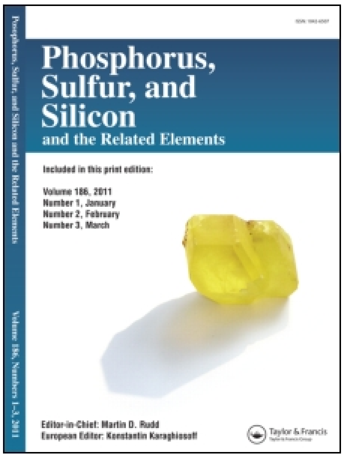

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Organometallic Compounds with Bridged or (Dimethylaminoethyl)-Substituted Cyclopentadienyl Ligands

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ORGANOMETALLIC COMPOUNDS WITH BRIDGED OR (DIMETHYLAMINOETHYL)-SUBSTITUTED CYCLOPENTADIENYL LIGANDS

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We report here the synthesis and structure of organometallic compounds with bridged or dimethylaminoethyl-substituted cyclopentadienyl ligands. A short survey of p- and d-block complexes with pentafulvalenediyl or silicon-linked cyclopentadienyl systems is followed by a discussion of cyclopentadienyl compounds containing the bi(poly)dentate ligands $C_5R_4CH_2CH_2NMe_2$ (R = H, Me) and s- or p-block elements. Compounds of the type $(C_5R_4CH_2CH_2NMe_2)M$ (M = Li, K, Tl), $(C_5R_4CH_2CH_2NMe_2)_2Ca$, $(C_5R_4CH_2CH_2NMe_2)ElMe_3$ (El = Si, Sn), and $(C_5R_4CH_2CH_2NMe_2)MX_2$ (M = Al, Ga, In; X = H, Me, Et, Cl, Br, I) have been obtained. Those with group 2 and group 13 elements as central atoms show an intramolecular coordination of the nitrogen atom and monomeric structures; sufficient volatilities make them potential candidates for MOCVD-processes.

Key Words: Bridged cyclopentadienyls; dimethylaminoethyl-functionalized cyclopentadienyls; metal complexes; intramolecular coordination

INTRODUCTION

There is no doubt that cyclopentadienyl systems are one of the most important ligands in the chemistry of s, p, d, and f-block elements.[1-4] In recent years, we have concentrated our interest in cyclopentadienyl chemistry on the synthesis and the use of modified cyclopentadienyl systems. In more detail, we have prepared organometallic compounds with several bridged and with some side chain-functionalized cyclopentadienyl ligands. The reasons for our activities are manifold:

Linked cyclopentadienyl systems with more or less flexible bridges are expected to bind metal centres in close proximity in the presence or absence of a metal-metal bond and thus to allow intramolecular interactions between adjacent metal centres. Furthermore, mediation of electronic communication between metal centres even without a direct metal-metal bond is expected with the help of the π-systems of the rather rigidly connected Cp ligands.

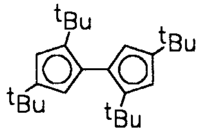
Cyclopentadienyl systems with a donor-functionalized side chain may be useful under several aspects. Firstly, additional intramolecular coordination of a donor to an unsaturated metal centre can stabilize catalytically relevant intermediates. Secondly, intramolecular coordination can influence structure and chemistry of corresponding compounds. Thirdly, donor-functions in the side chain may allow fixation of Cp-systems to differently structured surfaces. Finally, protonation or alkylation of basic side chain-centres can promote water-solubility of corresponding Cp-metal complexes.

In the following, we report on the synthesis and on the structure of some recently prepared modified Cp-compounds.

RESULTS AND DISCUSSION

Bridged Cyclopentadienyl Ligands and some Metal Complexes

The C(Cp)-C(Cp) bridged dicyclopentadienyl system **1** has been used so far in the chemistry of s, p, and d-block elements. In the context of non-classical metal-metal interactions, π-complexes with tin(II) and thallium(I) as metal centres have been described.[5,6] The x-ray crystal structure of the tin(II) compound is depicted in Figure 1[5]; this compound is best regarded as consisting of two isolated, C-C linked stannocene units. The thallium (I) complex consists of two cyclopentadienyl thallium units which are connected by a central C-C bond. The monomeric subunits form a two-dimensional polymer with a zick-zack chain of Tl atoms and a periphery of cyclopentadienyl ligands.[6] Dinuclear complexes showing **1** as ligand have been prepared so far with iron[7a,b], chromium[7a], molybdenum[7a,c], tungsten[7a], and nickel[7d]. Due to steric constraints of the *tert*-butyl substituents, a rotation of the Cp ligand around the central C-C bond is impossible. Thus, a *cis*-orientation of the central atoms is preserved even in the absence of a metal-metal bond.



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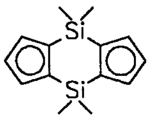

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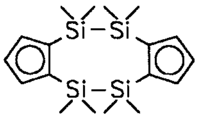

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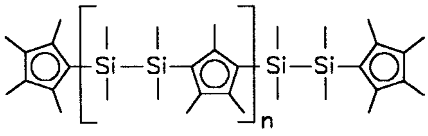


4 n = 0,1,2

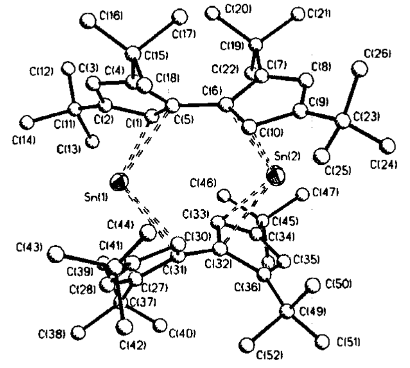


FIGURE 1 Molecular structure of $(t\text{-}Bu_4C_{10}H_4)_2Sn_2$

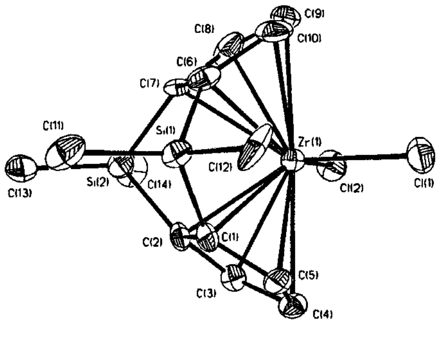


FIGURE 2 Molecular structure of a doubly bridged zirconocene dichloride

Several mono- and oligonuclear metal complexes have been prepared of the doubly bridged cyclopentadienyl ligand **2**.[8] It turns out that in the dinuclear complexes a communication between the relevant metal centres is present, but rather weak.[9] The compounds are best described as valence-localized systems (class I according to Robin and Day). The butterfly-like flexibility of the ligand system **2** allows the isolation not only of dinuclear complexes, but also of mononuclear complexes with a bent-sandwich type structure. As an example, the x-ray crystal structure of a zirconocene dichloride complex is shown in Figure 2.[8c] Independently, ligand **2** has also been investigated by the group of Köhler.[10]

The doubly Si-Si-bridged dicyclopentadienyl system **3** is available only very recently.[11] Bent-sandwich type complexes with germanium, tin, and lead have been obtained as well as a ferrocene derivative. Interestingly, complexes with cyclopentadienyl rings connected with each other by disilane bridges in 1.3-position can be obtained from the same starting compound following a different synthetic route. A cyclophane-type structure for the $Co(CO)_2$ complex is shown in Figure 3.[11] Investigations concerning the electronic communication in this class of compounds are in progress.

A synthetic route to ligands of type **4** in which several cyclopentadienyl units are linked by Si-Si-bridges has been elaborated only recently.[12] Examples for the application of these ligands in π-complex chemistry are still rare. A dinuclear Si-Si-bridged ferrocene is presented in Figure 4.[12]

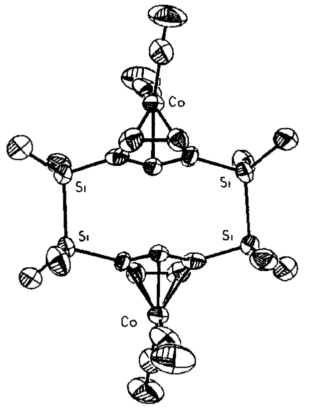


FIGURE 3 Molecular structure of a doubly bridged cobalt carbonyl complex

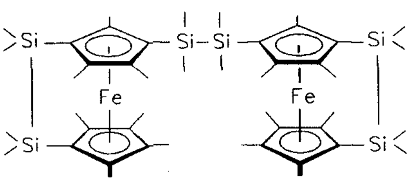
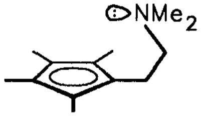


FIGURE 4 Molecular structure of a Si-Si-bridged, dinuclear ferrocene

Dimethylaminoethyl-Substituted Cyclopentadienyl Ligands

Very recently, we have introduced the bi(poly)dentate cyclopentadienyl ligand **5**[13] (possessing both a hard and a soft donor function) into the chemistry of s-, p-, d-, and f-block elements with some typical examples.[14] The corresponding ligand **6**[15] derived from the parent cyclopentadiene has been used in the chemistry of d- and f-block elements.[15a,16] A detailed review on these (dimethylaminoethyl)cyclopentadienyl ligands in compounds of s- and p-block elements will appear in near future.[17]



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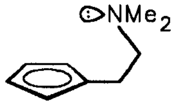
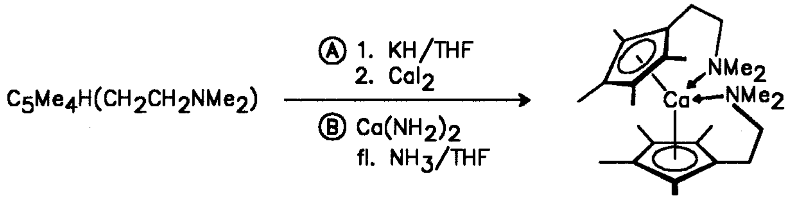


6

The cyclopentadienes $C_5R_4H(CH_2CH_2NMe_2)$ ($R = H$, Me) can be deprotonated with *n*-butyllithium or potassium hydride. The resulting alkali metal cyclopentadienides are important substrates for the synthesis of Cp element compounds containing ligands **5** and **6** (via metathesis reactions).

The calcocene **7** has been obtained by two different routes[14a]; it shows a bent metallocene geometry with intramolecularly coordinating nitrogen atoms. The bulky Cp ligand and the Lewis-base coordination favour the formation of a monomeric molecule.



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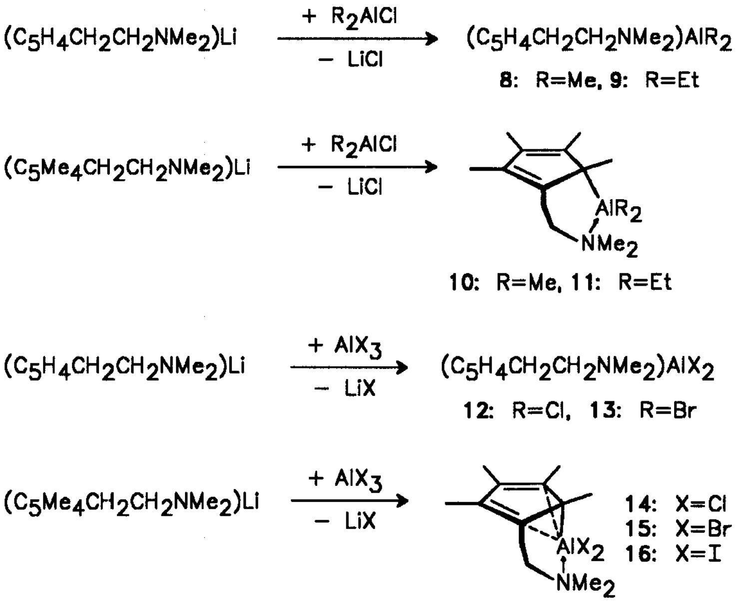
Special emphasis has been put on the synthesis of compounds with group 13 elements as central atoms. Both donor-substituted cyclopentadienyl systems **5** and **6** have been used successfully in the preparation of the (cyclopentadienyl)alanes **8-16**.[14a,c,18] The colourless and moisture-sensitive solids are readily soluble in common organic solvents; the Cp-methylated species are unexpectedly stable towards air.



8: R=Me, **9**: R=Et

10: R=Me, **11**: R=Et

12: R=Cl, **13**: R=Br

14: X=Cl
15: X=Br
16: X=I

The structures of the Cp-methylated compounds **10**, **11**, and **14-16** have been studied in detail.[18] The electron deficient aluminium atom is stabilized by an intramolecular coordination of the nitrogen atom. This effect results in monomeric molecules in solution and in the solid state. X-ray crystal structures of **10** and **14** are shown in Figure 5. Apparently, the intramolecular base stabilization (formation of a six-membered ring) and the sterically demanding Cp ligand prevent the formation of dimers. One major difference between the two structures is observed: In contrast to the trialkyl substituted

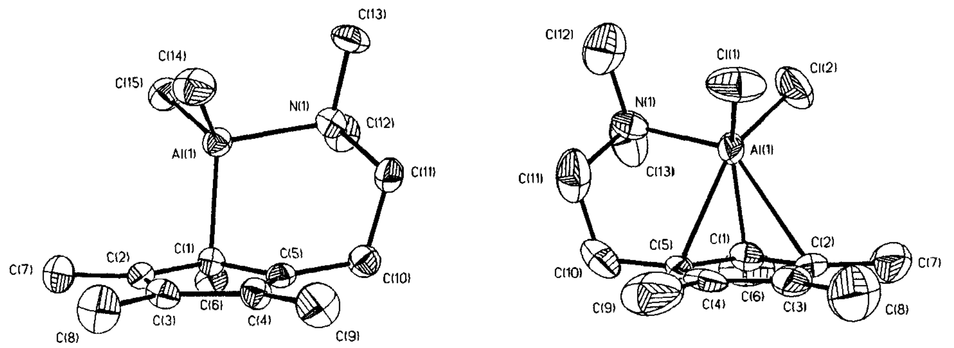
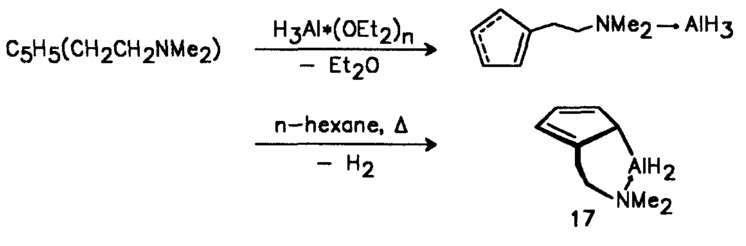


FIGURE 5 Molecular structure of (η^1:η^1-$C_5Me_4CH_2CH_2NMe_2$)$AlMe_2$ (**10**, left) and ($\eta^{2/3}$:η^1-$C_5Me_4CH_2CH_2NMe_2$)$AlCl_2$ (**14**, right)

alane **10**, the Cp ring in **14** is η^2/η^3-bonded to the metal centre (instead of η^1). This situation is neccessary to compensate for the enhanced electron deficiency caused by the electronegative halogen substituents. Obviously, not only the dimethylamino group, but also the electronically flexible cyclopentadienyl ligand can exert a stabilizing effect.

The Cp-substituted alane **17** (the first (cyclopentadienyl)alane known so far) has been prepared by a completely different method.[14c] It is a colourless, highly air- and moisture-sensitive, but thermostable solid which can be readily sublimed. Again, an η^1:η^1-coordination mode is observed.



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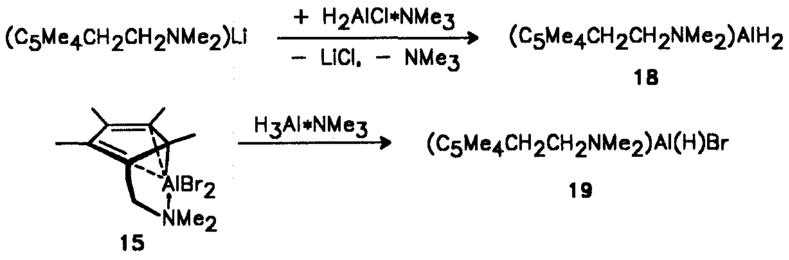
The corresponding alane **18** with the methylated ligand **5** can be prepared by a different synthetic route.[19] So far, compound **18** is characterized only by ^1H and ^{27}Al NMR data and by a low quality x-ray diffraction study. From this information a dimeric structure with η^1-bonded cyclopentadienyl rings and a coordinating dimethylamino group is indicated to be present in solution as well as in the solid state. The substitution of a halogeno ligand in **15** by a hydrido ligand leads to the mixed halogeno(hydrido)aluminium species **19**.[19] NMR data indicate a coordination number of five to six for the aluminium atom. A dimeric structure with bridging bromine ligands and η¹-bonded cyclopentadienyl ligands is assumed.



$$(C_5Me_4CH_2CH_2NMe_2)Li \xrightarrow[-\ LiCl,\ -\ NMe_3]{+\ H_2AlCl*NMe_3} (C_5Me_4CH_2CH_2NMe_2)AlH_2$$

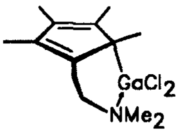
18

15

$$\xrightarrow{H_3Al*NMe_3} (C_5Me_4CH_2CH_2NMe_2)Al(H)Br$$

19

The chemistry of gallium and indium compounds with the ligand systems **5** and **6** has not been explored so far to a great extend. Examples for the application of these ligands are compounds **20-24**[14c,18]; their structure has been evidenced by several x-ray crystal analyses. All complexes show monomeric structures and an intramolecular base stabilization.



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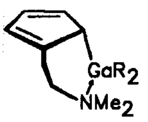
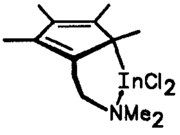


21: R=Cl
22: R=Me



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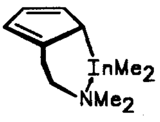

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The thallium derivatives **25** and **26** are very air-sensitive and well soluble in organic solvents; details of their structures are not known.[14d] The high solubility and the sensitivity towards air suggest monomeric or oligomeric structures in solution.

$$C_5R_4H(CH_2CH_2NMe_2) \xrightarrow[-\ EtOH]{+\ TlOEt} (C_5R_4CH_2CH_2NMe_2)Tl$$

25: R=H
26: R=Me

Among the many imaginable compounds with group 14 elements as central atoms, only the (cyclopentadienyl)trimethylsilanes and -stannanes **27-30** have been synthesized so far.[14d] The cyclopentadienyl ligands are bound to the metal atom in an η¹-fashion; no coordination of the amino group is observed. Compounds **27-30** (as well as **25** and **26**) are potential Cp-transfer reagents and are thus interesting for the synthesis of other cyclopentadienyl complexes.

$$C_5R_4H(CH_2CH_2NMe_2) \xrightarrow[\text{2. }Me_3SiCl\text{ or }Me_3SnBr]{\text{1. KH or }n\text{-BuLi}} (C_5R_4CH_2CH_2NMe_2)ElMe_3$$

27: R=H, El=Si
28: R=H, El=Sn
29: R=Me, El=Si
30: R=Me, El=Sn

A detailed discussion of NMR spectroscopic information of the many compounds mentioned above and an interpretation of solid state structures will be given in ref. [17].

Although it is not the scope of this survey to describe d- and f-block complexes of the functionalized ligand **5**, some examples are depicted in Figure 6.[14a,b,20,21] According to the electronic needs of the metal atoms, the dimethylamino group can coordinate intramolecularly to the corresponding metal centre (in addition to the cyclopentadienyl

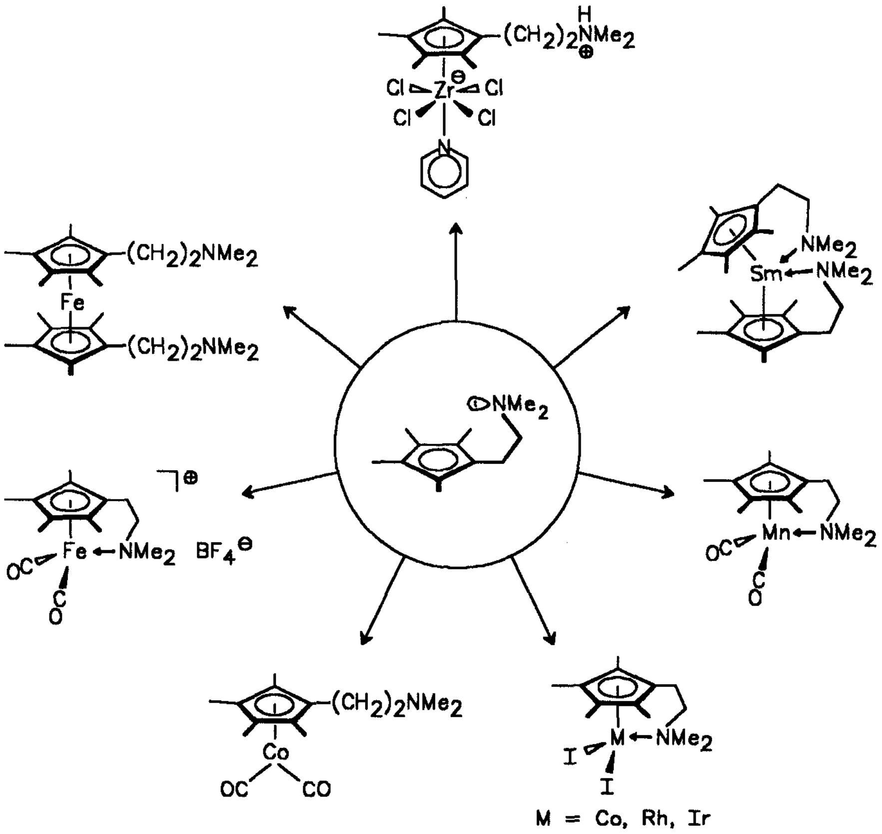

FIGURE 6 Schematic representation of complexes containing the $C_5Me_4CH_2CH_2NMe_2$ ligand **5** and d- or f-block elements

system). As a result, new types of complexes have been obtained. In the case of reversible side-arm participation (as has been proved in one case[14b]), it seems possible to stabilize highly reactive intermediates relevant for catalytic processes.

CONCLUSION

In this paper, we have described organometallic compounds with bridged or (dimethylaminoethyl)-substituted cyclopentadienyl ligands. The electronic and steric requirements of the novel ligand systems favour the formation of unprecedented molecular structures. Thus, the ligand systems **1-4** allow (for example) the synthesis of dinuclear complexes with a *cisoide* geometry of the metal atoms. In compounds containing ligands **5** or **6**, an additional *intra*molecular interaction of the dimethylamino group with coordinatively unsaturated centres is observed. Some of the compounds described here are catalytically active species or are volatile enough to be interesting for MOCVD purposes.

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