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Review

Group 4 bent metallocenes and functional groups—Finding convenient pathways in a difficult terrain

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Contents

Abstract

Current approaches toward the development of functional group chemistry with sensitive Group 4 bent metallocenes are discussed. This includes polymerization reactions of functionalized olefins, electrophilic attack at the metallocene Cp-rings, the introduction of functional groups via fulvene routes, the reactions of pendant functional groups, including CH-activation reactions, Mannich-type carbon–carbon coupling reactions, olefin metathesis reactions and photochemical [2 + 2] cycloadditions. The formation of chelate–PR_2-bridged metal–metal bonded early–late heterobimetallic bent metallocene derivatives is presented and some of their reactions are discussed.

Keywords: Group 4 metallocenes; Functionalized Cp-ligands; Heterobimetallic systems

1. Introduction

Synthetic transformations of molecular compounds often rely on the specific features of their characteristic functional groups. Much of synthetic organic chemistry is typical functional group chemistry. This is less developed in organometallic Group 4 metallocene chemistry, where reactive organic functional group chemistry, if it is involved at all, is mostly used at the ligand stage before the final transmetallation step. Organic functional group chemistry at the Group 4 metallocene stage has been rather limited so far, mostly because these organometallic derivates of the oxophilic early metals are very sensitive to the typical reaction conditions often used in organic functional group conversions. In Group 4 bent metallocenes the organometallic core is the essential functional group with its reactive σ-ligands [1] whereas other typical functional organic substituents have not frequently played a role in this chemistry.

This is about to change. There are increasing reports about reactions of typical organic functional groups in conjunction with early metal bent metallocene systems [2]. This has led to some interesting extensions of the use of the Group 4 metallocenes, most noteworthy in areas of homogeneous catalysis.

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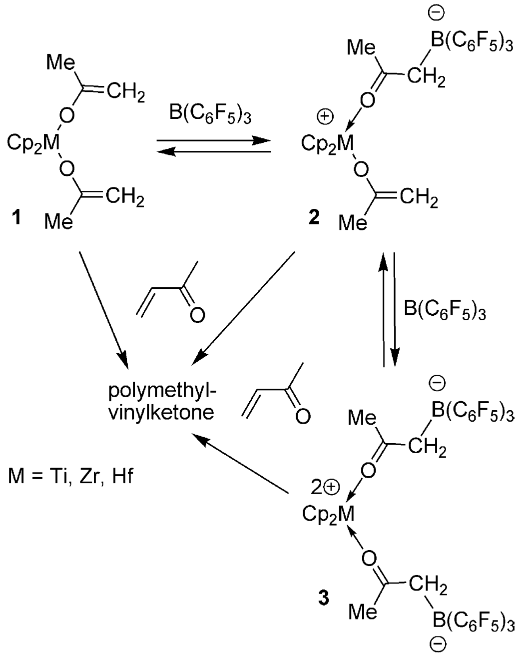
In this account we will present and discuss some of this recent development, mostly illustrated by examples that we have investigated in recent years.

2. Catalytic reactions

The Group 4 bent metallocenes have become well known for their function as very reactive and selective homogeneous metallocene Ziegler–Natta catalysts for olefin polymerization. Ethene and a variety of α-olefins are polymerized very effectively with these systems [3]. The active species are coordinatively unsaturated alkyl zirconocene cations, zwitterions, or ion pairs [4].

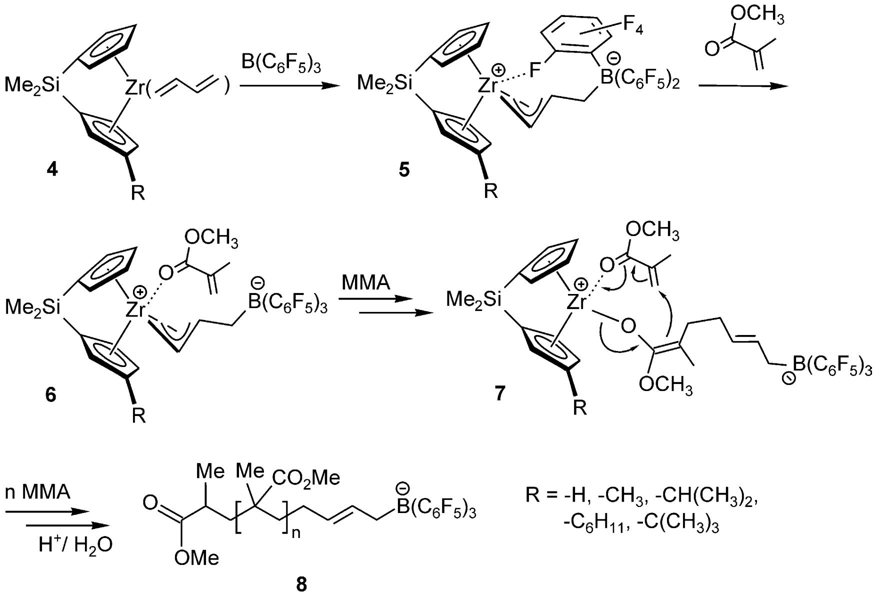
There has also been some development in the use of bent metallocenes as catalysts for the polymerization of functionalized alkenes. These reactions proceed by a different type of mechanism, involving active metal enolate systems [5–10]. In some early investigations we had prepared bis(propenolato)zirconocene (**1**) which was treated with $B(C_6F_5)_3$. This strong Lewis acid selectively adds to the nucleophilic terminal enolate carbon center of **1** to form **2** and subsequently **3**. The latter was characterized by X-ray diffraction. With an excess of $B(C_6F_5)_3$ activated titanium, zirconium or hafnium enolates **1** rapidly polymerize the methylvinylketone monomer with rather high activities (see Scheme 1) [11].

The metallocene-catalyzed polymerization of methylmethacrylate (MMA) is more important. Yasuda et al. had shown that $(Cp_2{}^*SmH)_2$ catalyzes the isospecific polymerization of MMA [5]. Collins and Ward had found that PMMA can be formed at zirconocene Ziegler–Natta-type catalysts by means of a group transfer polymerization mechanism [6]. Soga et al. described PMMA formation at zirconocene/dialkyl zinc catalyst systems [7]. Höcker and coworkers [8] as well as Gibson and co-workers [9] observed the formation of isotactic PMMA at chiral Me_2Si-bridged *ansa*-zirconocenes employing specific activation protocols. Chen et al. characterized the structural and chemical features of zirconocene–esterenolate complexes which are relevant to these reactions [10].



Scheme 1.

We have activated the (butadiene)-*ansa*-zirconocenes **4** (mixture of s-*trans*- and s-*cis*-η^4-C_4H_6 complex isomers [12]) by treatment with $B(C_6F_5)_3$ [13]. The borane added to a butadiene terminus to form the betaine system **5**. (see



Scheme 2.

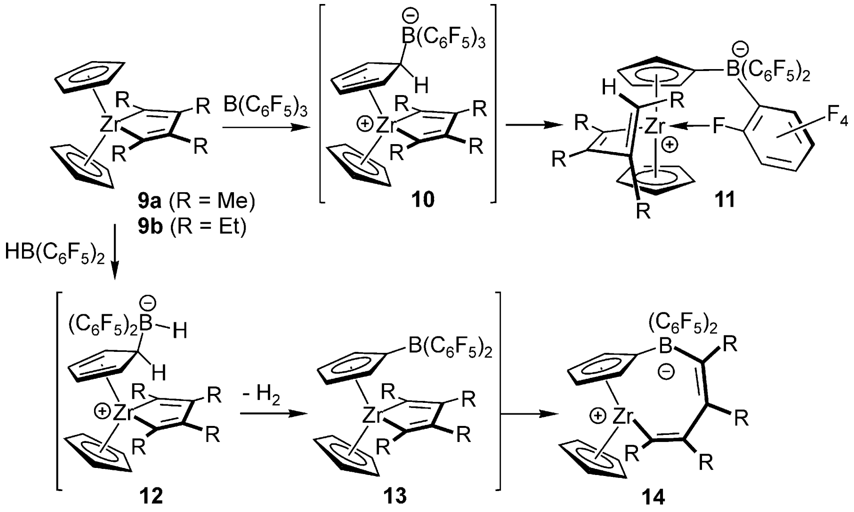
Scheme 2) The zwitterionic complex **5** is an active MMA polymerization catalyst. Initially it adds one equivalent of the α,β-unsaturated ester monomer to form the adduct **6**, which in one case (R = H) was actually observed spectroscopically. Then an intramolecular Michael addition occurred to form the zwitterionic zirconium-enolate (**7**), which then repetitively added methylmethacrylate to form the growing polymer chain in a living polymerization process. Hydrolysis eventually liberated the polymer (**8**), which in this case still contained the borate terminus as was shown by electrospray-MS. At these *ansa*-zirconocene catalysts increasingly isotactic polymethylmethacrylates were formed with an increasing steric bulk of the controlling substituent at the metallocene backbone (R = methyl, isopropyl, cyclohexyl, *tert*-butyl). With the aid of a competing series of experiments starting from the corresponding [$Me_2SiCp(C_5H_4R)ZrCH_3^+$] [$H_3CB(C_6F_5)_3^-$] catalysts it was shown that the stereochemical outcome of the PMMA formation was markedly anion dependent, which indicated a specific involvement of ion pairs in the actual carbon–carbon bond forming step [14].

3. Electrophilic attack at the Cp-ligands

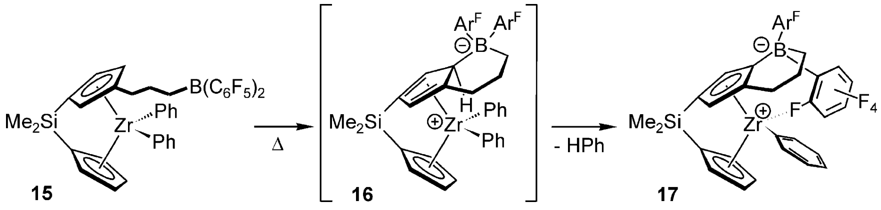
Cp–metal complexes can often very easily be functionalized at the π-cyclopentadienyl ring. Attack by nucleophiles at the [$CpMX_n^+$] cations of many middle to late d-metals [15] and the electrophilic aromatic substitution reactions at the ferrocene Cp-rings [16], respectively, are very typical examples. In contrast, examples of electrophilic functionalizations at the Cp-rings of the intact Group 4 bent metallocenes are still very rare.

We had observed an early example when we reacted the bis(cyclopentadienyl)zirconacyclopentadiene (**9a**) with $B(C_6F_5)_3$. The σ-ligand system in **9a** is so effectively shielded from outside attack, that the usual σ-ligand abstraction reaction by $B(C_6F_5)_3$ is not observed. Instead the electrophilic borane adds to a Cp-ring probably to generate **10**. Subsequently, the remaining *endo*-H at this C_5H_5[B] ring is intramolecularly abstracted by the adjacent Zr-bound σ-ligand to form the observed substitution product (**11**) (see Scheme 3) [17]. A similar reaction was observed when **9b** was treated with $HB(C_6F_5)_2$. We must assume that borane addition to a Cp-ring takes place to generate **12**, which then apparently loses dihydrogen. Subsequent intramolecular σ-ligand abstraction then leads to the eventually observed product (**14**) (Scheme 3) [18].

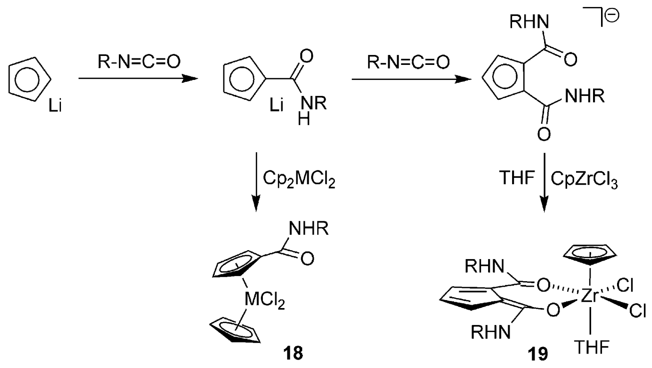
A similar reaction was observed when complex **15**, obtained by a hydroboration reaction employing $HB(C_6F_5)_2$, was kept for some time at room temperature in solution. The pendant borane intramolecularly added to its parent π-C_5H_4-ring. Subsequent elimination of benzene then directly led to the formation of **17** (characterized by X-ray diffraction) [19] (Scheme 4).



Scheme 3.



Scheme 4.



Scheme 5.

4. Bent metallocenes with pendant functional groups

Since the direct substitution at the Cp-rings is problematic at the metallocene stage (see above), functional groups had been introduced at an earlier stage and carried on through the Group 4 metallocene synthesis. This was often achieved by means of a fulvene route. Early work by Hafner et al. had opened convenient entries to functionalized fulvene systems that were later used (e.g. by Rausch et al.) to prepare titanocenes and zirconocenes with e.g. a –COCH$_3$ functionality at a Cp-ring [20].

Although this method has often been very useful, it shows its limitations in a number of cases. We had found that Cp-anion-addition to organic isocyanates can be used for the synthesis of carboxamide-substituted metallocenes (see Scheme 5, formation of **18**) [21]. However, the addition of two alkylisocyanate equivalents results in a fulvenoid anion that no longer expresses a Cp-anion-character towards e.g. zirconium. In contrast to the mono-functionalized [C$_5$H$_4$–CONHR]$^-$ reagent, the [*o*–C$_5$H$_3$(CONHR)$_2$]$^-$ reagents bind exclusively to zirconium via their chelate oxygen atoms to yield **19**, which demonstrates a limit of this otherwise generally very promising synthetic approach (Scheme 5) [22].

Levulinic acid amide (**20**) was converted to the fulvene (**21**) that contains a remote carboxamide function. Subsequent conversion to a functionalized cyclopentadienide was achieved by "soft" nucleophilic methylation followed by deprotonation. Transmetallation to titanium or zirconium then yielded the respective bent metallocenes (**23**) (see Scheme 6). In these neutral 16-electron complexes the pendant –CONR$_2$ functional group does not interact with the metal center. In contrast, abstraction of Cl$^-$ gave a cation (**24**) that strongly coordinated the carboxamide oxygen to preserve its favoured 16-electron configuration (see Fig. 1) [23].

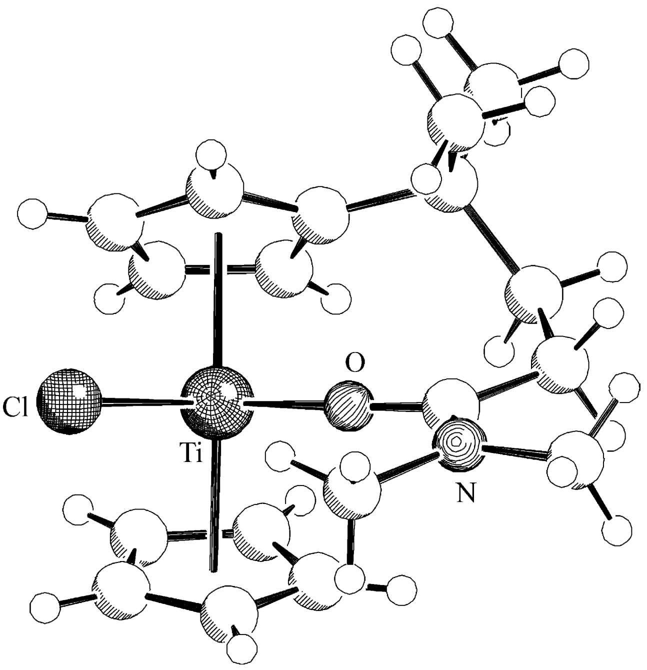
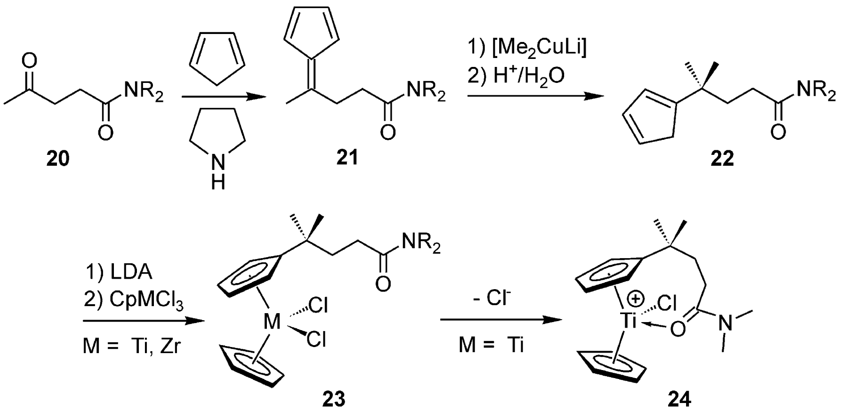
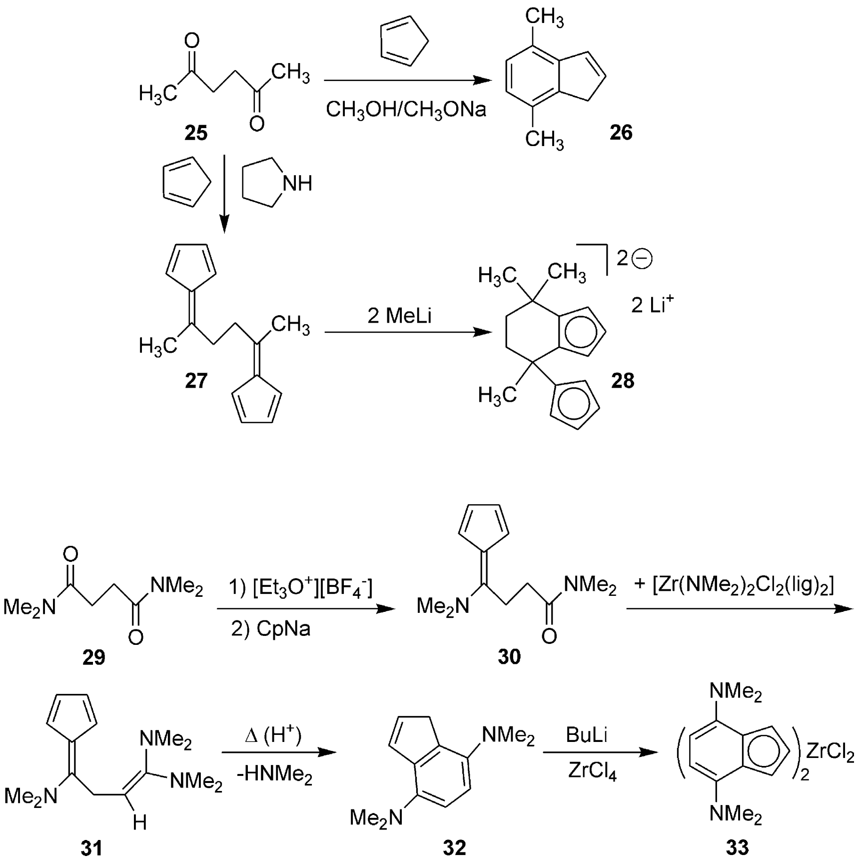


Fig. 1. Molecular structure of complex **24** [BF$_4$$^-$].

This type of a ligand synthesis shows some interesting variants, where the remote C=O functional groups have become involved. Thus, treatment of the 1,4-diketone (**25**) with cyclopentadiene and base under "Thiele conditions" [24] eventually gave the substituted indene (**26**) via a mono-fulvene intermediate, whereas the bis-fulvene (**27**) was readily obtained under "Stone/Little conditions" [25]. Its subsequent treatment with methyl lithium then gave the new



Scheme 6.



Scheme 7.

linked bis-Cp-ligand system (**28**) (Scheme 7). Compounds **26** and **28** have been extensively used in metallocene chemistry and catalysis.

Conversion of the succinamide (**29**) to the mono-fulvene (**30**) initiated an interesting alternative reaction pathway: its reaction with [$Cl_2Zr(NMe_2)_2(lig)_2$] gave **31**, which under the applied reaction conditions rapidly underwent ring closure and condensation to yield the 4,7-bis(dialkylamino)indene (**32**). This novel ligand system was successfully employed in metallocene syntheses (see Scheme 7 and Fig. 2) [26].

The fulvene route also made dialkylaminomethyl-substituted zirconocenes easily available. As a typical

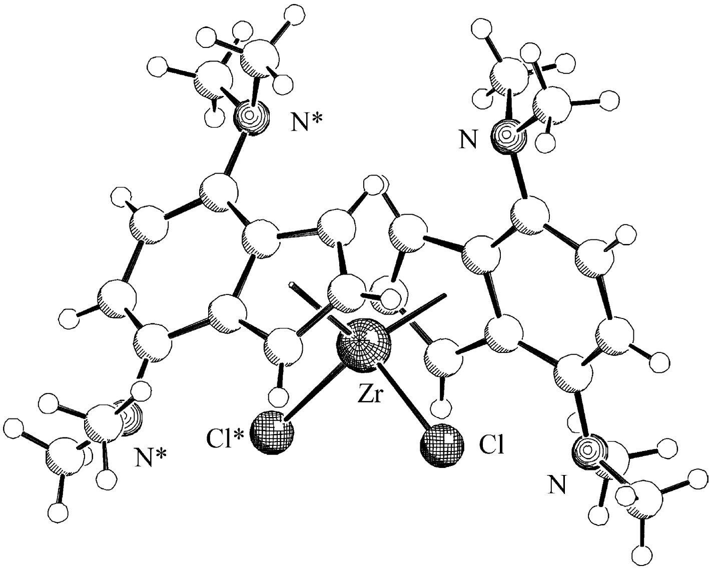
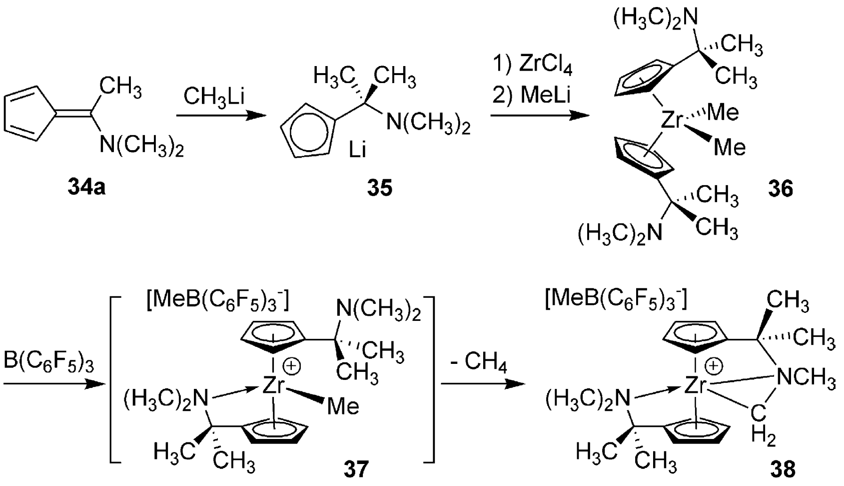


Fig. 2. A view of the molecular structure of complex **33**.



Scheme 8.

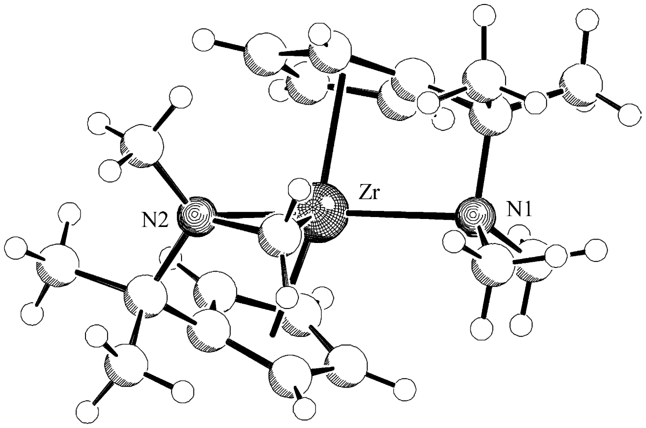


Fig. 3. Molecular structure of complex **38** (only the cation is depicted).

example the 6-dimethylaminofulvene (**34**) cleanly added methyl lithium to yield the amino-functionalized Cp-ligand system (**35**). Transmetallation to zirconium followed by alkylation gave the metallocene (**36**) [27] (Scheme 8). The cations derived from this and a variety of related zirconocenes with pendant dialkylamino-groups at their Cp-ligands all readily underwent a typical C–H activation process to yield η^2-iminium-type systems. Thus, treatment of **36** with $B(C_6F_5)_3$ generated an unstable $[Zr]^+$–CH_3 intermediate that rapidly reacted further by C–H activation at the pendant –$N(CH_3)_2$ functionality with loss of methane to yield **38** [28] (see Fig. 3). The chemistry of a variety of such compounds featuring internal η^2-$CH_2N(R)$– coordination was extensively investigated. Such systems were found to readily insert a variety of unsaturated reagents (olefins, conjugated dienes, organic carbonyl compounds, etc.) [29].

5. Carbon–carbon coupling reactions at pendant functional groups

We have found two types of typical organic functional group reactions that can easily be carried out at the intact Group 4 bent metallocene ligand framework to make interesting new metallocenes available by carbon–carbon bond formation.

The first is a Mannich-type coupling reaction. Treatment of a variety of substituted 6-alkyl-6-aminofulvens (**34**) with a suitable base resulted in a clean deprotonation with formation of the respective enamino-substituted cyclopentadienide reagents (**39**). The reaction of some of these systems with e.g. $ZrCl_4$ under carefully controlled conditions led to the formation of the respective Group 4 bent metallocenes bearing enamino-functional groups at their Cp-rings [30]. The molecular structure of a typical example is depicted in Fig. 4. Some of these complexes turned out to be rather unstable. Thus, exposure of e.g. the morpholino- or piperidino-derivatives (**40′**) to catalytic amounts of a Lewis acid (e.g. $ZrCl_4$) or a Brønsted acid resulted in a rapid Mannich-type condensation reaction with elimination of one molar equivalent of the corresponding amine to yield the unsaturated C_3-bridged *ansa*-zirconocene systems (**41**) [31,32] (Scheme 9 and Fig. 5).

In many other cases, the enamino-Cp-containing metallocenes were so unstable that they were not isolated nor even detected spectroscopically. Thus, treatment of dimethylaminoethenyl-Cp anion equivalent (**39a**) with $ZrCl_4$ (or $TiCl_4$) directly yielded the *ansa*-metallocene systems **41** (M = Zr or Ti). Many other examples of this interesting metallocene complex type could also be obtained in good yield in a one-pot variant of this Mannich reaction at the Group 4 bent metallocene nucleus.

The intramolecular metallocene Mannich coupling reaction was found to be synthetically very useful. It has been applied for the preparation of a variety of Group 4 *ansa*-metallocene Ziegler catalyst precursors. Lately it has found increasing use in ferrocene chemistry where it has opened very simple synthetic entries to ferrocene-based chelate ligands and other systems [33].

Olefin metathesis is another reaction type that has been found to be suited for carrying out carbon–carbon coupling

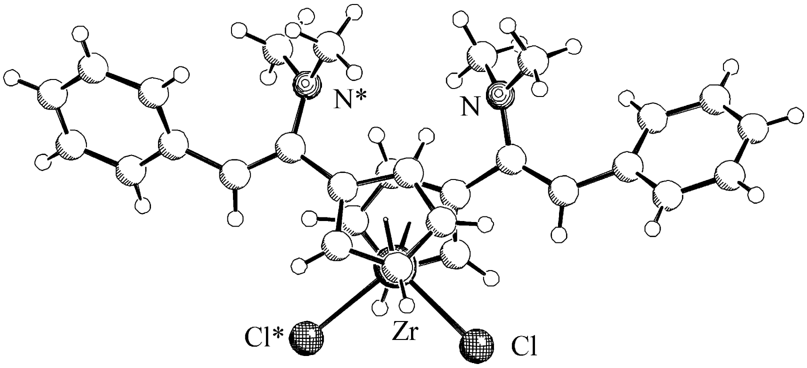
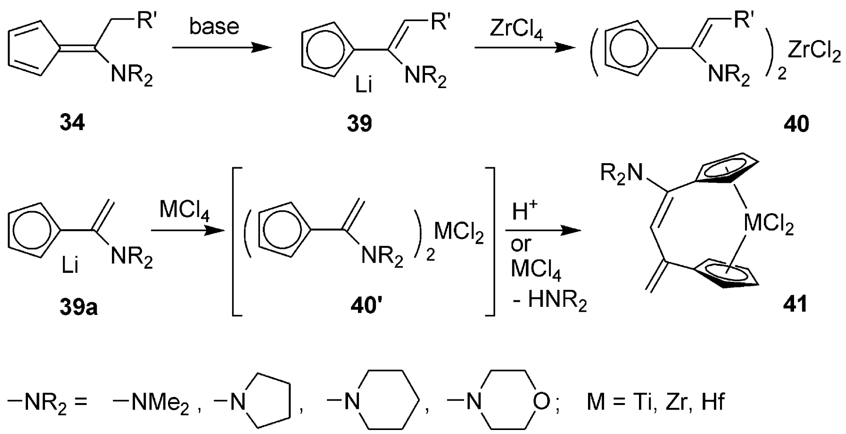


Fig. 4. Molecular geometry of an example of complex **40** (R′ = Ph, R = CH_3).



Scheme 9.

reactions at the sensitive Group 4 bent metallocenes. Here the starting materials are very easily available by nucleophilic substitution routes (see Scheme 10). The reaction of ω-hexenyl-cyclopentadienide (**42**) with 0.5 M equivalents of $ZrCl_4$ gave the open, non-bridged bent metallocene dichloride complex (**43**). Intramolecular olefin metathesis was catalyzed by means of $Cl_2(PCy_3)_2Ru = CHPh$ [34] to give the “large *ansa*-metallocene” system (**44**) with liberation of ethene. The X-ray crystal structure analysis of **44** revealed the presence of a *trans*-C=C double bond inside the large *ansa*-bridge. Similarly, bis(allyl-C_5H_4)$ZrCl_2$ (**46**) yielded the unsaturated C_4-bridged *ansa*-metallocene (**47**) upon treatment with the same metathesis catalyst [35].

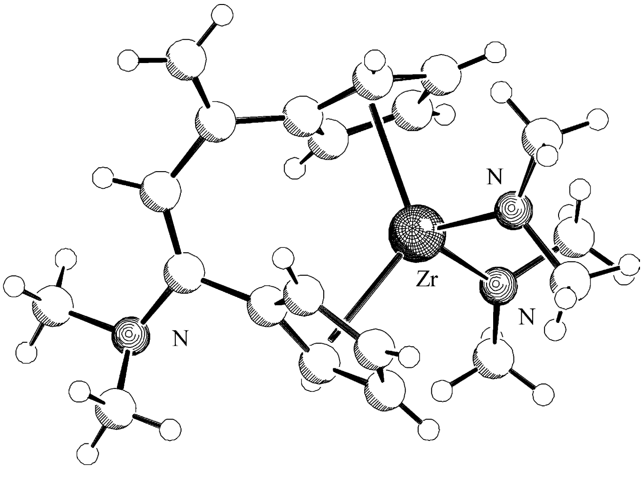
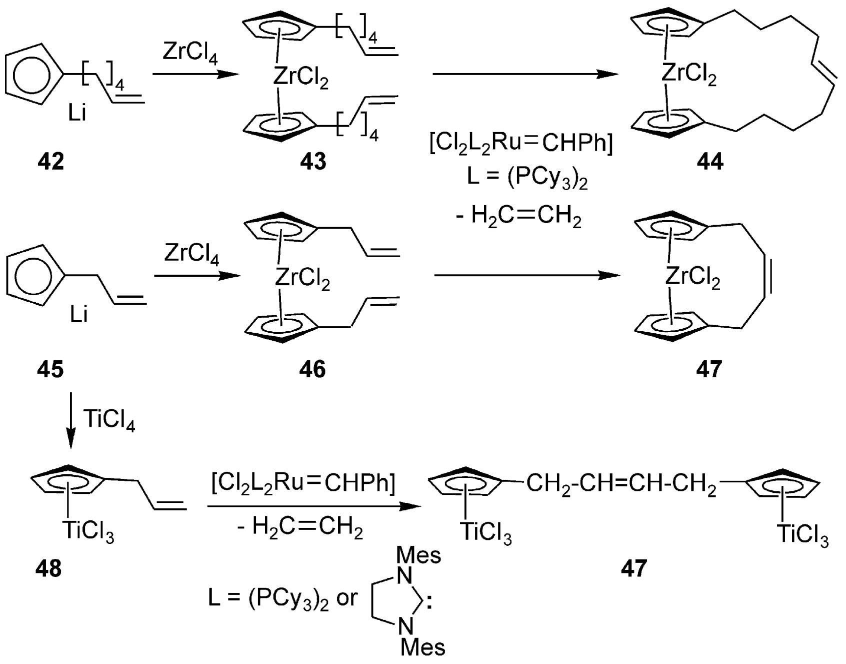


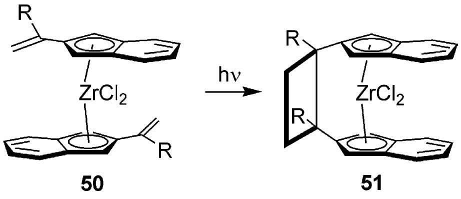
Fig. 5. Molecular geometry of an example of complex **41** (R = CH_3, M = Zr, X = –NMe_2).

Treatment of the Cp-allyl$^-$ reagent (**45**) with $TiCl_4$ gave (C_5H_4-allyl)$TiCl_3$ (**48**). Intermolecular metathetical coupling with loss of ethene was observed with the $Cl_2(PCy_3)_2Ru = CHPh$ catalyst to yield a *cis*/*trans*-mixture of the dimetallic product **49**. Use of the more reactive Grubbs II catalyst system [34] in this case yielded almost pure *trans*-**49**. Similar reaction features were observed when the Cp(C_5H_4-allyl)$TiCl_2$ system or a related *ansa*-zirconocene was employed [36].

Metal-catalyzed cross-coupling was used to attach alkenyl groups in conjugated position at the indenyl moiety at the ligand stage. The corresponding bis(alkenylindenyl)$ZrCl_2$ complexes (**50**) underwent a very efficient intramolecular photochemical [2 + 2] cycloaddition reaction to almost quantitatively yield the *ansa*-metallocenes **51** [37] (Scheme 11). In some cases, similar photochemical [2 + 2] ring closure reactions could be carried out at bis(alkenyl-C_5H_4)$ZrCl_2$ systems as well [38].



Scheme 10.



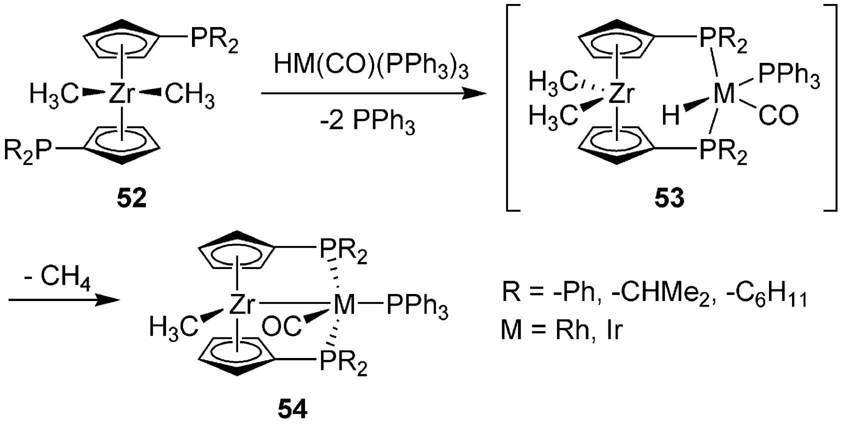
Scheme 11.

6. Early–late heterobimetallics

Cyclopentadienide is readily phosphorylated by means of treatment with $ClPR_2$ followed by base [39]. On this basis the corresponding zirconocene complexes $[(C_5H_4{-}PR_2)_2Zr(CH_3)_2]$ (**52**) were easily available. They have turned out to be suitable reagents for the preparation of a variety of very interesting new heterobimetallic complexes featuring a metal–metal bond between the Group 4 metal and a late transition metal element [40].

The $-PR_2$ functionalized zirconocenes (**52**) react with $[HM(CO)(PPh_3)_3]$ (M = Ir, Rh) by replacement of two PPh_3 ligands at the late metal to initially form the heterobimetallic chelate products (**53**) (the Ir system was actually observed and characterized spectroscopically) [41]. These primary adducts are not stable, however, but subsequently lose CH_4 to form the Zr–Rh metal–metal bonded systems **54** (see Scheme 12 and Fig. 6). The diphenylphosphino-substituted example of this class of compounds was actually characterized by X-ray diffraction [42] (see Fig. 6).

There is evidence that the metal–metal bond in the complexes **54** in some reactions itself serves as a functional group. In one case (**54′**: M = Rh, R = iso-propyl) we were able to show that iso-propanol added to the Zr–Rh linkage, without initially affecting the $Zr{-}CH_3$ moiety, to form **55**.



Scheme 12.

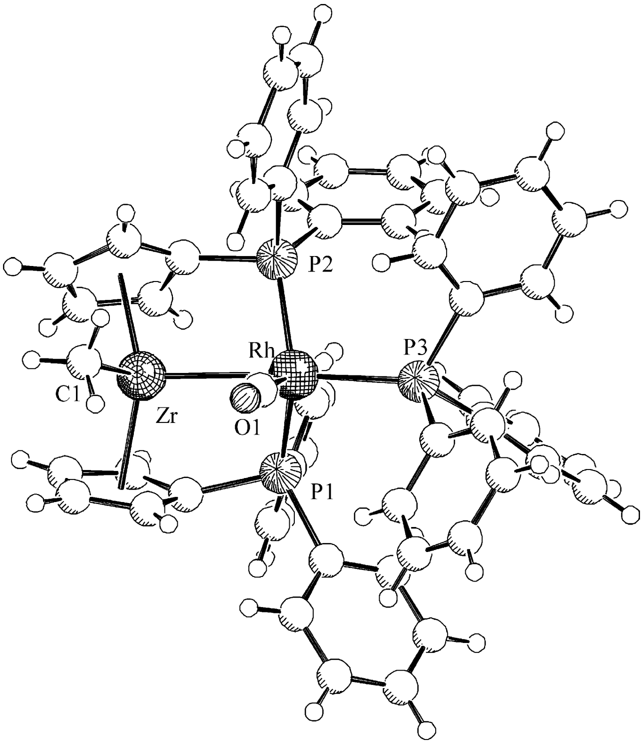


Fig. 6. Molecular structure of an example of the early-late heterobimetallic Zr–Rh complexes **54** (R = Ph).

Subsequently, this intermediate then reacted further by elimination of methane with re-forming the Zr–Rh bond to eventually yield the substitution product **56** (see Scheme 13) [41].

The complexes **54** (with M = Rh) also undergo some remarkable carbon–carbon coupling reactions along the Zr–Rh framework. In e.g. CH_2Cl_2 solution in some cases (R = alkyl) rapid formation of a Rh-bonded acetyl ligand is observed to occur with loss of the PPh_3 ligand. For stabilization the system abstracts two Cl atoms from the solvent to form the unique reaction products **59**. Fig. 7 shows the molecular structure of an example (R = iso-propyl) in the solid state. We assume that this reaction proceeds via reactive intermediates such as **57** and **58** to eventually arrive at the observed product **59** after Cl abstraction from the solvent (see Scheme 14) [42].

Treatment of the complexes **54** with carbon monoxide resulted in a rapid exchange reaction of the PPh_3 ligand at rhodium for carbon monoxide (see Scheme 15 and Fig. 8). We assume that this reaction also proceeds *via* the intermediate **57** that is under these conditions effectively trapped by CO to yield complex **60**.

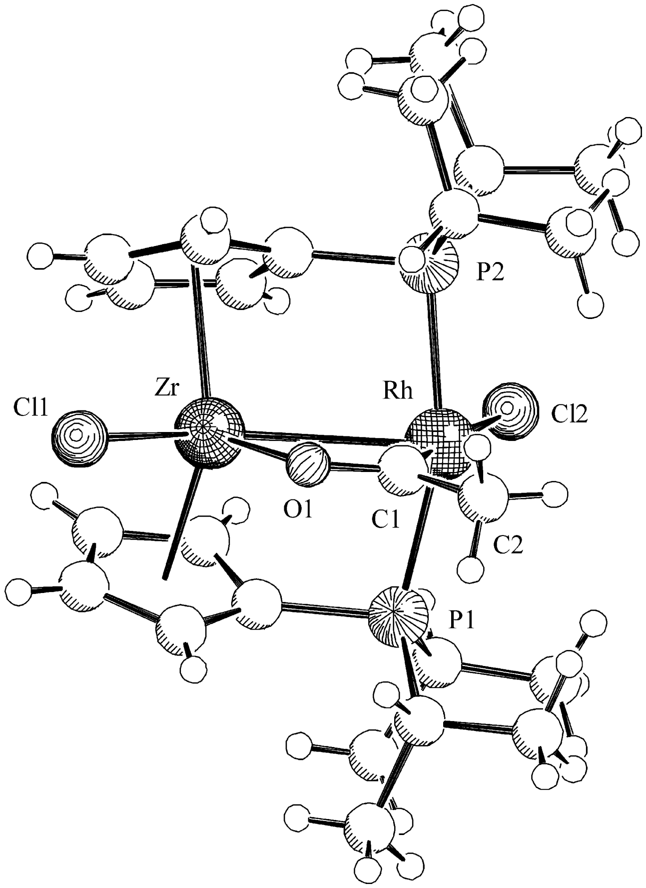
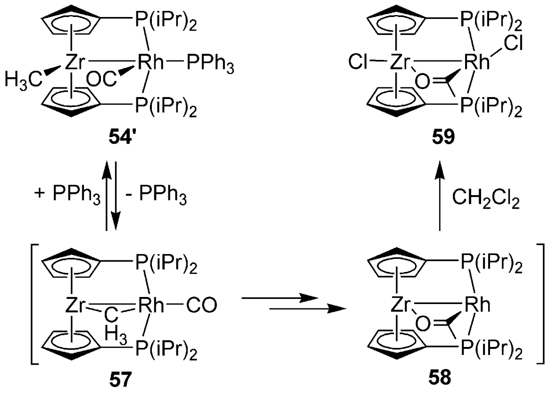
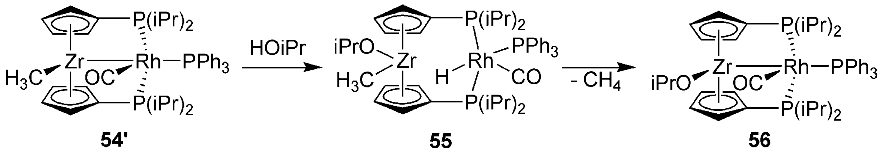


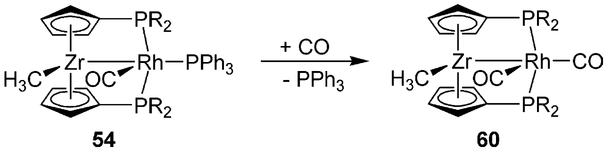
Fig. 7. A view of the molecular structure of complex **59** (R = iso-propyl).



Scheme 14.



Scheme 13.



Scheme 15.

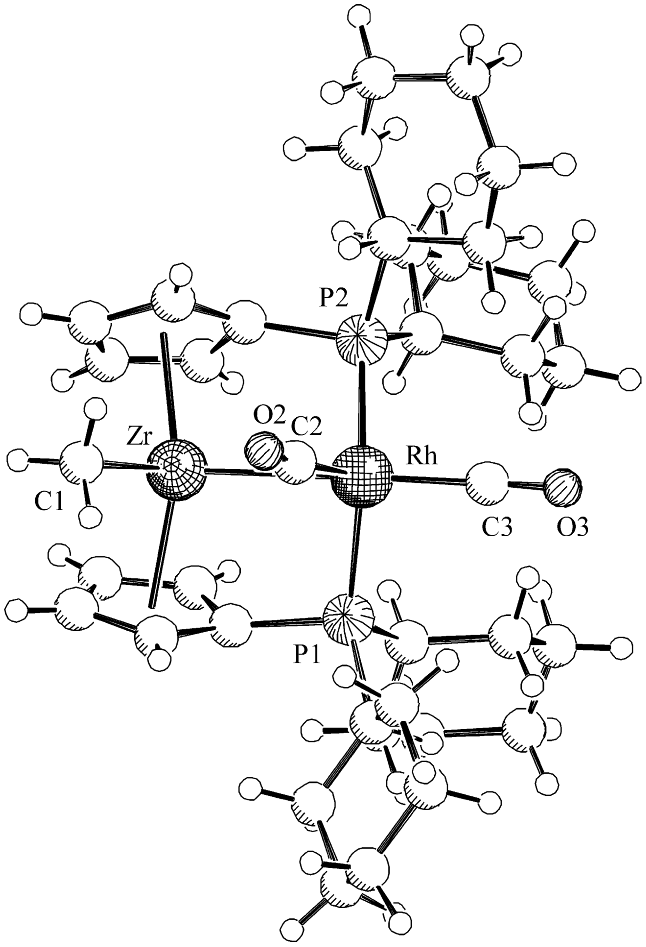


Fig. 8. Molecular structure of complex **60** (R = cyclohexyl).

7. Some conclusions

The examples presented and discussed here together with a variety of related systems reported elsewhere probably indicate an emerging area of a functional group chemistry of the Group 4 metallocenes from the literature. It appears that there are now a number of viable pathways available to synthesize a number of bent metallocenes that feature a variety of functional groups at their π-ligand framework. As demonstrated by first examples, some of these can now efficiently be used for carrying out typical functional group chemistry at the periphery of these otherwise very sensitive organometallic systems, be it C–H activation, olefin metathesis or even the Mannich reaction, i.e. a reaction from the most important family of the aldol-type carbon–carbon coupling reactions. These recent developments make us hopeful that we will see some expansion of bent metallocene chemistry beyond the current important applications in organic synthesis and catalysis, that will make good use of the many possibilities that will be synthetically opened by further developing a functional group chemistry at these special members of the large metallocene family.

Acknowledgements

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