Aminoethyl-Functionalized Cyclopentadienyl Complexes of d-Block Elements☆

Peter Jutzi* and **Thomas Redeker**

Fakultät für Chemie der Universität Bielefeld,
Universitätsstraße 25, D-33615 Bielefeld, Germany
Fax: (internat) + 49(0)521/106-6026
E-mail: P.Jutzi@uni-bielefeld.de

Received December 18, 1997

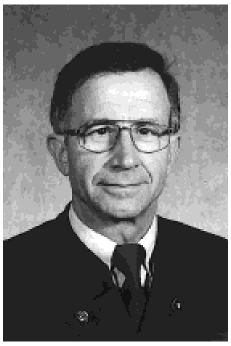
Keywords: Aminoethyl-functionalized cyclopentadienyl complexes / d-Block elements / Hemilabile N-ligands / Intramolecular coordination / Tethered aminoethyl groups / Water-soluble organometallics

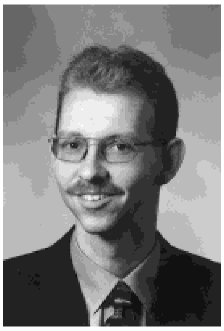
The introduction of an aminoethyl side chain into cyclopentadienyl compounds of many d-block elements leads to interesting changes in structure and reactivity compared to the parent species: (i) A hemilabile bonding situation is observed in complexes with low-valent transition-metal centers; (ii) amino-group coordination to an adjacent metal or nonmetal center creates novel types of bimetallic compounds; (iii) complexes with a tethered ammoniumethyl group often show good solubility in protic solvents, relevant with regard to organometallic chemistry in water. These features together with others are described in this review, which informs about the synthesis and properties of this new type of transition-metal complexes.

Introduction

Undoubtedly, the cyclopentadienyl group, C_5H_5 (Cp), is one of the most important ligands in organometallic chemistry.[1] In the last decade, an increasing number of new ring-substituted cyclopentadienyl fragments has appeared in the literature. Variations in the Cp-ligand periphery often result in dramatic changes in physical and chemical properties of the corresponding compounds. These changes can be attributed to electronic and steric effects caused by the partial or full replacement of the hydrogen atoms by other groups.[2]

The chemistry of Cp complexes containing a donor-functionalized side chain is a rapidly growing area that is currently being explored by several research groups.[3][4][5][6][7][8][9] This review concentrates on complexes of d-block elements containing aminoethyl-substituted Cp ligands. The first complexes of this type were introduced by Green et al. in 1983; the dimethylamino func-





Prof. Dr. P. Jutzi studied chemistry at the Technical University of Munich and received his Ph.D. degree under the supervision of Prof. Dr. M. Schmidt at the University of Marburg .After his habilitation at the University of Würzburg in 1971 he was appointed associate professor in 1974. In 1978 he moved as full professor of Inorganic Chemistry to the University of Bielefeld. His scientific interest is in the field of experimental organometallic chemistry. Topics of research are: I) Cyclopentadienyl chemistry of p- and d-block elements, II) nanometer-sized materials.

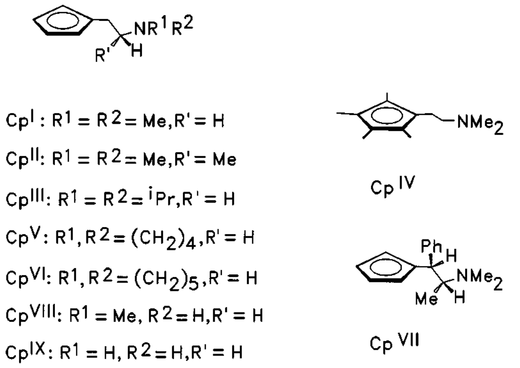
Dr. Thomas Redeker studied chemistry at the University of Bielefeld and received his Ph.D degree in early 1997. The thesis entitled "Metallocenes of the elements titanium and zirconium with the diisopropylaminoethylcyclopentadienyl ligand" was performed in Prof. Jutzi's laboratories, supported by a fellowship of the "Fonds der Chemischen Industrie" and awarded with the "Abschlußzertifikat" of the "Fonds der Chemischen Industrie". Currently, he is working in the group of Prof. Dr. H. D. Kaesz (UCLA, USA) as a postdoctoral fellow. His project, the MOCVD of titanium films, is supported by a grant from the "Deutsche Forschungsgemeinschaft".

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

1434–1948/98/0606–0663 $ 17.50+.50/0

tion was attached to a functionalized Cp ring only in the last step of the synthesis.[7a] The first synthesis of an aminoethyl-functionalized cyclopentadiene was described by Wang and co-workers in 1991. They prepared complexes with the (dimethylaminoethyl)cyclopentadienyl ligands Cp^{I} and Cp^{II} (Figure 1).[7f] Our laboratory contributed to this new field with compounds bearing the ligands Cp^{III} and Cp^{IV} (Figure 1).[9] Cyclopentadienyl ligands Cp^{V} and Cp^{VI} with pyrrolidyl and piperidyl functions as pendant groups were introduced by Herrmann and co-workers (Figure 1).[8c] The chiral dimethylaminoethyl-functionalized cyclopentadienyl ligand Cp^{VII} was described by van der Zeijden only recently (Figure 1).[8b][8l] The cyclopentadienyl ligand Cp^{VIII} with only one methyl substituent at the nitrogen atom was also introduced by Wang and co-workers.[8u] Tyler and Avey synthesized complexes with the Cp^{IX} ligand which contains the parent amino function.[7h]

Figure 1

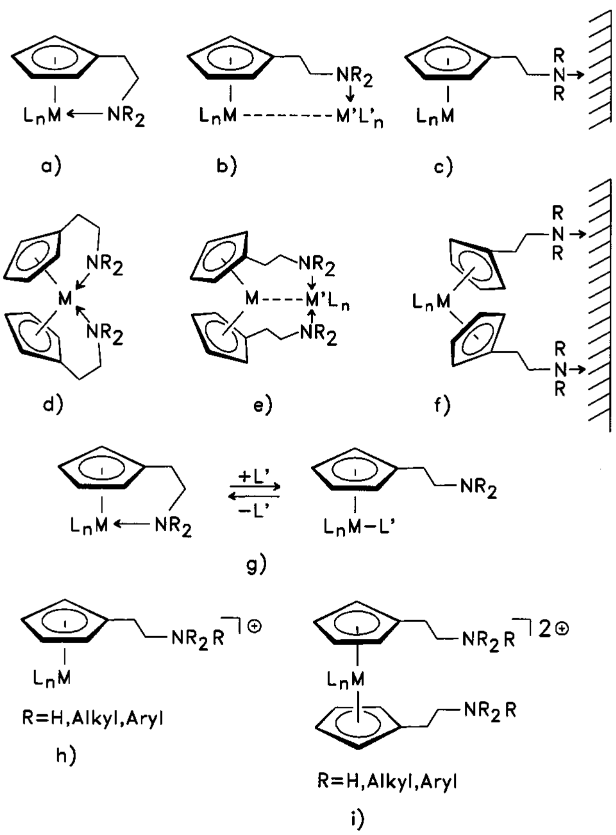


Apart from the general interest in novel ligand systems, we are investigating aminoethyl-functionalized Cp ligands for the following reasons (see Figure 2):

– The nitrogen atom of the aminoethyl group can coordinate to a metal center and block a vacant coordination site (see Figure 2a, d). Otherwise highly reactive intermediates or reaction products will be stabilized by this interaction, thus allowing unprecedented structures and chemical properties. Interesting bonding situations are expected as a function of the formal oxidation state of the respective metal. As documented by many examples, a cyclopentadienyl ligand stabilizes transition metals in high as well as in low oxidation states. On the other hand, the amino group favours coordination to metals in a high oxidation state (hard–hard interactions according to Pearson's concept). To metals in a low oxidation state, only weak interactions are anticipated, which might be strenghtened by the chelate effect; in this case, the aminoethyl-functionalized Cp ligand should behave as a hemilabile ligand. To metals in a high oxidation state, rather strong interactions are expected, which might allow the isolation of compounds even with cationic (aminoethyl)cyclopentadienyl units. In general, a ligated amino group will render the central atom much more electron-rich.

– The hemilabile bonding situation will allow an easy ligand exchange, as described in Figure 2g. The reversible coordination to a reactive metal center is of special interest in connection with catalytic processes; it seems possible to stabilize a highly reactive, electronically and sterically unsaturated intermediate by weakly occupying the vacant coordination site, until the actual substrate coordinates and replaces the amino group. Such processes might increase the lifetime and also the selectivity of the catalyst. A versatile catalyst design is conceivable by modifying the aminoethyl group.

Figure 2



– The amino function can coordinate to an adjacent electron-deficient metal (or nonmetal) center (Figure 2b, e). The resulting homo- or hetero-bimetallic complexes might be stabilized by different kinds of additional interaction; synergetic effects are expected.

– The amino group allows an interaction with Lewis or Broensted acidic surfaces (see Figure 2c, f); this effect is of special interest with regard to the heterogenisation of homogenous catalysts.

– Pendant amino or ammonium groups might have drastical consequences concerning the solubility of respective complexes. The development of an organometallic chemistry in water[10] can be promoted by the application of protonated or alkylated (arylated) aminoethyl-functionalized Cp compounds (see Figure 2h, i).

– Amino or ammonium groups in the side chain might exert electronic and steric effects and thus might induce changes in the chemistry compared to that of the parent compounds. Electronic and steric effects can be altered by variation of the substitution pattern at the cyclopentadienyl as well as at the amino fragment.

– The presence of N–H bonds in the side chain (Figure 1, compounds Cp^{VIII}, Cp^{IX}) allows further functionalization of the amino group by substitution reactions.

– The presence of protonated amino groups (Figure 2h, i; R′ = H) in principal permits proton-transfer reactions and thus opens new synthetic pathways.

This listing of effects unequivocally explains the current interest in aminoethyl-functionalized Cp complexes. In the following, we present a complete survey of d-block element complexes containing aminoethyl-functionalized cyclopentadienyl systems. Synthetic and structural aspects as well as important properties of these compounds are described with special emphasis to the effects of the tethered aminoethyl function.

Titanium and Zirconium Complexes

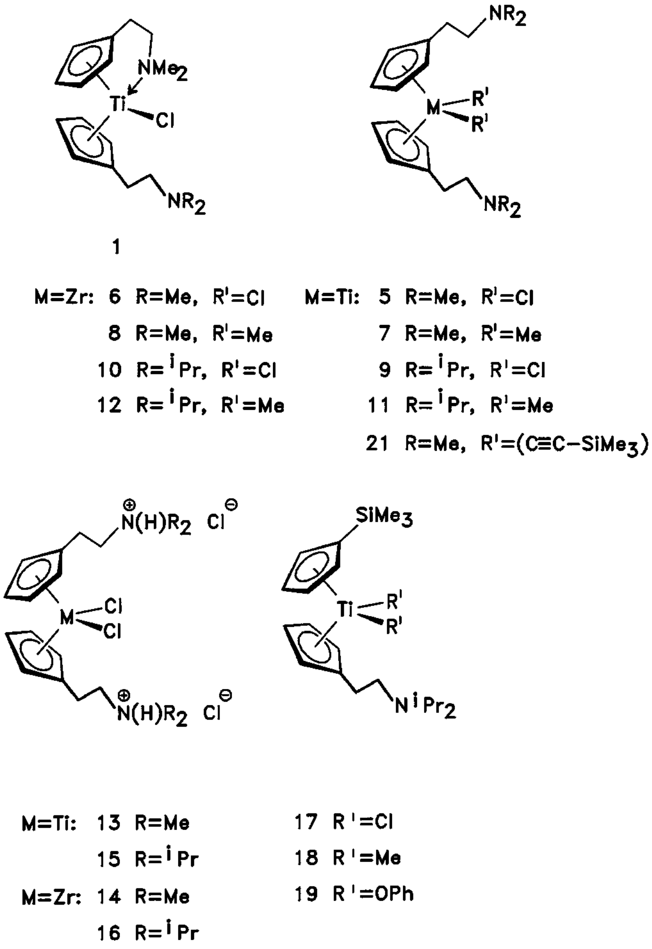
We started our efforts in this field synthesizing titanium compounds with the Cp^{I} and the Cp^{III} ligand. The titanium(III) complexes Cp$^{I}{}_2$TiCl (**1**) (Figure 3) and Cp$^{III}{}_2$TiCl (**2**) were prepared by the reaction of Cp^{I}Li and Cp^{III}Li, respectively, with $TiCl_3$.[9m] A single-crystal X-ray structure analysis of **1** revealed a pseudo-tetrahedral coordination sphere and thus the interaction of only one of the two amino groups with the titanium center.[9m] The structure of **2** containing the bulkier diisopropylaminoethyl-functionalized cyclopentadienyl ligand Cp^{III} is still unknown.[9w] The extreme air sensitivity of **2** compared to **1** indicates the non-coordinating nature of the amino function. The organo derivatives Cp$^{I}{}_2$TiR (**3**: R = Me; **4**: R = Bz) could be synthesized by simple substitution reactions.[9m] Only very recently, the titanium(III) compound $[(Me_2NCH_2CH_2)Me_4C_5][C_5H_5]TiCl$ with an intramolecular amino-group coordination was synthesized and structurally characterized.[8aa]

In metallocene dichlorides of the type Cp$^{I}{}_2$MCl$_2$ (**5**: M = Ti; **6**: M = Zr) (Figure 3), the intramolecular interaction of the amino group turns out to be rather weak. Intermolecular interaction finally dominates due to the formation of insoluble coordination polymers; the structures of these species are still unknown.[8z][9m] The corresponding dimethyl-substituted compounds Cp$^{I}{}_2$MMe$_2$ (**7**: M = Ti; **8**: M = Zr) are highly reactive and were therefore only characterized by ^{1}H-NMR spectroscopy.

The metallocene dichlorides Cp$^{III}{}_2$MCl$_2$ (**9**: M = Ti; **10**: M = Zr) (Figure 3) could be characterized completely.[9q] A single-crystal X-ray structure analysis of the titanium species **9** reveals a monomeric structure with no intramolecular coordination of the diisopropylamino functions to the metal center. The non-coordinating nature in **9** and **10** can be attributed to steric effects of the isopropyl substituents.

The dialkylaminoethyl functions in this type of metallocene complexes dramatically change the physical as well as the chemical properties. In contrast to the parent complexes Cp$_2$MCl$_2$, both types Cp$^{I}{}_2$MCl$_2$ and Cp$^{III}{}_2$MCl$_2$ are extremely air- and moisture-sensitive. This is due to the effect of the amino groups which facilitate the hydrolysis by enhancing the concentration of the attacking OH$^-$ nucleophiles and by trapping the arising hydrogen chloride.

Figure 3



1

M=Zr: **6** R=Me, R'=Cl
8 R=Me, R'=Me
10 R=^{i}Pr, R'=Cl
12 R=^{i}Pr, R'=Me

M=Ti: **5** R=Me, R'=Cl
7 R=Me, R'=Me
9 R=^{i}Pr, R'=Cl
11 R=^{i}Pr, R'=Me
21 R=Me, R'=(C≡C–SiMe$_3$)

M=Ti: **13** R=Me
15 R=^{i}Pr
M=Zr: **14** R=Me
16 R=^{i}Pr

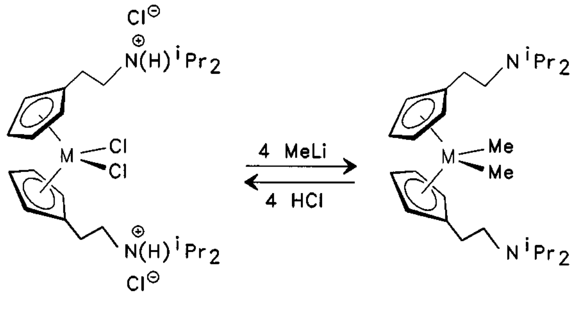
17 R'=Cl
18 R'=Me
19 R'=OPh

The methyl-substituted metallocenes Cp$^{III}{}_2$MMe$_2$ (**11**: M = Ti; **12**: M = Zr) (Figure 3) could be formed straightforwardly by the reaction of the corresponding metallocene dichlorides with methyllithium.[9q] The titanium derivative **11** exhibits a remarkable thermal stability. In contrast to the temperature- and light-sensitive complex Cp$_2$TiMe$_2$, for which an autocatalytic, "catastrophic" decomposition is reported[11], **11** is stable for several days under inert gas at room temperature. To explain this phenomenon, we propose a protecting effect of the N*i*Pr$_2$ group, which prohibits an α-elimination decomposition. Until now, an intramolecular coordination could not be proved unequivocally.

The metallocene dichlorides **5**, **6**, **9** and **10** could be converted quantitatively into the corresponding hydrochlorides Cp$^{I}{}_2$MCl$_2$ × 2 HCl (**13**, **14**) and Cp$^{III}{}_2$MCl$_2$ × 2 HCl (**15**, **16**) (Figure 3).[9q] In these compounds the protonated amino groups lead to drastic changes in the physical and chemical properties as compared to those of the non-protonated species. The hydrochlorides show an excellent solubility and stability in polar solvents such as chloroform or acetonitrile. Furthermore, solvolysis of the M–Cl bonds in protic solvents such as methanol or even water is prevented.

This is due to the effect of the ammonium groups which function as Broensted acids and reduce the concentration of the attacking OH^- nucleophiles, which are responsible for the hydrolytic process. Because of their exceptional stability, the hydrochlorides possess a long shelf life. Furthermore, they are useful starting materials for the synthesis of catalytically relevant species. For example, the metallocene dichloride dihydrochlorides **15** and **16** could be transformed with four equivalents of methyllithium into the dimethyl compounds **11** and **12** (Scheme 1).[9q] It is remarkable that a quantitative retransformation of the dimethyl compounds **11** and **12** back to the hydrochlorides **15** and **16** could be achieved by reaction with four equivalents of HCl in methanolic solution. No decomposition products were observed.

Scheme 1



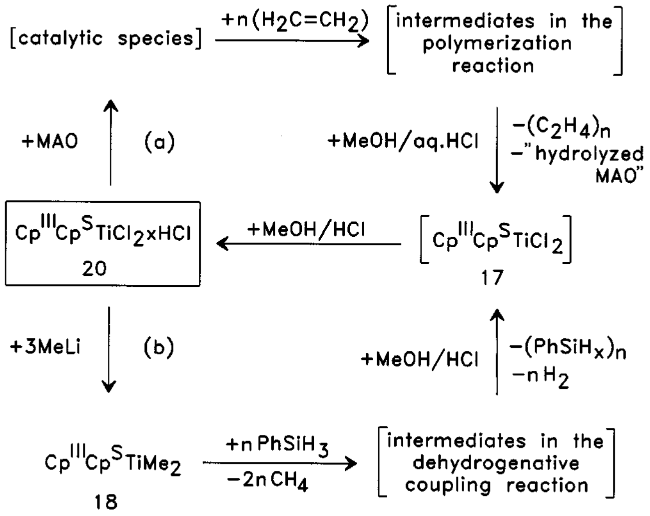
15,16 M=Ti,Zr 11,12

The mixed bent-sandwich complex $Cp^{III}Cp^{S}TiCl_2$ (**17**) ($Cp^{S} = CpSiMe_3$) containing only one (diisopropylaminoethyl)cyclopentadienyl ligand could be obtained by treating a solution of the halfsandwich complex $Cp^{S}TiCl_3$ with one equivalent of $Cp^{III}Li$ (Figure 3).[9r] The corresponding substituted derivatives $Cp^{III}Cp^{S}TiR_2$ [R = Me (**18**); PhO (**19**)] (Figure 3) as well as the hydrochloride $Cp^{III}Cp^{S}TiCl_2 \times HCl$ (**20**) can be synthesized in analogy to the symmetric titanocene complexes as described above.[9q] Only very recently, other titanocene derivatives with the Cp^{IV} ligand were synthesized and structurally characterized. They all show a non-coordinating amino group, but intermediate ligation was postulated to explain the observed reaction products.[8aa]

The metallocene dichlorides as well as the hydrochlorides containing the Cp^{III} ligand are catalyst precursors for the polymerization of ethylene; the productivities of the catalyst systems are comparable to those of the parent metallocene derivatives.[9q][9r] Furthermore, high catalytic activity in the dehydrocoupling of phenylsilane is observed for the methyl- and phenoxy-substituted derivatives.[9q][9r] The poly(phenylsilanes) obtained exhibit analytical data similar to those prepared with the parent catalyst system.

After the reaction, the catalytic species or its decomposition products generally remain in the polymer (leave-in catalysts) or are destroyed during the separation process and thus cannot be employed again. In our case, the influence of the diisopropylaminoethyl side chain provides sufficient stability to allow for efficient recycling of the precatalysts by a simple extraction procedure with methanol and aqueous HCl, as shown in Scheme 2 for complex **20**.[9v]

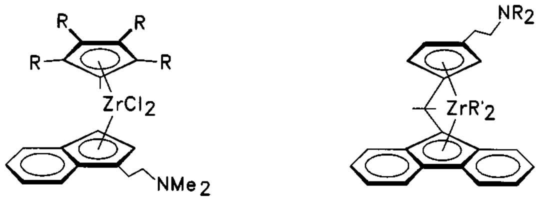
Scheme 2



Enders et al. described the reaction of the polymeric titanocene $Cp^{I}_2TiCl_2$ (**5**) with two equivalents of $LiC{\equiv}CSiMe_3$ to afford the temperature-sensitive, monomeric bis(alkynyl)titanocene derivative $Cp^{I}_2Ti(C{\equiv}CSiMe_3)_2$ (**21**) (Figure 3).[8z] The reaction of **21** with AgCl and $Cu(SC_6H_4CH_2NMe_2)_2$, respectively, yielded the heterobimetallic titanium-silver and titanium-copper complexes $[Cp^{I}_2Ti(C{\equiv}CSiMe_3)_2][AgCl]$ (**22**) and $[Cp^{I}_2Ti(C{\equiv}CSiMe_3)_2][Cu(SC_6H_4CH_2NMe_2)_2]$ (**23**); a coordination of the N functions to the metal centers could not be observed.[8z]

Further mixed aminoethyl-functionalized zirconocene complexes have been prepared by Tanaka et al.[8t] $Cp(IndCH_2CH_2NMe_2)ZrCl_2$ (**24**) and $Cp^*(IndCH_2CH_2NMe_2)ZrCl_2$ (**25**) (Ind = C_9H_6, Cp* = C_5Me_5) (Figure 4) could be obtained by the reaction of the appropriately substituted indenyllithium with Cp^*ZrCl_3 and $CpZrCl_3$.[8t] NMR spectroscopy did not reveal any indication of an amino-group coordination. These complexes, activated with 2 equiv. of *n*BuLi, catalyze the dehydrocoupling polymerization of phenylsilane to afford high-molecular-weight poly(phenylsilanes). ^{29}Si-NMR spectroscopy indicates that the microstructure of the resulting polymers is predominantly syndiotactic.[8t]

Figure 4



24 R=H
25 R=Me

26 R=Me,R'=Cl
27 R=ⁱPr,R'=Cl
28 R=Me,R'=Me
29 R=ⁱPr,R'=Me

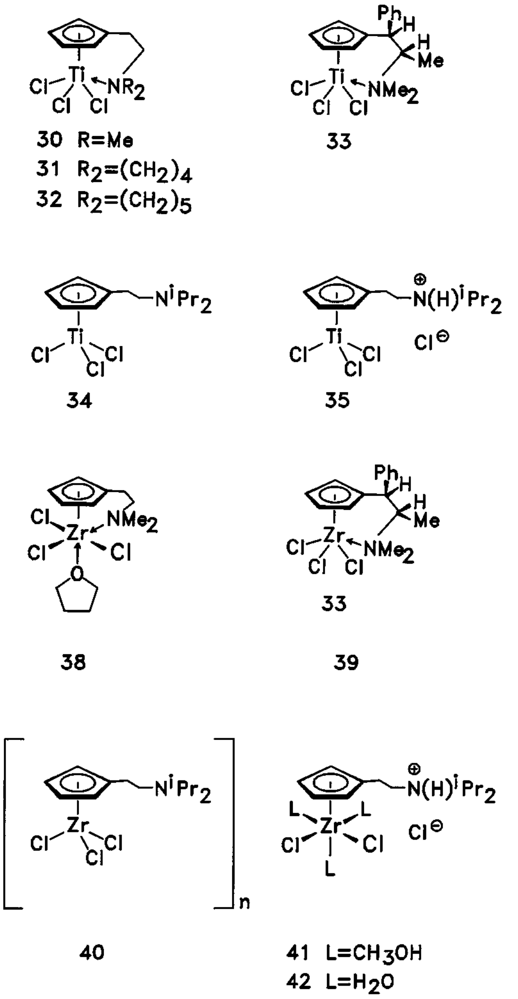
In the context of our studies of metallocene complexes with early transition metals we focussed our efforts also on the synthesis of ansa-zirconocenes. There is considerable interest in the preparation of ansa-zirconocenes as precursors for olefin polymerization catalysts;[12] the bridging unit as well as the substituents of both Cp rings greatly influence the activity and the stereoselectivity of the polymerization reaction.

Very recently, we synthesized the compounds $[(C_{13}H_8)CMe_2(C_5H_3CH_2CH_2NMe_2)]ZrCl_2$ (**26**) and $[(C_{13}H_8)CMe_2(C_5H_3CH_2CH_2N\mathit{i}Pr_2)]ZrCl_2$ (**27**), which are the first examples of dialkylaminoethyl-functionalized ansa-zirconocenes (Figure 4).[9x] Single-crystal X-ray analyses reveal the monomeric structure of these complexes. The amino groups are not coordinating to the zirconium center. The dialkyaminoethyl-functionalized side chains in β-position to the C_1 bridge might be essential for affecting the stereoselectivity in the polymerization of propylene. The dimethyl derivatives **28** and **29** (Figure 4) were obtained in high yields by the reaction of **26** and **27**, respectively, with two equivalents of methyllithium.[9x] Complexes **28** and **29** are highly moisture-sensitive, orange-yellow oils with a good solubility in nonpolar aprotic solvents such as toluene. Examinations of these complexes with respect to their potential use in catalytic reactions are in progress.

Although group-4 metallocenes dominate the homogeneous Ziegler-Natta polymerizations of ethylene and propylene, also halfsandwich complexes are employed as precursors in many catalytic reactions. In this context, several titanium and zirconium halfsandwich complexes containing dialkylaminoethyl functionalized cyclopentadienyl ligands were synthesized.

The compound $Cp^{I}TiCl_3$ (**30**) is the first titanium halfsandwich complex with an intramolecularly coordinating amino function, as reported by Rausch and co-workers (Figure 5).[7n] The amino group affects significantly the catalytic reactivity of **30** as compared to that of the parent complex $CpTiCl_3$. The system **30**/MAO (MAO: methylaluminoxane) shows a considerably lower activity towards styrene and an impressively increased activity towards ethylene and propylene. This is most likely due to the coordination behaviour of the amino group which influence the coordination of the incoming monomer.[7n] Cyclopentadienyl complexes of titanium with tethered pyrrolidinyl and piperidinyl functions were introduced by Herrmann and co-workers.[8c] The titanium halfsandwich complexes $Cp^{V}TiCl_3$ (**31**) and $Cp^{VI}TiCl_3$ (**32**) were prepared by the reaction of the silylated cyclopentadiene precursor with $TiCl_4$. X-ray crystal-structure results confirm the intramolecular nitrogen coordination to the titanium(IV) center (Figure 5). Van der Zeijden designed the chiral dimethylaminoethyl-functionalized cyclopentadienyl titanium halfsandwich complex $Cp^{VI}TiCl_3$ (**33**) by the reaction of the trimethylsilyl derivative $Cp^{VII}SiMe_3$ with $TiCl_4$ (Figure 5).[8l] In the titanium compound **33** the nitrogen side chain is only weakly coordinated, NMR spectroscopy indicates a fluxional coordination of the amino side arm. This is in contrast to $Cp^{I}TiCl_3$ (**30**), where a rigid intramolecular coordination is observed.

Figure 5



In the halfsandwich complex $Cp^{III}TiCl_3$ (**34**), synthesized by our group,[9u] the amino group is obviously not strongly coordinating intramolecularly to the titanium center (Figure 5); however, a weak intermolecular coordination was observed. The different coordination behaviour of **34** as compared to **30**−**33** can be attributed to steric effects of the bulkier isopropyl substituents at the amino function. Complex **34** reacted with one equivalent of HCl under protonation of the amino group to give the monomeric hydrochloride $Cp^{III}TiCl_3 \times HCl$ (**35**), which shows excellent solubility in polar solvents (Figure 5).[9u] Similar O-brigded dimers $[Cp^{I}TiCl]_2O \times 2HCl$ (**36**)[7n] and $[Cp^{VII}TiCl]_2O \times 2HCl$ (**37**)[8l] were obtained by the reaction of the halfsandwich complexes **30** and **33,** respectively, with traces of water.

In the trichlorozirconium complex $Cp^{I}ZrCl_3 \times THF$ (**38**) an intramolecular coordination of the amino group takes place. (Figure 5). The monomeric structure of the THF adduct was proved by a single-crystal X-ray structure investigation.[9m] Van der Zeijden also synthesized the chiral zirconium species $Cp^{VII}ZrCl_3$ (**39**) (Figure 5).[8l] In contrast to the corresponding titanium species $Cp^{VII}TiCl_3$ (**33**), the amino group is firmly coordinated to the metal center. Moreover, **39** still behaves as a moderate Lewis acid and catalyzes the Diels-Alder reaction of methacroleine with cyclopentadiene, but without measurable enantiomeric excess.[8l]

The zirconium compound $[Cp^{III}ZrCl_3]_x$ (**40**) (Figure 5) containing the bulkier diisopropylaminoethyl group forms a coordination polymer, comparable to the situation found for the analogous titanium species **34**.[9u] Compound **40** reacted with one equivalent of HCl under protonation of the amino group to give the monomeric air- and moisture-stable hydrochloride **41**, which crystallized with two additional methanol molecules in the coordination sphere of the zirconium atom (Figure 5).[9u] The reaction of **41** with water, which involves exchange of the donor ligands, led to the formation of the air- and water-stable hydrochloride **42** (Figure 5).[9u]

The extremely high air and moisture sensitivity of all described neutral halfsandwich complexes is worth mentioning. In contrast, the halfsandwich complexes with a protonated amino function are stable against air and moisture and soluble in protic solvents such as methanol. These properties of the protonated sandwich and halfsandwich compounds may be of special interest with regard to organometallic chemistry in water.

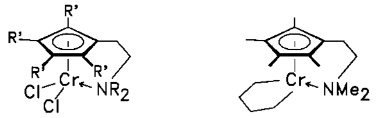
Vanadium, Chromium and Molybdenum Complexes

Only recently Enders and co-workers[8z] described the synthesis of the first dimethylaminoethyl-functionalized vanadocene and chromocene derivatives. The reaction of two equivalents of the metallated Cp^I ligand with in-situ prepared VCl_2 and $CrCl_2$, repectively, afforded the paramagnetic vanadocene and chromocene compounds $Cp^I{}_2M$ [M = V (**43**); M = Cr (**44**)]. The paramagnetic behaviour (spin-only value) is comparable to that of the parent complexes Cp_2Cr and Cp_2V. NMR data did not reveal any coordination of the N functions.

The first dimethylaminoethyl-functionalized bis(cyclopentadienyl)molybdenum complex was already synthesized by Green et al. in 1983.[7a] The functionalized molybdenum complex $[Mo(C_5H_4CH_2CH_2I)_2I_2]$ (**45**) (Scheme 3) reacted with dimethylamine and subsequently with ammonium hexafluorophosphate to give the ionic compound $[Mo(Cp^I)(C_5H_4CH_2CH_2NMe_2H)H]^{2+}[PF_6]^-{}_2$ (**46**) with the dimethylamino group intramolecularly coordinating to the molybdenum center. The structure of **46** as proposed on the basis of ^{1}H-NMR data is shown in Scheme 3.

Only very recently, the synthesis of halfsandwich complexes of chromium (type **46a−d**, Figure 5a) with an intramoleculary coordinating amino group was reported. These compounds were obtained as deep blue species by the reaction of $Cr(THF)_3Cl_3$ with the corresponding cyclopentadienyl alkali metal salts. In the mixture with MAO (MAO: methylaluminoxane), highly effective catalysts for olefin polymerisation are formed. Surprisingly, full catalytic activity is already reached in a molar Al/Cr ratio of 45−300:1.[*]

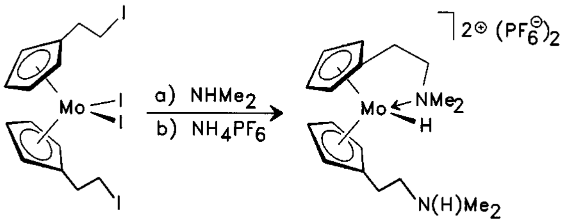
Figure 5a



46a : R'=H,R2=Me2
46b : R'=Me,R2=Me2
46c : R'=Me,R2=(CH2)4
46d

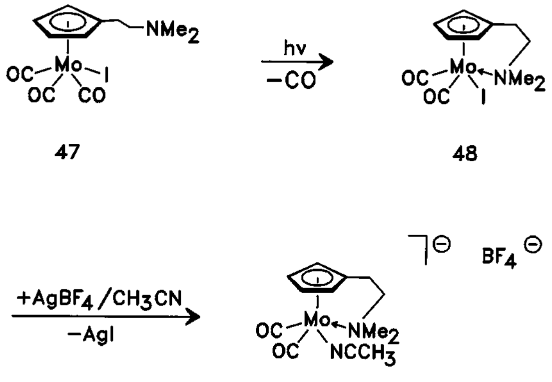
Wang and co-workers[7f] synthesized various molybdenum halfsandwich complexes in which the pendant dimethylaminoethyl group is coordinating intramolecularly to the metal center. Reaction of $Mo(CO)_6$ with Cp^ILi and subsequently with iodine led to the tricarbonyl complex $Cp^IMo(CO)_3I$ (**47**), which was transformed into the dicarbonyl compound $Cp^IMo(CO)_2I$ (**48**) (Scheme 4) by irradiation. Treatment of **48** with silver tetrafluoroborate led to the ionic molybdenum complex **49** (Scheme 4).[7f] An intramolecular coordination of the amino group takes place in **48** as well as in **49**.[7f]

Scheme 3



45
46

Scheme 4



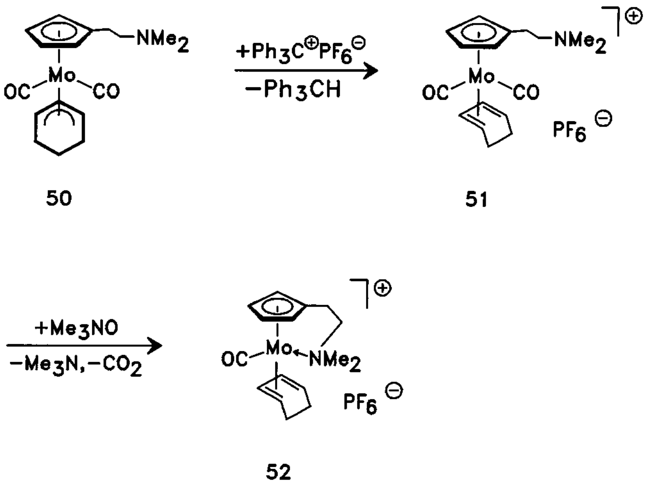
47
48
49

The dimethylaminoethyl-functionalized cyclopentadienylmolybdenum complex $(C_6H_9)Cp^IMo(CO)_2$ (**50**) (Scheme 5) was prepared by adding Cp^ILi to $(C_6H_8)Mo(CO)_2(CH_3CN)_2Br$.[7g] Reaction of **50** with trityl hexafluorophosphate provided the ionic compound $[(C_6H_8)Cp^IMo(CO)_2]^+[PF_6]^-$ (**51**) by hydride abstraction (Scheme 5). Treatment of **51** with trimethylamine *N*-oxide

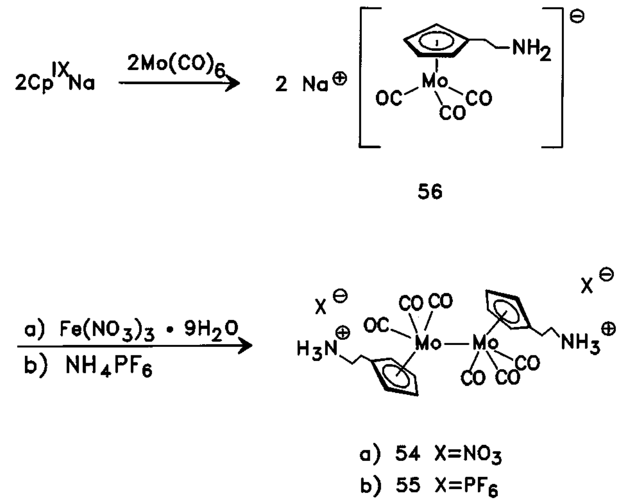
---

[*] Note added in proof: P. Jolly, K. Ionas, G. P. I. Verkovnic, German Patent 19630580 A1, **1998**.

Scheme 5



Scheme 6



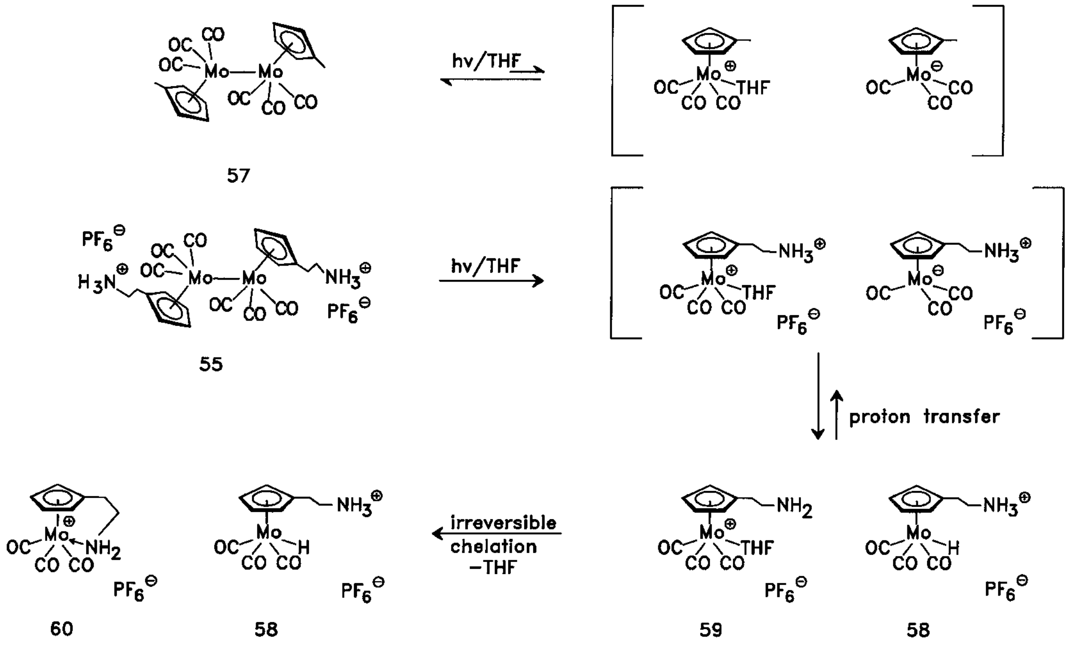
removed carbon monoxide to give $[(C_6H_8)(C_5H_4CH_2CH_2NMe_2)Mo(CO)]^+[PF_6]^-$ (**52**). (Scheme 5). A single-crystal X-ray structure analysis of **52** confirmes the intramolecularly coordinating dimethylamino group and the *exo* conformation of the cyclohexadiene ligand.[7g] Cationic dienylmolybdenum complexes are pertinent substrates for organic syntheses. Complexes of type **52** are particularly interesting because the electrophilicity is weakened as a result of amine coordination. Furthermore, the metal center is now chiral.

The dinuclear molydenum complex $[Cp^{IV}Mo(CO)_2]_2$ (**53**) was synthesized by our group.[9k] The structure analysis revealed that the side chains do not coordinate to the central metal atoms and lie on opposite sides of the Mo−Mo axis.[9k]

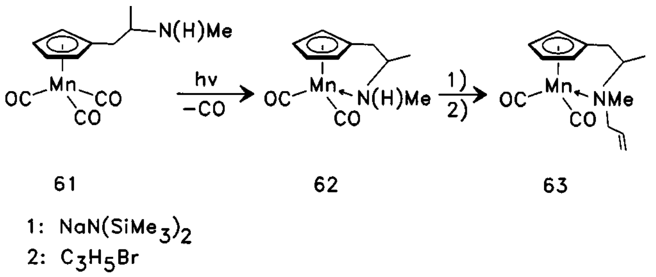
Avey and Tyler described the synthesis of the ammonioethyl-functionalized dimeric molybdenum complexes $Cp^{IX}{}_2Mo_2(CO)_6 \times 2$ HX (**54**: X = NO_3; **55**: X = PF_6) by reaction of $Cp^{IX}Na$ with $Mo(CO)_6$ and by subsequent oxidation of the anion $[Cp^{IX}Mo(CO)_3]^-$ (**56**) with $Fe(NO_3)_3 \cdot 9\ H_2O$ in water. The exchange of the anion in **54** with NH_4PF_6 afforded **55** (Scheme 6).[7h] It is noteworthy that in contrast to **55,** which is soluble in common organic solvents like THF, complex **54** is soluble and stable in aqueous solution.

Interestingly, the photochemistry of **55** differs from that of the parent complex $Cp^x{}_2Mo_2(CO)_6$ (**57**) ($Cp^x = C_5H_4Me$). Mechanistic work established that the different reactivities can be ascribed to a supramolecular effect of the tentacle ligand.[7l] Irradition of either dimer complex led to photolytic cleavage of the metal−metal bond. The photogenerated 17-electron radical complexes then reacted with THF (the solvent) to form 19-electron adducts; disproportionation then followed. The initial products were $[Cp^xMo(CO)_3(THF)]^+$, $[Cp^xMo(CO)_3]^-$ and

Scheme 7



Scheme 8



$[Cp^{IX}Mo(CO)_3(THF)]^+$, $[Cp^{IX}Mo(CO)_3]^-$, respectively (Scheme 7). In the case of the dimer **57**, a facile back reaction of these products ensued, and the net result was no reaction, even in the presence of an excess of $[C_6H_5CH_2CH_2NH_3]^+[PF_6]^-$.[7l] In the case of the tentacle dimer $Cp^{IX}{}_2Mo(CO)_6 \times 2\ HPF_6$ (**55**), proton transfer from the ammonium group to the anion yielded $Cp^{IX}Mo(CO)_3H \times HPF_6$ (**58**) and $[Cp^{IX}Mo(CO)_3THF]^+[PF_6]^-$ (**59**), and then facile coordination of the free amine by displacing the THF ligand effectively blocked the back reaction by forming $[Cp^{IX}Mo(CO)_3]^+[PF_6]^-$ (**60**) irreversibly.

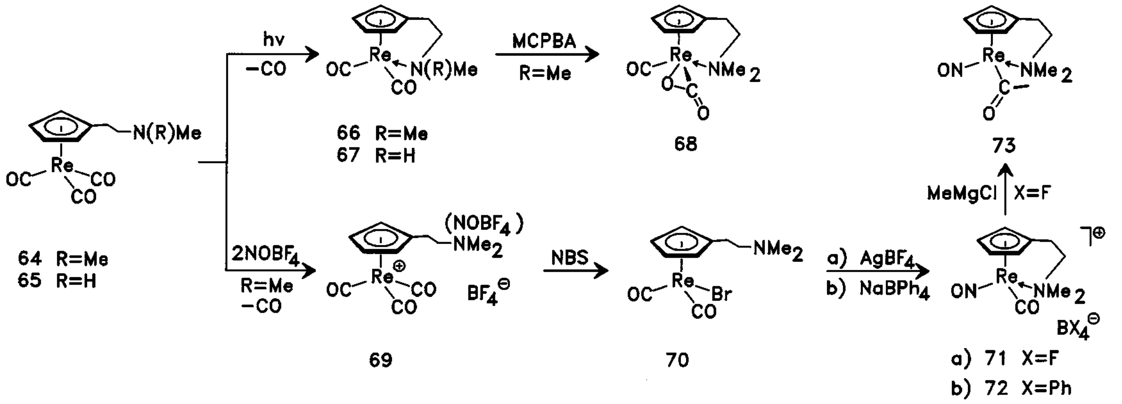
The described cooperative interaction between the tentacle ligands and the unstable initial products of disproportionation to yield stable products is regarded as an example of supramolecular reactivity.[7l]

Manganese and Rhenium Complexes

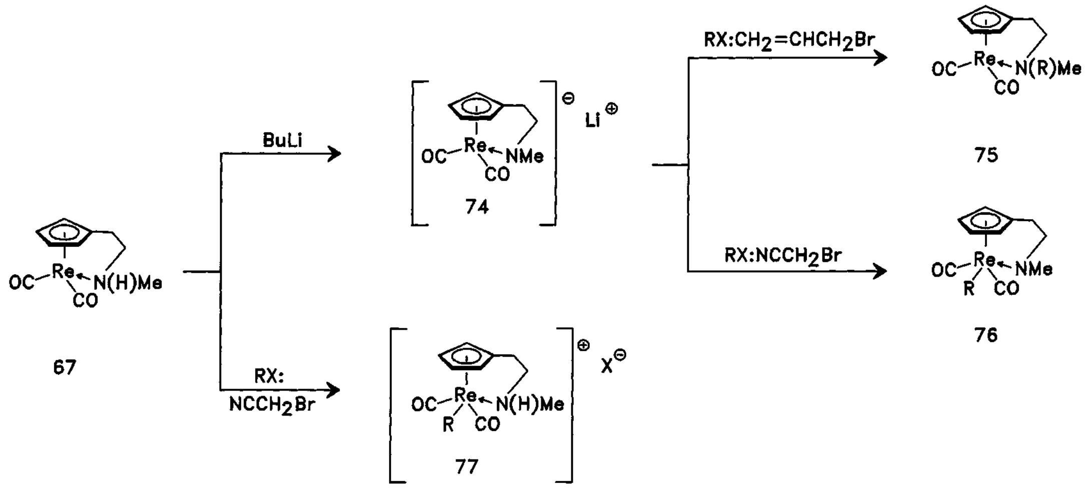
Wang et al.[7e] synthesized the manganese complex $Cp^{VIII}Mn(CO)_3$ (**61**) by treating $Mn(CO)_5Br$ with $Cp^{VIII}Li$ (Scheme 8). Irradiation of **61** removed carbon monoxide and gave rise to an intramolecular amine-group ligation to provide complex **62** (Scheme 8).[7e] Deprotonation of **62** with $NaN(SiMe_3)_2$ and subsequent addition of allyl bromide led to the alkylation product **63** (Scheme 8). The X-ray analysis clearly shows that allylation occurred at the nitrogen atom and not at the manganese center.[7e] The sequence **62** → **63** is an example of further amino-group functionalization in complexes with aminoethyl-substituted Cp ligands still containing N−H functions.

The first rhenium complexes containing an *N*-functionalized cyclopentadienyl ligand and further interesting reaction sequences were reported by Wang et al.[8d] The lithium salts $Cp^{I}Li$ and $Cp^{VIII}Li$ were shown to react with $Re(CO)_5Br$ to provide the halfsandwich complexes $Cp^{I}Re(CO)_3$ (**64**) and $Cp^{VIII}Re(CO)_3$ (**65**) (Scheme 9). Irradiation of **64** and **65** afforded the complexes $Cp^{I}Re(CO)_2$ (**66**) and $Cp^{VIII}Re(CO)_2$ (**67**), respectively, in which the

Scheme 9



Scheme 10



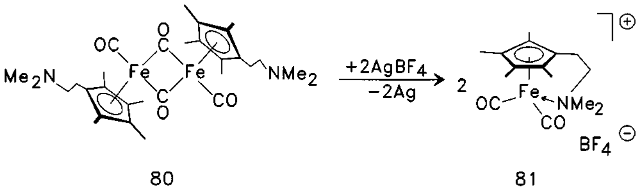
amino group is bound intramolecularly to the rhenium center (Scheme 9).[8d][8u] Oxidation of **66** with 3-chloroperoxybenzoic acid (MCPBA) provided the complex Cp$^{\mathrm{I}}$Re(CO)(CO$_2$) (**68**) (Scheme 9), the first example of a mononuclear CO$_2$ complex in rhenium chemistry. The structure of **68** is confirmed by X-ray crystallography.[8u] Reaction of **65** with two equivalents of NOBF$_4$ gave the nitrosylrhenium complex [Cp$^{\mathrm{I}}$Re(NO)(CO)$_2$]$^+$[BF$_4$]$^-$ × NOBF$_4$ (**69**),[8k] which was treated with NBS to afford the bromo complex Cp$^{\mathrm{I}}$ReBr(NO)(CO) (**70**) (Scheme 9). Removal of the bromide ion with AgBF$_4$ resulted in amino-group coordination to give the ionic complex [Cp$^{\mathrm{I}}$Re(CO)(NO)]$^+$[BF$_4$]$^-$ (**71**) (Scheme 9). The X-ray diffraction study of the corresponding tetraphenylborate [Cp$^{\mathrm{I}}$Re(CO)(NO)]$^+$[BPh$_4$]$^-$ (**72**) confirms the amino-group coordination.[8k] Reaction of the rhenium complex **71** with alkylating reagents occurred at the carbonyl carbon atom to provide acyl complexes. For instance, the reaction with methylmagnesium chloride led to the acyl derivative Cp$^{\mathrm{I}}$Re(NO)(COMe) (**73**) in which the amino group is still coordinating (Scheme 9).[8k] It is worth mentioning that the corresponding triphenylphoshane complex did not react with alkylmetal reagents to provide acyl complexes. Obviously, the influence of the amino function is necessary for this synthetic pathway.

Deprotonation of the N−H function in **67** with *n*BuLi led to the ionic compound **74** (Scheme 10), which reacted with electrophiles such as CH$_2$=CHCH$_2$Br at the nitrogen center to provide the complex [C$_5$H$_4$CH$_2$CH$_2$N(Me)(CH$_2$=CHCH$_2$)]Re(CO)$_2$ (**75**) with to different substituents at the nitrogen atom (Scheme 10).[8u] This is another example of a further functionalization of an aminoethyl-substituted Cp ligand. However, **74** reacted with electrophiles such as BrCH$_2$CN to give the alkylrhenium compound Cp$^{\mathrm{I}}$Re(CO)$_2$CH$_2$CN (**76**) (Scheme 10). Thus, the regioselectivity is dependent on the nature of the electrophile and can be explained on the basis of the hard-soft acid-base principle.[8u] Reaction of the neutral complex **66** with BrCH$_2$CN gave exclusively the alkylrhenium compound [Cp$^{\mathrm{I}}$Re(CO)$_2$CH$_2$CN]$^+$[Br]$^-$ (**77**).[8u] It is remarkable that the parent rhenium complex CpRe(CO)$_3$ does not react with BrCH$_2$CN. Thus, the electron donation of the amino ligand is important to promote the reactivity towards carbon electrophiles.

Iron Complexes

Treatment of FeCl$_2$ in THF with two equivalents of the lithiated ligand Cp$^{\mathrm{IV}}$Li yielded the dimethylaminoethyl-functionalized ferrocene Cp$^{\mathrm{IV}}_2$Fe (**78**).[9a] The analogous ferrocene Cp$^{\mathrm{I}}_2$Fe (**79**) could be synthesized in a similar manner.[7s] Not unexpectedly, no amino-group coordination is observed; the 18-electron rule is obeyed in both complexes by η^5-Cp bonding. Reaction of Cp$^{\mathrm{IV}}$H with Fe(CO)$_5$ led to the formation of the dimeric dicarbonyl(cyclopentadienyl)iron complex [Cp$^{\mathrm{IV}}$Fe(CO)$_2$]$_2$ (**80**). In this compound, no intramolecular displacement of a CO ligand by the amino groups could be initiated.[9c] However, the cationic cyclopentadienyl iron halfsandwich complex [Cp$^{\mathrm{IV}}$Fe(CO)$_2$]$^+$[BF$_4$]$^-$ (**81**), which was obtained by the reaction of **80** with AgBF$_4$, is stabilized by an intramolecular coordination of the amino group (Scheme 11).[9c]

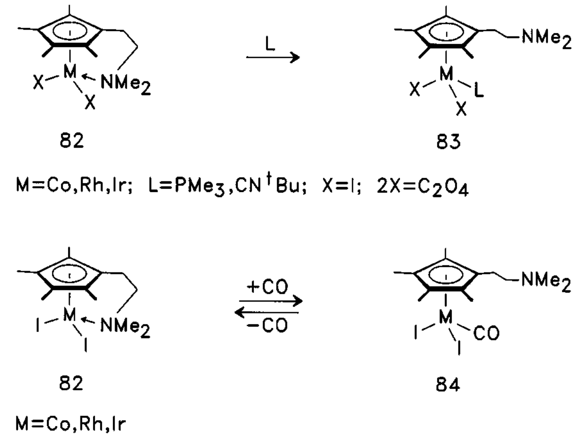
Scheme 11



Cobalt, Rhodium and Iridium Complexes

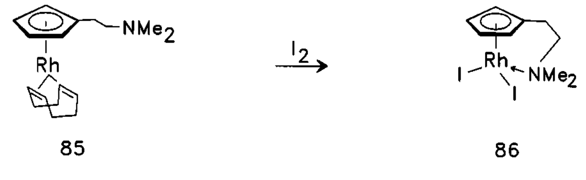
Several halfsandwich complexes with the Cp$^{\mathrm{IV}}$ ligand and with the central atoms cobalt, rhodium and iridium were obtained by classical synthetic routes.[9b][9h] In compounds of the type Cp$^{\mathrm{IV}}$ML$_2$ (M = Co, Rh, Ir; L = CO, C$_2$H$_4$) with the metals in the oxidation state +1, amino-group coordination is generally not observed. In compounds with the metals in the oxidation state +3, coordination depends on the further ligands present. The interplay between the donor ligands and the metal center can be tuned to a certain extent. An irreversible displacement was observed in the reaction of complexes of the type Cp$^{\mathrm{IV}}$MX$_2$ (**82**) (M = Co, Rh, Ir; X = I; X$_2$ = C$_2$O$_4$) with stoichiometric amounts of trimethylphosphane or *tert*-butyl isonitrile to afford Cp$^{\mathrm{IV}}$M(L)X$_2$ (**83**). With carbon monoxide, the displacement reaction leading to Cp$^{\mathrm{IV}}$M(CO)I$_2$ (**84**) is reversible (Scheme 12).[9b][9h]

Scheme 12



Poilblanc et al. described the synthesis of the rhodium(I) complex Cp$^{\mathrm{I}}$Rh(cod) (**85**) (Scheme 13) by reaction of Cp$^{\mathrm{I}}$Na with [Rh(cod)Cl]$_2$.[8w] Oxidation with iodine resulted in the formation of the rhodium(III) complex Cp$^{\mathrm{I}}$RhI$_2$ (**86**) (Scheme 13) with a coordinating amino group.

Scheme 13

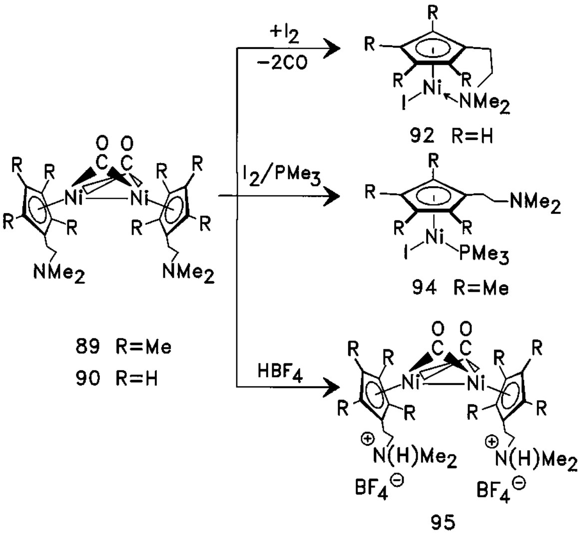


The reaction of **85** with HCl afforded the corresponding water-soluble hydrochloride $Cp^{I}Rh(cod) \times HCl$ (**87**). It is noteworthy that a reversible transformation to **85** could be achieved by treating **87** with a slight excess of *n*-butyllithium. The water-soluble rhodicinium complex $Cp^{I}_2RhCl \times 2\ HCl$ (**88**) was obtained by the reaction of the cyclopentadiene $Cp^{I}H$ with $Na_3RhCl_6 \times 12\ H_2O$.[8w]. Generally, the synthesis of this kind of compounds requires previous deprotonation of the cyclopentadiene by an auxiliary base. In case of the preparation of **88**, the role of the auxiliary basic reagent is probably adopted by the free amino group attached to the cyclopentadiene. The solubility of **87** and **88** in water is interesting in the context of a screening for antitumor activity.[8w]

Nickel, Palladium and Platinum Complexes

We were successful in the preparation of the dimeric carbonylnickel(I) complex $[Cp^{IV}Ni(CO)]_2$ (**89**) (Scheme 14) by the reaction of $Ni(CO)_4$ with $Cp^{IV}Li$ and subsequent oxidation with CuCl.[9n] The analogous complex $[Cp^{I}Ni(CO)]_2$ (**90**) (Scheme 14) containing the Cp^{I} ligand could be synthesized by Fischer and co-workers by a synproportionation of the nickelocene Cp^{I}_2Ni (**91**) with $Ni(CO)_4$.[8n][8o][8p] As expected, in both complexes no coordination of the pendant dimethylamino groups is observed.

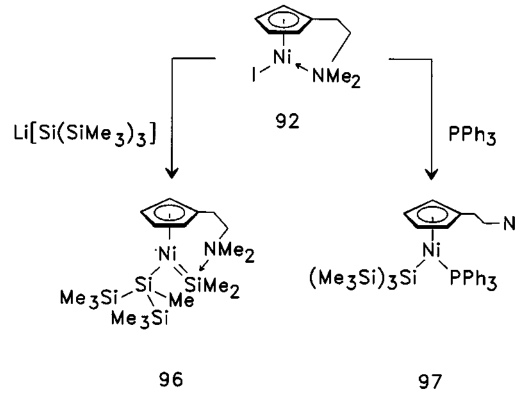
Scheme 14



Cleavage of **90** with iodine gave the monomeric nickel complex $Cp^{I}NiI$ (**92**) with a coordinating amino group (Scheme 14).[8n][8o][8p] The CO-free complex **92** might be an interesting starting material for MOCVD studies. Attemps to prepare the correseponding permethylated complex $Cp^{IV}NiI$ (**93**) failed.[9g] Cleavage of **89** with iodine in the presence of PMe_3 afforded the monomeric nickel(II) halfsandwich complex $Cp^{IV}Ni(PMe_3)I$ (**94**) (Scheme 14).[9n] Complex **89** reacted with two equivalents HBF_4 under protonation of the amino groups to give the ionic, air stable compound $[Cp^{IV}Ni(CO)]_2 \times 2HBF_4$ (**95**) (Scheme 14), which shows excellent solubility and stability in polar solvents such as nitromethane and acetonitrile.[9n]

The reaction of **92** with $[(thf)_3Li\{Si[Si(CH_3)_3]_3\}]$ finally afforded the nickel halfsandwich complex **96** (Scheme 15). This is the first example in which the amino function coordinates to an element (silicon) directly attached to the central metal. The structure of **96** is proven by a single-crystal X-ray structure analysis. When **92** was treated with $[(thf)_3Li\{Si[Si(CH_3)_3]_3\}]$ in the presence of PPh_3, the "normal" substitution product $Cp^{IV}Ni(PPh_3)I$ (**97**) was obtained (Scheme 15).[8n][8o][8p]

Scheme 15

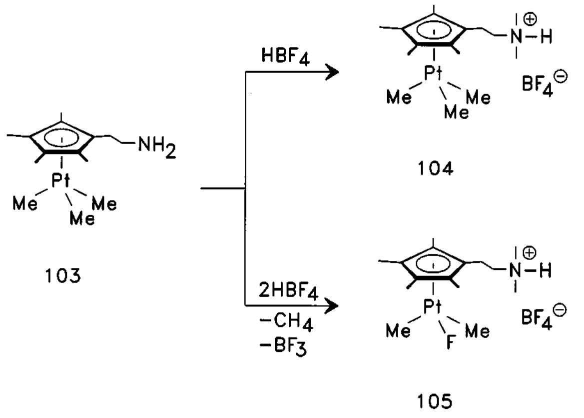


The reaction of **92** with PPh_3 and with low-valent indium bromide in the presence of NaI afforded the complex μ-$Cp^{I}Ni(PPh_3)InI_2$ (**98**) (Figure 16) with intramolecular coordination of the dimethylamino group.[8n][8o][8p] Another complex in which the amino group is coordinating to the adjacent electron-deficient metal center is the heterobimetallic compound μ-$Cp^{I}Ni(CO)GaCl_2$ (**99**) (Figure 6) which was obtained by the reaction of $[Cp^{I}Ni(CO)]_2$ (**90**) with Ga_2Cl_4.[8n][8o][8p] Both complexes **98** and **99** might be interesting as MOCVD precursors for nickel-indium and nickel-gallium alloy thin films.

Figure 6

In the chemistry of palladium only dimethylaminoethyl-functionalized cyclopentadienyl complexes with the permethylated Cp^{IV} ligand are known. Reaction of $[Pd(CO)Cl]_n$ with $[Cp^{IV}MgCl]_2$ gave the thermally labile dimeric palladium complex $(Cp^{IV}PdCO)_2$ (**100**) in a mixture with $Cp^{IV}H$.[9n] The synthesis of the palladium halfsandwich complex $Cp^{IV}PdC_3H_5$ (**101**) demonstrated that even in complexes with the palladium metal in the +2 oxidation state, the amino group could not compete with a π-allyl ligand.[9n] The preparation of the dimeric platinum(I) complex $[Cp^{IV}Pt(CO)]_2$ (**102**) failed.[9g] However, the halfsandwich complex $Cp^{IV}PtMe_3$ (**103**) with a Pt^{IV} metal center was obtained in the reaction of $[IPtMe_3]_4$ with $Cp^{III}Li$ (Scheme 16).[9n] In this complex the 18-electron rule is obeyed, and thus no coordination of the amino group is expected. The reaction of **103** with one equivalent of HBF_4 did not result in an elimination of methane and subsequent amino coordination, but led to the formation of $Cp^{IV}PtMe_3 \times HBF_4$ (**104**) with a protonated amino group, which shows an excellent solubility in polar solvents (Scheme 16).[9n] With two equivalents of HBF_4, however, elimination of methane did occur, and **103** was transformed into the fluoro-substituted compound $Cp^{IV}Pt(F)Me_2 \times HBF_4$ (**105**) (Scheme 16).[9n]

Scheme 16



Conclusion

Similarly to the parent cyclopentadienyl ligand, aminoethyl-functionalized systems can be used as complexing agents for almost any transition metal. There are several good reasons to tether an amino group, as already pointed out in more detail in the introduction; many of the potential effects discussed have already been realized in very recent investigations. The possibility to modify at the cyclopentadienyl core as well as at the amino side group offers an enormous synthetic flexibility. In complexes containing (aminoethyl)cyclopentadienyl ligands, the following effects are of special interest:

– A hemilabile bonding situation is typical of compounds of low-valent transition metals. Amino-group coordination stabilizes otherwise highly reactive intermediates by a weak interaction (soft metal–hard ligand). The reversibility of this process should allow to control the reactivity and also the catalytic properties of the relevant metal complex in more detail.

– The amino group can bind to another metal (non-metal) center and thus create or stabilize novel types of bimetallic complexes.

– Compounds with a tethered ammonium group often show an exceptional stability against air and moisture and a high solubility in protic solvents; this phenomenon is important with regard to organometallic chemistry in water.

These features, together with the others described in this article, augur well for the development of a rich and interesting future chemistry of aminoethyl-functionalized cyclopentadienyl complexes of the transition metals.

The experimental work reported from our group was accomplished by *Jürgen Dahlhaus*, *Jürgen Kleimeier*, *Marc Oliver Kristen*, *Christian Müller*, and *Thomas Redeker*; X-ray crystal-structure analyses were performed by *Beate Neumann* and *Hans-Georg Stammler*. The dedication and expertise of these co-workers is very gratefully acknowledged. We thank *Marion Welschof* for preparing the drawings. Funding was kindly provided by the *Deutsche Forschungsgemeinschaft*, by the *Fonds der Chemischen Industrie*, and by the University of Bielefeld. We are grateful to the *BASF AG*, to the *Degussa AG*, and to the *Wittko AG* for gifts of chemicals.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

[1] P. Jutzi, *J. Organomet. Chem.* **1990**, *400*, 1–17.

[2] For recent reviews see: [2a] P. Jutzi, *Adv. Organomet. Chem.* **1986**, *26*, 217–295. – [2b] C. Janiak, H. Schumann, *Adv. Organomet. Chem.* **1991**, *33*, 291–393. – [2c] J. Okuda, *Top. Curr. Chem.* **1991**, *160*, 97–145. – [2d] N. J. Coville, K. E. du Plooy, W. Pickl, *Coord. Chem Rev.* **1992**, *116*, 1–271. – [2e] J. Okuda, *Nachr. Chem. Tech. Lab.* **1993**, *41*, 8–14.

[3] Publications concerning alkenyl- and alkinyl-functionalized cyclopentadienyl ligands: [3a] J. F. Buzinkai, R. Schrock, *Organometallics* **1987**, *6*, 1447–1452. – [3b] J. Okuda, K. H. Zimmermann, *J. Organomet. Chem.* **1988**, *344,* C1-C4. – [3c] F. X. Kohl, R. Dickbreder, P. Jutzi, G. Müller, B. Huber, *Chem. Ber.* **1989**, *122*, 871–878. – [3d] J. A. Miguel-Garcia, P. M. Maitlis, *J. Chem. Soc., Chem. Commun.* **1990**, 1472–1473. – [3e] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1990**, *123*, 1641–1648. – [3f] M. Ogasa, D. T. Mallin, D. W. Macomber, M. D. Rausch, R. D. Rogers, A. N. Rollins, *J. Organomet. Chem.* **1991**, *405*, 41–52. – [3g] H. Lehmkuhl, J. Näser, G. Mehler, T. Keil, F. Danowski, R. Benn, R. Mynott, G. Schroth, B. Gabor, C. Krüger, P. Betz, *Chem. Ber.* **1991**, *124*, 441–452. – [3h] G. Erker, R. Aul, *Chem. Ber.* **1991**, *124*, 1301–1310. – [3i] J. Okuda, K. H. Zimmermann, *Chem. Ber.* **1992**, *125*, 637–641. – [3j] H. G. Alt, J. Han, U. Thewalt, *Organomet. Chem.* **1993**, *456*, 89–95. – [3k] J. Okuda, K. E. du Plooy, P. J. Foscano, *J. Organomet. Chem.* **1995**, *495,* 195–202. – [3l] R. E. v. H. Spence, W. E. Piers, *Organometallics* **1995**, *14*, 4617–4624. – [3m] K. A. Butakoff, D. A. Lemenovskii, P. Mountford, L. G. Kuz′mina, A. V. Churakov, *Polyhedron* **1996**, *15*, 489–499.

[4] Publications concerning *P*-functionalized cyclopentadienyl ligands: [4a] C. Charrier, F. Mathey, *J. Organomet. Chem.* **1979**, *170*, C41–C43. – [4b] J. C. Leblanc, C. Moıse, A. Maisonnat, R. Poilblanc, C. Charrier, F. Mathey, *J. Organomet. Chem.* **1982**, *231*, C43–C48. – [4c] D. M. Bensley, Jr., E. A. Mintz, *J.Organomet. Chem.* **1988**, *353*, 93–102. – [4d] J. Szymoniak, J. Besançon, A. Dormond, C. Moıse, *J. Org. Chem.* **1990**, *55*, 1429–1432. – [4e] M. Lin, K. A. Fallis, G. A Anderson, N. P. Rath, M. Y. Chiang, *J. Am .Chem. Soc.* **1992**, *114*, 4687–4693. – [4f] T. Cuenca, J. C. Flores, P. Royo, *J. Organomet. Chem.* **1993**, *462*,191–201. – [4g] R. T. Kettenbach, W. Bonrath, H. Butenschön, *Chem. Ber.* **1993**, *126*, 1657–1669. – [4h] I. Lee, F. Dahan, A. Maissonat, R. Poilblanc, *Organometallics* **1994**, *13*, 2743–2750. – [4i] D. Fryzuk, S. S. H. Mao, P. B. Duval,S. J. Rettig, *Polyhedron* **1995**, *14*, 11–23. – [4j] A. H. Cowley, C. S. King, A. Decken, *Organometallics* **1995**, *14*, 20–23. – [4k] J. Foerstner, R. Kettenbach, R. Goddard, H. Butenschön, *Chem. Ber.* **1996, 129**, 319–325. – [4l] O. J. Curnow, G. Huttner, S. J. Smail, M. M. Turnbull, *J. Organomet. Chem.* **1996**, *524*, 267–270. – [4m] I. Lee, F. Dahan, A. Maisonnat, R. Poilblanc, *J. Organomet. Chem.* **1997**, *532*, 59–170.

[5] Publications concerning *O*-functionalized cyclopentadienyl ligands: [5a] Q.Huang, Y. Qian, *Synthesis* **1987**, 910–912. – [5b] C. Qian, Z. Xie, Y. Huang, *J. Organomet. Chem.* **1987**, *323*, 285–294. – [5c] Y. Qian, G. Li, W. Chen, B. Li, X. Jin, *J. Organomet. Chem.* **1989**, *373*, 185–191. – [5d] D. Deng, C. Qian, G. Wu, P. Zheng, *J. Chem. Soc., Chem. Commun.* **1990**, 880–881. – [5e] D. Deng, B. Li, C. Qian, *Polyhedron* **1990**, *9*, 1453–1455. – [5f] H. Qichen, Q. Yanlong, L. Guisheng, T. Yongi, *Transition Met. Chem.* **1990**, *15*, 483–485. – [5g] R. Fandos, A. Meetsma, J. H. Teuben, *Organometallics* **1991**, *10*, 59–60. – [5h] Z. Xie, C. Qian, Y. Huang, *J. Organomet. Chem.* **1991**, *412*, 61–69. – [5i] C. Qian, B. Wang, D. Deng, G. Wu, P. Zheng, *J. Organomet. Chem.* **1992**, *427*, C29-C32. – [5j] U. Siemeling, *J. Organomet. Chem.* **1992**, *429*, C14-C18. – [5k] U. Siemeling, *J. Chem. Soc., Chem. Commun.* **1992**, 1335–1336. – [5l] Qian, G. Li, *Polyhedron* **1993**, *12*, 967–970. – [5m] D. Deng, C. Qian, F. Song, Z. Wang, G. Wu, P. Zheng, S. Jin, Y. Lin, *J.*

Organomet. Chem. **1993**, *458*, 83−88. – [5n] D. Laske, R. Duchateau, J. H. Teuben, A. L. Spek, *J. Organomet. Chem.* **1993**, *462*, 149−153. – [5o] U. Siemeling, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1993**, 126, 1311−1316. – [5p] D. Deng, X. Zheng, C. Qian, J. Sun, L. Zheng, *J. Organomet. Chem.* **1994**, *466*, 95−100. – [5q] C.Qian, X. Zheng, Wang, D. Deng, J. Sun, *J. Organomet. Chem.* **1994**, *466*, 101−105. – [5r] D. Deng, Y. Jijang, C. Qian, G. Wu, P. Zheng, *J. Organomet. Chem.* **1994**, 470, 99−107. – [5s] P. Van de Weghe, C. Bied, J. Collin, J. Marçalo, I. Santos, *J. Organomet. Chem.* **1994**, *475*, 121−126. – [5t] U. Siemeling, G. Hüffmann, J.Organomet. Chem. **1994**, *475*, 229−232. – [5u] C. Qian, B. Wang, D. Deng, J. Hu, J. Chen, G. Wu, P. Zheng, *Inorg. Chem.* **1994**, *33*, 3382−3388.

[6] Recent publications concerning *O*-functionalized cyclopentadienyl ligands: [6a] Y. Mu, W. E. Piers, L. R. MacGillivary, M. J. Zawarotko, *Polyhedron* **1995**, *14*, 1−10. – [6b] U. Siemeling, *Chem. Ber.* **1995**, *128*, 1135−1136. – [6c] J. Christoffers, R. G. Bergman, *Angew. Chem.* **1995**, *107*, 2423−2425; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2226−2227. – [6d] A. A. H. van der Zeijden, C. Mattheis, R. Fröhlich, *Organometallics* **1997**, *16*, 2651−2658. – [6e] P. Foster, M. D. Rausch, J. C. W. Chien, *J. Organomet. Chem.* **1997**, *527*, 71−74. – [6f] O. V. Gusev, L. N. Morozova, T. A. Peganova, M. Yu. Antipin, K. A. Lyssenko, A. F. Noels, S. R. O'Leary, P. M. Maitlis, *J. Organomet. Chem.* **1997**, *536−537*, 191−196.

[7] Publications concerning *N*-functionalized cyclopentadienyl ligands: [7a] A. Baretta, K. S. Chong, F. G. N. Cloke, A. Feigenbaum, M. L. H. Green, *J. Chem. Soc., Dalton Trans.* **1983**, 861−864. – [7b] T. J. Clark, T. A. Nile, D. McPhail, A. McPhail, *Polyhedron* **1989**, *8*, 1804−1806. – [7c] P. J. Shapiro, E. Bunel, W. P. Schäfer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867−869. – [7d] J. Okuda, *Chem. Ber.* **1990**, *123*, 1649−1651. – [7e] F. Wang, T.-Y. Lee, Y.-S. Wen, L.-K. Liu, *J. Organomet. Chem.* **1991**, *403*, 353−358. – [7f] T.-F. Wang, T.-Y. Lee, *J. Organomet. Chem.* **1992**, *423*, 31−38. – [7g] T.-F. Wang, Y.-S. Wen, *J. Organomet. Chem.* **1992**, *439*, 155−162. – [7h] A. Avey, D. R. Tyler, *Organometallics* **1992**, *11*, 3856−3863. – [7i] C. Qian, J. Guo, C. Ye, J. Sun, P. Zheng, *J. Chem. Soc., Dalton Trans.* **1993**, 3441−3445. – [7j] W. A. Herrmann, R. Anwander, F. C. Munck, W. Scherer, *Chem. Ber.* **1993**, *126*, 331−337. – [7k] R. Anwander, W. A. Herrmann, W. Scherer, F. C. Munck, *J. Organomet. Chem.* **1993**, *462*, 163−174. – [7l] A. Avey, T. J. R. Weakley, D. R. Tyler, *J. Am. Chem. Soc.* **1993**, *115*, 7706−7715. – [7m] A. K. Hughes, A. Meetsma, J. H. Teuben, *Organometallics* **1993**, *12*, 1936−1945. – [7n] J. C. Flores, J. C. W. Chien, M. D. Rausch, *Organometallics* **1994**, *13*, 4140−4142. – [7o] G. Paolucci, R. D′Ippolito, C. Ye, C. Qian, J. Gräper, D. R. Fischer, *J. Organomet. Chem.* **1994**, *471*, 97−104. – [7p] U. Böhme, K.-H. Thiele, *J. Organomet. Chem.* **1994**, *472,* 39−41. – [7q] H. Adams, N. A. Bailey, M. Colley, P. A. Schofield, C. White, *J. Chem. Soc., Dalton Trans.* **1994**, 1445−1451. – [7r] J. Okuda, *Comments Inorg. Chem.* **1994**, *16*, 185−205. – [7s] S. Rees, Jr., W. Lay, K. A. Dippel, *J. Organomet. Chem.* **1994**, *483*, 27−31.

[8] Recent publications concerning *N*-functionalized cyclopentadienyl ligands: [8a] S. Barry, A. Kucht, H. Kucht, M. D. Rausch, *J. Organomet. Chem.* **1995**, *489*, 195−199. – [8b] A. A. H. van der Zeijden, *Tetrahedron Asymm.* **1995**, 913−918. – [8c] W. A. Herrmann, M. J. A. Morawietz, T. Priermeier, K. Mashima, *J. Organomet. Chem.* **1995**, *486*, 291−295. – [8d] T.-F. Wang, J. P. Juang, K. J. Lin, *Bull. Inst. Chem., Acad. Sin.* **1995**, *42*, 41−48. – [8e] K.-H. Thiele, Ch. Schließburg, B. Neumüller, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1106−1110. – [8f] U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1995**, *128,* 481−485. – [8g] H. J. G. Luttikhedde, R. P. Leino, C.-E. Wileu, J. H. Näsman, M. J. Ahlgreu, T. A. Pakkanen, *Organometallics* **1996**, *15*, 3092−3094. – [8h] K. E. du Plooy, K. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* **1995**, *14*, 3129−3131. – [8i] H. Pleino, D. Burth, *J. Organomet. Chem.* **1996**, *519*, 269−272. – [8j] J. Okuda, K. E. du Plooy, W. Massa, H.-C. Kang, U. Rose, *Chem. Ber.* **1996**, *129*, 275−277. – [8k] T.-F. Wang, C.-Y. Lai, Y.-S. Wen, *J. Organomet. Chem.* **1996**, *523*, 187−195. – [8l] A. A. H. van der Zeijden, *J. Organomet. Chem.* **1996**, *518*, 147−153. – [8m] M. Enders, R. Rudolph, H. Pritzkow, *Chem. Ber.* **1996**, *129*, 459−463. – [8n] R. A. Fischer, S. Nlate, H. Hoffmann, E. Herdtweck, J, Blümel, *Organometallics* **1996**, *15*, 5746−5752. – [8o] S. Nlate, E. Herdtweck, R. A. Fischer, *Angew. Chem.* **1996**, *108*, 1957−1959; *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1861−1863. – [8p] J. Weiß, E. Herdtweck, S. Nlate, M. Mattner, R. A. Fischer, *Chem. Ber.* **1996**, *129*, 297−303. – [8q] H. Schumann, F. Erbstein, R. Weimann, J. Demtschuk, *J. Organomet. Chem.* **1997**, *536−537*, 541−547. – [8r] T.-F. Wang, C.-C. Hwu, C.-W. Tsai, K.-J. Lin, *Organometallics* **1997**, *16*, 3089−3090. – [8s] A. Bertuleit, C. Fritze, G. Erker, R. Fröhlich, *Organometallics* **1997**, *16*, 2891−2899. – [8t] N. Choi, S. Onozawa, T. Sakakura, M. Tanaka, *Organometallics* **1997**, 16, 2765−2767. – [8u] T.-F. Wang, C.-Y. Lai, C.-C. Hwu, Y.-S. Wen, *Organometallics* **1997**, *16*, 1218−1223. – [8v] J. Okuda, T. Eberle, T. P. Spaniol, *Chem. Ber.* **1997**, *130*, 209−215. – [8w] A. I. Philippopoulos, N. Hadjiliadis, C. E. Hart, B. Donnadieu, P. C. Mc Gowan, R. Poilblanc, *Inorg. Chem.* **1997**, 36, 1842−1849. – [8x] P. C. McGowan, C. E. Hart, B. Donnadieu, R. Poilblanc, *J. Organomet. Chem.* **1997**, *528*, 191−194. – [8y] S. Sakanishi, D. A. Bardwell, S. Couchman, J. C. Jeffrey, J. A. McCleverty, M. D. Ward, *J. Organomet. Chem.* **1997**, *528*, 35−45. – [8z] M. Enders, K. Köhler, W. Frosch, H. Pritzkow, H. Lang, *J. Organomet. Chem.* **1997**, *538*, 163−170. – [8aa]R.Beckhaus, J. Oster, B. Ganter, U. Englert, *Organometallics* **1997**, *16*, 3902−3909.

[9] [9a] J. Dahlhaus, doctoral thesis, Universität Bielefeld, **1993**. – [9b] P. Jutzi, M. O. Kristen, J. Dahlhaus, B. Neumann, H.-G. Stammler, *Organometallics* **1993**, *12*, 2980−2985. – [9c] P. Jutzi, J. Dahlhaus, M. O. Kristen, *J. Organomet. Chem.* **1993**, *450*, C1−C3. – [9d] P. Jutzi, J. Dahlhaus,. M. Bangel, *J. Organomet. Chem.* **1993**, *460*, C13−C15. – [9e] J. Dahlhaus, P. Jutzi, M. Bangel, *J. Organomet. Chem.* **1993**, *474*, 55−58. – [9f] P. Jutzi. J. Dahlhaus, *Synthesis* **1993**, 684−686. – [9g] T. Redeker, diploma thesis, Universität Bielefeld, **1994**.– [9h] P. Jutzi, M. O. Kristen, B. Neumann, H.-G. Stammler, *Organometallics* **1994**, *13*, 3854−3861. – [9i] P. Jutzi, M. Bangel, *J. Organomet. Chem.* **1994**, *480*, C18-C19. – [9j] P. Jutzi, J. Dahlhaus, *Coord. Chem. Rev.* **1994**, *137*, 179−199. – [9k] H.-G. Stammler, P. Jutzi, B. Neumann, M. O. Kristen, *Acta Crystallogr.* **1995**, *C51*, 2496−2498. – [9l] H.-G. Stammler, P. Jutzi, B. Neumann, M. O. Kristen, H. Hölscher, *Acta Crystallogr.* **1995**, *C51*, 2494−2496. – [9m] P. Jutzi, J. Kleimeier, *J. Organomet. Chem.* **1995**, *486*, 287−289. – [9n] P. Jutzi, T. Redeker, H.-G. Stammler, B. Neumann, *J. Organomet.Chem.* **1995**, *498*, 127−137. – [9o] P. Jutzi, U. Siemeling, *J. Organomet. Chem.* **1995**, *500*, 175−185. – [9p] P. Jutzi, H. Schmidt, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1995**, *499*, 7−10. – [9q] P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15*, 4153−4161. – [9r] P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *Chem. Ber.* **1996**, *129*, 1509−1515. – [9s] P. Jutzi, M. Bangel, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15,* 747−752. – [9t] P. Jutzi, M. Bangel, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15,* 4559−4564. – [9u] P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, *J. Organomet. Chem.* **1997**, *533*, 237−245. – [9v] P. Jutzi, T. Redeker, *Organometallics* **1997**, *16*, 1343−1344. – [9w] Th. Redeker, doctoral thesis, Universität Bielefeld, **1997**. – [9x] P. Jutzi, C. Müller, B. Neumann, H.-G. Stammler, publication in preparation.

[10] [10a] M. Barton, J. M. Atwood, *J. Coord. Chem.* **1991**, *24*, 43−67. – [10b] P. Kalck, F. Monteil, *Adv. Organomet. Chem.* **1992**, *34*, 219−284. – [10c] W. A. Herrmann, C. Kohlpaintner, *Angew.Chem.* **1993**, *105*, 1588−1609; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1524−1544.

[11] [11a] K. Clauss, H. Bestian, *Justus Liebigs Ann. Chem.* **1962**, 654, 8−19. – [11b] F. N. Tebbe, G. W. Parshall, G. S. Reddy, *J. Am .Chem. Soc.* **1978**, *100*, 3611−3613. – [11c] U. Thewalt, T. Wöhrle, *J. Organomet. Chem.* **1994**, *464*, C17−C19.

[12] For recent reviews, see: [12a] R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325−387. – [12b] T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57−77 – [12c] M. Bochmann, *Nachr. Chem. Tech. Lab.* **1993**, *41*, 1220−1228. – [12d] R. Mühlhaupt, *Nachr. Chem. Tech. Lab.* **1993**, *41*, 1341−1351. – [12e] M. Aulbach, F. Küber, *Chem. Unserer Zeit* **1994**, *28*, 197−208. – [12f] P. C. Möhring, N. J. Coville, *J. Organomet. Chem.* **1994**, 479, 1−29. – [12g] G. Fink, R. Mühlhaupt, H.-H. Brintzinger, *Ziegler Catalysts*, Springer-Verlag, Berlin, **1995**. – [12h] H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* **1995**, 107, 1255−1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143−1170. – [12i] M. Bochmann, *J. Chem. Soc., Dalton Trans* **1996**, 255−270.

[97311]