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Coordination Chemistry Reviews 250 (2006) 1056–1070

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Review

# Syntheses and reactions of fulvene-derived substituted aminoalkyl-Cp and phosphinoalkyl-Cp-Group 4 metal complexes

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Received 14 October 2005; accepted 18 October 2005
Available online 6 December 2005

## Contents

## Abstract

6-Dialkylaminofulvenes add a variety of RLi reagents to form (dialkylaminoalkyl)cyclopentadienides $[C_5H_4CR^1R{-}NR'_2]Li$, which exhibit oligomeric chain structures in the solid state. Transmetallation yields the corresponding titanocene or zirconocene derivatives that often show interesting intramolecular CH activation reactions. Phosphide anion addition to 6-alkyl-fulvenes yields the analogous phosphinoalkyl-Cp reagents and subsequently their Group 4 metallocene complexes. Deprotonation of 6-dialkylamino-6-alkylfulvenes generates enamino-substituted Cp-ligands. Their metal complexes undergo intramolecular *Mannich* reactions to yield $C_3$-bridged ansa-metallocene products. Treatment of 6-dimethylaminofulvene with LiNHAr reagents leads to amine exchange and opens a synthetic route to “CpCN”$MX_2$ “constrained geometry” catalysts. LiNHR addition to some 6-alkylfulvenes represents an alternative entry to this important class of compounds. The corresponding “CpCP”$MX_2$ systems are derived from the analogous LiPHR addition reaction. Many typical reactions of the new fulvene-derived metal complexes are presented and discussed.

*Keywords:* Pentafulvenes; Cyclopentadienides; Group 4 metallocene complexes; Constrained geometry catalysts; Metallocene cations

## 1. Introduction

Fulvenes have been employed as π-ligands in metal complex chemistry [1]. More importantly, pentafulvenes (**1**) have also been used as valuable precursors for the generation of substituted cyclopentadienides (**2**) and subsequently the formation of their respective $\eta^5$-RCp metal complexes. Fulvene routes have especially found numerous applications in Group 4 metallocene and related chemistry [2].

The pentafulvenes may be regarded as all carbon analogues of the organic carbonyl compounds. Their C6 carbon center is electrophilic and can be attacked directly by suitable nucleophiles. In addition, the C–H bonds in the α-position to C6 feature an enhanced CH acidity and thus can be removed by a suitable base. Nucleophilic addition reactions have frequently been used to synthesize branched alkyl (or aralkyl) substituted Cp ligands and their corresponding early transition metal complexes [3]. The deprotonation route has opened very convenient pathways to interesting new alkenyl functionalized bent metallocene complexes via their alkenyl-Cp anion reagents (**2b**) [4] (Scheme 1).

Fulvene routes can be used to attach a variety of functional groups at the Cp-ring prior to the final transmetallation step. The

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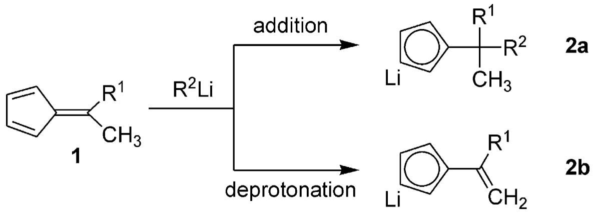
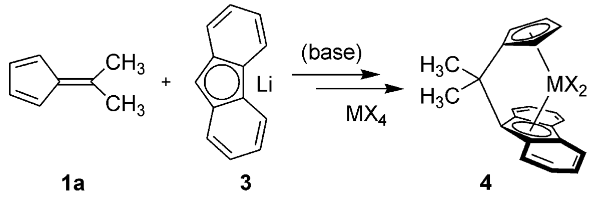
doi:10.1016/j.ccr.2005.10.008



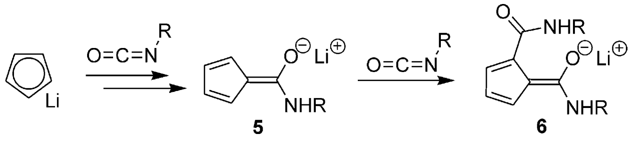
Scheme 1.



Scheme 2.

addition of fluorenyl anion, a carbanion with a sufficiently low basicity, to 6,6-dimethylfulvene (**1a**) is a prominent example. Subsequent deprotonation followed by transmetallation yields the $C_1$-bridged fluorenyl/Cp ansa-metallocene complexes that form the basis of highly reactive homogeneous *Ziegler-Natta* catalysts for the production of syndiotactic polypropylene. An early example published by *Ewen* and *Razavi* is depicted in Scheme 2 [5,6]. $C_2$-bridged ansa-metallocene complexes have been prepared by a sequence starting with reductive coupling of two pentafulvenes [7].

The reaction of cyclopentadienide with alkyl- and arylisocyanates gives rise to the formation of the fulvenoid addition products **5** [8]. These react with a variety of metal halides to yield carboxamide substituted $\eta^5$-Cp-X metal products [9,10]. In some cases even peptide-substituted $\eta^5$-Cp-pept. metal complexes were prepared in this way [11]. The systems **5** often add a second equivalent of the isocyanide reagent to form 1,2-functionalized fulvenoids (**6**) [12,13]. With late metal halides (Fe, Ru) these react to yield the respective linear tetrakis(carboxamide)metallocenes. In contrast, the systems **6** favour the formation of κO,O′-bonded non-metallocene chelate products when reacted with various Group 4 metal halides (see Scheme 3).



Scheme 3.

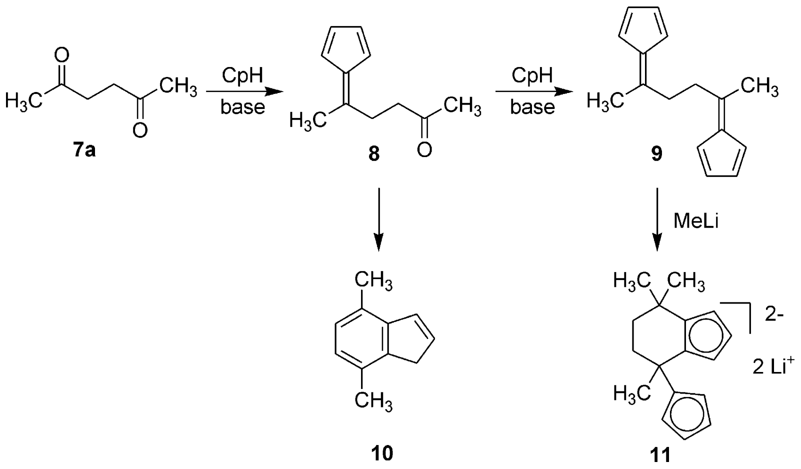
1,4-Dicarbonyl compounds (e.g. **7a**) undergo a condensation reaction with one equivalent of cyclopentadienide to yield the substituted indene derivatives via a mono-fulvene intermediate (**8**) [14]. With two Cp-anion equivalents the bis-fulvene (**9**) has been formed that was converted to the ansa-bis-Cp ligand system (**11**) upon treatment with methyl lithium (Scheme 4) [15,16].

In contrast, the carboxamido precursor (**12**) gave a mono-fulvene bearing a β-carboxamidoethyl substituent when treated with CpH under "*Stone*/*Little* conditions" [17]. Subsequent $CH_3$-anion addition gave the functionalized Cp-ligand (**14**) that was attached, e.g. to titanium to yield stable functionalized titanocene complex systems [18]. Activation of the related succinamide derivative (**15**) with *Meerwein*'*s* reagent followed by treatment with CpNa led to the formation of the carboxamido functionalized 6-dimethyl-amino-pentafulvene (**16**). Such systems were found to undergo a selective condensation reaction to form the 4,7-bis(dimethylamino)-substituted indene system (**17**) when treated with, e.g. $[Zr(NMe_2)_2Cl_2(L)_2]$ (**18**). The product **17** was used as a $\eta^5$-indenyl ligand after deprotonation [19] (Scheme 5).

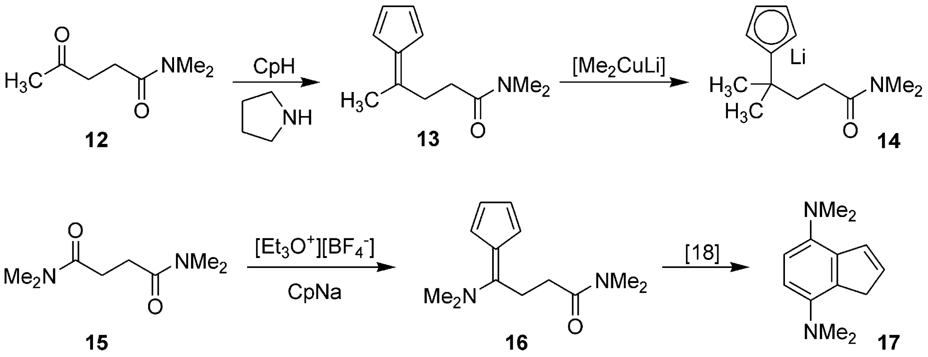
It turned out that 6-aminofulvenes in general were well-suited starting materials for the preparation of a variety of Cp-functionalized Group 4 metal complexes by making use of the specific chemical features of this class of compounds. In this account this will be illustrated by describing a variety of such examples (and related phosphorus containing compounds), many originating from my research group.

## 2. Cyclopentadienyl Group 4 metal complexes derived from substituted 6-aminofulvenes

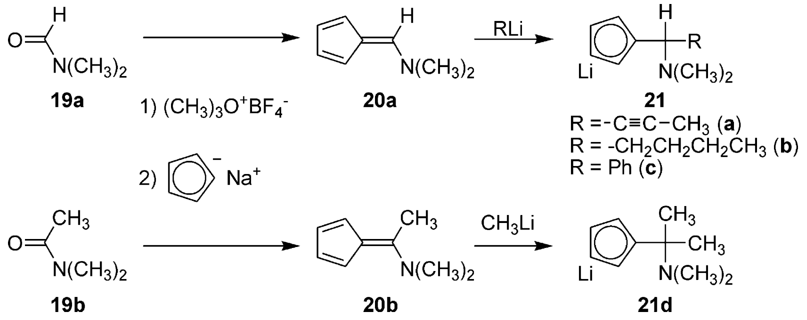
A variety of 6-dialkylaminofulvenes can readily be prepared by means of a route developed by Hafner et al. [20].



Scheme 4.



Scheme 5.



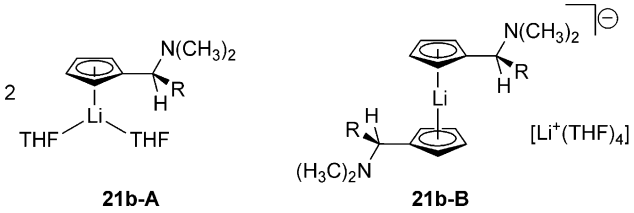
Scheme 6.

Thus, activation of dimethylformamide (**19a**) by treatment with *Meerwein's* reagent followed by the reaction with, e.g. sodium cyclopentadienide yields 6-dimethylaminofulvene (**20a**). Likewise, 6-dimethylamino-6-methylfulvene (**20b**) was obtained analogously starting from dimethylacetamide (**19b**). The aminofulvenes **20a** cleanly added a variety of carbon nucleophiles at C6 to yield the corresponding substituted (dimethylaminoalkyl)cyclopentadienides (**21a–c**, see Scheme 6) [21,22]. Treatment of the CH-acidic reagent **20b** with the basic alkyl lithium reagents can principally lead to α-deprotonation or nucleophilic addition. Mostly, the elimination route is preferred (see above), but under specific reaction conditions the addition of a carbon nucleophile at the fulvene carbon center C6 can be achieved. A typical example is the reaction of **20b** with methyl lithium in ether that leads to the formation of **21d**.

In THF solution equilibration between a mononuclear THF-stabilized structure **21A** and the lithiocene anion structure **21B** was observed by temperature dependent dynamic $^7$Li NMR spectroscopy. For the *n*-butyl substituted example **21b** the monomer **21b-A** features a single $^7$Li NMR resonance at a typical value of $\delta$ −7.8, whereas the lithiocene salt shows a 1:1 pair of $^7$Li NMR resonances at $\delta$ −0.8 and $\delta$ −13.0, the former being due to the [Li$^+$(THF$_4$)] counterion of the substituted lithiocene anion **21b-B** (see Scheme 7) [21,23].

In the crystal the compounds **21** exhibit associated oligomeric supersandwich-type structures [24]. Both electrostatic Li···Cp interaction and coordination of the pendent amino substituent to Li$^+$ is used to construct the observed chain structures. The recurring -aa-type structure of **21d** is a typical example (see Fig. 1, top). The Li$^+$ cation is almost symmetrically placed above a C$_5$H$_4$ ring (Li–C distances between 2.227(3) and 2.251(4) Å). In addition the Li$^+$ center is coordinated to the amino nitrogen atom of the next [C$_5$H$_4$-NMe$_2$$^-$] subunit (Li–N$^*$ 2.045(3) Å) and it features a short contact to one adjacent Cp-carbon atom (Li–C2$^*$ 2.667(3) Å). The recurrence of this structural motif makes up the indefinite chain structure of **21d**. Most of the systems **21** feature related recurring -aa-type linear frameworks. The (dimethylaminobenzyl)CpLi system (**21c**) represents an interesting exception, showing a chain structure of a principally different -ab-type (see Fig. 1, bottom) with alternating lithiocene anion and (diamino)Li($\eta^2$-Cp)$_2$-type substructural moieties making up the indefinite organometallic framework.

Transmetallation of the reagents **21** with, e.g. the Group 4 metal halides yields the corresponding substituted metallocene complexes. Thus, the reaction of **21d** with TiCl$_4$ or ZrCl$_4$ cleanly gave rise to the formation of the metallocene dichloride complexes **22a** and **22b** (see Scheme 8) [25,26]. X-ray crystal structure determinations revealed the formation of conventional 16-electron bent metallocene complexes. In **22a**,**b** there was



Scheme 7.

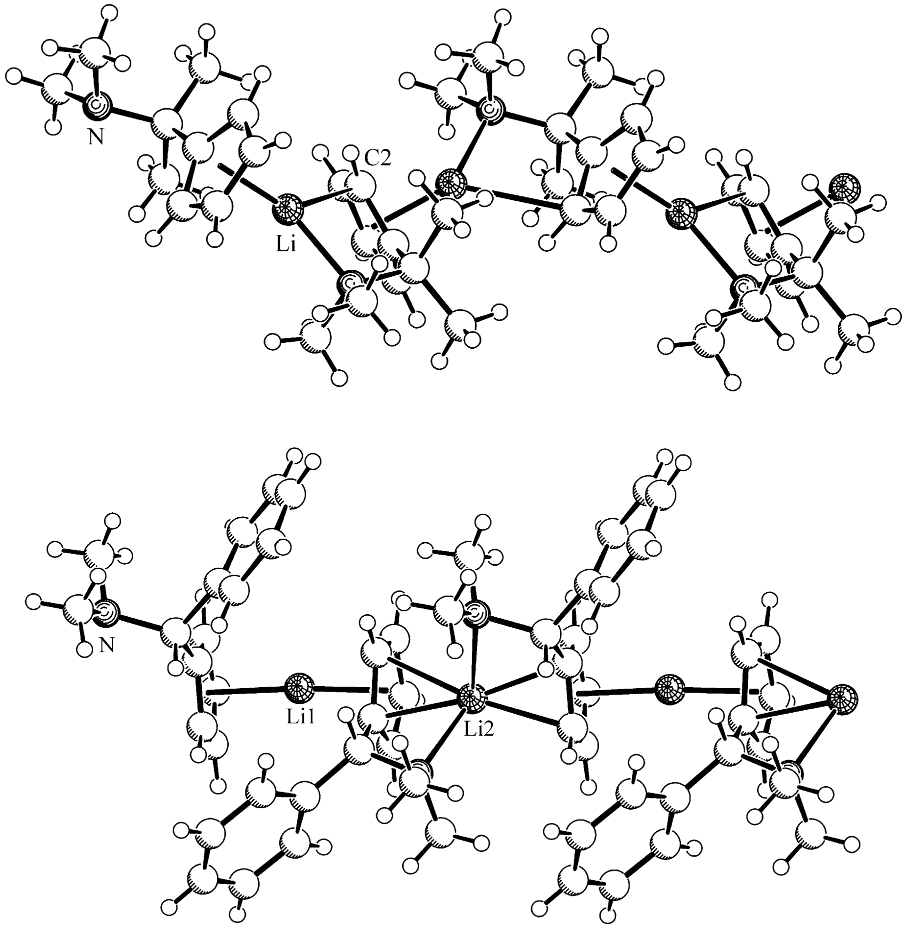


Fig. 1. Indefinite chain structures of **21d** (top) and **21c** (bottom) in the crystal.

no nitrogen–metal interaction detected. This was changed upon formation of the respective neutral Ti(III) complex **23** [25] as well as the cationic Zr(IV)$^+$ complex **25** (see Scheme 8) [26]. In both cases strong internal nitrogen coordination was observed (**23**: Ti–N 2.420(2) Å, **25**: Zr–N 2.369(3) Å) that retained the typical pseudo-tetrahedral framework structures of these bent metallocene complexes (see Fig. 2).

Treatment of the functionalized zirconocene dichlorides **22b** and **24** with methyl lithium gave the corresponding dimethylzirconocene complexes **26** and **27**, respectively. The reaction of **26** with $B(C_6F_5)_3$ resulted in the abstraction of a methyl anion equivalent from zirconium. However, the expected cationic primary product (**28**) was not stable under the reaction conditions but rapidly reacted further by a CH activation pathway [26].

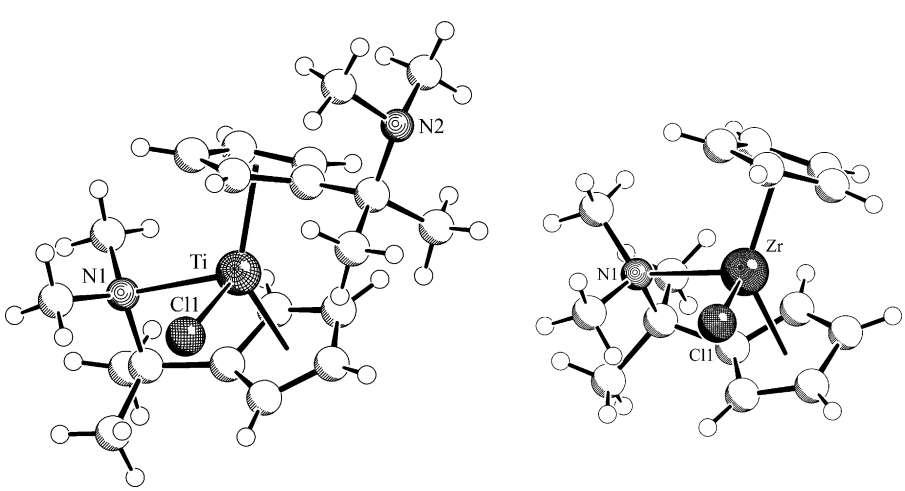
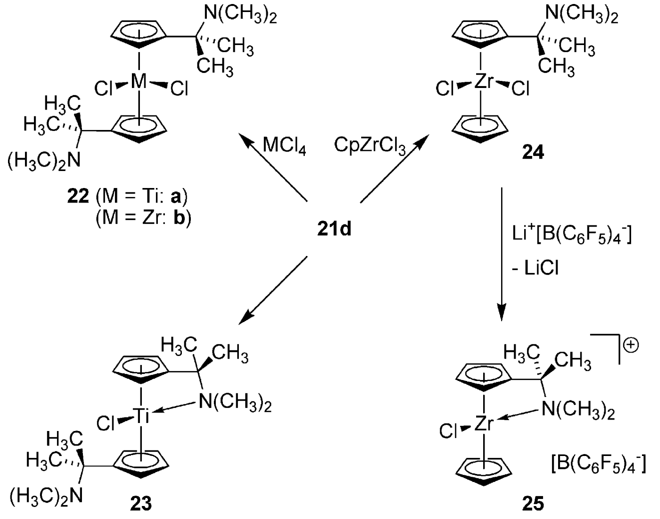


Fig. 2. A comparison of the molecular structures of the internally stabilized neutral Ti(III) complex **23** (left) and the cationic Zr(IV)$^+$ complex **25** (right, only the cation is depicted).



Scheme 8.

Attack of [Zr]–$CH_3$ at an adjacent –$NMe_2$ methyl group with liberation of methane yielded the $\eta^2$-iminium-type CH activation product **29**. It features a metallacyclic three-membered ring structure in solution ($^{13}C$ NMR, [Zr]$CH_2$[N]: $\delta$ 49.1, $^1J_{CH} = 147$ Hz) as well as in the solid state (Zr–$CH_2$(N): 2.251(1) Å, see Fig. 3). The reaction sequence starting from **24** is similar. Again the reaction proceeds by rapid subsequent methane evolution. The resulting $\eta^2$-iminium-type product (**30**) can be stabilized by the addition of external donor ligands. The tert.-butylisocyanide adduct (**31b**) was characterized by X-ray diffraction (see Fig. 3 and Scheme 9) [26].

The CH-activation products (e.g. **29**, **30**) contain a reactive zirconium-carbon bond at the easily accessibly open front side of the bent metallocene wedge. They consequently react with a variety of unsaturated organic reagents to form the respective insertion products. As a typical example, the cation **30** readily reacts with conjugated dienes to yield **32**. Styrene is inserted to yield the product **33** where some extra stabilization is achieved by $\eta^3$-coordination of the resultant benzylic subunit (see Scheme 10 and Fig. 4) [26].

## 3. Phosphorus containing systems

The analogous P-containing ligand systems can in many cases readily be prepared by nucleophilic phosphide addition to the electrophilic C6 carbon atom of the unfunctionalized pentafulvene substrates. A typical example is the $LiPAr_2$ addition to 1,2,3,4-tetramethylfulvene – which is conveniently prepared by

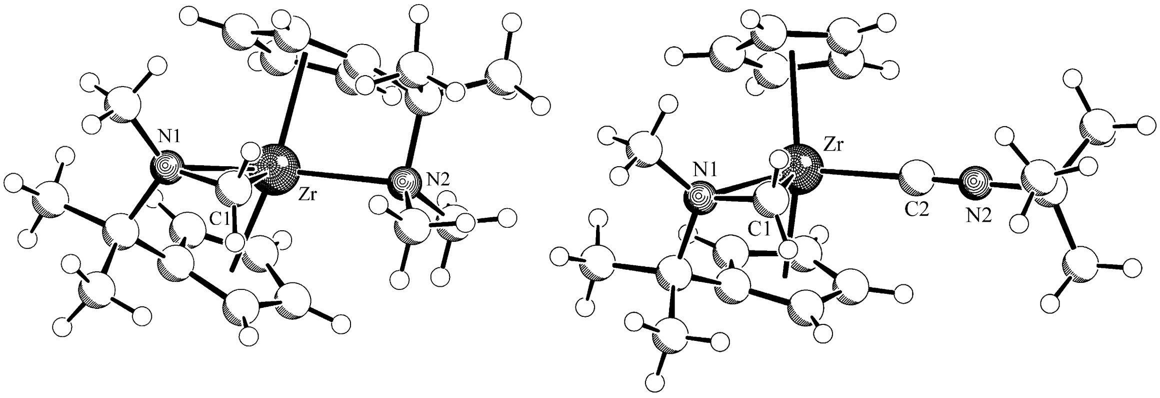
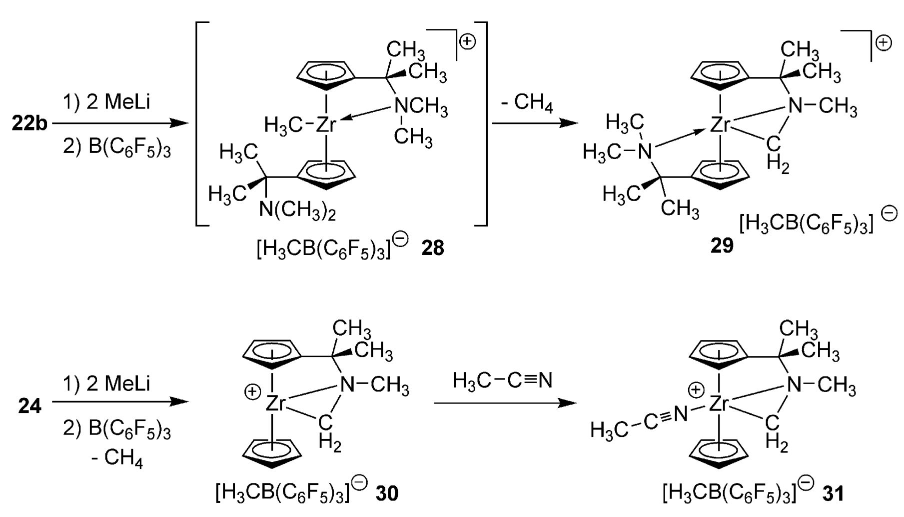
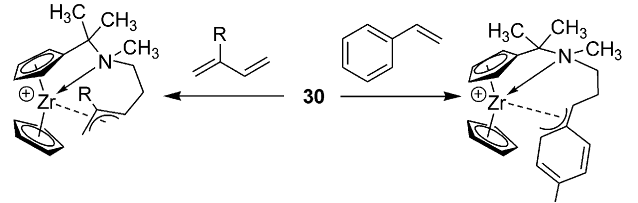


Fig. 3. Molecular structures of the $\eta^2$-iminium-type zirconocene cation complexes **29** (left) and **31b** (right), only the cations are depicted.



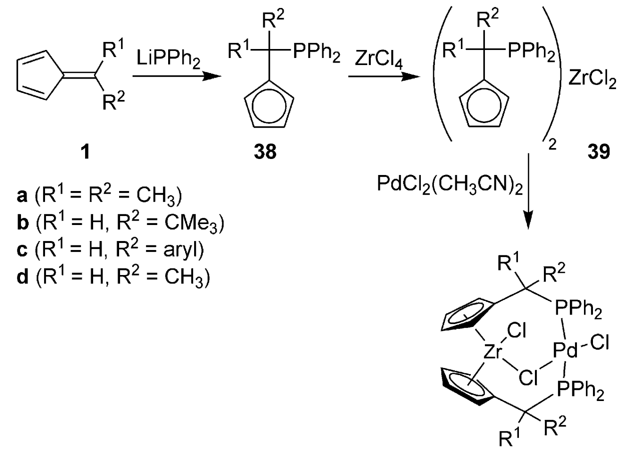
Scheme 9.



**32**
R = H (**a**), $CH_3$ (**b**)

**33**
R = H (**a**), $CMe_3$ (**b**)

Scheme 10.



**1** **38** **39**

**a** ($R^1 = R^2 = CH_3$)
**b** ($R^1$ = H, $R^2 = CMe_3$)
**c** ($R^1$ = H, $R^2$ = aryl)
**d** ($R^1$ = H, $R^2 = CH_3$)

**40**

Scheme 12.

hydride abstraction from $Me_5C_5$ anion – to yield the anionic $C_5Me_4(CH_2PAr_2)$ ligand system **36** (Scheme 11) [27]. Subsequent transmetallation to Zr then gave **37**.

The fulvenes **1** add $LiPPh_2$ cleanly to yield the phosphinoalkyl-Cp anion equivalents **38**. Transmetallation gives the phosphino-substituted zirconocenes that may serve as flexible bidentate chelate ligands. Addition to, e.g. $PdCl_2(CH_3CN)_2$ yielded the heterobimetallic complexes **40**. The X-ray crystal structure analysis of a typical example (**40b**) has revealed a μ-Cl bridged structural framework (see Fig. 5 and Scheme 12) [28].

Treatment of **39a** with methyl lithium gave **41** from which one methyl group was readily abstracted with $B(C_6F_5)_3$ to yield the cation complex **42** [26,29]. An X-ray crystal structure analysis revealed that both $-PPh_2$ groups in **42** were symmetrically coordinated to zirconium. Subsequent treatment with another equivalent of $B(C_6F_5)_3$ removed the remaining σ-methyl ligand at zirconium with formation of the bis(phosphinoalkylCp) stabilized organometallic dication system **43**. The reactive dication complex **43** can be stabilized by donor ligand addition (e.g. by acetonitrile to form **45**). Complex **43** is so reactive that it is able to abstract chloride from dichloromethane solvent to yield **44** (see Scheme 13) [29].

## 4. Enamino substituted Cp-systems

The competition between nucleophilic addition to, e.g. 6-dimethylamino-6-methylfulvene (**20b**) and α-deprotonation is critically dependent on the reaction conditions. As described above, treatment of **20b** with methyl lithium in ether gave the addition product **21d** (see Scheme 6). In contrast the reaction of **20b** with MeLi in THF or, alternatively, treatment of **20b** with LDA gave rise to the formation of the (aminoalkenyl)CpLi

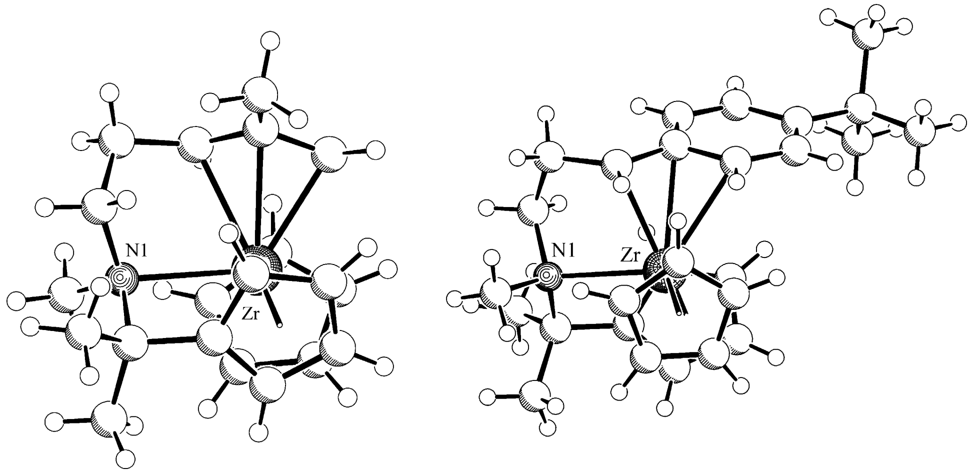
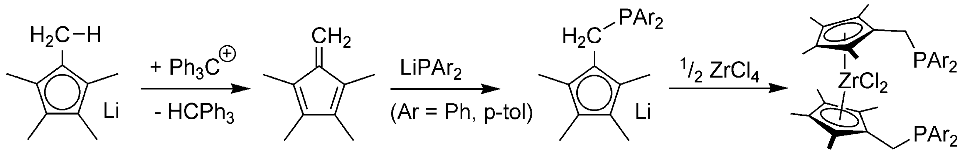


Fig. 4. Views of molecular structures of the complexes **32b** (left) and **33b** (right).



**34** **35** **36** **37**

Scheme 11.

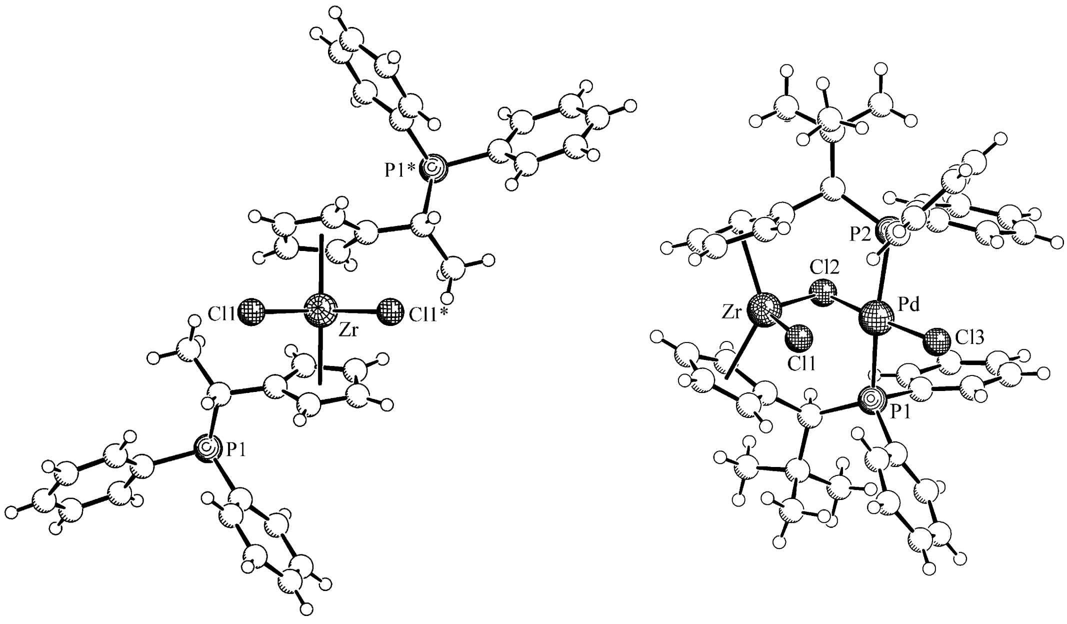


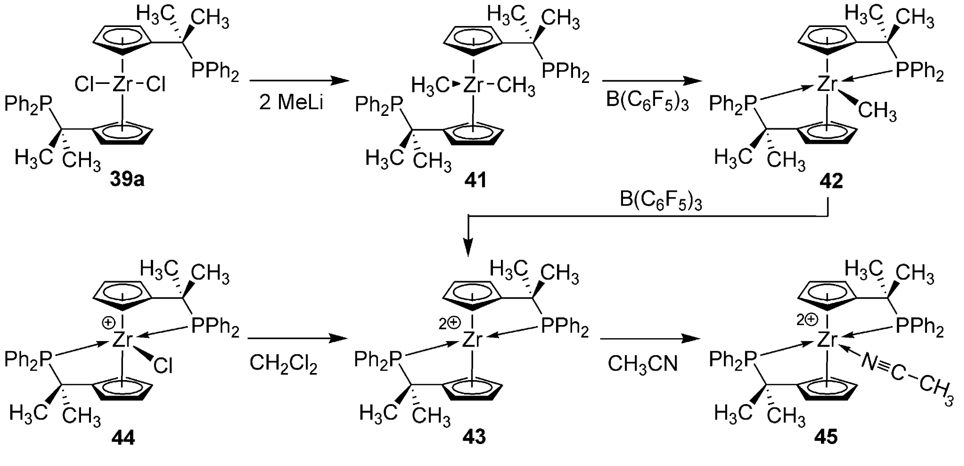
Fig. 5. Views of the molecular structures of the complexes **39d** (left) and **40b** (right).

product **46a** (see Scheme 14) [30]. The deprotonation pathway is also favoured in the case of the 6-diethylamino-6-methylfulvene (**20c**) to yield **46b**, even with MeLi in ether. Transmetallation of **46b** with $ZrCl_4$ gave the (enamino-Cp)$_2$$ZrCl_2$ product **47b** (see Scheme 14 and Fig. 6). The similar reaction of the reagent **46a** with $CpZrCl_3$ gave the mono-enamino-substituted metallocene product $[C_5H_4{-}C(NMe_2){=}CH_2]CpZrCl_2$ (**48**). It was reacted with "butadiene-magnesium" [31] to generate a (butadiene)-metallocene complex (**49**) [32] that was not stable under the applied reaction conditions due to a very rapid subsequent intramolecular CH-activation reaction at a *N*-$CH_3$ methyl group to eventually give the observed final product **50**.

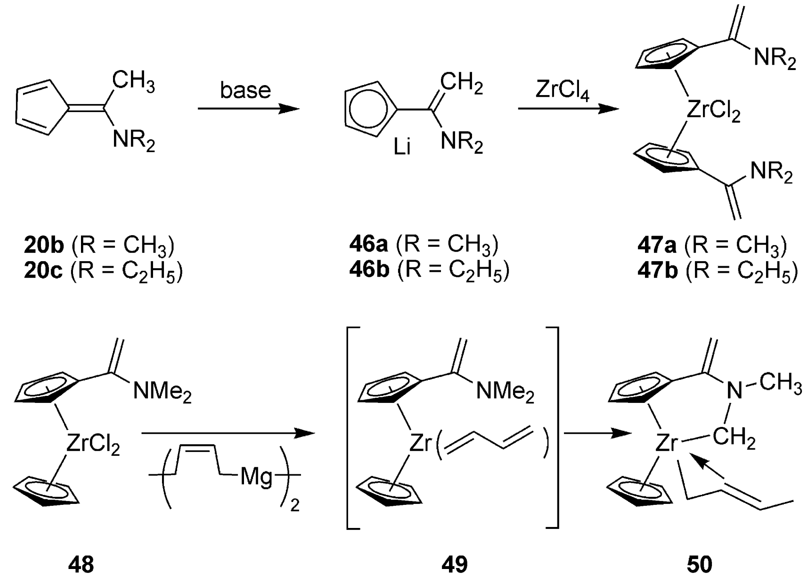
The bis(enamino-Cp)$ZrCl_2$ systems allowed for a unique development of a CC-coupling methodology at the framework of the bent metallocene units. This may represent a development toward establishing a typical organic functional group chemistry at the very sensitive Group 4 metallocene complexes, here using a typical reaction type from the important family of the aldol condensation type of reactions.

The enamino-Cp ligands **46c** and **46d** were prepared by the usual fulvene route. Transmetallation gave the functionalized metallocene complexes **47c**,**d**. Treatment of each of these compounds by catalytic amounts of either a *Brønsted* acid ($[PhNMe_2H^+][BPh_4^-]$) or a *Lewis* acid ($ZrCl_4$) resulted in the rapid occurrence of a *Mannich*-type CC-coupling [33] and condensation reaction to yield the respective $C_3$-bridged unsaturated ansa-metallocene complexes **51c** and **51d** with elimination of piperidine or morpholine, respectively (see Scheme 15) [34,35].

The intramolecular *Mannich* coupling of the parent (dimethylamino)ethenyl-substituted system occurs even much more facile. It can usually be achieved as a one pot reaction in conjunction with the transmetallation step, making use of the presence of the strongly *Lewis* acidic Group 4 metal halides to act as a suited catalyst for the *Mannich*-type CC-coupling sub-



Scheme 13. All cations with $[H_3CB(C_6F_5)_3^-]$ counter anion.



Scheme 14.

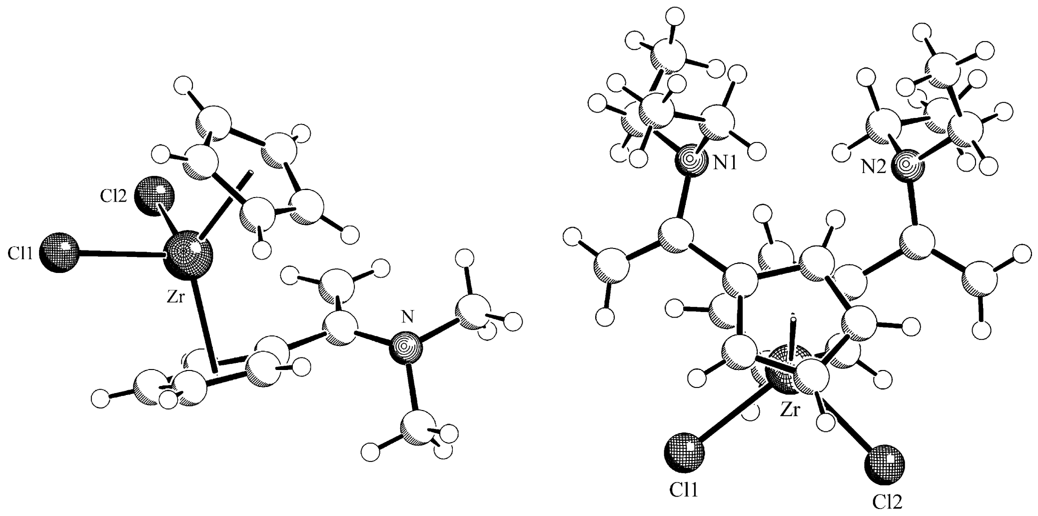


Fig. 6. Views of the molecular structures of the enamino-substituted bent metallocene complexes **48** (left) and **47b** (right).

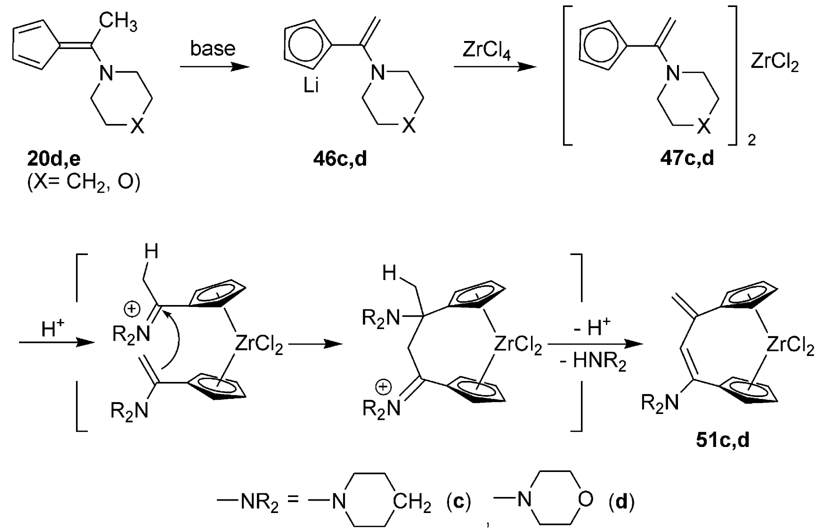
sequent to the formation of the ($C_5H_4$–C($NMe_2$)=$CH_2$)$_2$$MCl_2$ systems (**47**). Both the corresponding ansa-metallocene complexes **51a** (M = Zr) and **51b** (M = Hf) were readily obtained by the one pot procedure and isolated in good yield (Scheme 16 and Fig. 7) [35].

This reaction type turned out to be so advantageous that it was even adapted to ferrocene chemistry, although alternative [3]ferrocenophane syntheses had been available for some time [36]. Treatment of 1,1′-diacetylferrocene (**52**) with a suitable secondary amine in the presence of a catalytic quantity of, e.g. $TiCl_4$ readily gave the respective unsaturated [3]ferrocenophane amine by the intramolecular *Mannich* condensation reaction (e.g. **53a** from **52**, dimethylamine and $TiCl_4$, see Scheme 17 and Fig. 7) [37].

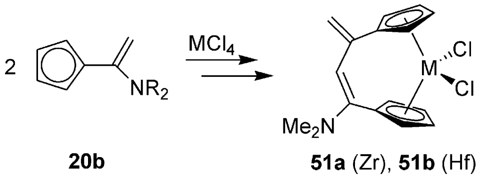
This [3]ferrocenophane synthesis provided the basis for a very successful entry to chiral ferrocene-based chelate ligands for asymmetric catalysis. The sequence started with a trans-selective catalytic hydrogenation of the framework followed by resolution of the resulting racemate and transformation/introduction of the required functional groups. Pd complexes of, e.g. the enantiomerically pure ligand system **55** were successfully employed in asymmetric hydrogenation or asymmetric alternating CO/propene polymerization yielding an optically active polyketone [38].

## 5. CpCN and CpCP constrained geometry systems

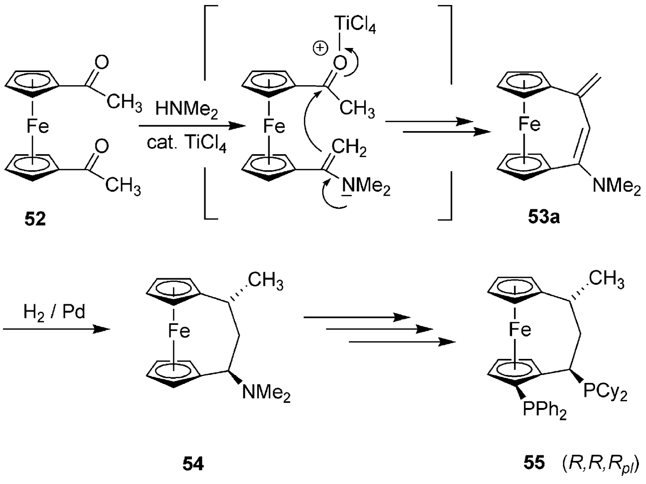
Group 4 metallocene *Ziegler-Natta* catalysts have become of great significance in the recent years [39]. Their silylene-bridged Cp/amido Group 4 metal complex analogues—the “constrained geometry systems” represent an important subgroup of this general catalyst family [40,41]. The “CpSiN”$MX_2$ systems (**56**)



Scheme 15.



Scheme 16.



Scheme 17.

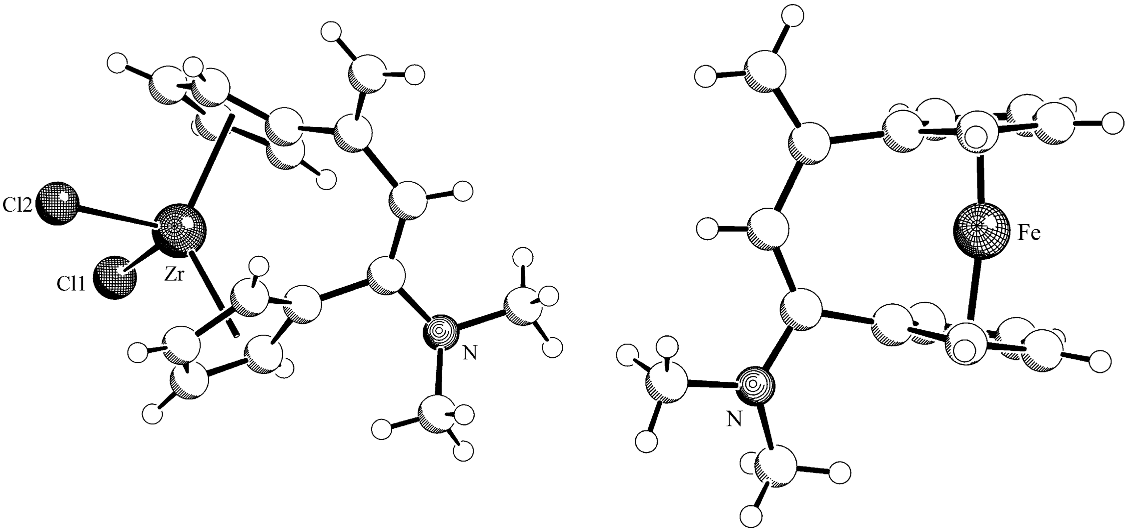
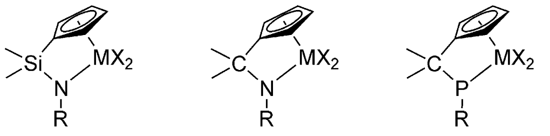


Fig. 7. Views of the $C_3$-bridged unsaturated ansa-zirconocene **51a** (left) and the related [3] ferrocenophane **53a** (right).

are much more open than the corresponding ansa-metallocene complexes. They have found significant use in catalytic ethene/1-alkene copolymerization applications. Much less had been known about the related "CpCN" or "CpCP" systems (**57**, **58**), where the silicon bridge of the ubiquitous Cp/amido catalyst precursors was formally replaced by a $C_1$-bridge. It has recently been shown that such systems can be obtained in straightforward synthetic ways by means of fulvene routes.



"CpSiN"$MX_2$ (**56**) "CpCN"$MX_2$ (**57**) "CpCP"$MX_2$ (**58**)

Scheme 18.

Some of these recent developments shall briefly be outlined in this section (Scheme 18).

An early example of a derivative of a "CpCN" dianion equivalent was prepared by a variant of the isocyanate addition reaction, depicted in the Introduction (see Scheme 3). Fluorenyl lithium (**60**) was added to *tert*-butyl isocyanate to yield **61**. Subsequent reduction of the amide functionality gave the 6-aminodibenzofulvene derivative **62** that was then further reduced to eventually yield the ligand precursor **63**. Treatment of **63** with *tert*-butyl lithium gave rise to the formation of the dianion **64** (see Scheme 19 and Fig. 8) that was characterized by X-ray diffraction. Unfortunately, this route to a "CpCN" dianion ligand system proved unsuited for a practical "CpCN"$MX_2$ synthesis because of several competing pathways that led to complicated anionic product mixtures [42].

A practical preparative pathway was opened by amine exchange of 6-dimethylamino-6-methylfulvene (**20b**) by treatment with excess $NH_3$. The resulting parent 6-amino-6-methylfulvene (**20f**) was *N*-silylated and then α-deprotonated with LDA to yield **66**. Transmetallation with $MCl_4$ (M = Ti, Zr) led to the formation of the "spiro"-system **67**, whereas treatment with the $[Cl_2Zr(NEt_2)_2(THF)_2]$ reagent (**69**) cleanly yielded the $sp^2$-C-bridged "CpCN"$ZrX_2$ constrained geometry catalyst precursor **68** (Scheme 20) [43].

$sp^3$-C-bridged "CpCN"$MX_2$ systems were prepared by either of two related alternative synthetic routes. The first also involved an amine exchange reaction, albeit in this case starting from the "non-enolizable" 6-dimethylaminofulvene precursor **20a**. Its treatment with, e.g. lithium anilide (**70**) gave rise to the formation of the anionic exchange product **71**. The X-ray crystal structure analysis of **71** showed a dimeric electrostatic $\eta^5$-Cp/$\kappa$N-type structure in the solid state (see Fig. 9) [44]. The anion **71** is probably best described by a resonance hybrid of a fulvenoid (A) and an imino-Cp-type structure (B) [observed d(C6–N): 1.295(3) Å]. Consequently, a variety of R-Li reagents (MeLi, aryl-Li) add to C6 of the mono-anionic reagents **71** to form the dianionic "CpCN" ligand systems **72**. Transmetallation with $[Cl_2Ti(NMe_2)_2]$ then gave the $C_1$-bridged constrained geometry systems **73** [45]. Replacement of the pair of $-NMe_2$ groups at titanium was achieved by subsequent treatment with $Cl_2SiMe_2$ to yield the "CpCN"$TiCl_2$ systems **74** (see Scheme 21) [46]. These were then transformed to the "CpCN"$Ti(CH_3)_2$ derivatives (**75**, see Fig. 10) which proved to be precursors of active homogeneous *Ziegler-Natta* catalysts. The performance of these catalysts depended critically on the activation methods applied [45].

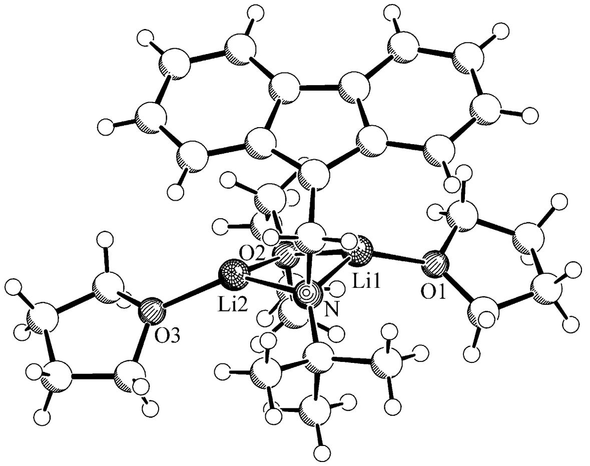
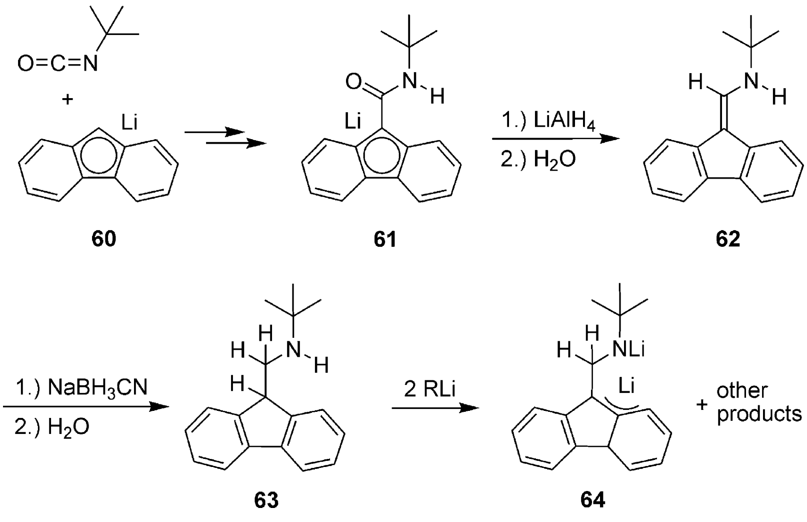
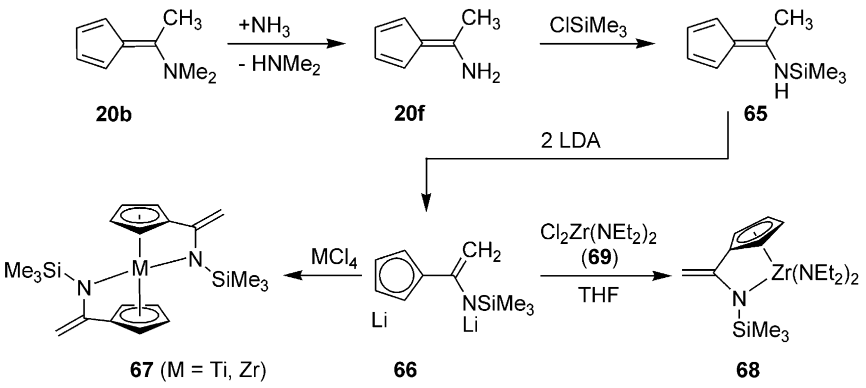


Fig. 8. Molecular structure of the "dibenzo-CpCN" dianion equivalent **64**.

An alternative synthetic route to "CpCN"$MX_2$ systems starts from 6-alkylfulvenes (e.g. **1b**). In this case the addition of lithium amides LiNHR (R = alkyl or aryl) results in the formation of the mono-anions (**76**) that were further deprotonated by LDA to



Scheme 19.



Scheme 20.

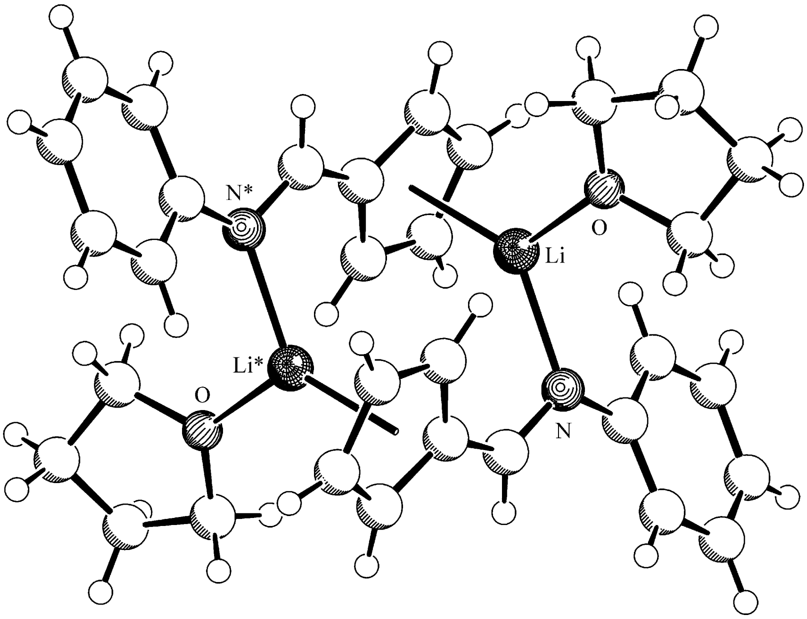
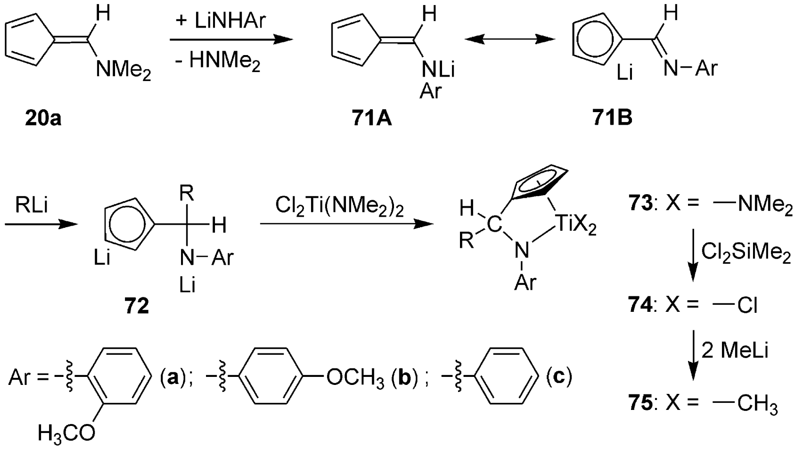


Fig. 9. Dimeric molecular structure of the reagent **71c** (Ar = phenyl) in the crystal.

yield the dianions (**77**). Transmetallation with [$Cl_2Ti(NMe_2)_2$] – and in one case with [$Cl_2Zr(NMe_2)(THF)_2$] [45] – then gave way to the formation of the respective "CpCN"$MX_2$ systems (see Scheme 22) [47]. The "CpCN"$MX_2$-derived homogeneous *Ziegler-Natta* catalysts showed in several respect features different from their conventional "CpSiN"$MX_2$ analogues [45].

Treatment of sodium cyclopentadienide with ethyl acetate yields "acetylcyclopentadienide" (**81**), an anionic system that



Scheme 21.

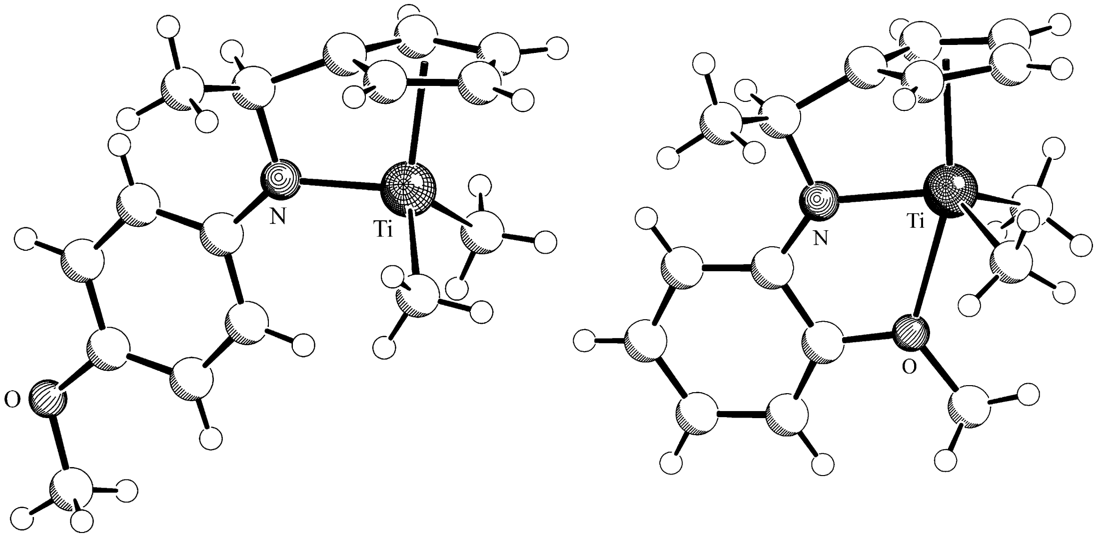
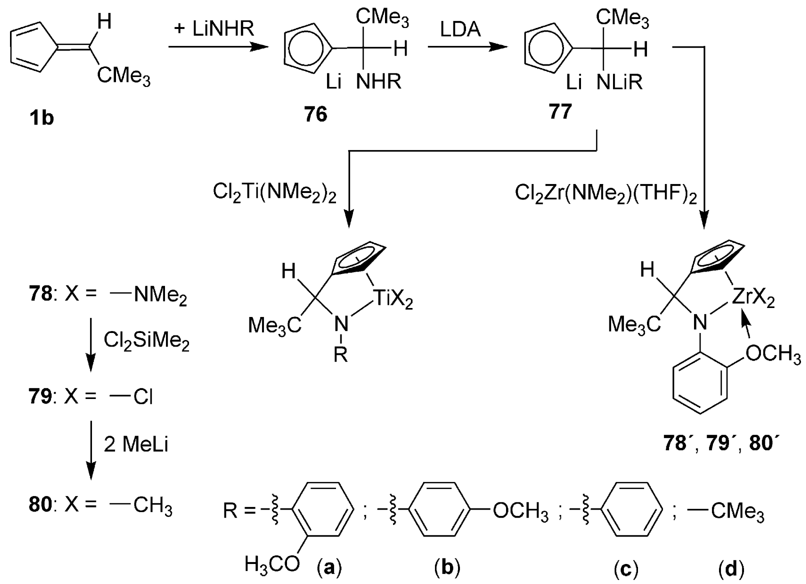


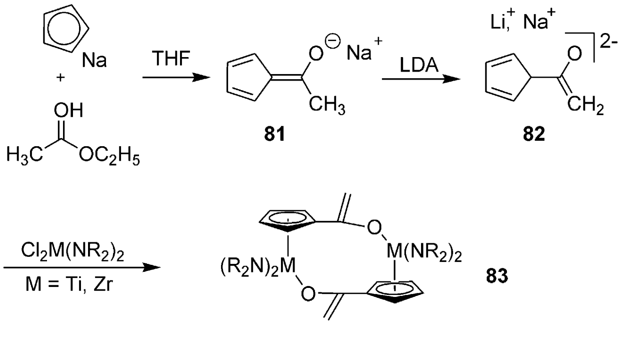
Fig. 10. A comparison of the molecular structures of the “CpCN”Ti($CH_3$)$_2$ complexes **75a** (right) and **75b** (left).



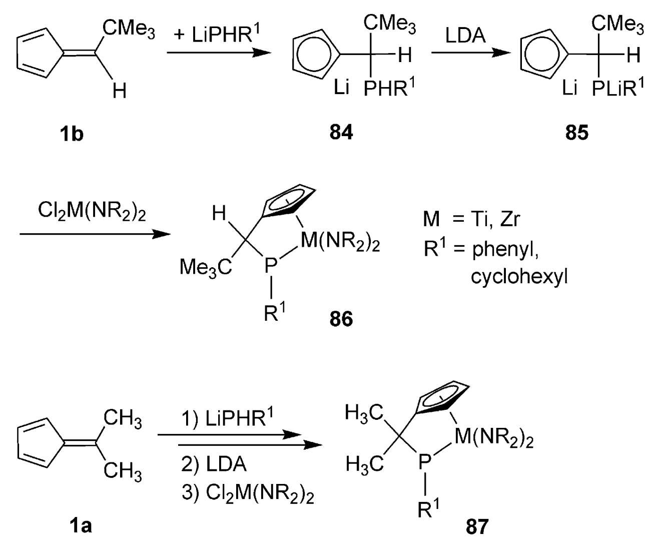
Scheme 22.

exhibits a considerable fulvenoid structure [20,48]. Its treatment with LDA results in a clean α-deprotonation with formation of the dianionic reagent **82**. Transmetallation gave the “CpCO”$MX_2$ systems (**83**). However, their analysis revealed a cyclodimeric structure in solution as well as the solid state. Nevertheless, activation with methylalumoxane (MAO) gave active olefin homo- and copolymerization catalysts. At 90 °C an ethene/1-octene copolymer was formed that had up to 20% of the linear 1-alkene component incorporated [49] (Scheme 23).

“CpSiP”$MX_2$ systems were recently prepared by means of a conventional route [50]. Their “CpCP”$MX_2$ analogues have become available by variations of the fulvene route to Cp-type ligand systems. Addition of LiPHR reagents to the “non-enolizable” 6-*tert*-butylfulvene (**1b**) followed by deprotonation (LDA) and transmetallation gave the “CpCP”M($NR_2$)$_2$ systems (**86**) [51–53] The low basicity of the lithium phosphido reagents even allowed for the successful $PHR^-$ addition (R = phenyl or cyclohexyl) to 6,6-dimethylfulvene to eventually yield the corresponding isopropylidene-bridged “CpCP”$MX_2$ compounds **87**. All these systems gave interesting olefin copolymerization catalysts upon suitable activation [51] (Scheme 24).



Scheme 23.



Scheme 24.

## 6. Some conclusions

Unfunctionalized alkyl-substituted fulvenes have long been used as substrates for the preparation of cyclopentadienide ligands. The extension of this methodology to various functionalized fulvene systems, as illustrated by various nitrogen and phosphorus bearing pentafulvene systems and their derivatives described in this article, has substantially increased the synthetic potential of this general route. With regard to the chemistry of early transition metal metallocene complexes and related systems this has opened two significant principal synthetic entries. Firstly, a variety of interesting new functional groups and functionalized frameworks could be constructed prior to the transmetallation step to yield the respective functionalized Group 4 metal complex systems. This often constitutes a very important synthetic procedure since the very sensitive Group 4 bent metallocene complexes had previously not allowed for any substantial organic functional group chemistry to be carried out at the π-ligand framework after transmetallation to the d-metal. It will remain essential to introduce a variety of specific functional groups at the stage of the preceding ligand framework assembly steps due to the high sensitivity of the Group 4 metal targets.

The described work has, however, also demonstrated that first steps have successfully been taken to overcome this serious synthetic limitation of early transition metal metallocene chemistry [54]. Advanced fulvene chemistry has, e.g. opened novel pathways to eventually carry out intramolecular *Mannich* coupling reactions at the framework of the intact Group 4 bent metallocene complexes. Carrying out such reactions from the important family of the organic aldol-type condensation reactions successfully at these very sensitive substrates must be regarded a significant advancement of organometallic synthetic methodology, that will probably have substantial implication for the future design of novel advanced catalyst systems. Reactions of functionalized fulvene-derived systems have marked the beginning of this development—fulvene chemistry is expected to continue to play a significant role in this development for some time in the future.

## Acknowledgements

G.E. cordially thanks his many coworkers and collaborating colleagues for their valuable contributions to the own work by the Erker group that is described in this article. Generous support of some of this work by the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt Foundation and the Fonds der Chemischen Industrie is gratefully acknowledged.

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