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Results and perspectives in the chemistry of side-chain-functionalized cyclopentadienyl compounds

Christian Müller, Derk Vos, Peter Jutzi *

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse 25, D-33615 Bielefeld, Germany

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Abstract

Cyclopentadienyl (Cp) compounds of s-, p-, d-, and f-block elements with donor functionalities in the side-chain of the Cp fragment have attracted a lot of attention during the last decade. In this article, the structure and reactivity of representative compounds with tethered NR_2, OR, PR_2, SR, and CH=CHR groups are described; one, two (in 1,3 position) or five donors are attached with C_n or SiC_n spacers to the Cp fragment. Intra- or intermolecular donor–acceptor interactions can be classified with the help of the HSAB concept. A 'hard–soft' coordination promotes hemilability and causes interesting effects concerning reactivity. Side-chain-functionalized compounds find application in catalysis, CVD and related techniques, molecular recognition, organometallic chemistry in water, and dendrimer synthesis. Perspectives in these fields are presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Functionalized cyclopentadienyl compounds; Intramolecular coordination; Intermolecular coordination; Molecular recognition; Catalysis; Water solubility; Dendrimers

1. Introduction

During the last decade, the introduction of functional groups at the C_5 perimeter of a cyclopentadienyl (Cp) fragment has become an interesting tool to sometimes modify drastically the chemical and physical properties of classical Cp complexes of s-, p-, d-, and f-block elements. In our group, we have concentrated on the investigation of Cp compounds with one, two (in 1,3 position) or five donor functionalities in the side-chain, as indicated in Fig. 1. Dialkylamino and alkenyl groups act as donor centers and the side-chain (spacer) consists of up to three carbon atoms.

In this article, we report on recent results and trends in the field of correspondingly functionalized Cp compounds, and offer perspectives for quite different applications. We include results and trends from the chemistry of comparable OR-, PR_2-, and SR-functionalized compounds containing C_n and SiC_n spacer units, which has been investigated by other groups.

2. Intramolecular coordination

2.1. π-Cyclopentadienyl complexes

2.1.1. Bonding features and synthetic strategies

The coordination of a tethered donor fragment to a metal center is entropically favored compared with the coordination of a free donor molecule. Furthermore, intramolecular coordination (Fig. 2, left side) is generally preferred to intermolecular coordination (Fig. 2, right side), but an increase in chelate ring strain and a decrease in solubility might enforce the formation of coordination polymers.

In cyclopentadienyl complexes of transition metals, the Cp ligand is known to stabilize metal fragments in

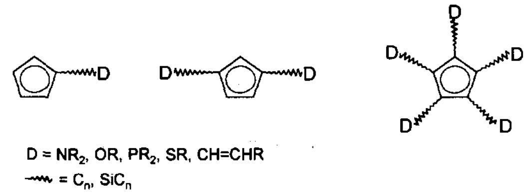

Fig. 1.

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* Corresponding author. Fax: +49-521-1066026.
E-mail address: peter.jutzi@uni-bielefeld.de (P. Jutzi)

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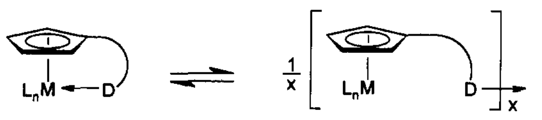


Fig. 2.

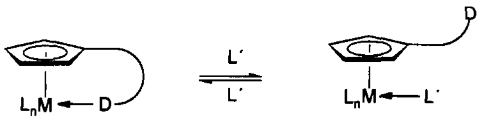


Fig. 3.

both low and high oxidation states and is usually regarded as substitutionally inert. The effect of an additional donor group, however, strongly depends on the nature of the metal and of the donor group. The strength of the interaction can be estimated on the basis of Pearson's HSAB concept of 'hard' and 'soft' acids and bases [1]. 'Hard' ligands combine preferentially with 'hard' metal centers, and 'soft' ligands favor the interaction with 'soft' metal centers. On the other hand, otherwise unfavored 'hard–soft' combinations are stabilized to a certain extent by the chelate effect; this unusual binding situation leads to interesting electronic effects at the respective metal center with consequences for the chemical reactivity. Of course, the side-chain donor can be easily substituted in such types of complexes. This results in a hemilabile behavior [2], where the side-chain functionality can either act as a donor or as a spectator ligand (Fig. 3).

The hemilabile situation is expected in compounds where a 'hard' donor, such as an amino or alkoxy group, coordinates to a 'soft' metal center, as present in complexes with a late transition metal in low oxidation states. Vice versa, hemilability is anticipated when a 'soft' donor, such as a phosphino, thio, or alkenyl group, interacts with a 'hard' center, as present in complexes with early transition metals in high oxidation states. Of course, there exist many 'borderline' bonding situations, where the donor–acceptor interaction is difficult to predict. A substitutionally labile group is capable of temporarily blocking a coordination site and therefore allows tuning of the reactivity of the metal center. The fluxional 'opening and closing' character (see Fig. 3) provides interesting perspectives in terms of stabilization of reactive, unsaturated species, of substrate activation, of chemical sensing, and of homogeneous catalysis.

2.1.2. *Compounds with a dialkylaminoalkyl side-chain*

Many examples of dialkylaminoalkyl-substituted Cp complexes with s-, p-, d-, and f-block elements have been described in the literature [3]. A representative selection is collected in Fig. 4.

The calcocene **1** and the samarocene **2** have recently been published by our group [4]. The coordination of the amino side-chains prevents an association to oligomers. No strong intermolecular contacts are observed in the solid-state structure of **1**, in contrast to Cp^*_2Ca [5]. The molecular character of such types of compounds enhances their volatility and offers application as precursors in the chemical vapor deposition (CVD) process. Similar criteria in terms of intramolecular stabilization count for compounds **3** and **4**. The monomeric lanthanum complex **3**, reported by Herrmann and co-workers, contains three dimethylaminoethyl substituted cyclopentadienyl groups; only two amino groups coordinate to the metal center and thus prevent the usual formation of oligomers [6]. Lanthanoid complexes of type **4**, reported by Schumann et al., are more stable towards air and moisture than the parent compounds; unfortunately, they do not catalyze the polymerization of ethylene anymore [7].

The influence of the alkyl substituents at the amino group has been studied in complexes **5**–**7**. Rausch and co-workers have described the titanium half-sandwich complex **5**, which is monomeric in the solid state and in solution [8], analogous to the parent compound $CpTiCl_3$ [9]. In combination with MAO, **5** is a very active catalyst in the polymerization of ethylene; the role of the dimethylamino group in the polymerization process has not been elucidated yet. We have reported on the synthesis of the titanium and zirconium half-sandwich complexes **6** and **7** [10], with a diisopropylamino group in the side-chain. These compounds prefer an intermolecular coordination, which results in the formation of coordination polymers. Beckhaus et al. have investigated the influence of the oxidation state of the central metal on the coordination behavior [11]. The oxidation of **8** to **20** is connected with decomplexation. Although 16-valence-electron complexes of early transition metals, like **20**, are electronically unsaturated, intramolecular donor coordination has not been reported so far. Addition of $LiCH{=}CH_2$ to **20** leads back to the starting compound **8** with a coordinating amino group (Scheme 1).

The 16-valence-electron alkylmetallocenium cations of the types **9**–**11** have been recently synthesized in our group [12]. Coordination of the dialkylaminoethyl ligand is proven by NMR experiments. As expected on the basis of the HSAB concept, the amino group coordination is rather strong and prevents hemilability. An active catalyst for the polymerization of ethylene has been obtained upon addition of AlR_3. This effect is most probably due to the coordination of the Lewis acidic aluminum alkyl to the amino group and demonstrates the possibility of activating a dormant catalytically active site [13]. An interesting aspect concerning the effect of spacer length has been reported by Erker and co-workers [14]. Treatment of **12**, in which the Cp

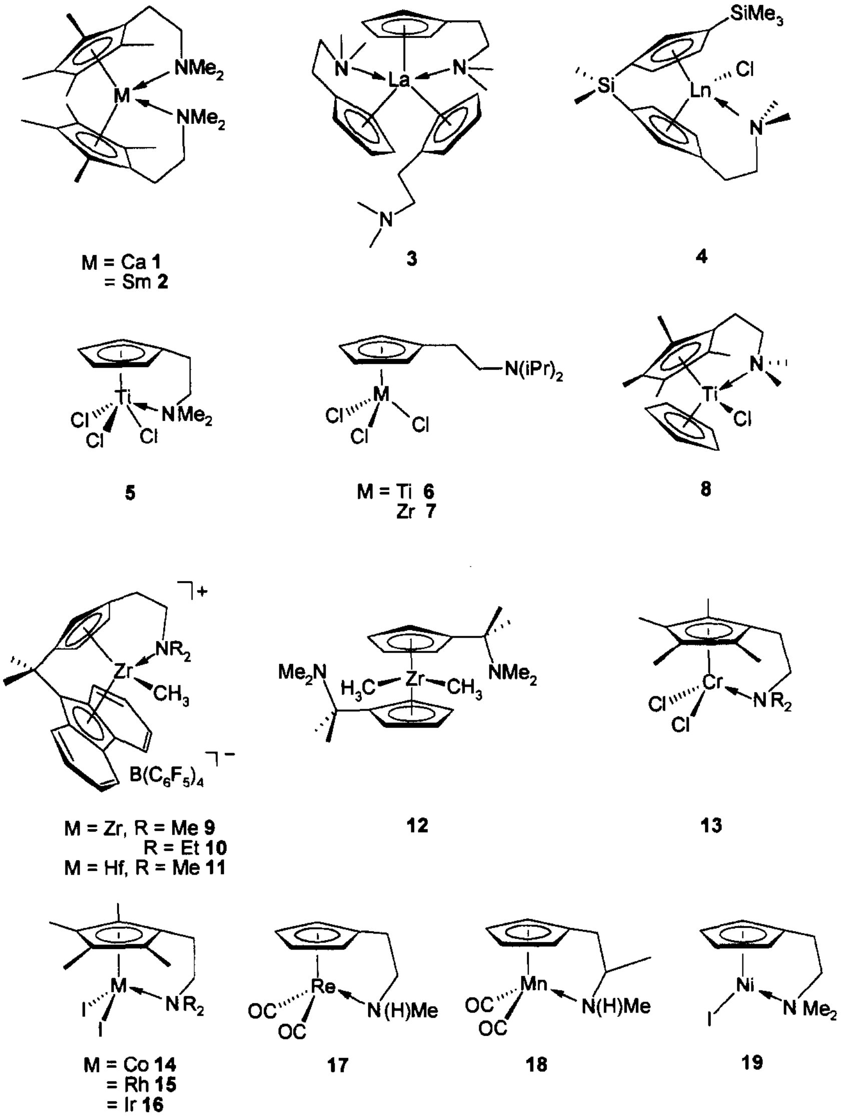
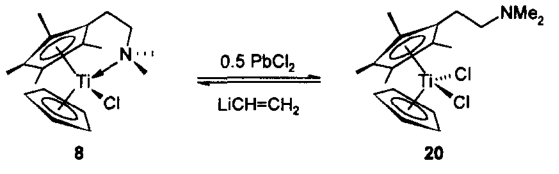


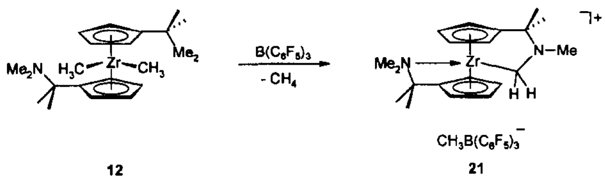
Fig. 4.

rings are substituted by dimethylaminomethyl groups, with the strong Lewis acidic tris(pentafluorophenyl)-borane leads to an ionic intermediate, which undergoes a surprising reaction sequence: C–H activation under loss of methane instead of coordination of the second dimethylamino group yields the spiro-metallocene **21** (Scheme 2).

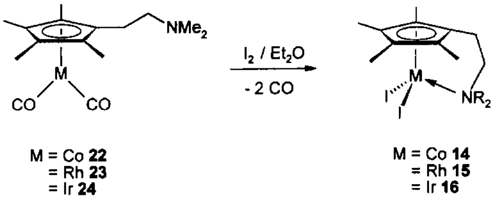
The chromium half-sandwich complex **13** has been reported by Jolly et al. [15]. In combination with MAO, this system acts as a highly active catalyst for the polymerization of ethylene. Interestingly, full catalytic activity is already reached at Cr:Al ratios of 1:45–300! Again, the role of the amino side-chain in the polymerization process remains unknown. The bonding characteristics of the $C_5H_4(CH_2CH_2)NMe_2$ ligand in late transition-metal compounds have been extensively studied in our group [16]. The amino side-chain does not coordinate in complexes **22**–**24** of the type



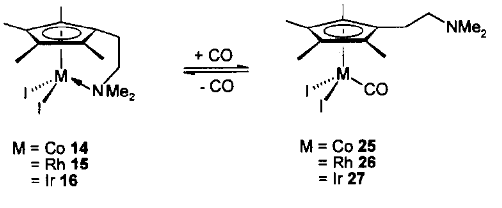
Scheme 1.



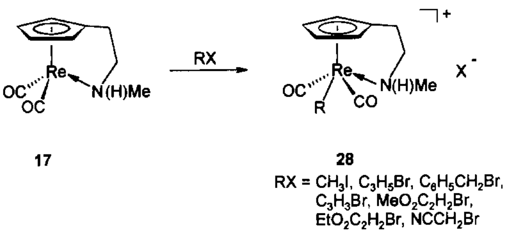
Scheme 2.



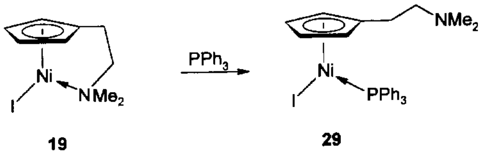
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

$[C_5H_4(CH_2CH_2)NMe_2]L_2M$, ($L = CO$, C_2H_4; $M = Co$, Rh, Ir) (Scheme 3). On the other hand, coordination takes place in **14**–**16** with the metal center in the oxidation state +III. Once more, this behavior can be explained with the HSAB concept.

Interestingly, a hemilabile situation has been observed in the systems **14**–**16**/CO, where the amino group can be reversibly displaced (Scheme 4) [16a]. In a more general context, 'intramolecular coordination on demand' might be a useful strategy, especially for the tailoring of catalytically active metal centers.

Wang et al. have contributed significantly to the area of amino-substituted Cp ligands [17]. Besides many other examples, they have reported on compound **17**, in which the 'hard' amino group is coordinated to a 'soft' Re(I) center. The enhanced nucleophilicity of the metal now enables alkylation with substrates RX [18], as shown in Scheme 5. The same group has presented the manganese complex **18** [19]. Once more, the coordination of an N donor to a monovalent metal center is supported by the chelate effect.

One of the few examples of intramolecular amino group coordination to a Group 10 element has been reported by Fischer and co-workers [20]. The labile dimethylaminoethyl group in the nickel(II) complex **19** can easily be displaced by a triphenylphosphine ligand (Scheme 6).

2.1.3. Cp complexes with an alkoxyalkyl side-chain

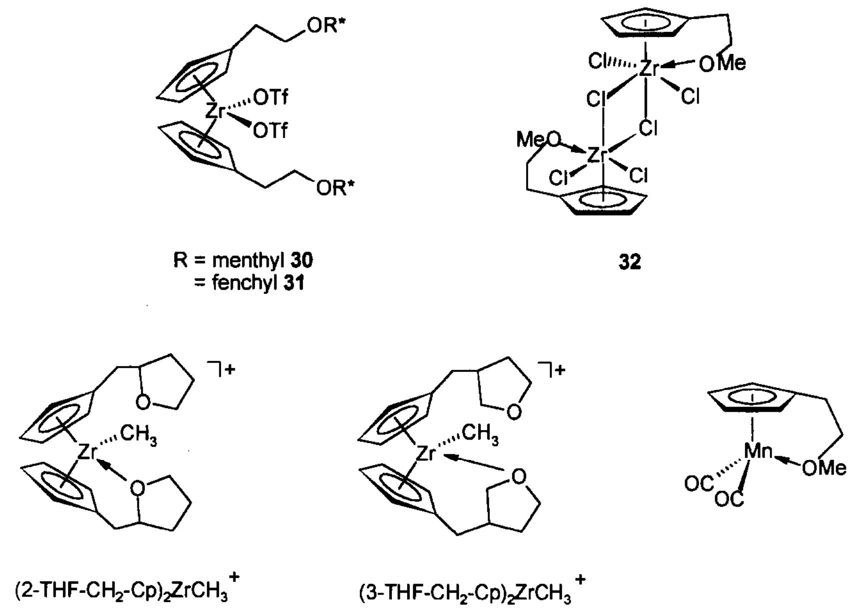
Various half-sandwich and sandwich complexes with oxygen-containing moieties in the Cp side-chain have been reported in the literature [21]. Some typical examples are depicted in Fig. 5.

Van der Zeijden et al. have reported on the synthesis of chiral metallocene triflate complexes of the type **30** and **31** [22], which were used as catalysts in Diels–Alder reactions. An intramolecular coordination of the ether moiety during the catalytic process was expected to effect an asymmetric induction (Scheme 7), which so far could not be verified. In general, this concept offers interesting perspectives for synthetic applications.

The same group has reported on the dimer **32** [23], which carries methoxyethyl functionalities. Due to the coordinated ether group, a decreased sensitivity towards air and moisture was observed. Compound **32** is a suitable catalyst for Diels–Alder and hydrocyanation reactions. The solid-state structure of **32** reveals a chloro-bridged dimer, while the analogous amino-substituted compound [24] as well as the parent compound $CpZrCl_3$ are polymeric species [9]. The influence of the alkyl spacer length on hemilability has been investigated by molecular modeling studies on the zirconocenium cations **33** and **34** [25]. On the basis of semi-empirical, ab initio, and DFT calculations, the 2-THF complex **33** (C_2 spacer) is more stable than the 3-THF complex **34** (C_3 spacer). As shown by Johnston and co-workers, the coordinating methoxyethyl group in the Mn(I) complex **35** can be substituted by the triethylphosphite ligand to obtain compound **36** (Scheme 8) [26]. In general, the coordination of an alkoxyalkyl group to a highly Lewis acidic metal center is problematic. It is known from organosilicon chemistry that a strong electrophile might cause an ether cleavage, which leads to an irreversible blocking of a coordination site by formation of a covalent silicon–oxygen bond [27]. In transition-metal chemistry, this phenomenon has synthetically been applied for the preparation of constrained geometry catalysts [28].

2.1.4. Cp complexes with a diorganylphosphinoalkyl side-chain

The use of phosphinoalkyl substituted Cp groups as bidentate ligands in Main Group as well as in early and late transition-metal compounds has been described in the literature by several groups [29]. In many examples the coordination of the 'soft' donor group to a 'soft'



R = menthyl **30**
= fenchyl **31**

32

(2-THF-CH$_2$-Cp)$_2$ZrCH$_3$$^+$

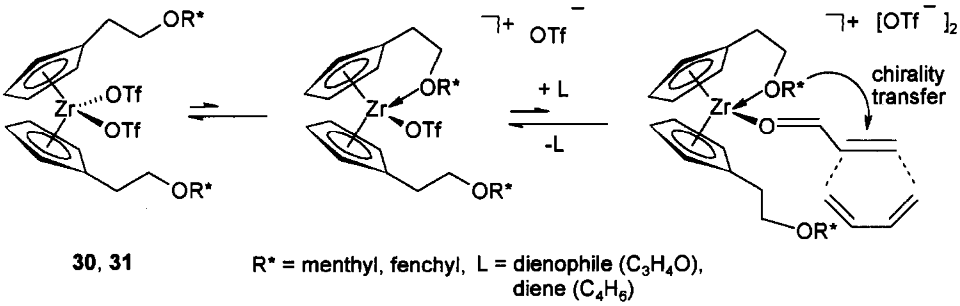
33

(3-THF-CH$_2$-Cp)$_2$ZrCH$_3$$^+$

34

35

Fig. 5.



30, 31

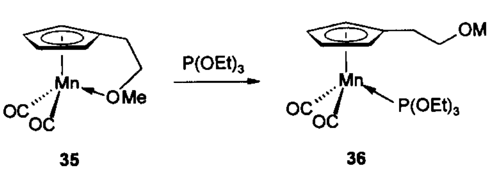
R* = menthyl, fenchyl, L = dienophile (C$_3$H$_4$O), diene (C$_4$H$_6$)

Scheme 7.

metal center has been observed. On the other hand, various compounds, in which an interaction with 'hard' early and late transition metals in high oxidation states occurs, have been synthesized. The collection in Fig. 6 is restricted to some prominent examples. Most of them show different structural features and reactivities compared with those observed for dialkylamino-functionalized species.

Karsch et al. have recently reported on the potassium super-sandwich complex **37** with an intramolecularly coordinated diphenylphosphinoethyl group [30]. An additional THF molecule is necessary to complete the coordination sphere of the alkali metal. Fryzuk et al. have presented a very interesting novel 'pincer' ligand with two P donor groups in 1,3 position of the cyclopentadienyl ring [31]. This ligand has been extensively used in the chemistry of early transition metals; it can stabilize unusual binding situations or highly reactive metal centers, as demonstrated by the synthesis of the first isolable zirconium alkylidene complex **38** [32]. Reactions of **38** with various substrates such as ethylene, acetone, CO, or *t*-butylisonitrile have been described [33].

The diphenylphosphinomethyl-substituted zirconocene dimethyl **39** has been synthesized by Erker and co-workers [34]. Compound **39** was converted into the phosphino stabilized zirconocene cation **46**; treatment of **46** with B(C$_6$F$_5$)$_3$ yielded the dicationic system **47** (Scheme 9). Interestingly, compounds **46** and **47** are not catalytically active in the olefin polymerization process. In the similar amino-substituted system **12**/**21**, (see Scheme 2), C–H activation instead of intramolecu-



35

36

Scheme 8.

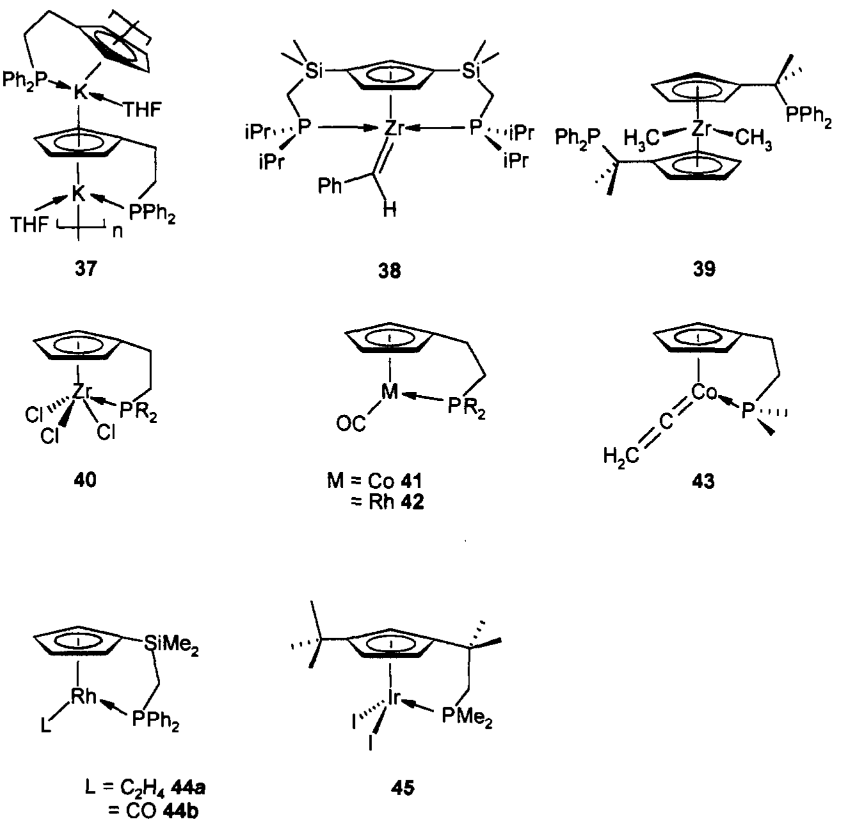
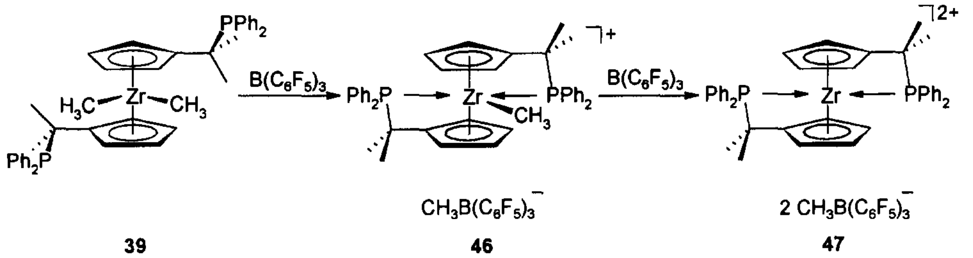
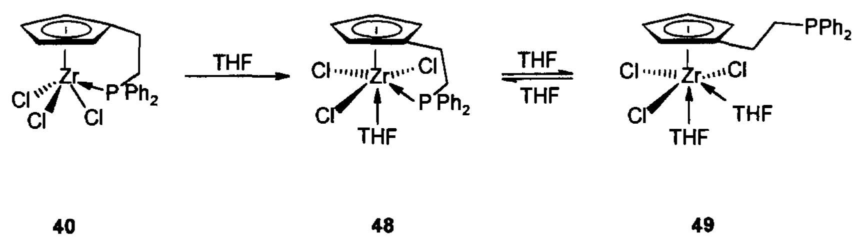


Fig. 6.



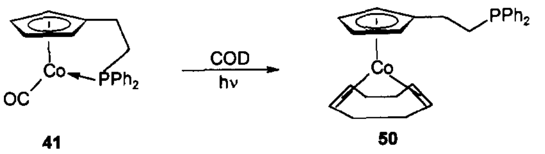
Scheme 9.



Scheme 10.

lar coordination has been observed. However, a direct comparison is prohibited due to a different substitution pattern at the donor atoms.

The half-sandwich complex **40** has been synthesized by Krut'ko et al. [35]. In contrast to the monomeric compound **40**, dimeric or polymeric structures are observed for the corresponding dimethylaminoethyl- [24] or methoxyethyl-functionalized systems [23]. The formation of the adduct **48** can easily be achieved by treatment of **40** with THF. An equilibrium mixture of **48** and **49** is present in THF as solvent (Scheme 10). No comparable situations are observed in cases of the



Scheme 11.

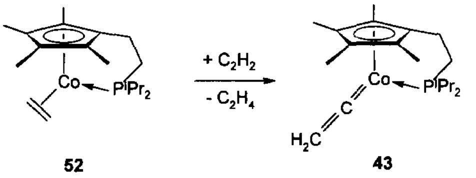
corresponding NMe_2-, OMe-, and SMe- functionalized complexes [35].

Butenschön and co-workers have extensively studied the coordination behavior of phosphino-substituted sandwich and half-sandwich Cp complexes. Surprisingly, a substitutionally labile character of the donor group was found in the chemistry of many Co(I) half-sandwich complexes [29]. As an example, both the CO and the phosphino group in **41** are displaced by the bidentate 1,5-cyclooctadiene (COD) ligand, yielding complex **50** (Scheme 11) [36].

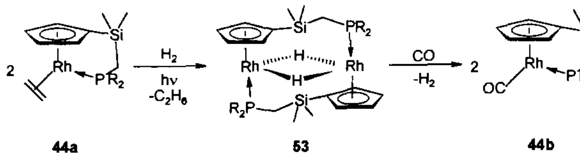
Poilblanc and co-workers have reported on the synthesis of the chelate complex **42**, which dimerizes to the diastereomers **51a** and **51b** [37]. NMR investigations show that **51a** and **51b** can be converted into the monomer **42** upon heating (Scheme 12).

Butenschön et al. have prepared the vinylidene Co complex **43** by an unexpected alkyne-vinylidene rearrangement in the presence of ethylene (Scheme 13) [38]. This reaction type is not observed in comparable half-sandwich complexes containing a non-linked phosphino ligand; it is demonstrated that the chelating diisopropylphosphinoethyl group drastically effects the reactivity of the metal center.

Jones and co-workers have described the synthesis of the rhodium complex **44a** [39]. Irradiation of **44a** in the presence of H_2 yielded the dimeric hydride complex **53** as the major product; upon treatment of **53** with CO, the mononuclear complex **44b** was obtained (Scheme 14).



Scheme 13.



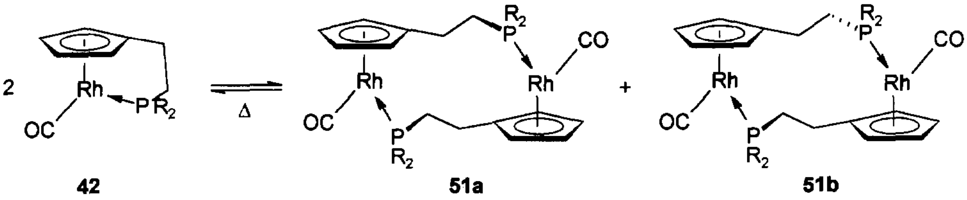
Scheme 14.

Mobley and Bergman have reported on the planar chiral iridium complex **45**, which is a suitable precursor for C–H activation reactions [40]. Treatment of **45** with zinc and acetic acid in methanol leads to the formation of the dihydrido iridium complex **54**. Photolytically activated **54** reacts with cyclohexane to give complex **55** diastereoselectively (Scheme 15).

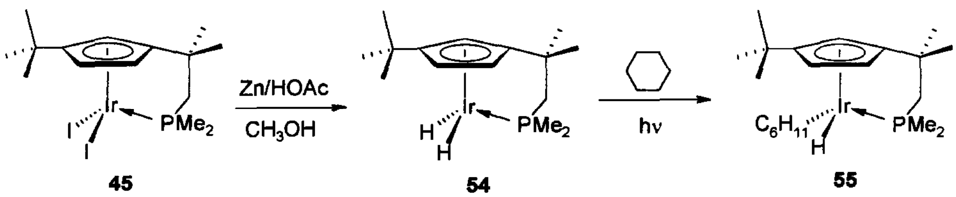
2.1.5. *Cp complexes with on organothioalkyl side-chain*

Comparatively few thioalkyl-substituted Cp complexes have been described so far [29]. Some typical examples are collected in Fig. 7. A coordination behavior similar to that of phosphino-substituted complexes is expected, with a tendency for weaker interaction.

The coordination of a 'soft' phenylthioethyl group to the 'hard' cationic Mo(IV) center in complex **56** has been presented by Green and co-workers [41]. In contrast to the expected weak interaction, no hemilability was observed. Hemilability of a thienylmethyl substituted Cp system in the half-sandwich Ru(II) complex **57** has been shown by Rauchfuss and co-workers [42];



Scheme 12.



Scheme 15.

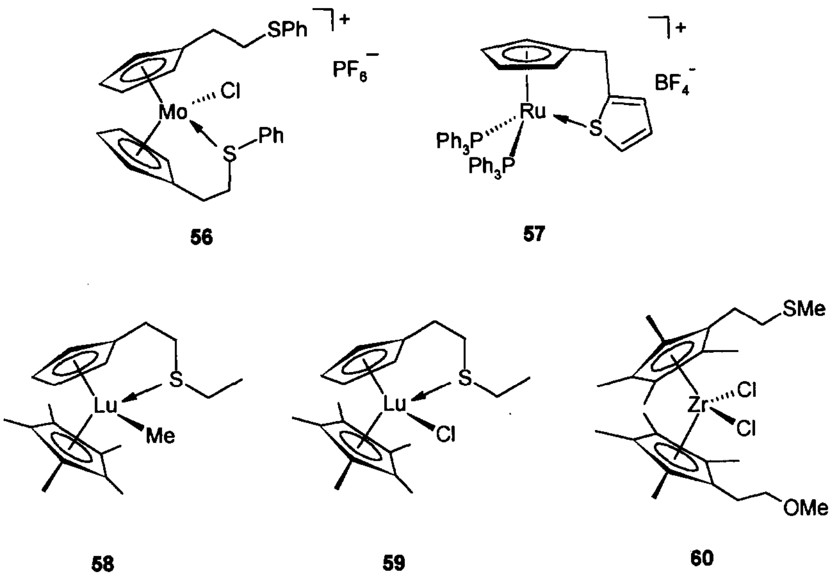
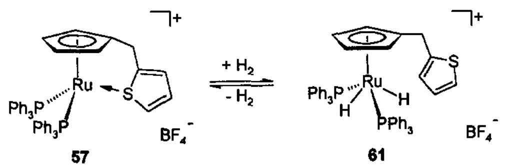
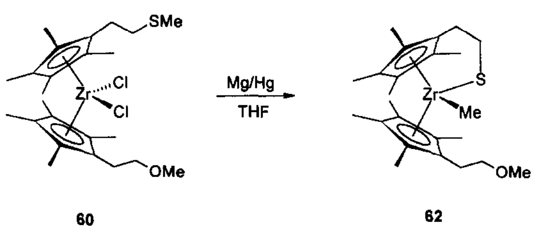


Fig. 7.



Scheme 16.



Scheme 17.

oxidative addition under the formation of **61** is observed upon reaction with H_2 (Scheme 16). The reversibility of this process is worth mentioning.

Schumann and co-workers have reported on the different coordination behavior of the side-chain donor in the metallocenes **58** and **59** [43]. The Lewis acidity of the Lu(III) center in **58** is slightly reduced by the methyl substituent; thus, permanent coordination of the sulfur atom is observed. The interaction in the 'hard' metal–'soft' ligand system **59** shows the expected hemilabile character.

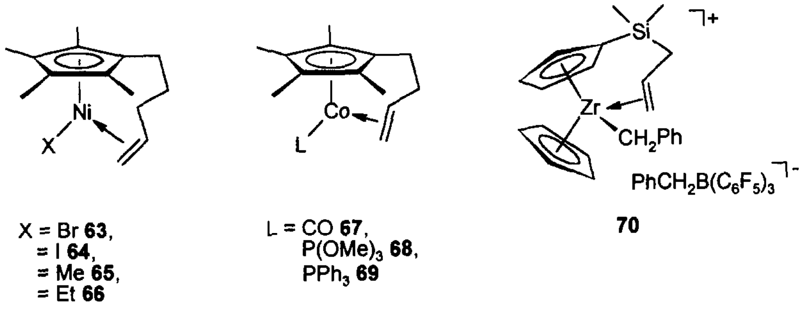
The competition between a sulfur and an oxygen donor group in the coordination to a zirconium center has been investigated by Krut'ko et. al. [44]. Treatment of **60** with magnesium amalgam in THF leads to complex **62**. The intermediate 'soft' zirconocene prefers interaction with the 'soft' sulfur ligand, which reacts under oxidative addition (Scheme 17). Similar to the situation described in Section 2.1.3. for OR-functionalized Cp systems, the oxidative addition of SR units competes with simple coordination. Only small traces of the corresponding O–Me bond cleavage product were detected.

2.1.6. Cp complexes with an ω-alkenyl side-chain

In the chemistry of alkenyl-substituted compounds, either stabilization of reactive species or further reactions (e.g. insertion) of the double bond are expected. Both situations have been reported in the literature [45]. The examples depicted in Fig. 8 are restricted to the former.

The Ni(II) complexes **63**–**66** with a coordinated pentenyl side-chain have been reported by Lehmkuhl et al. [46]. They were found to be substitutionally inert and thus are much more stable than the corresponding structural analogues without a Cp donor linkage. In contrast, Okuda and co-workers have reported on the labile behavior of the butenyl side-chain in the Co(I) complexes **67**–**69** [47]. Hence, reaction of **68** and **69** with I_2 leads to the oxidative addition products **71** and **72**, respectively. Treatment of **71** and **72** with Na/Hg leads back to **68** and **69**, respectively (Scheme 18). The reaction sequence nicely demonstrates that the 'soft' alkenyl group prefers coordination to the 'soft' Co(I) center, in contrast to the observed preference of the 'hard' dimethylamino group for the 'hard' Co(III) center, as presented in Scheme 3.

Substitution of the CO ligand and of the coordinated butenyl group was observed in the reaction of **67** with two equivalents of *tert*-butyl phosphaethyne (^{t}BuC≡P), yielding compound **73** with [^{t}BuCP]$_2$ as a four-electron π-ligand (Scheme 19) [47d].

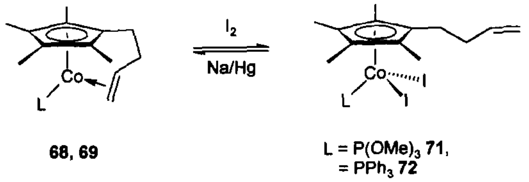


X = Br **63**,
= I **64**,
= Me **65**,
= Et **66**

L = CO **67**,
P(OMe)$_3$ **68**,
PPh$_3$ **69**

70

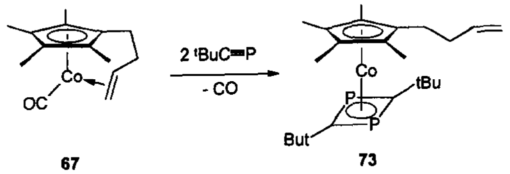
Fig. 8.



68, 69

L = P(OMe)$_3$ **71**,
= PPh$_3$ **72**

Scheme 18.



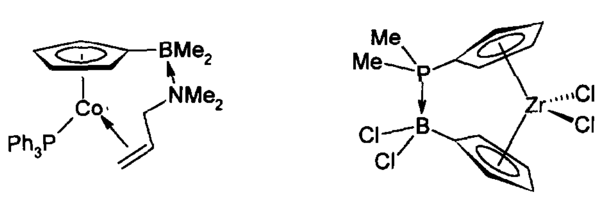
67 **73**

Scheme 19.

One of the very few examples for the documentation of alkene coordination to a catalytically relevant alkylzirconocene cation has been described by Royo and co-workers [48]. The metal–alkene interaction in **70** was investigated by variable temperature NMR experiments. It is still open whether **70** is catalytically active in the Ziegler–Natta polymerization process.

2.1.7. Cp complexes with donor–acceptor linkages in the side-chain

The linkage of suitable donor and acceptor functionalized groups offers the possibility for the synthesis of novel chelate ligand systems (Fig. 9). This concept has been realized in the preparation of the Co(I) complex **74** [49], as described by Klang and Collum. The difunctional aminopropene coordinates to the Co(I) center via the alkenyl moiety and to the Lewis acidic boron center via the amino group.



74 **75**

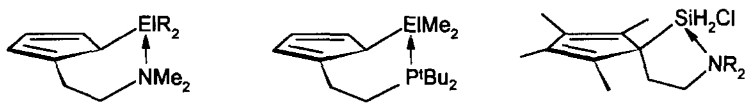
Fig. 9.

Donor–acceptor linkage allows the synthesis of the novel *ansa*-zirconocene dichloride **75**, as described by Starzewski et al. [50]. The bridge in **75** consists of a strong coordinative P–B interaction. In combination with MAO, **75** is a thermally stable, highly efficient catalyst for the polymerization of ethylene. This new class of metallocene precatalysts provides the possibility of tuning a catalyst efficiently by varying the donor (e.g. O, N, P) and acceptor atoms (e.g. B, Al) in the bridge.

2.2. σ-Cyclopentadienyl compounds of Main Group elements

In compounds of Main Group elements, the σ-bound cyclopentadienyl ligand can be regarded as substitutionally labile [51]. Some of the important features of side-chain-functionalized Cp ligands, discussed in Section 2.1.1, play an important role in the chemistry of Main Group elements as well; intramolecular coordination of the donor group is able to prevent the formation of dimers or oligomers and therefore stabilizes monomeric species. Fig. 10 shows some compounds of Main Group elements with dialkylaminoethyl- or dialkylphosphinoethyl-functionalized cyclopentadienyl ligands.

The Group 13 element compounds **76**–**80** have been published by Cowley et al. [52] and by our group [53]. In these compounds, the stability against air and moisture is improved and ligand scrambling reactions are excluded; the side-chain is located in vinylic position of the cyclopentadienyl skeleton, whereas the Main Group element is exclusively bound to an allylic position. In the case of the silicon compounds **81** prepared by our group [54], both the Si atom and the side-chain are positioned at the allylic carbon atom. The observed constellations are most likely caused by the different coordination geometries at the relevant Main Group element centers. In all compounds, the intrinsically labile El–Cp bond is further weakened by electron donation from the amino group to the Main Group element. Compounds **77a** and **82** are precursors for the

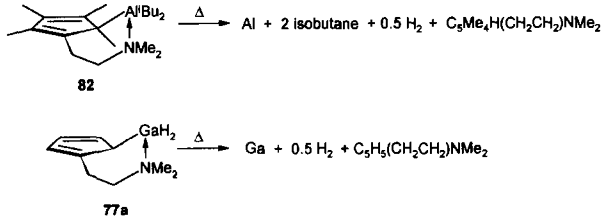


El = Al, R = H **76a**, R = Me **76b**
= Ga, R = H **77a**, R = Me **77b**
= In, R = Me **78a**

El = Ga **79**
= In **80**

R = Me **81a**, R = Et **81b**

Fig. 10.



Scheme 20.

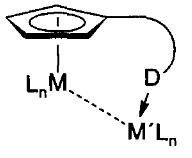


Fig. 11.

thermal and for the photochemical deposition of aluminium or gallium in CVD and related processes (Scheme 20) [55].

3. Intermolecular coordination

3.1. Di- and oligonuclear π-Cp complexes

Donor-functionalized cyclopentadienyl groups are suitable ligands for the synthesis of homo- and heterobimetallic complexes. While one metal center is coordinated by a η^5-Cp moiety, the other one is complexed by the donor functionality (Fig. 11). This constellation allows the study of cooperative interactions between two rather close metal centers, which might result in important changes of chemical and physical properties.

Some heterobimetallic complexes are shown in Fig. 12. They are based on metallocene cores; the second metal is coordinated by a tethered diorganophosphino group. Special interest in the context of metal–metal interactions and electronic communication is put on combinations of early and late transition metals, as present in the tetranuclear complex **83** published by Cowie and co-workers [56]. The Rh(CO)Cl unit might influence the metallocene-based polymerization of olefins and thus might provide interesting perspectives in terms of tuning the catalytically active site. A similar behavior is expected for compound **84** [57]. Heterobimetallic complexes such as **85** may have sensor functions if the redox properties of the ferrocene units are changed upon coordination of the second metal fragment [36]. The topic of molecular recognition will be briefly discussed in Section 3.2.

The dinuclear complexes **86** and **87**, published by Fischer et al. [58], have been used as single source precursors in the metal organic chemical vapor depostion (MOCVD) process to prepare thin layers of NiIn and NiGa alloys (Fig. 13). It might be possible to

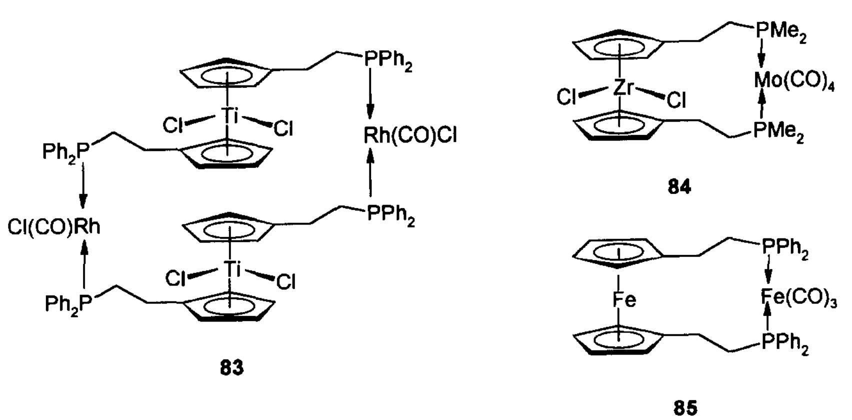
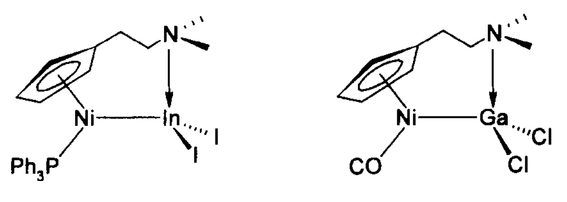


Fig. 12.



86 **87**

Fig. 13.

influence the stoichiometry of the deposited layer by the molecular structure of its precursor. Combinations of transition metals with Group 13 elements can provide metal contacts to III/V semiconductor surfaces [59].

3.2. Molecular recognition

The field of molecular recognition is a fast expanding research area [60]. The development of electrochemical sensors, which are capable of binding charged or neutral guest molecules, is a challenging task for all synthetic chemists. Very often these sensors are built up from a chelating unit, which is responsible for the guest binding, and a reporter group, which provides for the electrochemical information (Fig. 14).

Metallocenes have proved to be suitable reporter groups. Especially ferrocenyl compounds have often been used as redox antenna for guest molecule binding [61]. Some ferrocene-containing sensors with nitrogen donors in the side-chain are depicted in Fig. 15.

The pyridyl-supported complexation of a metal cation can vary the half-wave potential of the ferrocene unit, as demonstrated by Siemeling and co-workers [62]. On complexation of a Cu^+ ion, the redox potential of **88** is anodically shifted about 400 mV. The magnitude of this shift is undoubtedly due to the close proximity of the Fe and the Cu atom. Similar anodic shifts of the half-wave potential can be realized upon coordination of various alkaline earth and transition metals [63]. Beer et al. have reported on a series of bis(ferrocenyl) receptors based on (aminomethyl)ferrocene [64], linked by different spacer groups. The authors have studied the interaction of hydrated metal perchlorates/tetrafluoroborates towards the bis(ferrocenyl) receptors in acetonitrile as solvent. Receptor protonation or metal coordination was shown to depend on the nature of the spacer between the two ferrocenyl moieties. For **89b** complexation of Ni^{2+}, Cu^{2+} and Zn^{2+} was favored over protonation, while in the case of **89a** protonation of the amine receptor occurred. Plenio et al. have described the synthesis of 1,2-ferrocenylmethylenediyl diamino tetraacetate (1,2-FDTA) **90** [65]. Again, complexation of metal ions (especially earth alkaline metals) leads to an anodic shift of the ferrocene's half-wave potential. The selectivity of **90** for Ca^{2+} over Mg^{2+} is even larger than that of EDTA itself and makes this system a potential amperometric sensor. The same authors have presented other systems with two redox-active ferrocenyl units, which can act as a regulatory unit for sodium cations [66].

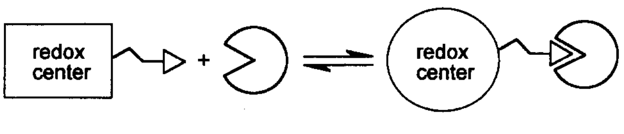
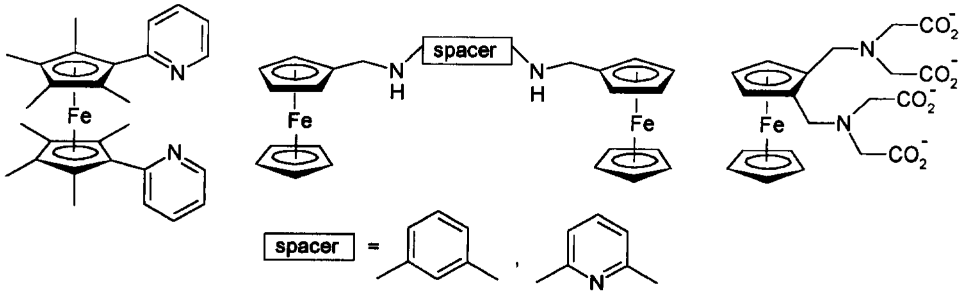


Fig. 14.

3.3. Effect of donor–acceptor interaction on catalysis

The synthesis of transition-metal catalysts for the polymerization of olefins has become an important and rapidly growing research area in the last decades [67]. A novel concept of modifying active centers in single-site catalysts has recently been detected in our group. The reversible connection of an additional molecule to the ligand sphere of the catalytically active species results in the presence of two kinds of catalysts due to different coordination spheres around the metal centers. As a consequence, alterations in chain propagation and chain termination reactions occur, which result in the production of polymers with different molecular weights (Fig. 16). *Ansa*-zirconocene dichlorides, which are substituted by a dialkylaminoethyl group, provide



88 **89a** **89b** **90**

Fig. 15.

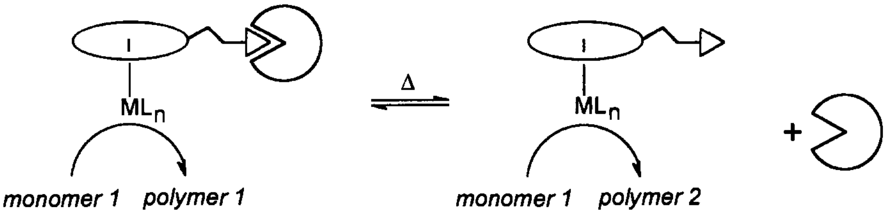
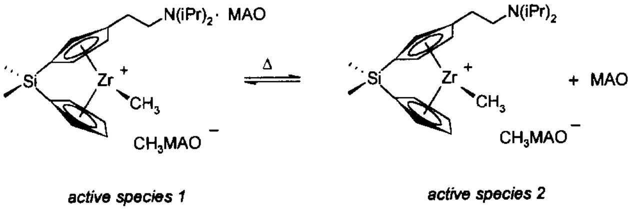


Fig. 16.



Scheme 21.

the possibility of switching between two catalytically active sites [13]. This leads to the production of two different kinds of polyethylenes, 'low-molecular-weight' PE ($M = 30\,000$–$60\,000$ g mol^{-1}) and 'high-molecular-weight' PE ($M = 1\,000\,000$–$2\,500\,000$ g mol^{-1}). Their relative amounts can be controlled by the polymerization temperature. A reversible association of the Lewis acidic cocatalyst MAO with the amino functionality is responsible for this kind of temperature-controlled catalyst tuning. This strategy should not be restricted to the system shown in Scheme 21; similar effects are also expected in other transition-metal-catalyzed reactions.

4. Water solubility

Organometallic chemistry is usually connected with anaerobic and water-free conditions. Although the majority of organometallic compounds are indeed sensitive to air and moisture, the cyclopentadienyl group and its derivatives are known to provide kinetic stabilization of reactive metal centers. Thus, a lot of air- and moisture-stable Cp–metal complexes are known nowadays [68]. To make an organometallic compound even soluble in water, it has to carry polar substituents such as hydroxy, carboxy, amino, or amonio groups. Hence, the hydrophobic organometallic core must be 'wrapped' by hydrophilic functionalities (Fig. 17). Water solubility provides important and interesting features for biological applications, as well as for catalytic and stoichiometric reactions.

Some water-soluble organometallic complexes are shown in Fig. 18. We have shown that the titanocene dichlorides **91** and **92** are water soluble and stable [69]. They are suitable precatalysts for the polymerization of ethylene as well as for the dehydrocoupling of phenylsilane. Upon addition of HCl, the catalytically active species can be reconverted into the water-soluble precatalyst **92**, once the polymerization process has finished. This allows an efficient high-yield recycling of the titanocene compound after its use in the catalytic process.

Complex **93**, reported by Tyler and co-workers, is a precursor for the generation of 19-valence-electron species in aqueous solution [70]. These kind of compounds are potential reducing agents and therefore valuable species for electron-transfer initiations. Photochemical water splitting by such systems is a fascinating research area. It has been found that some Cp-containing organometallic complexes have cytostatic properties against a variety of tumors [71]. Generally, they can be classified in two categories: (a) neutral complexes like metallocene dihalides of Ti, V, Nb, Mo and (b) salt-like metallocenium complexes of Fe, Rh or Co. Sufficient aqueous solubility of such compounds is a prerequisite for their use in biological media. As an example, the water-soluble and -stable Rh^{III} complex **94** has been synthesized by Poilblanc and co-workers [72]. The water solubility can be facilitated not only by quarternization of amino groups. We have recently synthesized the deca(hydroxypropyl)ferrocene **95** by hydroboration reaction of the decaallylferrocene **107** with BH$_3$·THF and subsequent oxidative workup [73]. Compound **95** has potential application as a redox mediator in scanning electrochemical microscopy (SECM).

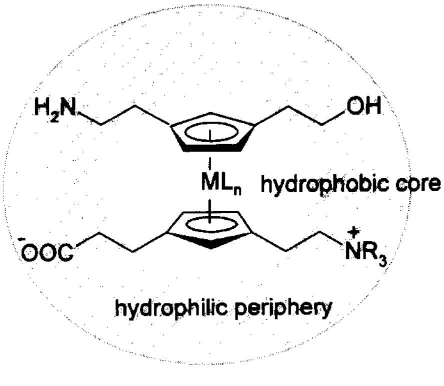
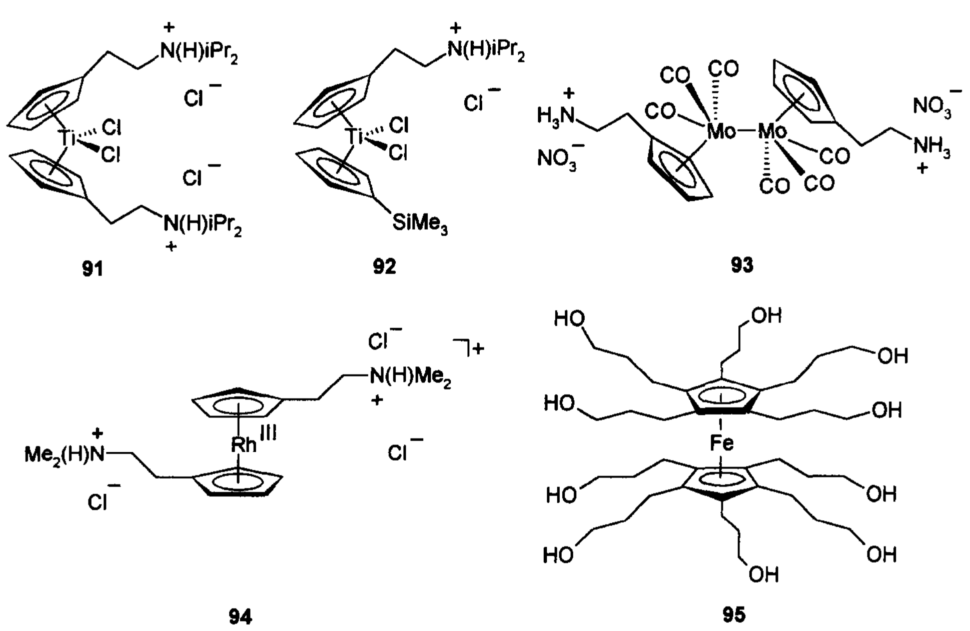


Fig. 17.



91 92 93

94 95

Fig. 18.

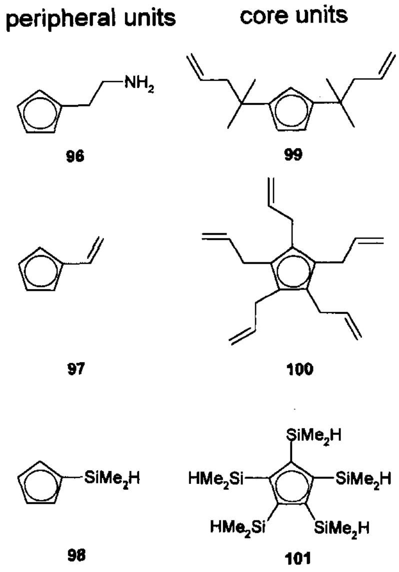
5. Dendrimers

During the last few years the research area of dendrimers has attracted a lot of attention [74]. These macromolecules possess a well-defined three-dimensional structure and carry a controlled number of functional groups. Dendritic macromolecules containing a specific number of redox-active metal centers are suitable candidates for applications in multi-electron redox catalysis, photoinduced electron transfer and molecular electronic devices.

A great number of dendrimers are known, which carry either a functionalized Cp fragment or the corresponding organometallic complex. These systems can be classified into three general categories: (a) dendrimers with peripheral redox-active Cp units; (b) dendrimers with redox-active Cp cores, and (c) dendrimers with redox-active Cp cores and with redox-active peripheral Cp units. Some useful construction tools for such dendrimers are depicted in Fig. 19 [75]. Cp units that carry only one functionality are suited to terminate the dendritic framework, whereas Cp units with up to five functionalities are suitable cores. In Fig. 19, we have included the $SiMe_2H$-functionalized Cp system **101**, which can easily be further functionalized by hydrosilylation reactions, and is therefore a suitable core or peripheral unit in the dendrimer strategy.

Dendrimers with peripheral redox-active Cp units are synthesized by linking a number of identical electroactive groups to a suitable framework. Usually the functional groups are attached to the core by hydrosilylation or metathesis reactions. The group of Cuadrado and Morán has reported on a series of dendrimers with organometallic substituents on the periphery [74c]. They prepared dendrimers with a silicon or poly(propylenimine) framework and connected up to 64 ferrocenyl units on the periphery by the synthetic approaches mentioned above. In Fig. 20, dendrimer **102** with eight peripheral ferrocene units is shown. According to electrochemical investigations, the ferrocenyl subunits are oxidized at the same potential and thus are non interacting. The oxidized form deposits on the electrode surface and forms electroactive films [76].

Dendrimers with a redox-active Cp core are relatively rare due to the synthetic difficulties encountered with the introduction of more than one functionizable group. Some useful core units are depicted in Fig. 21.

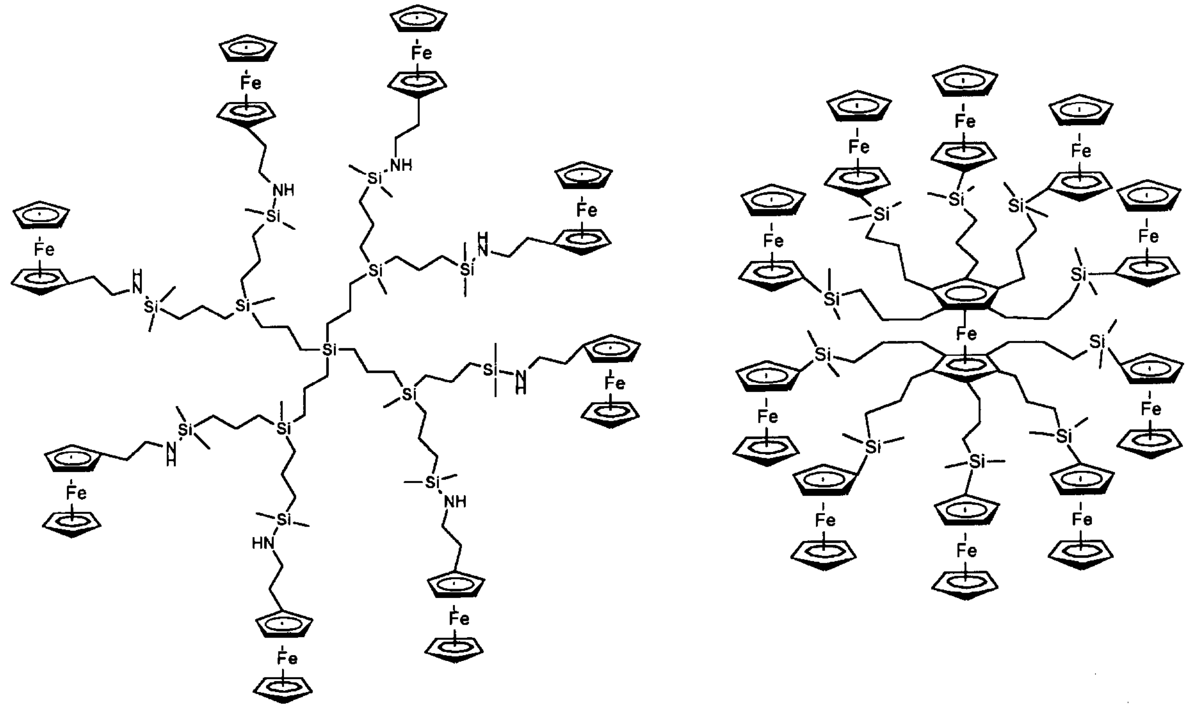


96 99

97 100

98 101

Fig. 19.



102 **103**

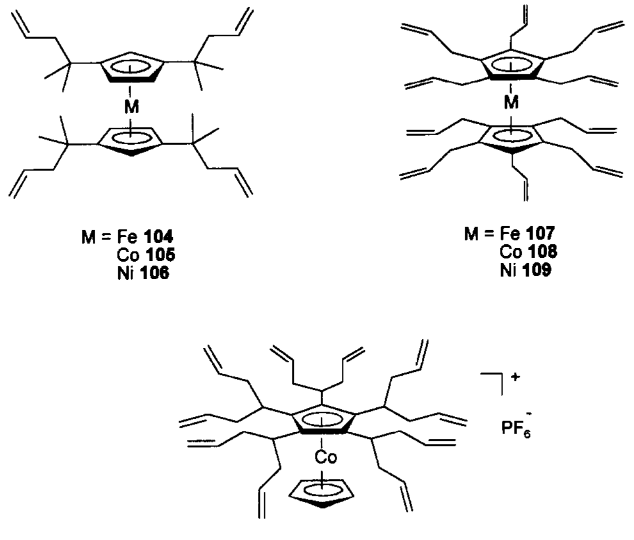
Fig. 20.

We have recently synthesized the tetraalkenyl-substituted metallocenes **104**–**106** [77] and the decaallyl metallocenes **107**–**109** [78]. The terminal double bonds offer the possibility of constructing macromolecular structures by established methods.

Astruc and co-workers have prepared the decaalkenyl-substituted cobaltocenium salt **110** (Scheme 22) [79]; a one-pot reaction of the pentamethylcobaltocenium salt **111** with allylbromide in the presence of KO^{t}Bu allows the introduction of ten functional groups. So far, no further functionalization of **110** has been described.

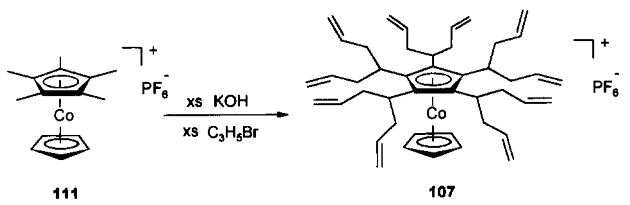
Dendrimers with redox-active Cp cores and peripheral Cp units can be synthesized with the help of the multiply alkenyl-substituted ferrocenes **104** and **107**. As an example, hydrosilylation of decaallylferrocene **107** with ten equivalents of dimethylferrocenylsilane leads to the formation of the decaferrocenyl functionalized ferrocene **103** (Fig. 20) [75c]. Cyclovoltammetric studies revealed separate oxidation waves for the central and the terminal ferrocene units. In chronoamperometric studies, the ratio of transferred electrons was determined to be ca. 1:10 [80]. In general, the ten alkenyl side-chains in **107**–**109** offer the possibility to built up dendrimers with $(n \times 10) + 1$ redox centers.

Another promising core fragment for $(n \times 10)$-fold functionalization of metallocenes is the penta-hydridosilyl-substituted cyclopentadienide system **101**, described by Sakurai and co-workers [75f]. Starting with



110

Fig. 21.



111 **107**

Scheme 22.

hydrosilylation reactions, the synthesis of different kinds of dendrimers seems to be possible.

6. Perspectives

Cyclopentadienyl units with tethered NR_2-, OR-, PR_2-, SR- and CH=CHR-functionalized ligands have already found versatile application in the chemistry of s-, p-, d- and f-block elements. Quite different strategies can be envisaged for the future, where the use of such bidentate ligands is indicated. The strength of interaction with metal centers can be estimated on the basis of the HSAB concept. Concerning intramolecular coordination, a hemilabile interaction is of special interest for catalytic purposes; weak interactions are a prerequisite to use corresponding compounds as precursors in the CVD or related processes. Concerning intermolecular coordination, metal–ligand as well as metal–metal interactions can be tuned in tailor-made bimetallic complexes; the corresponding compounds find application in sensor chemistry, as novel types of catalysts, and once more as precursors in the CVD process. Finally, suitably side-chain-functionalized Cp complexes can be used in dendrimer chemistry and in the organometallic chemistry in water. For the next decade, the use of side-chain-functionalized cyclopentadienyl ligands in many fields of chemistry is promising.

Acknowledgements

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