicotoriano, *J. Am. Chem. Soc.* **108**, 4666 (1986).
19. H. Werner, H. Otto and H.J. Kraus, *J. Organomet. Chem.* **315**, C57 (1986).
20. P. Jutzi, W. Leffers in prep.
21. P. Jutzi, F. Kohl, P. Hofmann, C. Krüger and Y.H. Tsay, *Chem. Ber.* **113**, 757 (1980).
22. I.L. Atwood, W.E. Hunter, A. Cowley, R.A. Jones and C.A. Stewart *J. Chem. Soc., Chem. Commun.* **925**, (1981).
23. P. Jutzi and B. Hielscher, *Organometallics* **5**, 1201 (1986).
24. P. Jutzi, R. Dickbreder and H. Nöth, *Chem. Ber.* in press.
25. P. Jutzi and B. Hielscher, *Organometallics* **5**, 2511 (1986).
26. P. Jutzi, D. Kanne, M. Hursthouse and A.I. Howes, *Chem. Ber.* **121**, 1299 (1988).
27. P. Jutzi, D. Kanne and C. Krüger, *Angew. Chem.* **98**, 163 (1986).
28. R. Blom, A. Haaland, P. Jutzi unpublished.
29. R. Gleiter unpublished.
30. P. Jutzi, U. Holtmann, H. Bögge and A. Müller, *J. Chem. Soc., Chem. Commun.* **305** (1988).
31. P. Jutzi, U. Holtmann and A. Möhrke, unpublished.