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(Dimethylaminoethyl)cyclopentadienyl ligands in compounds of *s*- and *p*-block elements

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CONTENTS

ABSTRACT

The chemistry of (dimethylaminoethyl)cyclopentadienyl-substituted compounds containing *s*- and *p*-block elements is reviewed. A survey of the syntheses, properties and structures of these compounds, classified according to the group numbers in the Periodic Table, is presented. Some comments on NMR spectroscopic aspects are presented together with a discussion of solid-state structures.

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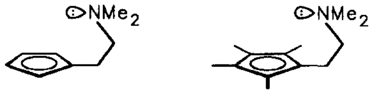
1. INTRODUCTION

The cyclopentadienyl group, C_5H_5 (Cp), is one of the most important ligands in organometallic chemistry. Its key role in this field can be judged from the vast number of cyclopentadienyl complexes (σ or π-bonded to the central atom) of virtually every element [1–4]. More than 80% of all known organotransition metal compounds contain the Cp system or a derivative thereof [5]. Cyclopentadienyl ligands stabilize metals in both high and low oxidation states and can bind to a metal through one to five of the ring carbon atoms. The easy change of hapticity (η^1-η^3, η^5) allows flexible adjustment of the cyclopentadienyl ligand to the electronic and steric requirements of the central atom, resulting in an extensive complex chemistry.

In recent decades, an increasing number of new ring-substituted cyclopentadienes have been reported. In principle, all five hydrogen atoms of the C_5H_5 fragment can be substituted in any fashion. Variations in the Cp ligand sphere often result in significant changes in chemical reactivity, stability, sensitivity to oxidation and many other properties. This effect can be attributed to both the electronic and the steric changes that accompany the replacement of a hydrogen atom by another group. Most of the ring substituents are simple hydrocarbon moieties, either alkyl or aryl groups. An example of particular impact is the permethylated cyclopentadienyl ligand, C_5Me_5 (Cp*) [6–9]. This widely used ligand allows the synthesis of complexes whose cyclopentadienyl analogues are too unstable to be isolated under standard conditions. Among the numerous reviews highlighting aspects of cyclopentadienyl compounds, there is only one which focuses on π bonding to main group elements [10]. Previous articles are oriented towards functionally substituted cyclopentadienyl ligands [11,12].

Currently, functionalized cyclopentadienyl systems with novel substitution patterns are being explored with great success, including our laboratory (see for example ref. 13 and references cited therein). We and others have developed synthetic strategies for cyclopentadienes with functional groups in the side-chain and for the synthesis of the corresponding complexes. This review concentrates on compounds of *s*- and *p*-block elements with the dimethylaminoethyl-substituted cyclopentadienyl ligands **I** and **II**.

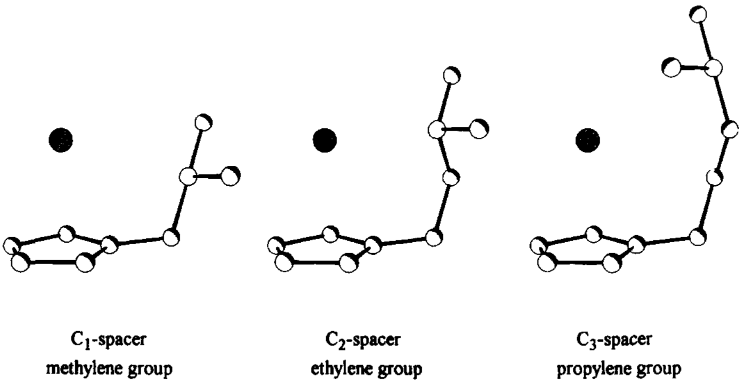


I II

Scheme 1.

Apart from the basic, general interest in novel ligand systems, one might imagine many fascinating applications for cyclopentadienyl metal compounds containing functional groups. The bi(poly)dentate ligands **I** and **II** possess both a hard and a soft donor function (following Pearson's [14] concept of hard and soft acids and bases) which may lead to interesting effects (exerted by the peripheral substituents) on both structure and reactivity. Furthermore, these ligands may enhance the solubility of the complexes in aqueous media, after protonation or alkylation of the dimethylamino group. Both aspects are the motivation for our activities.

In the two exocyclically substituted cyclopentadienyl systems under discussion, the cyclopentadienyl ring and the remote dimethylamino group are linked by a carbon chain, which is required as a spacer unit to prevent electron delocalization between the Cp and the functional moiety. Furthermore, the ethylene spacer is of appropriate length and flexibility to allow intramolecular coordination of the terminal donor atom to a metal centre. Whereas a methylene group probably is too short for an intramolecular interaction, a propylene group, although suitable with respect to its chain length, seems to be too flexible. Finally, the dimethylamino group was chosen to minimize terminal substitution on the Lewis basic atom and reduce steric crowding around the central atom.



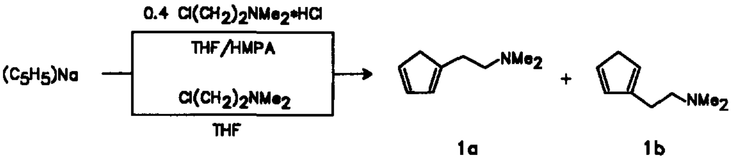
Scheme 2.

Below we present some recent results in the field, predominantly from our group at Bielefeld. Syntheses and properties of complexes with dimethylaminoethyl-substituted cyclopentadienyl ligands are described together with the results of X-ray crystal structure investigations.

2. LIGAND SYNTHESIS

2.1. [2-(N,N-Dimethylamino)ethyl]cyclopentadiene

General strategies for the synthesis of monosubstituted cyclopentadienyl ligands are reviewed in ref. 12. The reaction of cyclopentadienide salts (lithium, sodium, potassium or thallium cyclopentadienides or cyclopentadienylmagnesium halides) with alkyl halides or other alkylating reagents [15] represents a versatile method for the preparation of monoalkyl-substituted cyclopentadienes. [2-(*N*,*N*-dimethylamino)ethyl]cyclopentadiene (**1**) is easily prepared from sodium cyclopentadienide and 2-chloro-1-dimethylaminoethane hydrochloride in THF and HMPA [16]. In a modification of this method, 2-chloro-1-dimethylaminoethane is used instead of its hydrochloride [17,18]; the use of toxic HMPA and excess sodium cyclopentadienide is not necessary. Compound **1** is a colourless, light-sensitive liquid; it is only briefly stable under ambient conditions. Therefore, to avoid significant decomposition (and to inhibit potential dimerization), **1** is stored at low temperatures. ^{1}H NMR data suggest that two olefinic regioisomers, **1a** and **1b**, are present.



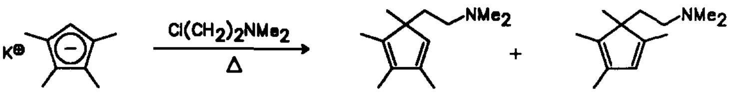
1a **1b**

Scheme 3.

2.2. *1-[2-(N,N-Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadiene*

In principle, four methods are conceivable for the preparation of tetramethylcyclopentadienes with a functionalized carbon side chain.

(1) As in the case of **1** 1-[2-(*N*,*N*-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadiene (**2**) should be obtainable by a nucleophilic substitution reaction starting from a cyclopentadienide salt. Therefore, 2-chloro-1-dimethylaminoethane has been reacted with potassium tetra-methylcyclopentadienide [19]. A mixture of isomeric [2-(*N*,*N*-dimethylamino)ethyl]tetramethylcyclopentadienes (**3**) is formed. The structure assignment of **3** is based on ^{1}H and ^{13}C NMR data and shows almost exclusively the presence of geminally disubstituted products. As no detectable amounts of 1,2,3,4,5-substituted isomers (with allylic hydrogen atoms) are present, **3** cannot be deprotonated and is therefore not suitable for the synthesis of cyclopentadienyl complexes.



3a **3b**

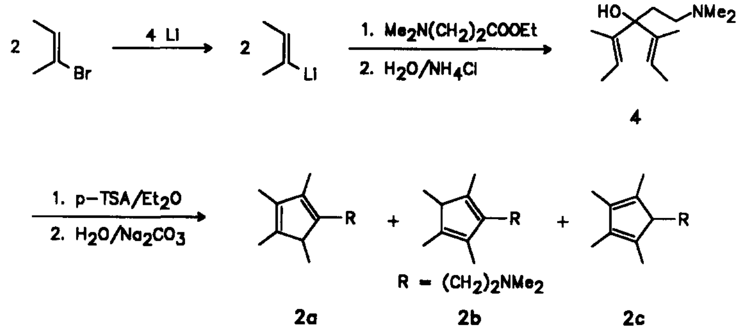
Scheme 4.

(2) 1,2,3,4-Tetramethylfulvene can be converted into a 1,2,3,4,5-substituted tetramethylcyclopentadiene or its anion by addition of organolithium compounds [20]. The reaction proceeds via nucleophilic attack at the carbon atom of the

exocyclic methylene group. For the synthesis of **2**, $LiCH_2NMe_2$ is needed as a reagent, which is not easy to prepare. Hence this route is not very attractive.

(3) Treatment of 2,3,4,5-tetramethylcyclopent-2-en-1-one [21,22] with organolithium compounds (e.g. $Li(CH_2)_3NMe_2$ [23]) gives 1,2,3,4,5-substituted tetramethylcyclopentadienes. However, the synthesis of **2** by this method is not possible, because the required organolithium compound $Li(CH_2)_2NMe_2$ is not accessible.

(4) We have chosen a combination of C_2 and C_1 units (where the functional group is already attached to C(1)) to build up the C_5 ring system. The condensation of appropriately substituted esters with but-2-enyllithium followed by an acid-catalysed dehydration and ring closure is a facile and efficient method. It was first described by Campbell et al. [24] and was later adapted by Threlkel and Bercaw [25]. The majority of alkyl- and aryl-substituted tetramethylcyclopentadienes, RC_5Me_4H (with allylic hydrogens), have been prepared in this way. We have introduced for the first time the use of heteroatom-substituted esters. Thus, we could prepare new alkylated cyclopentadienes possessing an *N*- or *O*-functionalized side-chain [19]. Treatment of *cis*- and *trans*-2-bromobut-2-ene with lithium sand in diethyl ether and subsequent addition of ethyl 3-dimethylaminopropionate, followed by hydrolysis, produces the dienol **4** (*cis* and *trans*). Without further purification, reaction of **4** with *p*-toluenesulphonic acid yields, after aqueous workup and subsequent distillation, the functionalized tetramethylcyclopentadiene **2** as a colourless, air- and thermostable liquid. The structure of **2** has been established by analysis of NMR data; a statistical mixture of the three possible isomers with an allylic hydrogen atom is present.

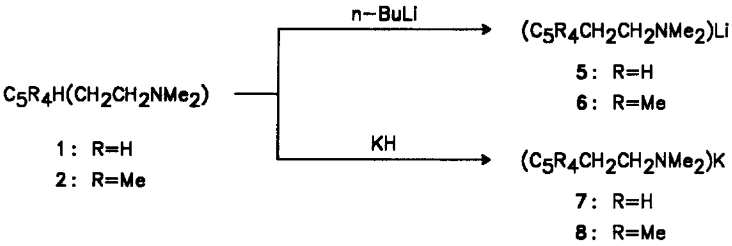


Scheme 5.

3. GROUP 1 AND 2 ELEMENTS AS CENTRAL ATOMS

3.1. Alkali metal compounds

The modified cyclopentadienes **1** [16,26] and **2** [13,23] react with potassium hydride or n-butyllithium in THF or diethyl ether to yield the alkali metal cyclopenta-

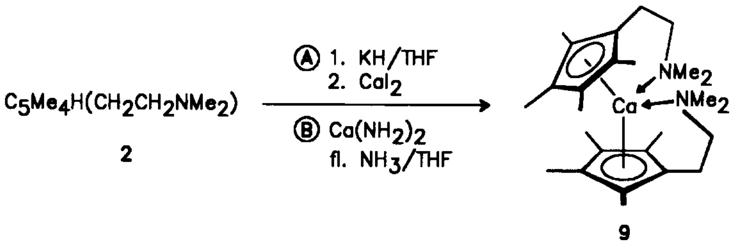


Scheme 6.

dienides **5–8**, respectively. The potassium salts **7** and **8** are extremely air-sensitive, colourless solids and are insoluble in common solvents, whereas the lithium compounds **5** and **6** are soluble in THF. Warming a solution of **6** in THF (which shows a yellow colour) above 0°C results in decomposition [23]. The high solubility of **6** even in cold THF (in contrast to the properties of $(C_5Me_5)Li$) suggests a monomeric or oligomeric structure in solution, presumably with intramolecular coordination of the amino function to the lithium atom. On the other hand, lithiation of **2** in diethyl ether gives a colourless suspension of **6** now as a thermally stable and hardly soluble species. So far, compounds **5–8** have not been characterized by ^1H, ^{13}C or ^7Li NMR spectroscopy and only IR and elemental analysis data have been reported for **7** [26]. Compounds **5–8** are important substrates for the synthesis of Cp element compounds containing ligands **I** and **II** (via metathesis reactions).

3.2. Alkaline earth metal compounds

Reaction of the potassium cyclopentadienide **8** with calcium diiodide in THF leads to $(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2)_2Ca$ (**9**) [13]. The calcocene can also be prepared from the reaction of the cyclopentadiene **2** and calcium amide in liquid ammonia. Compound **9** is a colourless, air- and moisture-sensitive solid; it is clearly



Scheme 7.

more stable than the analogous decamethylcalcocene $(C_5Me_5)_2Ca$. The compound can be sublimed at 110°C/5×10^{-3} mbar, but a major part is lost as a non-volatile residue. NMR data and the behaviour with donor solvents provide evidence for an intramolecular coordination of the dimethylamino group. In contrast to $(C_5Me_5)_2Ca$

[27], **9** does not form an adduct with THF. The single-crystal X-ray structure gives more insight into coordination and association modes of **9** in the solid state [28]. It can be viewed as an intramolecularly solvated monomeric calcocene (unlike the polymeric $(C_5H_5)_2Ca$[29]) involving η^5-Cp rings flanking the Ca core in a bent metallocene geometry [30] similar to the parent $(C_5Me_5)_2Ca$ [31]. The dimethylamino groups coordinate to the "open" side of the central calcium atom. The increase in coordination number obviously satisfies the need of the alkaline earth metal for coordination saturation. The bulky Cp ligand and the Lewis-base coordination favour the formation of a monomeric molecule.

4. GROUP 13 ELEMENTS AS CENTRAL ATOMS

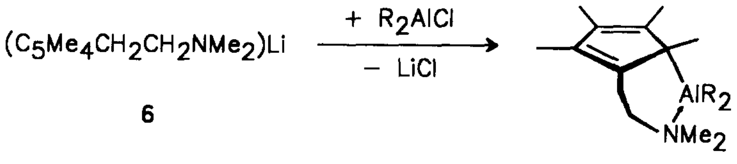
4.1. *Aluminium(III) compounds*

Lithiation of **1** and **2**, respectively, and reaction with stoichiometric amounts of the corresponding dialkylaluminium chloride lead to the cyclopentadienyl compounds **10**–**13** of type $(C_5H_4CH_2CH_2NMe_2)AlR_2$ (R = Me, Et) and (η^1:η^1-$C_5Me_4CH_2CH_2NMe_2(AlR_2$ (R = Me, Et) [13,32,33]. They are obtained as colourless, moisture-sensitive crystals which are readily soluble in hexane, THF, Et_2O or benzene; the Cp-methylated species **12** and **13** are unexpectedly stable against air.

$$\underset{\mathbf{5}}{(C_5H_4CH_2CH_2NMe_2)Li} \xrightarrow[-\ LiCl]{+\ R_2AlCl} (C_5H_4CH_2CH_2NMe_2)AlR_2$$

10: R=Me
11: R=Et

Scheme 8.



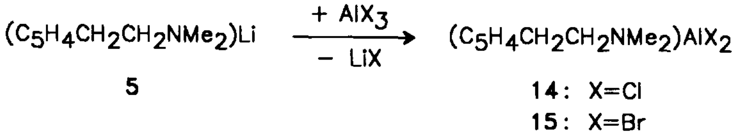
6

12: R=Me
13: R=Et

Scheme 9.

Whereas the structures of compounds **10** and **11** could not be characterized unambiguously (owing to their low solubility), the Cp-methylated analogues **12** and **13** have been studied in detail. The electron-deficient aluminium atom is stabilized by an intramolecular coordination of the nitrogen atom. This effect results in monomeric molecules in solution; cryoscopic molecular mass determinations in benzene show a degree of association of 1. One can conclude from NMR data that the Cp ligand is bonded to the aluminium in an η^1 fashion. The crystal structures of **12** and **13** (Fig. 1) [33] confirm an intramolecular base stabilization and the presence of monomeric species with an η^1-bonded Cp ring. Apparently, the Lewis-base coordination (formation of a six-membered ring) and the sterically demanding Cp ligand prevent the formation of dimers. The Al–N distances in **12** and **13** are comparable to those of related alane-amine adducts (e.g. $H_3Al{\cdot}NMe_3$ [34,35]). The Al–N distances between adjacent molecules are 690–790 pm; thus an additional intermolecular donor–acceptor interaction can be ruled out.

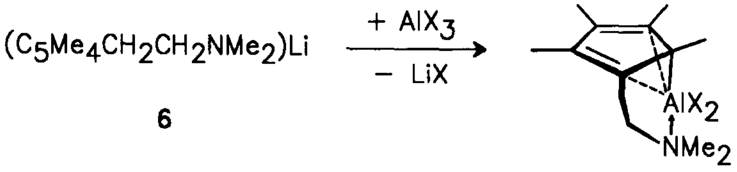
Deprotonation of the cyclopentadiene **1** or **2** with n-butyllithium and successive reaction with one equivalent of an aluminium trihalide, AlX_3, yield the (cyclopentadienyl)alanes $(C_5H_4CH_2CH_2NMe_2)AlX_2$ (X = Cl, Br) and $(\eta^{2/3}{:}\eta^1\text{-}C_5Me_4CH_2CH_2NMe_2)AlX_2$ (X = Cl, Br, I) **14**–**18** [32,33]. Compounds **14**–**18** are colourless solids.



$$\underset{\mathbf{5}}{(C_5H_4CH_2CH_2NMe_2)Li} \xrightarrow[-\ LiX]{+\ AlX_3} (C_5H_4CH_2CH_2NMe_2)AlX_2$$

14: X=Cl
15: X=Br

Scheme 10.



16: X=Cl
17: X=Br
18: X=I

Scheme 11.

The Cp-methylated species **16**–**18** are moderately air stable. Only the Cp-methylated compounds **16**–**18** have been structurally characterized. The alanes **14** and **15** are not sufficiently soluble to perform a cryoscopic molecular mass determination and it was not possible to obtain crystals suitable for X-ray structure analysis. The gross structural features of **16**–**18** resemble those of the alkyl substituted aluminium compounds **12** and **13** (intramolecularly base-stabilized, monomeric molecules) (see above). Only one major difference is observed: in contrast to the trialkyl-substituted alanes, the Cp ring is η^2/η^3-bonded to the metal centre. This coordination mode compensates for the enhanced electron deficiency caused by the electronegative halogen substituents. Obviously, the electronically flexible cyclopentadienyl ligand has a stabilizing effect in addition to the dimethylamino group. The crystal structure

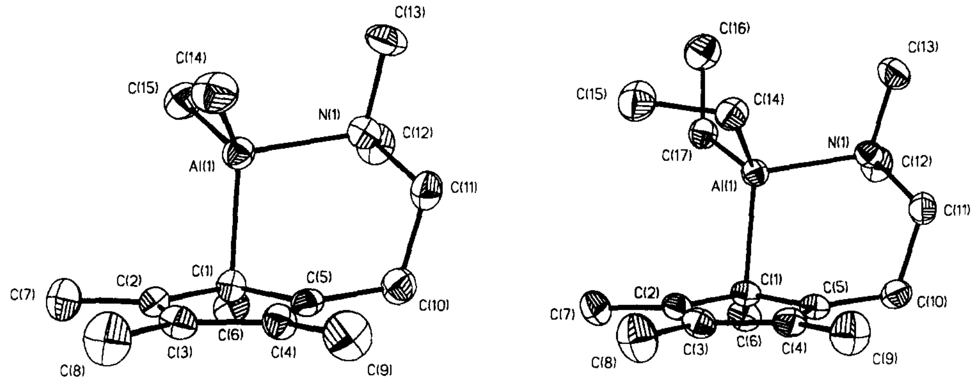
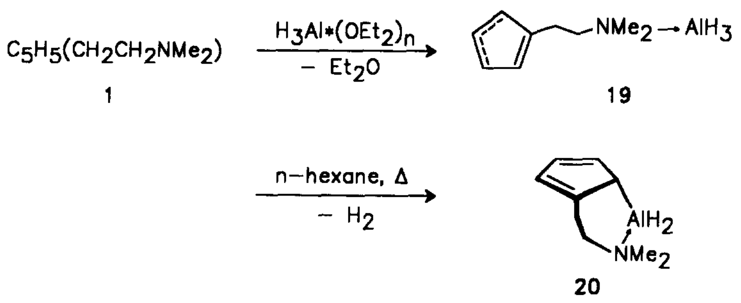


Fig. 1. Crystal structures of (left) **12** and (right) **13**. Selected distances (Å): for **12**, Al–C(1) 2.09, Al–N 2.07, C(1)–C(2) 1.45, C(2)–C(3) 1.37, C(3)–C(4) 1.43, C(4)–C(5) 1.39, C(1)–C(5) 1.46; for **13**, Al–C(1) 2.10, Al–N 2.08, C(1)–C(2) 1.44, C(2)–C(3) 1.38, C(3)–C(4) 1.42, C(4)–C(5) 1.38, C(1)–C(5) 1.46.

of **16** (Fig. 2) has been determined and the Al–N distance is significantly shorter than those in **12** and **13** and approaches that found in $Cl_3Al·NMe_3$ [36].

A completely different method is used for the synthesis of $(\eta^1:\eta^1$-$C_5H_4CH_2CH_2NMe_2(AlH_2)$ (**20**) [32]. Treatment of **1** with $H_3Al·(OEt_2)_n$ leads to the alane adduct **19**. On refluxing a solution of **19** in n-hexane for several hours, the Cp-substituted alane **20** is obtained (via H_2 elimination and formation of an aluminium-carbon bond). Compound **20** is the first reported (cyclopentadienyl)alane [37]. It is a colourless, highly air- and moisture-sensitive solid, but is sufficiently thermally stable to be sublimed at 60°C/0.01 mbar. An X-ray crystal structure analysis of **20** (see above) (Fig. 2) confirms the η^1:η^1-coordination mode deduced from NMR spectroscopic data and shows the expected bond lengths and bond angles within the (dimethylaminoethyl)cyclopentadienyl unit and the aluminium coordination sphere.



Scheme 12.

The corresponding alane **21** with the tetramethylcyclopentadienyl ligand can be prepared in an analogous fashion, although a different synthetic route gives higher yields [38]. The metathesis reaction of the lithium compound of **2** with $H_2AlCl·NMe_3$ provides **21** as a rather air-sensitive solid, which can be sublimed under reduced

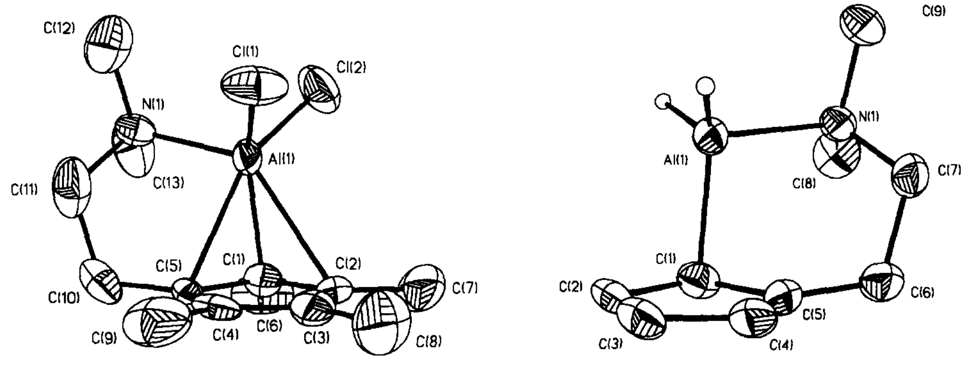


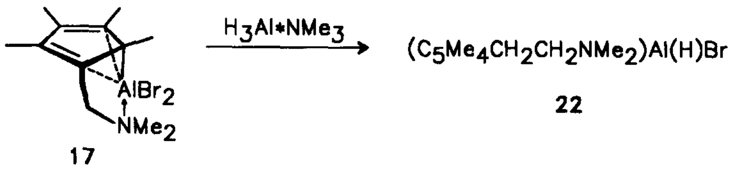
Fig. 2. Crystal structures of (left) **16** and (right) **20**. Selected distances (Å): for **16**, Al–C(1) 2.06, Al–C(2) 2.51, Al–C(5) 2.32, Al–N 2.01, C(1)–C(2) 1.40, C(2)–C(3) 1.32, C(3)–C(4) 1.40, C(4)–C(5) 1.35, C(1)–C(5) 1.40; for **20**, Al–C(1) 2.05, Al–N 2.02, C(1)–C(2) 1.46, C(2)–C(3) 1.38, C(3)–C(4) 1.40, C(4)–C(5) 1.37, C(1)–C(5) 1.46.

pressure. So far, **21** has been characterized only by ^{1}H and ^{27}Al NMR data and by a low-quality X-ray diffraction study, which indicates a dimeric structure with η^1-bonded cyclopentadienyl rings and a coordinating dimethylamino group both in solution and in the solid state.

$$\underset{\mathbf{6}}{(C_5Me_4CH_2CH_2NMe_2)Li} \xrightarrow[-\ LiCl,\ -\ NMe_3]{+\ H_2AlCl{\bullet}NMe_3} \underset{\mathbf{21}}{(C_5Me_4CH_2CH_2NMe_2)AlH_2}$$

Scheme 13.

The substitution of a halogeno ligand in **17** by a hydrido ligand leads to the mixed halogeno(hydrido)aluminium species, **22** [23]. Thus, in the reaction of **17** with the alane adduct $H_3Al{\cdot}NMe_3$, **22** is formed in almost quantitative yield as a colourless, rather air-sensitive solid. NMR data indicate a coordination number of five to six for the aluminium atom. A dimeric structure with bridging bromine ligands and η^1-bonded cyclopentadienyl ligands is assumed.

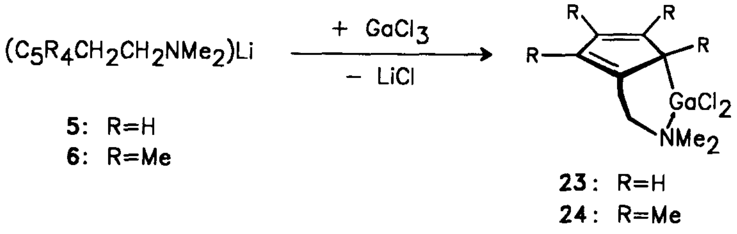


17

Scheme 14.

4.2. Gallium(III) compounds

The chemistry of gallium compounds with (dimethylaminoethyl)cyclopentadienyl ligands has not been fully explored. In analogy with the reactions of aluminium trichloride with the lithiated cyclopentadiene **5** or **6**, gallium trichloride reacts in diethyl ether to give the corresponding dichlorogallium compounds **23** and **24** [32,33]. They are obtained as colourless, more (**23**) or less (**24**) air-sensitive crystalline solids. ^{1}H and ^{13}C NMR investigations and molecular mass measurements indicate an intramolecular coordination of the dimethylamino group and a monomeric structure in solution for both compounds. An X-ray crystal structure analysis of **23** (Fig. 3) confirms that the assumptions made for **23** are valid also for the solid state: the dimethylamino group is coordinated to the gallium atom, which is η^1-bonded to the cyclopentadienyl ring. Bond distances and angles all are in the expected range. Experiments to introduce a second (dimethylaminoethyl)cyclopentadienyl ligand to a gallium centre have failed so far.



Scheme 15.

4.3. Indium(III) compounds

Indium compounds with (dimethylaminoethyl)cyclopentadienyl ligands have been obtained by two different routes: metathesis reaction of cyclopentadienyllithium

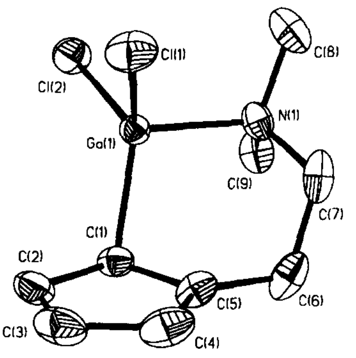
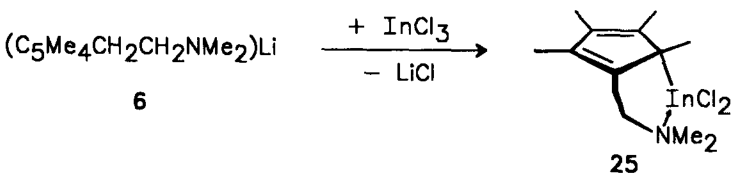


Fig. 3. Crystal structure of **23**. Selected distances (Å): Ga–C(1) 1.99, Ga–N 2.03, C(1)–C(2) 1.47, C(2)–C(3) 1.35, C(3)–C(4) 1.43, C(4)–C(5) 1.37, C(1)–C(5) 1.49.

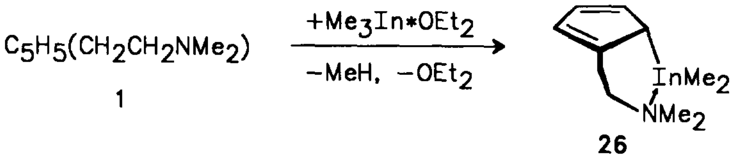
with indium trichloride and methane elimination from the parent cyclopentadiene and trimethylindium. Thus, reaction of indium trichloride with the lithium species **6** leads to the dichloroindium compound (η^1:η^1-$C_5Me_4CH_2CH_2NMe_2$)$InCl_2$ (**25**) which



Scheme 16.

is obtained in good yields as a yellow, crystalline, rather air-stable solid [32,33]. NMR data, molecular mass determination and solubility criteria indicate an intramolecular coordination of the dimethylamino group to the indium centre. This coordination mode is confirmed in the solid state by an X-ray crystal structure analysis (Fig. 4) [33].

Comparable results have been obtained for the analogous compound **26** with the parent ligand system. This species is formed as an air-sensitive, crystalline compound by the reaction of trimethylindium with (dimethylaminoethyl)cyclopentadiene (**1**) with elimination of methane [32].



Scheme 17.

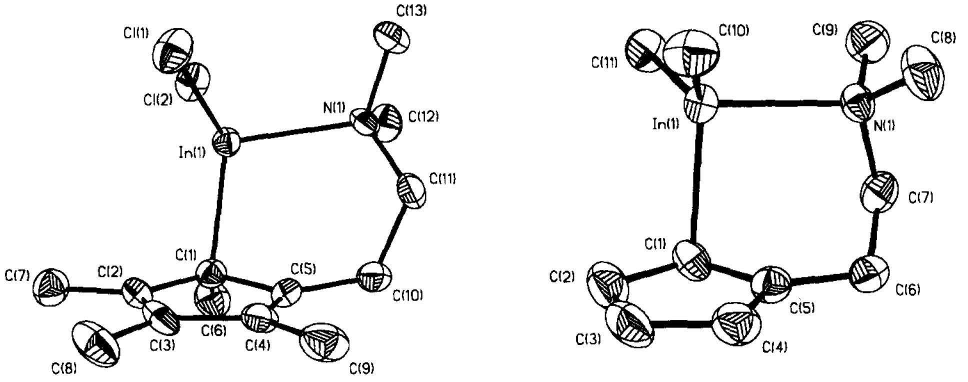
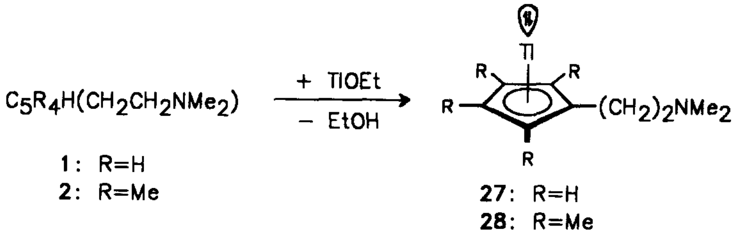


Fig. 4. Crystal structures of (left) **25** and (right) **26**. Selected distances (Å): for **25**, In–C(1) 2.18, In–N 2.27, C(1)–C(2) 1.47, C(2)–C(3) 1.35, C(3)–C(4) 1.45, C(4)–C(5) 1.36, C(1)–C(5) 1.48; for **26**, In–C(1) 2.34, In–N 2.36, C(1)–C(2) 1.44, C(2)–C(3) 1.38, C(3)–C(4) 1.40, C(4)–C(5) 1.40, C(1)–C(5) 1.44.

4.4. Thallium(I) compounds

Cyclopentadienylthallium compounds are widely used for Cp transfer to other elements and are therefore, together with the corresponding alkali metal compounds, of great synthetic value. The thallium compounds **27** and **28** with the two (dimethylaminoethyl)cyclopentadienyl ligands in question are easily prepared by the reactions of the functionalized cyclopentadienes **1** and **2**, respectively, with thallium ethoxide



Scheme 18.

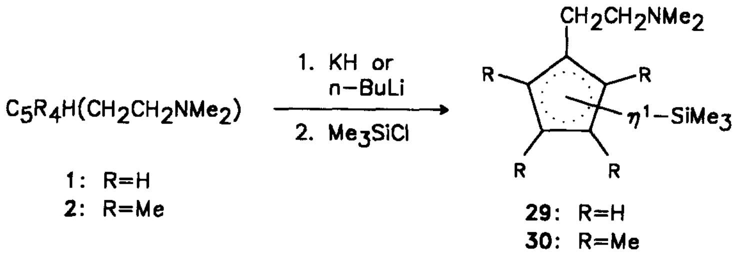
[39]. The colourless compound **27** and the yellow compound **28** are both very air sensitive and soluble in organic solvents. Details of their structures are not known. The high solubility and their sensitivity towards air suggest monomeric or oligomeric structures in solution. There is no conclusive evidence for an intramolecular coordination in either **27** or **28**.

5. GROUP 14 ELEMENTS AS CENTRAL ATOMS

Few compounds with Group 14 elements as central atoms have been synthesized, but they include those which seem to be interesting from a synthetic point of view, e.g. Cp-transfer agents.

5.1. Silicon(IV) compounds

The trimethylsilyl derivatives of **1** and **2** are prepared by reaction of the lithium or potassium salts **5**–**8** with trimethylchlorosilane [39]. Compounds **29** and **30** are

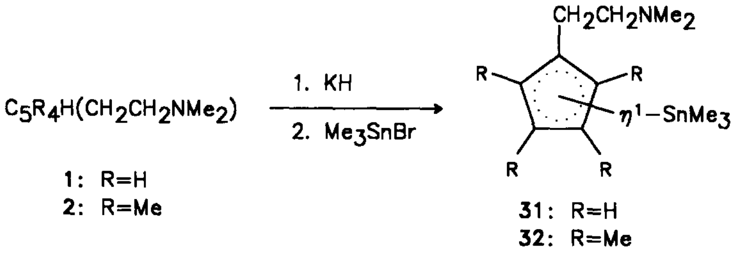


Scheme 19.

obtained in high yields as colourless to light-yellow liquids. The resulting products are air stable for short periods of time and are also thermally stable. The cyclopentadienyl ligands are bound to silicon in an η^1-fashion and coordination of the amino group is not observed. The dynamic behaviour of **29** and **30** is similar to that of other cyclopentadienyl silicon compounds [40].

5.2. *Tin(IV) compounds*

The trimethyltin derivatives of **1** and **2** are obtained in good yields by deprotonation with potassium hydride and subsequent reaction with trimethylbromostannane [39]. The resulting compounds **31** and **32** are light-yellow, thermally stable liquids, which are air stable for short periods of time. As observed for the silicon compounds, the cyclopentadienyl ligands are bound in an η^1-mode; no coordination of the amino groups takes place. The fast sigmatropic rearrangements observed are typical of cyclopentadienyl tin species [40].



Scheme 20.

6. NMR SPECTROSCOPIC INFORMATION

6.1. *Detection of an intramolecular coordination mode*

In solution, the intramolecular coordination of the nitrogen atom of the dimethylaminoethyl side-chain can be easily detected in the ^1H NMR spectra of the corresponding compounds. Intramolecular coordination leads to a significant downfield shift for the protons of the methyl and methylene groups bound directly to the nitrogen atom. In comparison with chemical shifts of compounds with non-coordinating amino groups or in the cyclopentadienes **1** and **2**, $\Delta\delta$ values in the range 0.14–0.59 ppm are observed. These effects are independent of the concentration of the solution and can be detected most clearly in $CDCl_3$. A collection of NMR data is given in Table 1.

TABLE 1

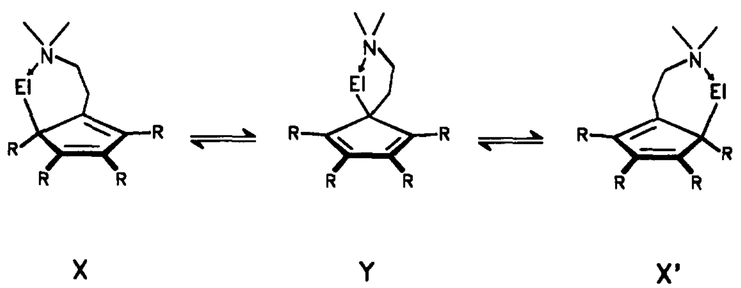
Correlation of ^1H NMR chemical shifts (δ, ppm) of the $CH_2N(CH_3)_2$ protons in the (dimethylaminoethyl)cyclopentadienyl compounds with the coordination behaviour (in $CDCl_3$ except where indicated otherwise)

Compound	δ (CH_2NMe_2)	δ (NMe_2)	Coordination
$C_5H_5(CH_2CH_2NMe_2)$ **1**	2.42–2.57	2.26–2.27	–
$C_5Me_4H(CH_2CH_2NMe_2)$ **2**	2.21–2.37	2.15–2.26	–
$(C_5Me_4CH_2CH_2NMe_2)_2Ca$ **9**	2.53	2.23	+
$(C_5H_4CH_2CH_2NMe_2)AlMe_2$ **10**	2.86–2.90	2.52	+
$(C_5H_4CH_2CH_2NMe_2)AlEt_2$ **11**	2.88–2.92	2.53	+
$(C_5Me_4CH_2CH_2NMe_2)AlMe_2$ **12**	2.70	2.38	+
$(C_5Me_4CH_2CH_2NMe_2)AlEt_2$ **13**	2.64–2.71	2.37	+
$(C_5H_4CH_2CH_2NMe_2)AlCl_2$ **14**	2.90–2.95	2.75	+
$(C_5H_4CH_2CH_2NMe_2)AlBr_2$ **15**	2.91–2.99	2.80	+
$(C_5Me_4CH_2CH_2NMe_2)AlCl_2$ **16**	2.79	2.59	+
$(C_5Me_4CH_2CH_2NMe_2)AlBr_2$ **17**	2.76–2.84	2.66	+
$(C_5Me_4CH_2CH_2NMe_2)AlI_2$ **18**	2.88	2.74	+
$(C_5H_4CH_2CH_2NMe_2)AlH_2$ **20**	2.89–2.94	2.57	+
$(C_5Me_4CH_2CH_2NMe_2)Al(H)Br$ **22**[a]	2.29–2.34	2.07, 2.27	
$(C_5H_4CH_2CH_2NMe_2)GaCl_2$ **23**	2.88	2.73	+
$(C_5Me_4CH_2CH_2NMe_2)GaCl_2$ **24**	2.75	2.65	+
$(C_5Me_4CH_2CH_2NMe_2)InCl_2$ **25**	2.68–2.77	2.59	+
$(C_5H_4CH_2CH_2NMe_2)InMe_2$ **26**	2.82	2.34	+
$(C_5H_4CH_2CH_2NMe_2)Tl$ **27**[a]	2.55	1.64	
$(C_5Me_4CH_2CH_2NMe_2)Tl$ **24**[a]	2.62	2.29	
$(C_5H_4CH_2CH_2NMe_2)SiMe_3$ **29**	2.41–2.57	2.24	–
$(C_5Me_4CH_2CH_2NMe_2)SiMe_3$ **30**	2.42	2.15–2.26	–
$(C_5H_4CH_2CH_2NMe_2)SnMe_3$ **31**	2.57–2.63	2.25	–
$(C_5Me_4CH_2CH_2NMe_2)SnMe_3$ **32**	2.32–2.37	2.21	–

[a] In C_6D_6.

6.2. Dynamic behaviour

The dynamic behaviour of η^1-cyclopentadienyl compounds is well understood [40]. Sigmatropic rearrangements which are more or less fast are the basis for the observed fluxionality. In all (cyclopentadienyl)aluminium, -gallium and -indium compounds known so far, fast rearrangements are observed which lead to averaged ^1H and ^{13}C NMR signals even at low temperatures. The situation is more complex in the intramolecularly coordinated Group 13 element compounds. The chain length of the corresponding dimethylaminoethyl substituent is not flexible enough to allow all carbon positions of the Cp ring to participate in sigmatropic rearrangements. Thus, the dynamic behaviour is restricted to the process $X \rightleftharpoons Y \rightleftharpoons X'$ shown. In this process, two carbon atoms of the cyclopentadiene ring always remain vinylic in character, whereas the other three carbon atoms are partly allylic (one third) and partly vinylic (two thirds). In the case of fast rearrangement rates, three resonances are expected in the ^{13}C NMR spectra for the ring carbon atoms. For the substituents R at the cyclopentadienyl system, two carbon resonances and two proton resonances ($R=CH_3$) or an AA′XX′-type spectrum ($R=H$) are expected.



Scheme 21.

It should be emphasized that within the class of main-group cyclopentadienyl compounds it is not possible to differentiate between highly fluxional η^1-structures and $\eta^{2,3,5}$-structures on the basis of ^1H and ^{13}C NMR data only. Thus, a π ground-state structure in solution cannot be ruled out for some of the compounds discussed here.

6.3. ^{27}Al NMR spectroscopy

Benn and co-workers [41,42] have shown that there is a correlation between the coordination number of the aluminium atom and the ^{27}Al NMR chemical shift in organoaluminium compounds of the type $(R_2AlY)_n$ with $Y=R$, OR, NR_2, H and halogen. Our investigations have demonstrated that this correlation is valid also for the class of (cyclopentadienyl)aluminium compounds of the type $CpAlY_2$ with $Y=$ R or halogen. The lower the coordination number at aluminium, the higher is the chemical shift value ($\delta^{27}Al$) (Table 2 lists (cyclopentadienyl)aluminium compounds and their ^{27}Al NMR parameters and coordination numbers as determined by X-ray analysis). It is assumed that the coordination number is the same in the solid state and in solution. If the degree of association in solution is known for the respective compound, the hapticity of the Cp–Al bond (η^1, $\eta^{2/3}$ or η^5) can be predicted. Hence ^{27}Al NMR spectroscopy is an important tool for the determination of the solution structure in this class of compounds.

7. ON THE WAY FROM σ TO π-BONDING: INTERPRETATION OF SOLID-STATE STRUCTURES

In cyclopentadienyl compounds of Group 13, 14 and 15 elements, the energy difference between σ- and π-structures becomes smaller on going to the heavier elements and on exchanging organic by inorganic ligands. This statement is the

TABLE 2

^{27}Al NMR chemical shifts (δ, ppm) of (cyclypentadienyl)aluminium compounds (in $CDCl_3$ except where indicated otherwise)

Compound	δ (^{27}Al)	Coordination number (solid state)
$(C_5H_4CH_2CH_2NMe_2)AlMe_2$ **10**	161.7	
$(C_5H_4CH_2CH_2NMe_2)AlEt_2$ **11**	159.5	
$(C_5Me_4CH_2CH_2NMe_2)AlMe_2$ **12**	155.2	4
$(C_5Me_4CH_2CH_2NMe_2)AlEt_2$ **13**[a]	152.9	4
$(C_5H_4CH_2CH_2NMe_2)AlCl_2$ **14**	116.7	
$(C_5H_4CH_2CH_2NMe_2)AlBr_2$ **15**[a]	121.2	
$(C_5Me_4CH_2CH_2NMe_2)AlCl_2$ **16**	55.7	5–6
$(C_5Me_4CH_2CH_2NMe_2)AlBr_2$ **17**	69.2	
$(C_5Me_4CH_2CH_2NMe_2)AlI_2$ **18**	79.2	
$(C_5H_4CH_2CH_2NMe_2)AlH_2$ **20**	142.7	4
$(C_5Me_4CH_2CH_2NMe_2)Al(H)Br$ **22**[a]	62.0	
$[(C_5Me_5)Al(Me)Cl]_2$ [45,46][a]	8.5	6
$[(C_5Me_5)AlCl_2]_2$ [49,50][a]	−52.8	8
$(C_5Me_5)AlMe_2 \cdot THF$ [23][a]	150.6	4

[a] In C_6D_6.

result of many experimental observations [40] and of theoretical calculations by Anh et al. [43] and Schoeller [44]. In this context, the molecular structures of Group 13 element compounds discussed in this paper can be compared with respect to the question of ground state σ- or π-bonding. The structural characteristics (see Table 3) are described by the angle α between the Group 13 element-carbon (Cp) vector and the carbon (Cp)–centre(Cp) vector, and by the angle β showing the deviation of the allylic methyl carbon from the Cp plane. Compounds with $\alpha < 90°$ are regarded as π-complexes and those with $\alpha > 90°$ as σ-bonded species, more or

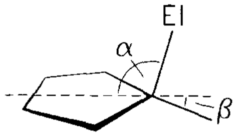
TABLE 3

Solid-state structural data

Compound	α[a]	β[a]
$(C_5Me_4CH_2CH_2NMe_2)AlMe_2$ **12**	94.6	25.9
$(C_5Me_4CH_2CH_2NMe_2)AlEt_2$ **13**	95.6	27.2
$(C_5Me_4CH_2CH_2NMe_2)AlCl_2$ **16**	79.1	19.7
$(C_5H_4CH_2CH_2NMe_2)AlH_2$ **20**	96.3	—
$(C_5H_4CH_2CH_2NMe_2)GaCl_2$ **23**	110.6	—
$(C_5Me_4CH_2CH_2NMe_2)InCl_2$ **25**	104.2	33.4
$(C_5H_4CH_2CH_2NMe_2)InMe_2$ **26**	97.6	—

[a] α = Angle between Group 13 element and Cp plane; β = angle between allylic methyl carbon and Cp plane.

less on the way from σ- to π-bonding. The decrease of the angle β is correlated with an increase of π-character in the respective Cp–element bond. In a strongly π-bonded complex, the angle β should become small owing to a change in hybridization from sp^3 to sp^2 at the relevant carbon atom. C–C bond lengths within the cyclopentadiene unit may also change on the way from σ- to π-bonding. The planarity of the C_5 perimeter in cyclopentadienyl compounds is not a useful criterion for the presence of a π-complex, because planar Cp rings are also found in typical σ-structures [40].



Scheme 22.

The aluminium atoms in **12** and **13** are σ-bonded to the Cp fragments. In contrast, π-bonding of the $\eta^{2/3}$ type is observed in **16** and a change in the C–C bond lengths within the Cp unit is observed. The basic structural features of the Cp fragment remain virtually unchanged on the transition from η^1 to $\eta^{2/3}$ bonding, presumably as a consequence of intrinsically rather weak π-interactions. Instead of C–C bond-length averaging, the typical cyclopentadiene pattern with C–C bonds including sp^2 and sp^3 hybridized carbon atoms is maintained. The type of π-structure found in **16** is not unknown in the chemistry of aluminium. For example, an η^2- or η^3-bonding has already been observed in the dimeric $[(C_5Me_5)(Al(CH_3)Cl]_2$ [45,46] and in the gas-phase structure of $(C_5H_5)AlMe_2$ [47,48]. Even an η^5-species has been reported with the dimeric $[(C_5Me_5)AlCl_2]_2$ [49,50]. Only very few η^1-structures are known. In the polymeric $[(C_5H_5)AlMe_2]_\infty$ the bridging Cp units are bound in an η^1 fashion [51]; the same situation is found in the monomeric adduct $(C_5Me_5)AlMe_2$·THF [23]. In the aluminium compound **20** the bonding is also of σ-type.

The gallium species **23** is characterized by Cp–element σ-bonding and by a rather short C(Cp)–Ga distance of 1.99 Å, as compared with the 2.22 Å distance in polymeric $(C_5H_5)GaMe_2$ [52]. The bond length is comparable to that found in the $(C_5Me_5)GaCl_2$ dimer [53] and in $Me_3Ga{\cdot}NMe_3$ [54]. In the indium compounds **25** and **26**, the Group 13 element is σ-bonded to the Cp ring. The C(Cp)–In bond length is significantly shorter in the chloro compound **25** than in the dimethyl compound **26**. This difference in bond lengths is attributed to the alteration of the Lewis acidity of the indium centre. Both distances are in the range of values found for the terminal and bridging In–Cp contacts in polymeric $(C_5H_5)_3In$ [55].

It is interesting that Cp–element σ-bonding seems to be preferred in compounds of the heavier Group 13 elements. This behaviour is similar to that found for the heavier Group 14 elements, whereas a pronounced tendency for π-bonding is observed for the heavier Group 15 elements in their trivalent state [56]. In cyclopentadienyl compounds of trivalent aluminium, gallium and indium a coordination number of at least four at the Group 13 element is characteristic. An intramolecular amino coordination can prevent many compounds with (dimethylaminoethyl)cyclopentadienyl ligands from oligomerization.

8. CONCLUSION

Only recently, the first compounds of Group 1, 2, 13 and 14 elements with (dimethylaminoethyl)cyclopentadienyl ligands have been synthesized. The electronic and steric requirements of the novel ligand systems favour the formation of unprecedented molecular structures. Thus, in compounds with Group 1, 2 and 13 elements, additional interaction of the dimethylamino group with the coordinatively unsaturated centres is observed. In most cases, this interaction occurs intramolecularly and prevents oligomerization. Owing to the lack of crystal structures or other conclusive data, intermolecular interaction cannot be ruled out in some cases. π–Bonded cyclopentadienyl systems of the η^5-type are present in the calcium compound and presumably also in the alkali metal and thallium compounds. The bonding between the cyclopentadienyl fragment and a Group 13 elements is generally of the σ-type, even with the heavier homologues (Ga, In). The only exceptions have been found in $CpAlHal_2$ compounds, where π-bonding of the $\eta^{2/3}$-type is observed. The bonding to the Group 14 elements is of σ-type with no further interaction of the amino group. The dynamic behaviour of the novel compounds due to sigmatropic rearrangements or haptotropic shifts is comparable to that of other cyclopentadienyl species of the relevant elements. In the case of amino coordination, dynamic processes are restricted to three of the five Cp-ring carbon atoms. Some of the compounds described here are volatile enough to be interesting for MOCVD purposes.

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