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Invited review

Cyclopentadienyl compounds with nitrogen donors in the side-chain

Peter Jutzi *, Ulrich Siemeling

Fakultät für Chemie der Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany

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Abstract

The coordination chemistry of cyclopentadienyl ligands bearing either a dimethylaminoethyl side-chain or a pendant pyridyl group is described. The influence of these *N* donor functionalities on the structure and the physical as well as chemical properties of relevant metal complexes is discussed. In several cases, a relatively weak intramolecular coordination of the pendant amine is found; the hemilabile coordination profile of the *N* functionalised cyclopentadienyl ligands towards d-block elements may prove useful for the development of single-component catalysts.

Keywords: *N*-functionalised cyclopentadienyl; Magnesium; Germanium; Titanium; Zirconium; Rhodium

1. Introduction

As was described in more detail in Vol. 400 of this journal [1], we have a long-standing interest in cyclopentadienyl chemistry. Undoubtedly, cyclopentadienyl are among the most important ligands in organometallic chemistry. Their steric and electronic properties can be tailored by the introduction of up to five substituents [2].

At the start of our research in this area we utilised the effects of alkyl and silyl substituents on the cyclopentadienyl ring for the stabilisation of highly reactive species (containing predominantly hypercoordinated Main Group elements in low oxidation states) [1,2a]. In recent years, we have extended our efforts to the use of two classes of oligodentate cyclopentadienyl systems, namely bridged oligo(cyclopentadienyl) ligands that contain identical (or very similar) coordination sites and side-chain functionalised cyclopentadienyl ligands that contain at least two distinctly different coordination sites.

Some typical examples of bridged oligo(cyclopentadienyl) ligands are shown in Fig. 1. Silatropic rearrangements are the key to the formation of the silicon-bridged species III–VI.

We have used these ligands mainly for the construction of homo- and hetero-oligometallic complexes in order to investigate intramolecular metal–metal interactions with particular reference to cooperative chemical and physical phenomena. The chemistry of these ligands was recently reviewed [3].

The chemistry of side-chain functionalised cyclopentadienyl systems is a rapidly growing area that is currently being explored by several research groups [4–8]. Our laboratories have contributed to the chemistry of such functionalised ligands by synthesizing the previously unknown species of types VII–X (Fig. 2).
Some parent unmethylated cyclopentadienyl ligands related to types VIII and IX have already been described in the literature [9].

In the group headed by one of us (U.S.), (oligo)pyridyl-functionalised cyclopentadienyl systems of types XI–XIV are also being investigated (Fig. 3). There were a few earlier examples of related systems containing unmethylated cyclopentadienyl units [10], and one permethylated species has been described [6a].

We are interested in such side-chain functionalised cyclopentadienyl ligands for various reasons. Firstly, the presence in these oligodentate ligands of both a soft (i.e. the cyclopentadienyl moiety) and a hard (i.e. the heteroatom) donor site may have a dramatic influence on both the structure and the reactivity of metal complexes of these ligands. Secondly, it is envisaged that the functionalised side-chain can be used to anchor such

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* Corresponding author.

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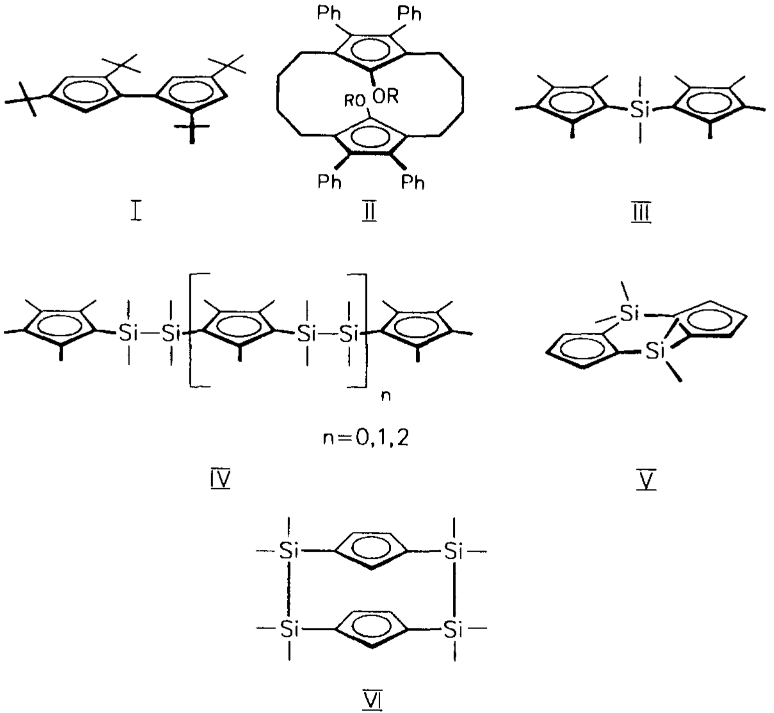


Fig. 1. Some typical examples of bridged oligo(cyclopentadienyl) ligands investigated in our laboratories.

cyclopentadienyl species to surfaces. Thirdly, the side-chain can greatly influence the solubility of relevant metal complexes and so development of an organometallic chemistry in unusual solvents (including aqueous media [11]) is a further aim of our project. Lastly, the construction of oligonuclear metal complexes should be feasible with such oligodentate ligands; this is especially true for the pyridyl- and oligopyridyl-functionalised cyclopentadienyl systems, since these units are known to have good coordination properties for a variety of metals.

The review below presents a preliminary report of recent work with dimethylaminoethyl- and pyridyl-substituted cyclopentadienyl compounds.

2. Dimethylaminoethyl-cyclopentadienyl compounds

We have been investigating the chemistry of ligands **1a** and **1b** with the aim of utilising the potential effects

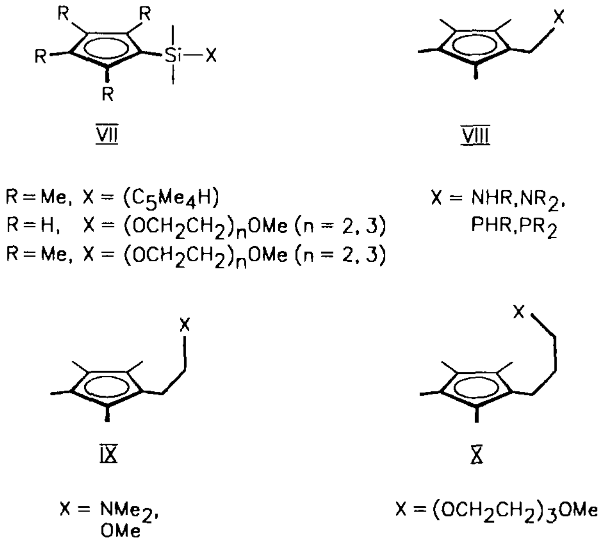


Fig. 2. Side-chain functionalised cyclopentadienyl systems developed in our laboratories.

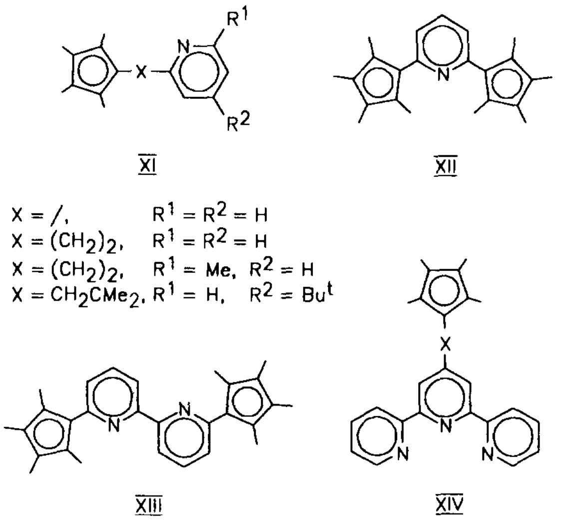


Fig. 3. (Oligo-)pyridyl-functionalised cyclopentadienyl systems under investigation.

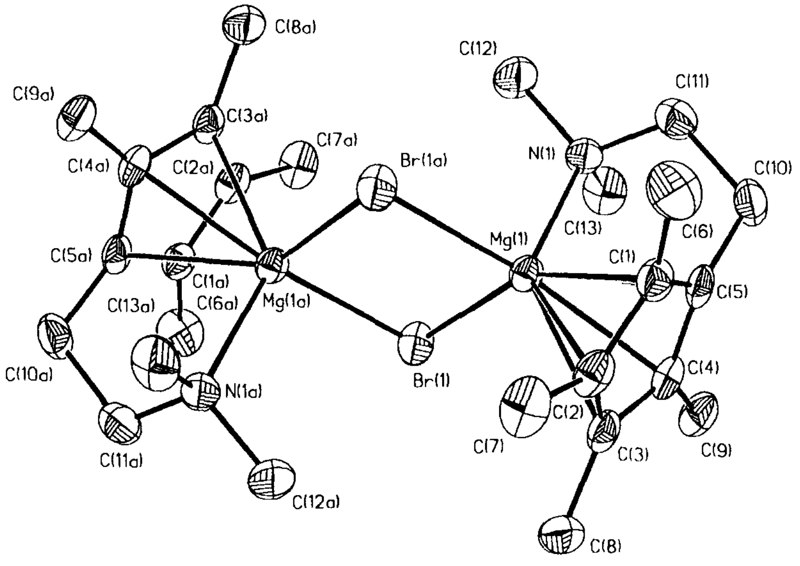


Fig. 4. Molecular structure of **3b**.

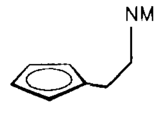
of the donor-functionalised side-chain. The nitrogen atom can act as a 2-electron donor site and can coordinate to metal centres; owing to the appropriate length and flexibility of the ethylene spacer unit between the cyclopentadienyl moiety and the NMe_2 unit, *intra*molecular coordination to a Lewis acidic metal centre bonded to the cyclopentadienyl ring is quite favourable. The nitrogen atom can act as a Lewis base not only towards Lewis acidic metal centres but also towards more classical Lewis acids such as H^+ and R^+. Protonation or alkylation of the N atom generates a cationic ammonium group, which will enhance the solubility of relevant metal complexes in very polar solvents such as water; additionally, the ammonium-substituted side arm will have electronic and steric properties distinctly different from those of the neutral NMe_2-substituted side arm. Furthermore, it is conceivable that the amino function could be used to immobilise complexes of **1a** and **1b** on acidic surfaces.

2.1. Compounds with s- and p-block elements

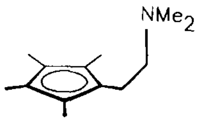
The chemistry of the ligands **1a** and **1b** involving s- and p-block elements has been reviewed recently [4c]. We will therefore present only some very recent results.

2.1.1. Grignard compounds [6r]

Metathesis of the side-chain functionalised cyclopentadienes **1a**H and **1b**H with simple alkyl magnesium halides yields the corresponding halogen-bridged dimeric Grignard compounds containing these ligands. Thus, $[(Me_2NCH_2CH_2)C_5H_4MgBr]_2$ (**2**) and $[(Me_2NCH_2CH_2)C_5Me_4MgX]_2$ (**3a**, X = Cl; **3b**, X = Br) were prepared by this route. The structure of compound **3b** was determined by a single-crystal X-ray diffraction study (Fig. 4). Not unexpectedly, each cyclopentadienyl group is bonded η^5 to its magnesium centre, which is additionally coordinated by the amino group tethered to its cyclopentadienyl ring. The halogen bridges in **3b** are broken by addition of an excess of THF, and the monomeric species **4** is obtained, the intramolecular nitrogen coordination having remained intact. The structure of **4** was determined by X-ray diffractometry and is shown in Fig. 5.



1a



1b

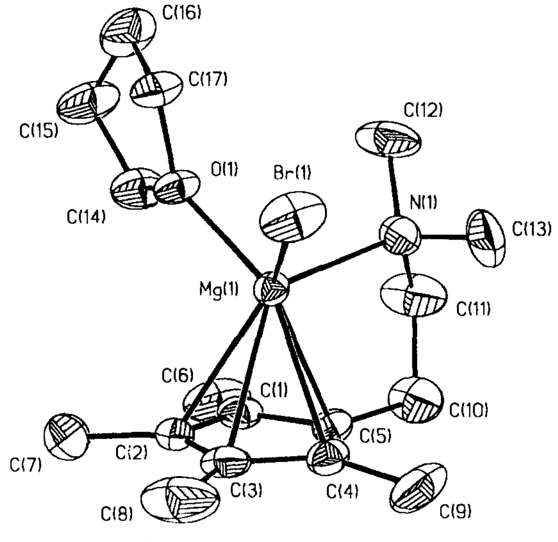


Fig. 5. Molecular structure of **4**.

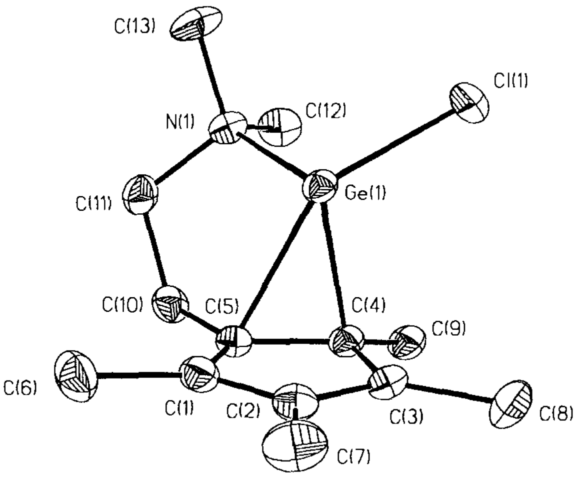


Fig. 6. Molecular structure of 5.

2.1.2. *Germylene chemistry [6t]*

An intriguing result has been obtained in germanium(II) chemistry. The structures of several germylenes of the type Me_5C_5GeR (R = Cl [12], $CH(SiMe_3)_2$ [13], $C(SiMe_3)_3$ [14], 2,4,6-$Bu^t_3C_6H_2$ [14]) have already been described in the literature. None of these germylenes forms adducts with aliphatic or aromatic amines; only the cationic species $Me_5C_5Ge^+$ gives adducts with pyridine and 2,2′-bipyridine [15].

Surprisingly, an intramolecular coordination of the amino group is observed in the compound $(Me_2NCH_2CH_2)C_5Me_4GeCl$ (**5**). This can be explained by a pronounced chelate effect of the oligodentate ligand **1b**. A single-crystal X-ray structure analysis of **5** reveals that the amino coordination has important structural consequences: the bonds to the coligands (i.e. the cyclopentadienyl π system and the chloro-substituent) are weakened quite considerably; the Ge–cyclopentadienyl interaction is between π- and σ-bonding, and the Ge–Cl bond is one of the longest ever found (237 pm). Fig. 6 shows the molecular structure of compound **5**.

It should be pointed out that, in contrast to the situation encountered with most d-block elements, with Main Group elements cyclopentadienyl ligands generally behave as good leaving groups. This is also true for the functionalised systems **1a** and **1b**, which in our experience can be readily substituted by other nucleophiles. Thus, in the chemistry of s- and p-block elements, **1a** and **1b** cannot be regarded as hemilabile ligands. Hemilabile coordination behaviour represents, however, a crucial aspect of the chemistry of their compounds with d-block elements, since cyclopentadienyl groups tend to coordinate very strongly to most transition metals irrespective of their oxidation states.

2.2. *Compounds with d-block elements*

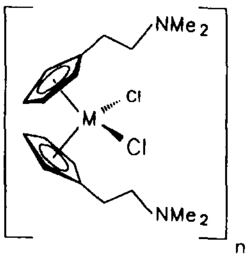
In respect of the chemistry of dimethylaminoethylcyclopentadienyl transition metal compounds, our primary interest was to find out the conditions for intramolecular coordination of the amino group. Below we briefly describe our preliminary findings on the complexes of titanium and zirconium, of cobalt, rhodium and iridium, and of nickel, palladium and platinum.

2.2.1. *Titanium and zirconium compounds [6p]*

Many types of cyclopentadienyl ligands had already been employed with d^4 metals in order to stabilise and/or activate relevant complexes in catalytic processes. Of special importance are bent-metallocene-type systems complexes, which have proved very useful for the polymerisation of α-olefins [16], and textbooks acknowledge that a labile 14-electron cationic alkyl complex is the catalytically active species in catalyst formulations based on titanocene or zirconocene derivatives [17]. Thus, one of our goals was to prepare corresponding titanocene and zirconocene derivatives with dimethylaminoethyl side-chains, and ultimately to generate cationic species stabilised by a weak intramolecular nitrogen coordination yet still active in catalysis. Such a ''reversible'' stabilisation of a reactive metal–ligand fragment bonded to the cyclopentadienyl moiety is based on appropriate hemilabile qualities of the functionalised cyclopentadienyl ligand.

The synthesis of such d^4 metal complexes turned out not to be easy. This was because of the interaction of the amino group with the metal substrate and also the presence of intermolecular coordination in the products leading to oligomeric and polymeric species that are difficult to characterise.

Interesting results were obtained mainly with the parent dimethylaminoethyl-cyclopentadienyl ligand **1a**. Complexes of type **6** made in THF by reaction of $TiCl_4$



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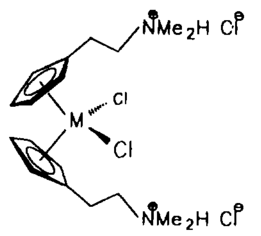

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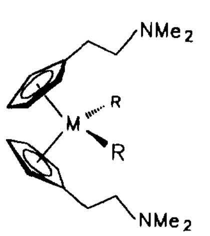

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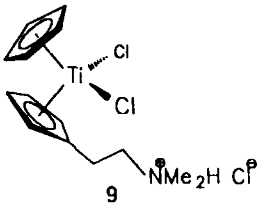

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and $ZrCl_4$ with **1aNa** and **1aLi**, respectively, turned out to be coordination polymers; they can be readily converted into the corresponding hydrochlorides of type **7**, which show good solubilities in polar solvents. Organo-substituted metallocenes of type **8** are formed in the reaction of the corresponding dichlorides of type **6** with organolithium reagents; they possess noncoordinating amino groups.

A titanium dichloride containing an unfunctionalised cyclopentadienyl ligand as well as a dimethylaminoethyl-cyclopentadienyl ligand is obtained in the reaction of $(C_5H_5)TiCl_3$ with $(Me_2NCH_2CH_2)C_5H_4$-$SiMe_3$ (**1aSiMe$_3$**), and was characterised as its hydrochloride **9**.

The paramagnetic titanium(III) complex **10** can be synthesised in high yield by reaction of **1aLi** with $TiCl_3$ in toluene. A single-crystal X-ray structural analysis of this compound revealed that only one of the two amino groups is coordinated to the titanium centre (Fig. 7). In the reaction of **10** with organolithium reagents the corresponding organo derivatives are formed through simple substitution of the chloro substituent. Metathesis of **10** with $AgBPh_4$ leads to the ionic compound $[(Me_2NCH_2CH_2)C_5H_4]_2Ti^+BPh_4^-$ (**11**), whose structure is still unknown.

In the half-sandwich tris(dimethylamino)titanium(IV) compound $[(Me_2NCH_2CH_2)C_5H_4]Ti(NMe_2)_3$ (**12**), obtained by reaction of **1aH** with $Ti(NMe_2)_4$ in toluene, the pendant amino group is not coordinated to the metal, whereas in the trichloro analogue such coordination is observed, as reported recently by Rausch et al. [6n].

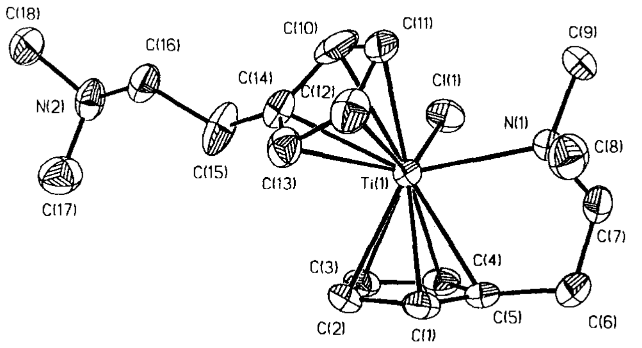


Fig. 7. Molecular structure of **10**.

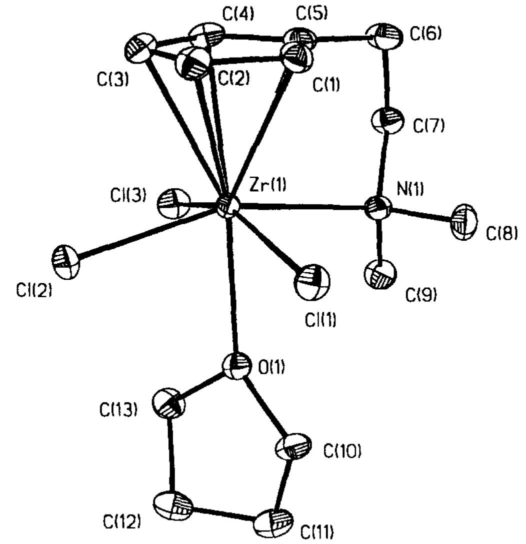


Fig. 8. Molecular structure of **13**.

The corresponding trichlorozirconium complex is able to coordinate an additional Lewis base. The structure of its THF adduct **13** was investigated by a single-crystal X-ray diffraction study and is shown in Fig. 8.

The hydrochloride **14** of a corresponding pyridine adduct, which contains the dimethylaminoethyl-tetramethylcyclopentadienyl ligand **1b**, adopts a zirconate-type structure (Fig. 9). In both cases, the zirconium centre is surrounded by six ligands in a pseudo-octahedral arrangement.

Not unexpectedly, our preliminary investigations show that the coordination behaviour of the pendant

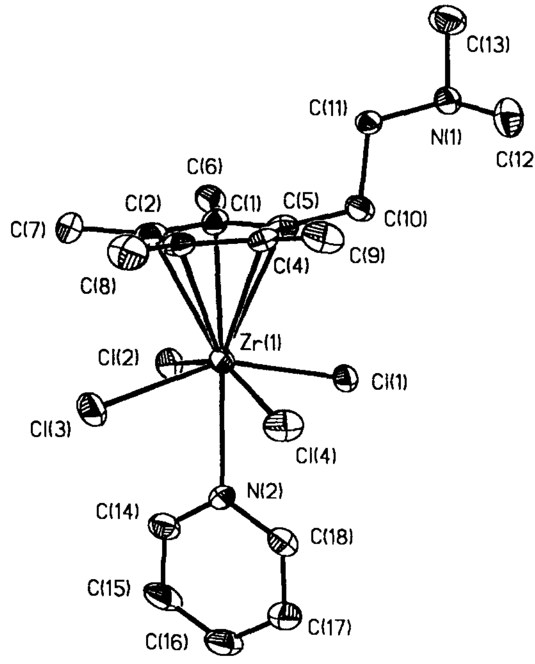


Fig. 9. Molecular structure of the cation of **14**.

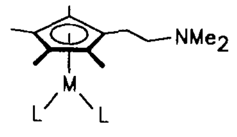
amino group in complexes of the dimethylaminoethylcyclopentadienyl ligand with titanium and zirconium depends strongly on the nature of the metal centre including its oxidation state and other ligands.

2.2.2. Cobalt, rhodium and iridium compounds [6m,18]

Numerous cyclopentadienyl complexes of cobalt [19], rhodium [20] and iridium [21] have been used in important stoichiometric and catalytic reactions. All of these reactions rely on the intermediate formation of electronically and coordinatively unsaturated species. It is of great interest to investigate the possibility of stabilising such reactive intermediates. We envisaged that the dimethylaminoethyl-cyclopentadienyl ligand system **1** would be excellently suited for a "reversible" stabilisation of reactive metal–ligand fragments based on a fairly soft electron-rich late transition metal coordinated to the cyclopentadienyl moiety of the ligand, because the pendant amino group (a hard σ-donor) is expected to coordinate only loosely to such metal centres. Thus, **1a** and **1b** should behave as truly hemilabile ligands with the late transition metals.

We have focused our efforts on the use of the permethylated system **1b** in the chemistry of cobalt, rhodium and iridium. Compounds of type **15** can be obtained in good yields by classical routes. No intramolecular displacement of a coligand L by the amino group could be detected with these species. In complexes of type **16** which contain the metal in the +III oxidation state, an intramolecular coordination is observed. Consequently, the 18-electron rule is obeyed by these compounds, obviating the necessity to form halogen-bridged dimers as observed, for example, for $[Me_5C_5RhCl_2]_2$ [22]. The structures of **16a–16c** and **16e** were determined from single-crystal X-ray diffraction data; the structures of the rhodium complexes **16b** and **16e** are shown in Fig. 10.

The lability of the coordinative nitrogen–metal bond in these species is demonstrated by irreversible displacement reactions with stoichiometric amounts of more strongly donating ligands such as phosphanes; these reactions occur already under very mild conditions. The nice interplay between the donor and acceptor qualities of the ligands and the metal centre can be utilised in the design of systems for which such displacements are reversible. Two such systems are shown in Scheme 1. In both cases the equilibrium constant is estimated to be close to unity at room temperature.



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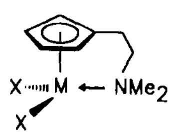
	M	L
a	Co	CO
b	Rh	CO
c	Ir	CO
d	Co	C_2H_4
e	Rh	C_2H_4
f	Ir	C_2H_4



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	M	2 X
a	Co	2 I
b	Rh	2 I
c	Ir	2 I
d	Co	C_2O_4
e	Rh	C_2O_4
f	Ir	C_2O_4

In summary, in the chemistry of cobalt, rhodium and iridium the coordination behaviour of the amino group of **1b** depends strongly on the formal oxidation state of the metal: no coordination is observed with Co, Rh and Ir in the +I oxidation state; in compounds with these metals in the +III oxidation state, the coordination behaviour is determined by the nature of the metal and the other ligands that it bears.

2.2.3. Nickel, palladium and platinum compounds [6s]

With the intriguing results obtained in the chemistry of cobalt, rhodium and iridium in mind, we were interested in finding out whether the amino group of the (dimethylaminoethyl)-tetramethylcyclopentadienyl ligand **1b** could coordinate to a nickel, palladium and platinum centre in the +I and +II oxidation states.

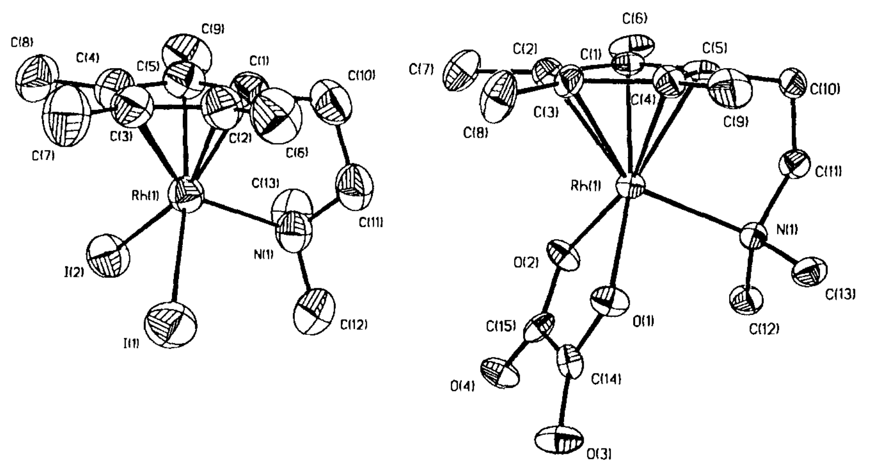
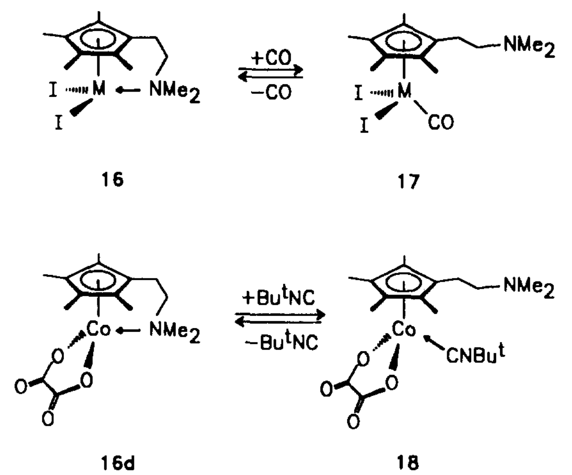


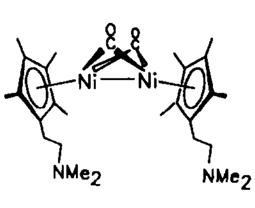
Fig. 10. Molecular structures of (a) **16b** and (b) **16e**.



Scheme. 1. Examples of reversible ligand displacement reactions for complexes of the dimethylaminoethyl-tetramethylcyclopentadienyl ligand **1b**.

We have been successful in the preparation of the carbonylnickel and -palladium compounds **19** and **20**, respectively, showing that the pendant amino group cannot substitute a CO ligand in compounds with the metal in the +I oxidation state. Attempts to prepare the CO-free compounds were unsuccessful. The syntheses of the complexes **21** and **22** demonstrate that even in compounds with the metal in the +II oxidation state the amino group cannot compete with a phosphane or a π-allyl ligand as a donor.

Attempts to prepare the corresponding platinum complexes failed. However, the compounds **23** and **24** with Pt(IV) as the central atom were obtained. In both species the 18-electron rule is obeyed, and so no amino-coordination is expected. It is noteworthy that in the reaction of **23** with HBF_4 protonation of the NMe_2 group is preferred over the elimination of methane and subsequent amino coordination. With two equivalents of HBF_4, however, elimination of methane does occur, and **23** is transformed to **24**, which to the best of our knowledge is the first cyclopentadienyl compound of platinum with a Pt–F bond.



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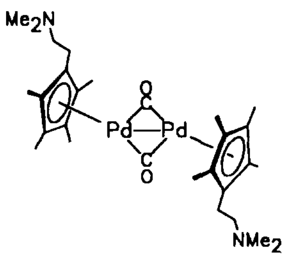

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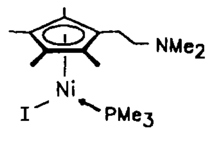

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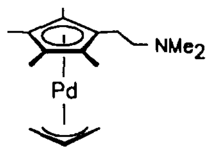

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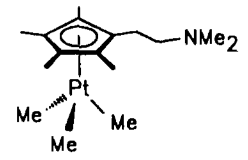

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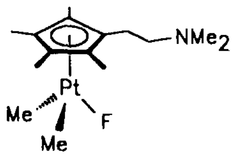

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3. Pyridyl-functionalised cyclopentadienyl compounds [6k,t]

The group headed by one of us (U.S.) has also been investigating the synthesis and chemical properties of permethylated cyclopentadienyl ligands bearing a pendant pyridyl group. In contrast to the corresponding unmethylated species, the parent cyclopentadienes do not form Diels-Alder dimers, and are therefore much easier to store. In addition, the steric and electronic influence of the methyl substituents will in most cases stabilise relevant metal complexes.

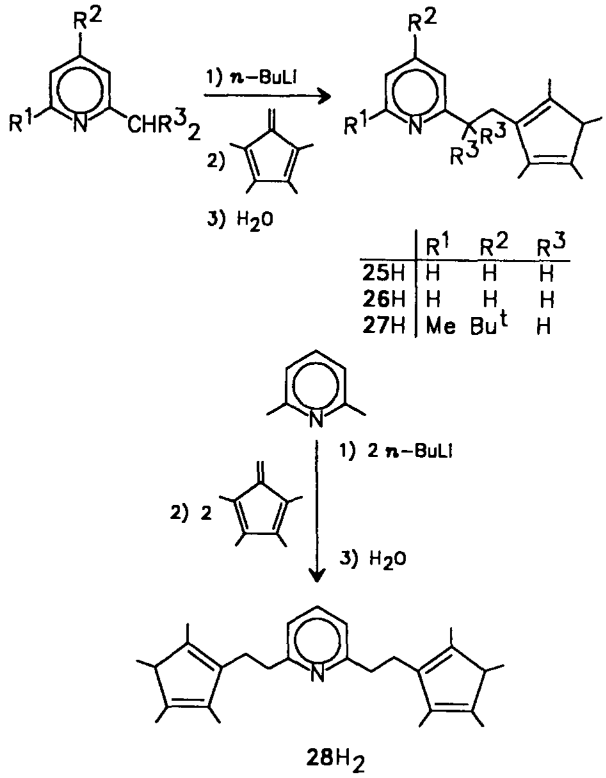
The potential effects of the donor-functionalised side-chain present in these ligands are essentially the same as those described in Section 2 for the dimethylaminoethyl substituent.

3.1. Synthesis of the parent cyclopentadienes

Two synthetic strategies have been employed for the synthesis of permethylated cyclopentadienes bearing a pendant pyridyl group. The first is based on the use of 2,3,4,5-tetramethylfulvene (TMF) as a synthetic equivalent of the cyclopentadienyl moiety. The cyclopentadienes **25H**–**27H** can be obtained by this route. Owing to deprotonation equilibria, the bis(cyclopentadiene) $\mathbf{28H_2}$ is formed as a side product in the latter case; this compound can be obtained in much higher yield by reaction of dilithiated 2,6-lutidine with two equivalents of TMF (Scheme 2). The products are obtained as statistical mixtures of the possible regioisomers.

The second synthetic strategy is based on the use of 2,3,4,5-tetramethylcyclopent-2-enone as equivalent for the cyclopentadienyl moiety. 2-Lithiopyridine reacts smoothly with this reagent, and the desired cyclopentadiene **29H** is obtained in high yield after acidic work-up (Scheme 3).

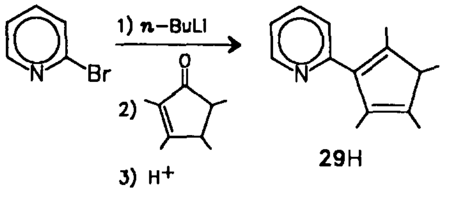
Interestingly, the isomer distribution for this compound is not statistical. One of the two possible isomers having the cyclopentadiene double bonds in conjugation with the pyridine unit is the major isomer (ca. 65%); the other of these isomers is by far the minor product (ca.



	R^1	R^2	R^3
25H	H	H	H
26H	H	H	H
27H	Me	Bu^t	H

$28H_2$

Scheme 2. Synthesis of the pyridyl-functionalised permethylated cyclopentadienes **25H**–**27H** and **$28H_2$**.



Scheme 3. Synthesis of the pyridyl-functionalised permethylated cyclopentadiene **29H**.

5%). The third isomer, in which the cyclopentadiene double bonds are not in conjugation with the pyridine ring, forms ca. 35% of the mixture. A possible explanation for this unusual isomer distribution is the presence of a hydrogen-bond interaction between the nitrogen atom and the cyclopentadienyl CH unit in the major isomer of **29H** as shown in Fig. 11 [23].

Neither of the two synthetic approaches gave the pyridyl-substituted cyclopentadienes with a single meth-

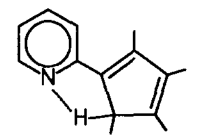


Fig. 11. Possible hydrogen-bond interaction in the main isomer of **29H**.

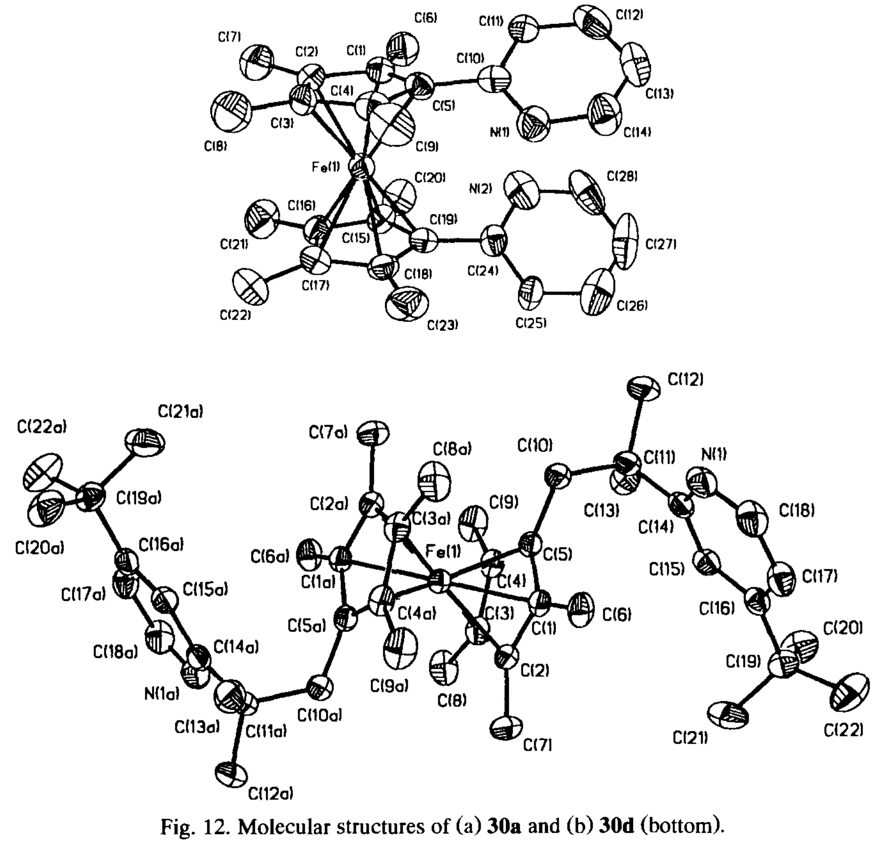
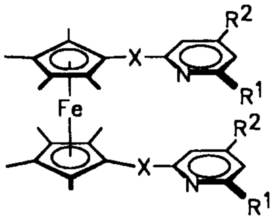


Fig. 12. Molecular structures of (a) **30a** and (b) **30d** (bottom).



30

	X	R^1	R^2
a	/	H	H
b	CH_2CH_2	H	H
c	CH_2CH_2	Me	H
d	CMe_2CH_2	H	Bu^t

ylene spacer unit between the pyridyl group and the cyclopentadienyl ring.

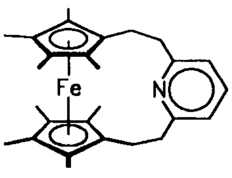
3.2. Metal compounds

The cyclopentadienes **27**H and **29**H are cleanly converted into the corresponding lithio derivatives **27**Li and **29**Li by reaction with one equivalent of n-BuLi. For reasons yet unknown, this reaction does not take place with **25**H, **26**H and **28**H_2. Their lithio derivatives are, however, formed in good yields in the addition reaction of the corresponding lithiated methylpyridines with TMF prior to aqueous work-up (cf Scheme 2); they can conveniently be used in situ for the preparation of a range of organometallic compounds.

Reaction of the lithio derivatives **25**Li–**27**Li and **29**Li with iron(II) chloride in THF leads to the formation of the corresponding pyridyl-substituted ferrocenes of type **30**.

Single-crystal X-ray structure analyses were performed for **30a** and **30d** (Fig. 12). The pyridine rings of compound **30a** are arranged in a stacked fashion, with a closest ring–ring contact of 316 pm, which is considerably shorter than the cyclopentadienyl interring distance of 332 pm. This effect may be indicative of secondary intramolecular interactions responsible for the conformation of the molecule in the solid state though the possibility that it is a result of crystal packing forces cannot be ruled out [24].

Reaction of **28**Li_2 with $FeCl_2$ in THF yields the ferrocenophane **31**.



31

The ferrocenes of type **30** can be used as redox-active bidentate ligands. For example, in the reaction of **30a** with $[Cu(NCCH_3)_4]BF_4$ and $[C_6H_5CN)_2PdCl_2]$, complexes of the stoichiometry $[Cu($**30a**$)_2]BF_4$ and $[Cl_2Pd($**30a**$)_2]$, respectively, are formed.

3.3. Summary and outlook

The permethylated pyridyl-substituted cyclopentadienyl ligands described in this review can be prepared very conveniently from readily accessible starting materials. The preliminary results obtained so far augur well for the development of a rich coordination chemistry based on these ligands, especially for the construction of oligonuclear organometallic assemblies. We are also studying related systems based on 2,2′-bipyridine and 2,2′ : 6,2″-terpyridine which should be even more interesting ligands in this respect.

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