

Ansa-Metallocenes by Intramolecular Ring Closure Reactions – Syntheses and Applications

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Summary: Examples of a functional group chemistry at the Group 4 bent metallocene frameworks are presented and discussed that allow for the preparation of ansa-metallocenes at the stage of the intact organometallic complexes. These examples include ansa-metallocene formation by means of intramolecular olefin metathesis reactions, by photochemical [2+2] cycloadditions of pendant olefinic moieties and even of a Mannich-type carbon–carbon coupling reaction of enamino substituents attached at the Cp-rings. Many of the resulting ansa-metallocene systems were employed as components of reactive homogeneous Ziegler–Natta olefin polymerization and copolymerization catalysts. The Mannich coupling reaction was also used in ^[3]ferrocenophane chemistry, eventually leading to novel chelate ligand systems that were employed in catalytic asymmetric polyketone formation.

Keywords: ansa-metallocenes; functional groups; olefin polymerization; zirconium

Introduction

Ansa-metallocenes of the Group 4 metals and related systems have extensively been applied as catalyst precursors for the generation of very active and often at the same time quite selective homogeneous Ziegler–Natta olefin polymerization catalysts.^[1] Mostly the necessary specific substituent pattern at the ligand framework is attached and constructed prior to the final transmetallation step. A typical organic functional group chemistry at the stage of the intact bent metallocene complexes is close to non-developed.^[2] In this situation we have asked ourselves if it were possible to develop a specific functional group chemistry at the Group 4 bent metallocene frameworks, designed to form the respective ansa-bridges, by carefully selecting specific functional groups and specific reaction types and reaction conditions that were compatible with the typical features and chemical needs of these rather sensitive organometallic systems.

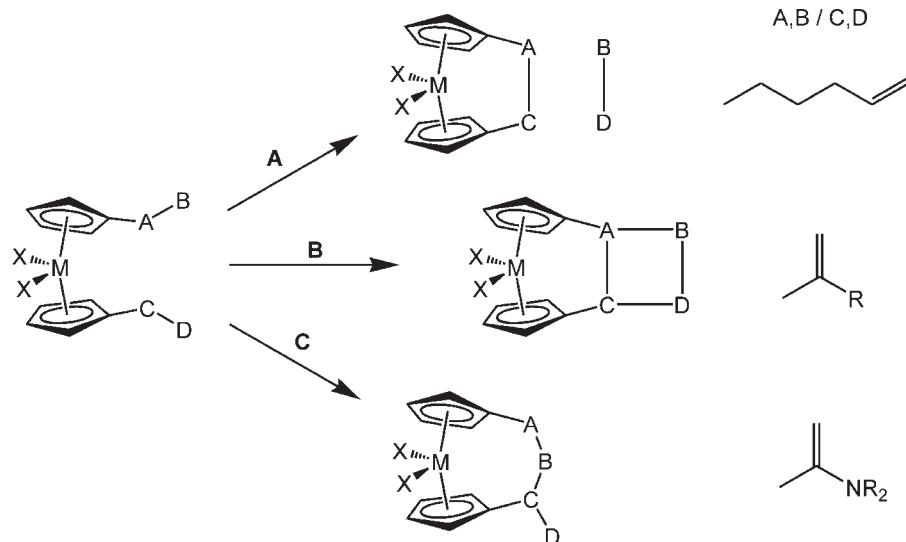
Some successful developments in this direction have recently been carried out by us. In this account we will briefly illustrate three lines of such synthetic organometallic developments and discuss selected examples. These will include olefin metathesis reactions (**A**), intramolecular photochemical [2+2] cycloadditions (**B**) and eventually an example from the important family of the aldol-type carbon–carbon coupling reactions, namely an intramolecular Mannich-type condensation (**C**) that all can be carried out in the ligand sphere of an intact Group 4 metallocene under the appropriate reaction conditions (see Scheme 1).

Results and Discussion

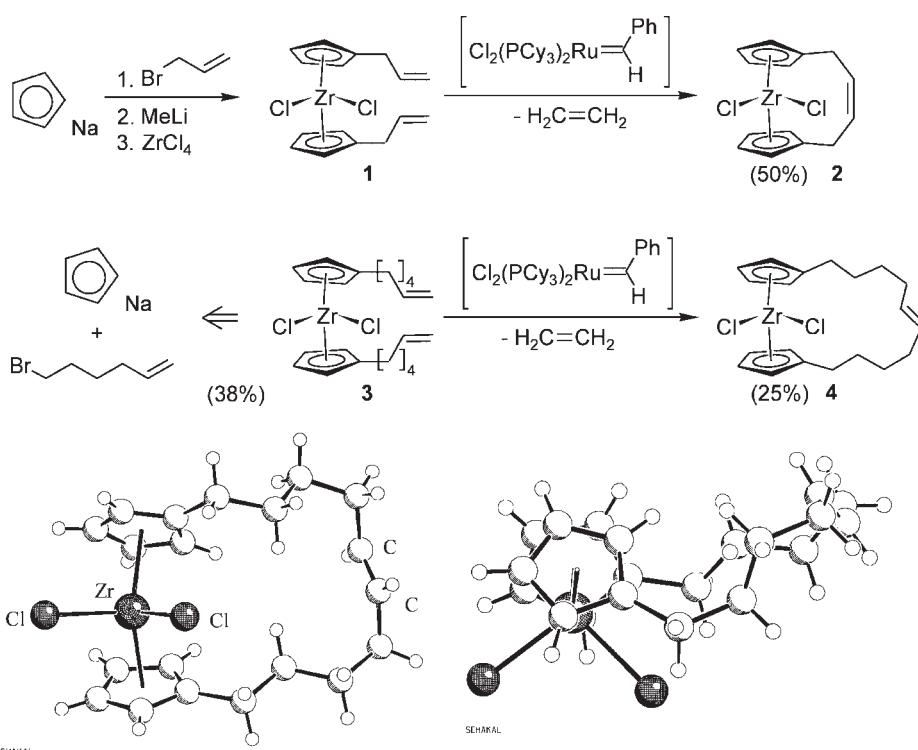
Olefin Metathesis Reactions

Over the recent years the metal carbene complex catalyzed olefin metathesis reaction has developed into a very powerful tool in organic synthesis.^[3] It tolerates a great number of functional groups, so why not even the sensitive Group 4 bent metallocenes. Conversely, the necessary functional reagent, e.g. the $-\text{CH}=\text{CH}_2$ functionality is

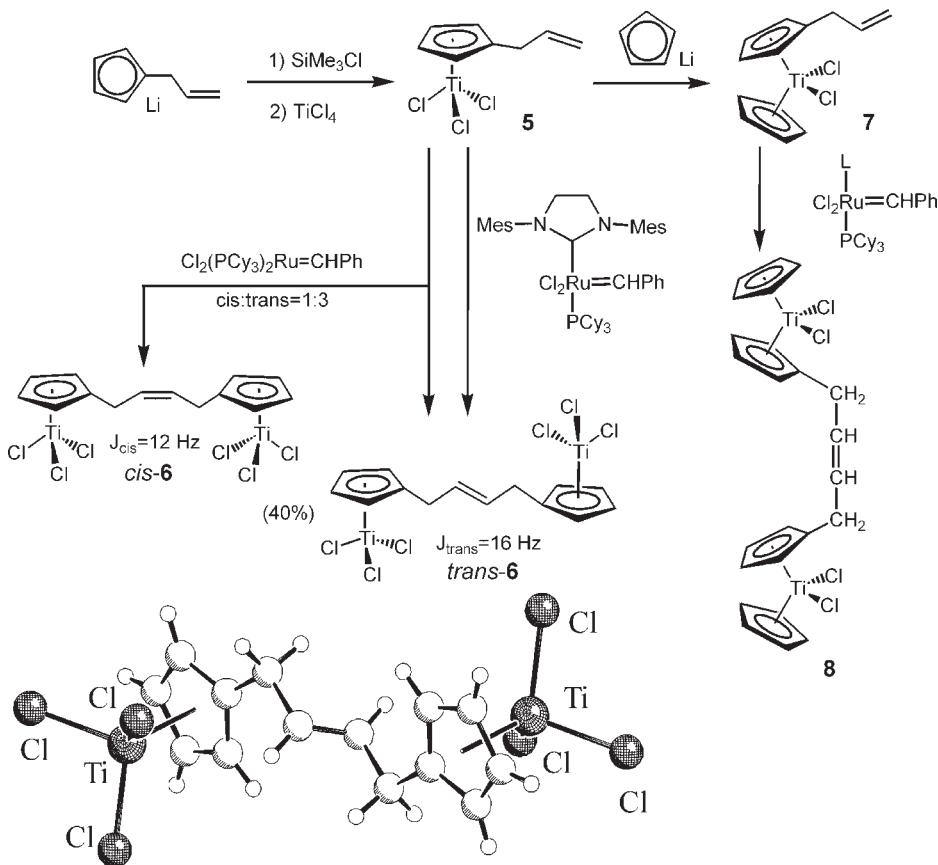
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**Scheme 1.**

General Scheme of Functional Group Coupling Reactions Carried out at the Group 4 Bent Metallocene Framework.

**Scheme 2.**

Formation of ansa-zirconocenes by intramolecular olefin metathesis.

**Scheme 3.**

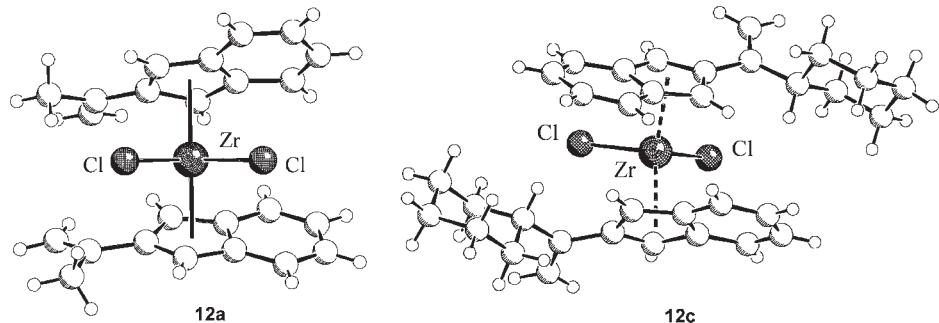
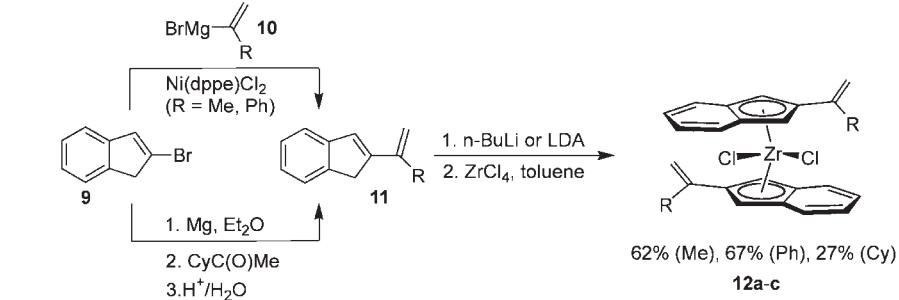
Intermolecular Metathesis Coupling Reactions of Group 4 Organometallic Systems.

compatible with the specific features of most titanocene, zirconocene and hafnocene systems.

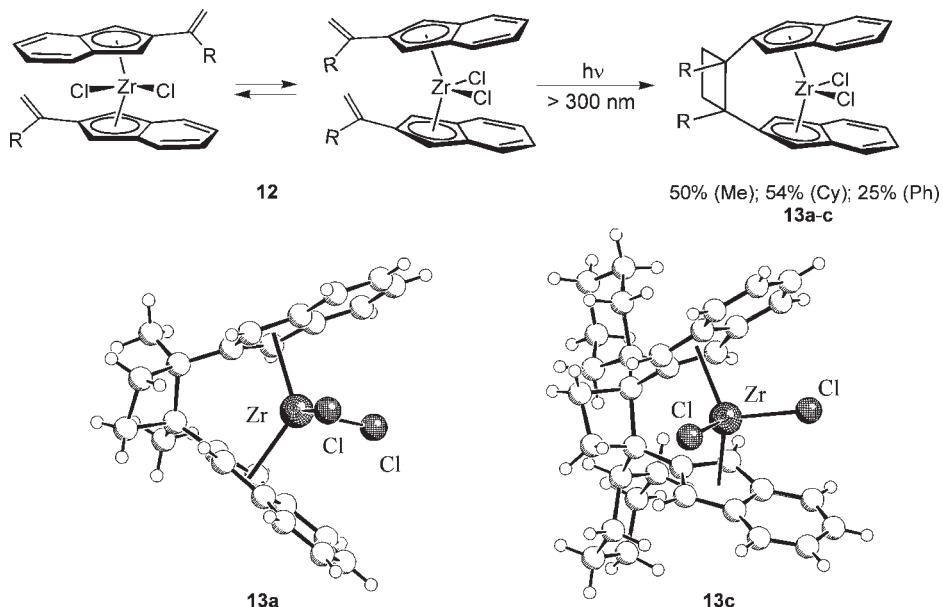
Bis(allyl-Cp) ZrCl_2 (**1**) was prepared in a straightforward way. Its treatment with the Grubbs I catalyst [$(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$] readily gave the olefin metathesis product (**2**, ca. 50% isolated) with formation of ethene.^[4] This ring closing metathesis reaction seems to be generally applicable for the preparation of ansa-metallocenes. Another typical example from our research group is the synthesis of the “large ansa-metallocene” (**4**) that features an unsaturated C_{10} -bridge between the pair of Cp-ligands at zirconium. Complex **4** was obtained in 25% yield upon treatment of bis(hexenyl-Cp) ZrCl_2 with the $[\text{Ru}]=\text{CHPh}$ metathesis catalyst. Both the com-

plexes **2** and **4** were characterized by X-ray crystal structure analyses. The newly formed $\text{C}=\text{C}$ double bond inside the ansa-bridge is cis-configurated in **2**, which is probably enforced by the ring-size, whereas complex **4** features a trans- $\text{C}=\text{C}$ double bond as part of the bridge.

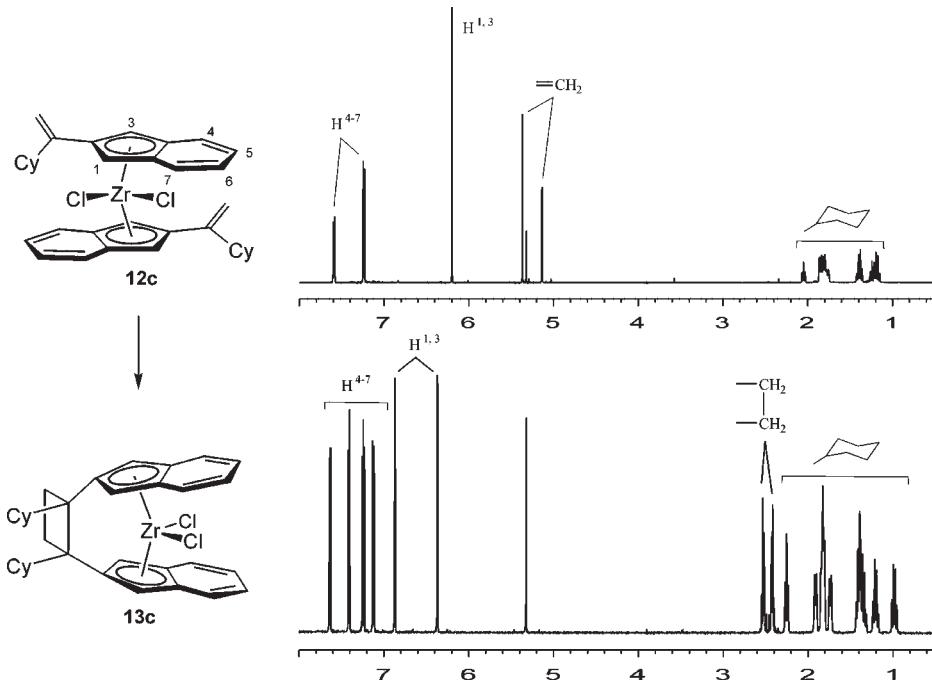
The olefin metathesis reaction was also used for the intermolecular coupling of suitably functionalized Group 4 metallocenes and related compounds.^[5] We regard the development of this synthetic organometallic methodology as important for the ongoing quest of cooperative effects in homogeneous Ziegler-Natta catalysis.^[6] For this reason we reacted (allyl-Cp) TiCl_3 (**5**) with the Grubbs I ruthenium-based olefin metathesis catalyst. The rapid reaction gave a ca. 1:3 mixture of the cis-**6** and

**Scheme 4.**

Synthesis and Structures of the Bis(2-alkenylindenyl) ZrCl_2 Complexes 12.

**Scheme 5.**

[2+2] Cycloaddition of the Bis(2-alkenylindenyl) ZrCl_2 Complexes.

**Scheme 6.**¹H NMR Spectra and Photochemical Conversion of **12c** to **13c**.

trans-**6** metathesis products (see Scheme 3). The corresponding reaction with the respective imidazol-2-ylidene-derived Grubbs II metathesis catalyst proceeded much faster and eventually yielded predominantly the trans-**6** product isomer.^[6] The intermolecular metathesis coupling reactions of the related metallocene complexes (e.g. **7** → **8**) proceeded equally facile and showed similar reaction characteristics.^[5,7] The metathesis product trans-**6** was characterized by X-ray diffraction.^[6]

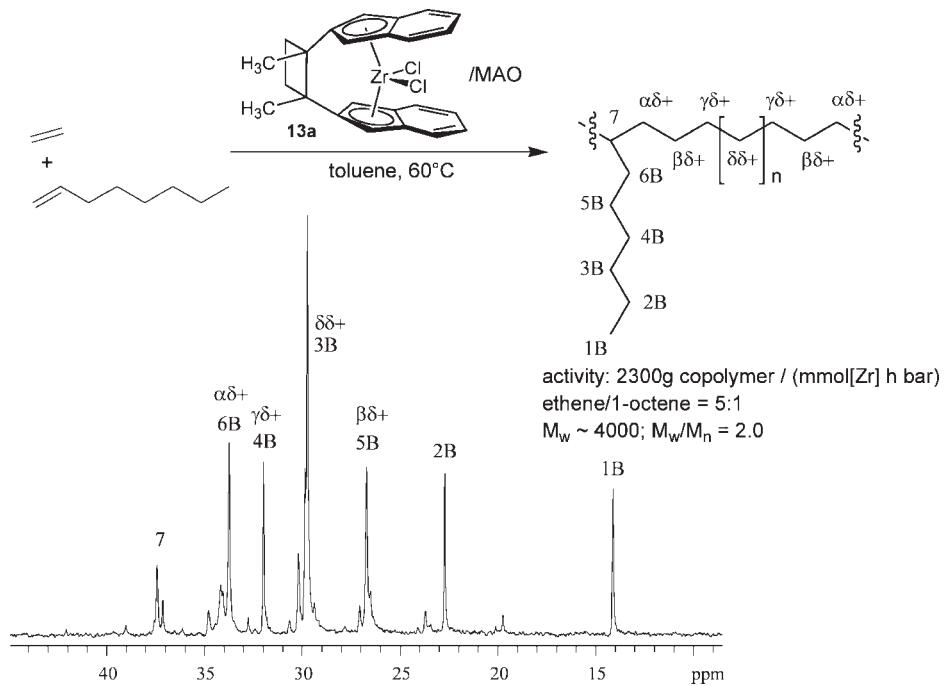
Photochemical [2+2] Cycloaddition Reactions

Photochemical [2+2] cycloaddition reactions of conjugated alkenyls have been used for the construction of cyclobutane ring systems.^[8] To apply this method to organometallic systems^[9] required the attachment of suitable alkenyl functional groups to the Cp- or indenyl rings of the respective Group 4 metallocene systems. This was achieved by classical synthetic routes. 2-Bromoindene (**9**) was cross-coupled with

a variety of alkenyl Grignard reagents (**10**) with the aid of a nickel catalyst to yield the 2-alkenyl-indene reagents **11**. In one case ($R = \text{cyclohexyl}$) the alternative route via generation of the indenyl Grignard reagent followed by carbonyl addition and elimination was more favorable. Subsequent deprotonation and transmetallation eventually yielded the bis(2-alkenylindenyl)ZrCl₂ complexes **12(a-c)**.^[10]

The functionalized bis(indenyl)zirconium complexes **12** undergo a rapid conformational equilibration in solution. Out of this equilibrium a rapid intramolecular [2+2] cycloaddition reaction is effected upon UV-irradiation to yield the corresponding cyclobutylene-bridged ansa-zirconocenes **13(a-c)**. These products were isolated as crystalline solids after recrystallization. The products **13a** and **13c** were characterized by X-ray diffraction (see Scheme 5).^[10]

In some cases the ansa-metallocene formation by intramolecular photochemical [2+2] cycloaddition is fast and goes

**Scheme 7.**Ethene/1-Octene Copolymerization with the **13a**/MAO Catalyst System.

rapidly to completion. Scheme 6 shows such an example. Irradiation of a solution of complex **12c** in CD_2Cl_2 at ambient temperature leads to a close to quantitative conversion to the ansa-metallocene product **13c** within ca. 30 min., as judged by the typical ^1H NMR spectra of these compounds.

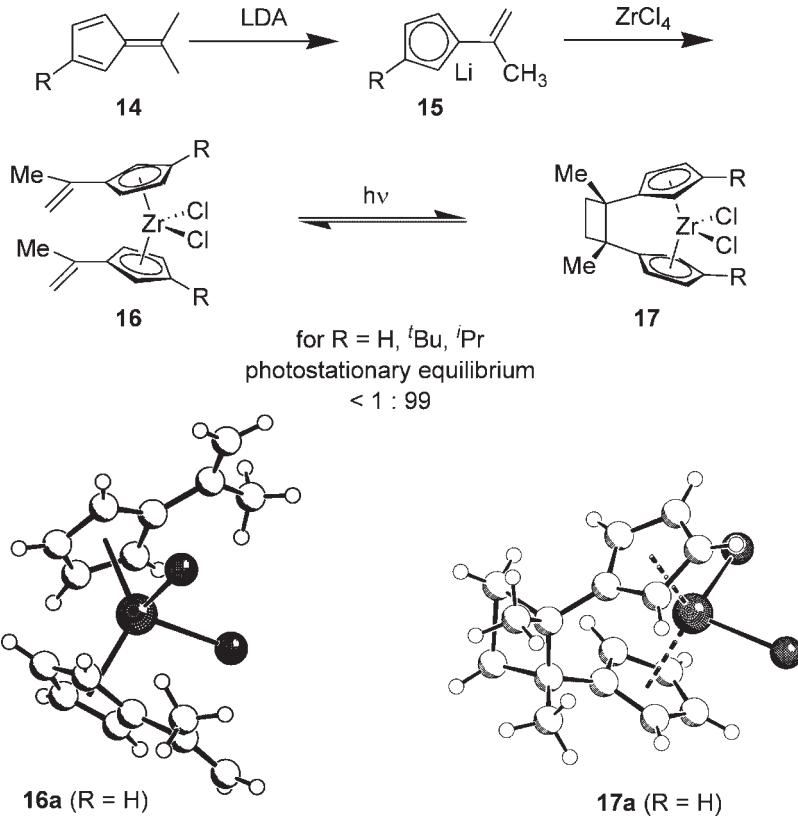
Upon MAO activation some of the resulting cyclobutylene-bridged ansa-zirconocenes give rather active α -olefin polymerization and copolymerization catalysts. The methyl-substituted system **13a** is a typical example. It provides an active catalyst system for ethene/1-octene random copolymerization. The rather low molecular weight product features a ca. 5:1 ethene/1-octene monomer component ratio (see Scheme 7).^[10]

The [2+2] cycloaddition reaction can also successfully be applied to the formation of ansa-zirconocenes from (alkenyl-Cp)₂ZrCl₂ complexes. These starting materials are best prepared by variations of the

fulvene route.^[11] Typically, a substituted 6,6-dimethylfulvene (**14**) was deprotonated to yield the corresponding alkenyl cyclopentadienide (**15**). Subsequent transmetalation then gave the bis(alkenyl-Cp)ZrCl₂ complexes **16** ($\text{R} = \text{H}$, ^iPr , ^tBu , Ph, naphthyl). In the case of the first three examples irradiation (HPK 125, Pyrex filter) resulted in a rapid and practically quantitative formation of the respective ansa-zirconocenes (**17**). The aryl-substituted systems gave photostationary equilibria between the corresponding substituted complexes **16** and **17**.^[12,13]

The photochemical [2+2] cycloaddition procedure can even be applied to the coupling of alkenyl-cyclopentadienides at the lithium complex state.^[14] This reaction represents one of the very rare examples of a real functional group chemistry at the stage of intact organolithium compounds.

It is well known that lithium cyclopentadienides in solution rapidly equilibrate with their respective lithiocene anions. In



Scheme 8.

Photochemical ansa-Metallocene Formation from Substituted (1-Methylethyl-Cp)₂ZrCl₂ Complexes

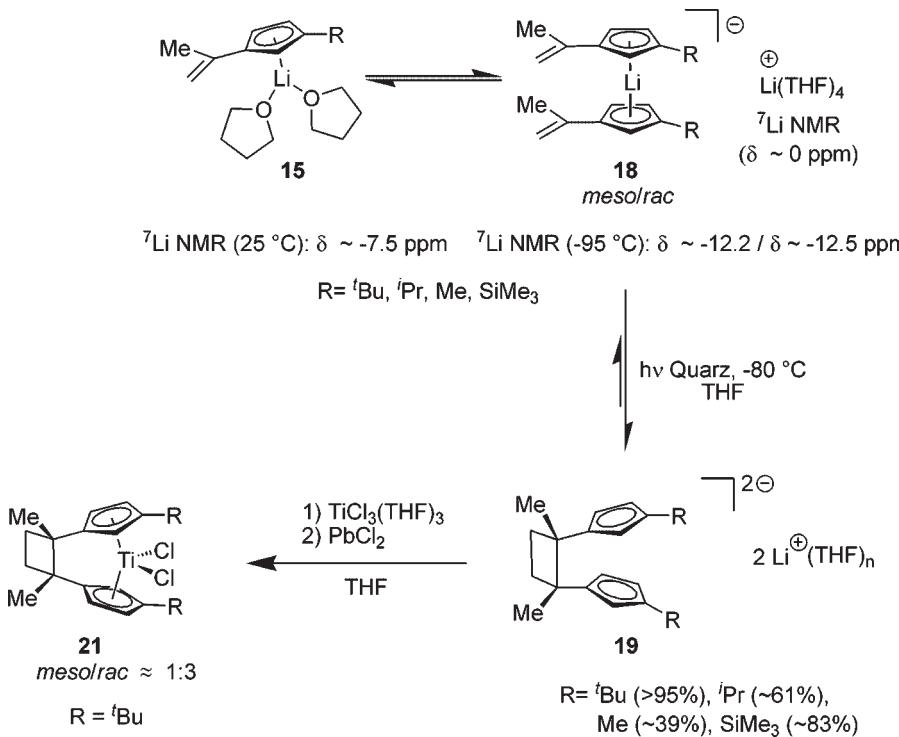
the case of the substituted (1-methylethyliden-Cp)Li reagents (**15**) this equilibration was analyzed by dynamic ^7Li NMR spectroscopy. It was shown that the **15** ↔ **18** equilibrium was strongly temperature-dependent and considerably shifted to the lithiocene anion side at low temperature. In some cases (e.g. $\text{R} = ^3\text{Bu}$) the equilibrium lay almost completely on the lithiocene anion side at -95°C . In that case, a pair of diastereoisomers (meso-/rac-**18**) was formed in a ca. 1:1 ratio, which gave rise to a pair of typical ^7Li NMR resonances at $\delta = -12.2/-12.5$.

Irradiation of e.g. **15b** ($R = ^3\text{Bu}$) under optimized reaction conditions at low temperature (-80°C , HPK 125, quartz filter, THF) resulted in the formation of a ca. 5:95 mixture of the starting material **15b** and the cyclobutylene-bridged [2+2] cycloaddition

product **19b** (see Scheme 9). The product (**19b**) was isolated from several photolysis experiments and transmetallated with $TiCl_3$ to yield the corresponding d-metal-containing system **20**. Subsequent oxidative chlorination then gave the diamagnetic (Ti IV) ansa-titanocene dichloride **21**. The photochemical [2+2] cycloaddition reaction at the lithiocene stage could be carried out with a variety of other alkenyl-functionalized lithiocene anions, but its efficiency turned out to be strongly dependent on the additional substituent pattern at the Cp -ring system. [14]

Mannich-Condensation Reactions at Metallocene Frameworks

A variant of the fulvene route was used to generate enamino-substituted cyclopentadienides and subsequently their Group 4



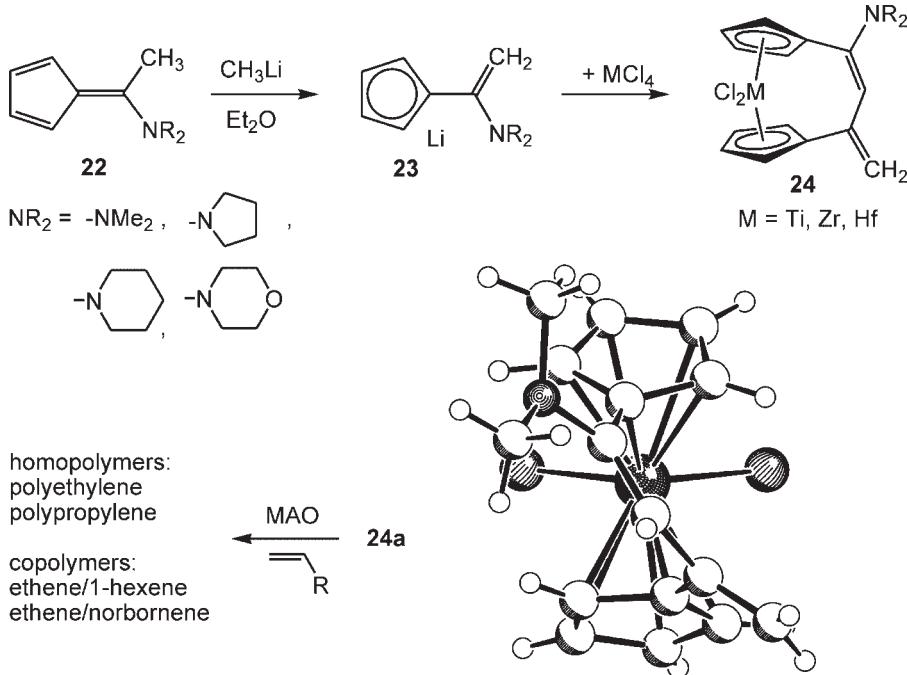
Scheme 9.

Photochemical [2+2] Cycloaddition at the Lithiocene Anion Stage.

metal complexes. However, under the standard reaction conditions this sequence took a surprising turn. Treatment of a series of substituted 6-amino-6-methylfulvenes (22)^[15] with a suitable base generated the expected enamino-Cp Li reagents. Their reaction with the Group 4 metal chlorides MCl_4 under the typical reaction conditions applied for many transmetalation reactions gave the unsaturated ansa-metallocene complexes **24(a-d)**. Apparently, a Mannich condensation reaction had taken place, leading to the C-C coupling product with subsequent elimination of one equivalent of the amine. The X-ray crystal structure analysis of an example (**24a**) showed that the resulting completely unsaturated ansa-bridge fits almost ideally in the space provided by the bent metallocene wedge. The complexes **24** were used to generate homogeneous Ziegler-Natta olefin polymerization catalysts after MAO activation.^[16]

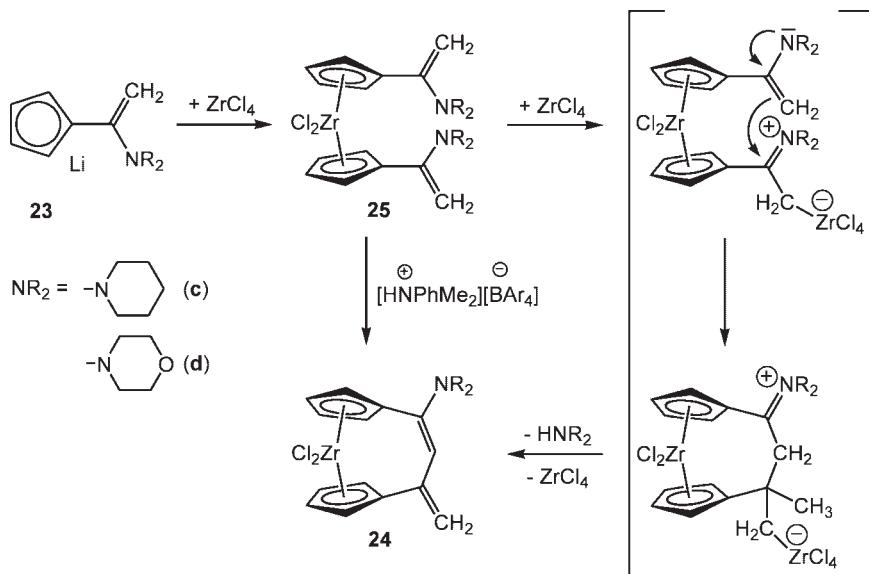
Under carefully controlled conditions we were able to prepare several bis(enamino-Cp) $ZrCl_2$ complexes,^[17] among them the morpholino- and piperidino-Cp systems **25(c,d)**. Treatment of each of these systems with either catalytic amounts of the Lewis acid $ZrCl_4$ or a Brønsted acid rapidly resulted in the formation of the C-C coupling products **24(c,d)** with liberation of one equivalent of the cyclic amine. This indicated that we had indeed succeeded in carrying out a Mannich-type C-C coupling and condensation reaction in the ligand sphere of a sensitive Group 4 bent metal-locene complex.

The metallocene Mannich coupling reaction has turned out to be so convenient that we have applied it extensively in ferrocene chemistry directed toward the preparation of new types of chelate ligands for asymmetric catalysis and polymerization catalysis.^[18] Treatment of 1,1'-diacetylferrocene (**26**) with e.g. dimethylamine,



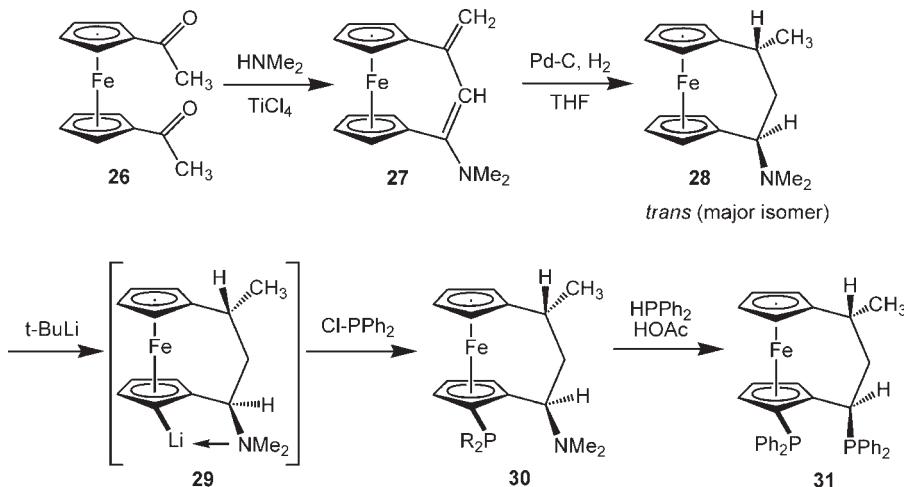
Scheme 10.

Formation and Structure of the ansa-Metallocenes 24.



Scheme 11.

Mechanism of the Mannich Coupling at the Group 4 Bent Metallocene Framework.



Scheme 12.

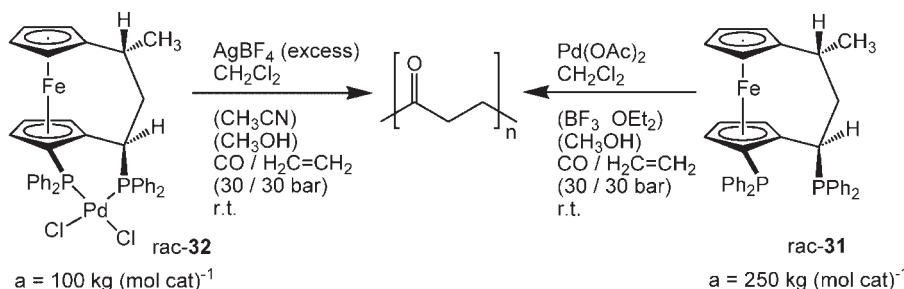
Preparation of ^[3]Ferrocenophane-Derived Chelate Ligands via a Mannich-Route.

catalyzed by TiCl₄, cleanly resulted in the formation of the unsaturated amino ^[3]ferrocenophane (**27**). Catalytic hydrogenation (Pd/C) gave a mixture of *cis*- and *trans*-**28**, with the latter being the predominant product (1:7). *Trans*-**28** underwent a directed metalation reaction when treated with tert. butyl lithium. Quenching of the reactive intermediate **29** with ClPPh₂ yielded the P,N-chelate ligand **30** (see Scheme 12). Subsequently, the *N*Me₂ group was exchanged by *–PR*₂ (R = Ph or cyclohexyl) by treatment with the respective HPR₂ reagent in acetic acid. This two-step substitution reaction takes place with overall retention of configuration at carbon, utilizing the strong anchimeric assistance of

the Fe-neighboring group in a two-step double inversion process.^[19,20]

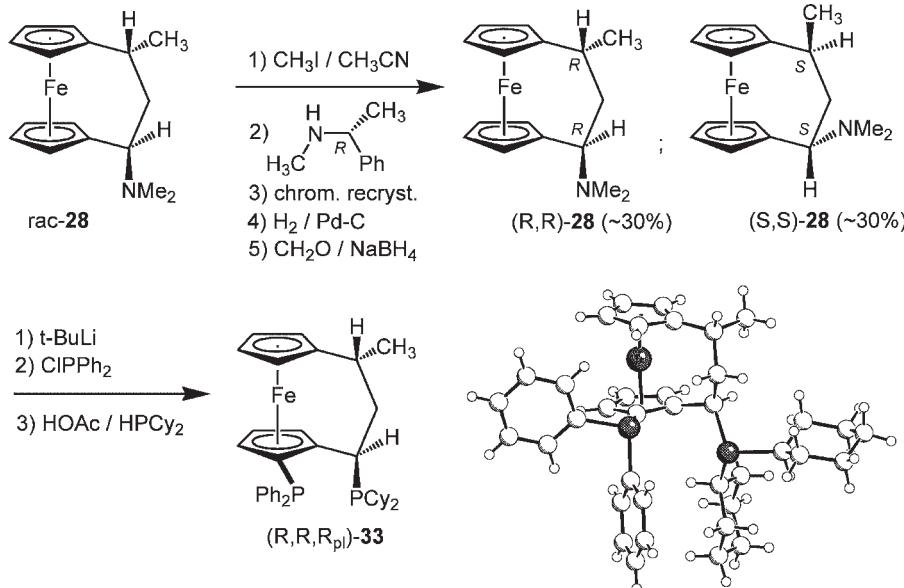
Treatment of the chelate ligand **31** with (cod)PdCl₂ gave the square-planar (chelate phosphine)PdCl₂ complex **32**. Upon suitable activation this turned out to be an active catalyst for alternating carbon monoxide/ethene copolymer formation (activity = 100 kg/mol cat). An even more active catalyst was obtained by an *in situ* procedure employing the free ligand (**31**) and palladium acetate in a typical activation protocol^[21] (see Scheme 13).

Optical resolution at the amino^[3] ferrocenophane (**28**) stage was achieved by means of very efficient five-step procedure, involving amine exchange with a chiral



Scheme 13.

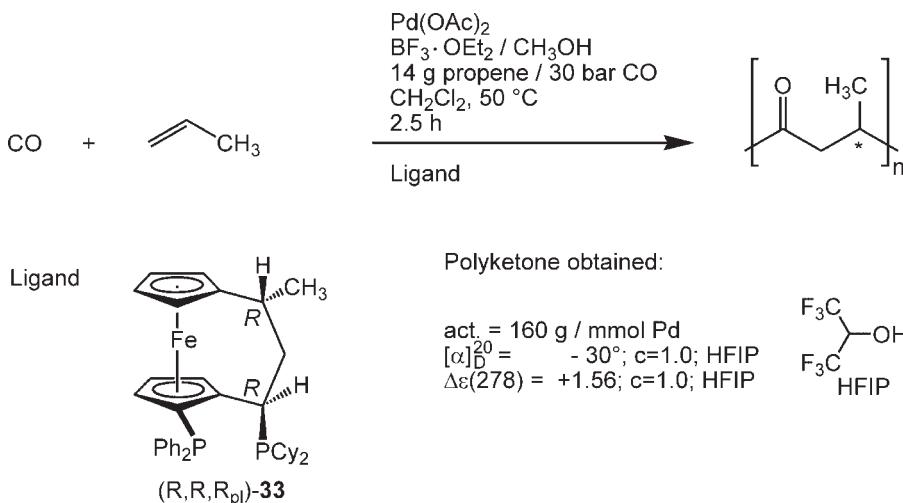
Alternating CO/Ethene Copolymer Formation.

**Scheme 14.**Synthesis of the Enantiomerically Pure Chelate Ligand (R,R,R_{pl})-33.

auxiliary, chromatographic separation of the resulting diastereoisomers and re-formation of the $-\text{NMe}_2$ substituent (see Scheme 14). A pure enantiomer of **28** was then readily converted to the new

chelate ligand **33** (characterized by X-ray diffraction).

The alternating copolymer formed from CO and propene features a main chain chirality. Consequently the use of an

**Scheme 15.**Formation of an Optically Active Alternating CO/Propene Polyketone at an Active (R,R,R_{pl})-33/Pd(II) Polymerization Catalyst.

enantiomerically enriched catalyst can then lead to optically active polymeric products.^[23] The new chelate ligand (R₁R₂R₃pl)-33 in conjunction with Pd(OAc)₂ in a typical activation protocol generates a very active CO/propene alternate copolymer forming catalyst that is highly selective. This catalyst system based on the new ^[3]ferrocenophane-derived chelate ligand systems apparently leads to high asymmetric induction in this stereoselective carbon-carbon coupling process.^[24]

Some Conclusions

The Group 4 metallocenes are rather sensitive systems. They contain a very reactive metal center, which in the past had made it difficult to find the right reaction conditions that would allow to carry out a typical organic functional group chemistry at the framework of the intact bent metallocenes. This appears to be changed. We and others have found increasing numbers of examples where one can actually perform carbon-carbon coupling reactions between typical functional groups attached at the Cp or indenyl ligands of e.g. zirconocene complexes. As we have shown this is not limited to the use of simple olefinic side chains, but we can even carry out CC-coupling reactions from the very important family of the aldol reactions (here a Mannich reaction) at Group 4 bent metallocene frameworks if care is taken to chose the suitable detailed reaction conditions. This makes us hopeful that we will see more of such organic functional group chemistry to help design and develop an increasing number of useful metallocene systems for catalysis.

Acknowledgements: G. E. thanks his coworkers and collaborators, whose names are listed in the respective references, for their many valuable contributions. It has been a pleasure to work together on these projects. Financial support from the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt-Stiftung, and the Fonds der Chemischen Industrie is gratefully acknowledged.

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