Stereochemistry and catalysis with zirconium complexes

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<u>Abstract</u> - Mono- and bis(η-cyclopentadienyl)zirconium complexes show interesting stereochemical features with regard to their use in organometallic and organic synthesis as well as in catalysis. An example is described where the zirconocene unit serves to stabilize a planar tetracoordinate carbon center. Next, various building blocks (a metal carbonyl, an organic carbonyl compound, a conjugated diene, plus one or two organic alkylating electrophiles) are assembled at the Cp_2Zr-moiety and stereoselectively coupled to give new functionalized heteroatom stabilized carbene complexes or directly organic products. Chiral $(R^*Cp)_2Zr$-derived metallocene/alumoxane Ziegler-type catalysts have been used for propene polymerization. It is shown that chain end control and enantiomorphic site control are not operating independently for determining the product stereochemistry. Additivity effects have been disclosed in a series of $[Cp-CHR^1R^2]_2ZrCl_2$-derived olefin polymerization catalysts with regard to the degree of stereocontrol exercised by the chiral metallocene unit. Finally, the preparation of the new chiral Lewis acid "(diborna-Cp)zirconium trichloride" and applications in enantioselective catalysis are described.

INTRODUCTION

This account will focus on stereochemical properties of various types of zirconium complexes containing stabilizing cyclopentadienyl ligands, their use for the preparation of novel organometallic compounds with unusual properties, for selectively assembling and connecting starting materials and reagents in stoichiometric organic syntheses, and for catalyzing the stereoselective carbon-carbon coupling of prochiral organic building blocks. Examples will be discussed derived from three different types of complex frameworks. At first, several derivatives of neutral bis(η-cyclopentadienyl)zirconium(IV) complexes will be presented, mainly focussing on stoichiometric chemistry at the mildly electrophilic d^0-configurated early transition metal center with a formal 16-electron count. Active catalysts are derived from this system of central importance by making it more electrophilic. This can be achieved in either of two ways which will be illustrated with selected examples. Removal of X^- from a suitable Cp_2ZrX_2 precursor leads to cationic Cp_2ZrX^+ systems, some of which serve as the active species in homogeneous Ziegler-Natta polymerization. Alternatively, the formal replacement of a stabilizing Cp-moiety for e.g. a halide ligand gives very reactive neutral organometallic Lewis acid systems which can be used in many ways for very selectively catalyzing the transformation of organic substrates.

$$d^0, \ 14e^- \qquad\qquad d^0, \ 16e^- \qquad\qquad d^0, \ 12e^-$$
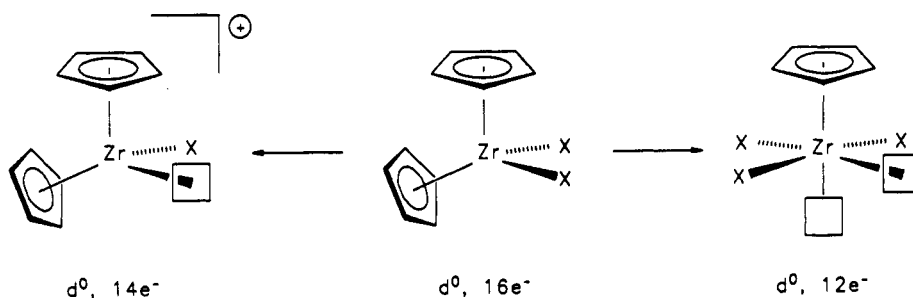
Selected examples from these topics will be presented and discussed in the following four chapters. The names of coworkers who have actually done most of the presented work will be given with each subtitle. All the structural work mentioned below was carried out by Professor Carl Krüger and his group at the Max-Planck-Institut für Kohlenforschung at Mülheim a. d. Ruhr, F.R.G., with whom we are having a long-standing intensive collaboration.

PLANAR TETRACOORDINATE CARBON (Roland Zwettler, Ralph Petrenz)

In the time past the Van't Hoff/Le Bel centennial it is more than ever a great challenge to experimentally realize compounds with very unusual coordination geometries of tetracoordinate carbon. In the seventies R. Hoffmann et al. have described the stereoelectronics of planar tetracoordinate carbon which is characterized by having an electron-deficient σ-system (four σ-bonds containing six electrons altogether) and a doubly occupied p-orbital (ref. 1).

Extensive calculations (namely by P.v.R. Schleyer et al. (ref. 2)) have revealed which metal substituents can provide a sufficient combination of σ-donor and π-acceptor properties (such as in 1,1-dilithiocyclopropane) to make planar tetracoordinate carbon more stable than the usual tetrahedral σ-bond arrangement. The few examples where the tetracoordinate planar ligand orientation at carbon was experimentally verified (ref. 3) all rely on dissipating electron density from the p-orbital by delocalization into a conjugated π-system (such as in the planarly bis-vanadium-substituted aromatic system depicted below). We have now found a very simple system making use of this effect. It is the first example where a single C=C double bond appears to provide sufficient stabilization for making planar tetracoordinate carbon (containing, of course, two metal substituents) experimentally observable.
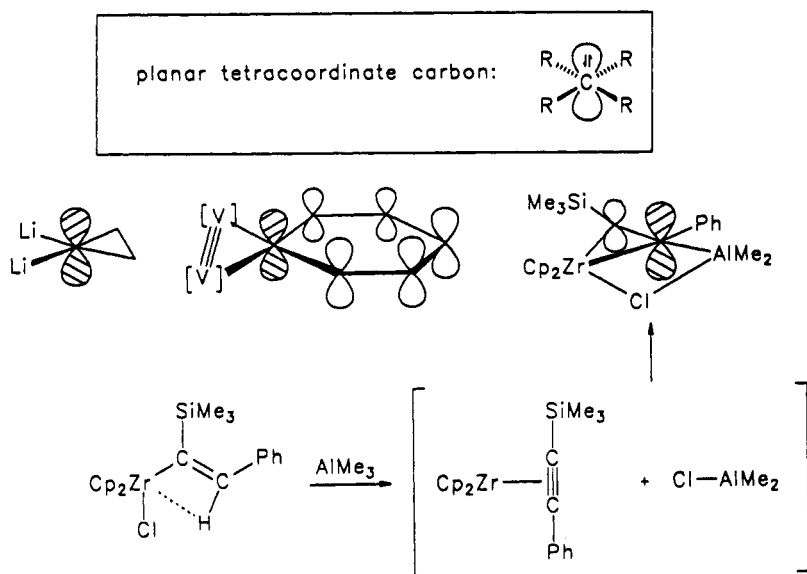
We have reacted β-agostic $Cp_2ZrCl[C(SiMe_3)=CHPh]$ with trimethylaluminum. Metathesis followed by methan formation probably generates a mixture of (η^2-alkyne)zirconocene and dimethylaluminumchloride in situ. This combination of reagents is not stable under the applied reaction conditions. Rapid addition takes place to form the doubly acetylene/chloride bridged bimetallic Zr/Al complex, which features a planar tetracoordinate carbon atom in the center.
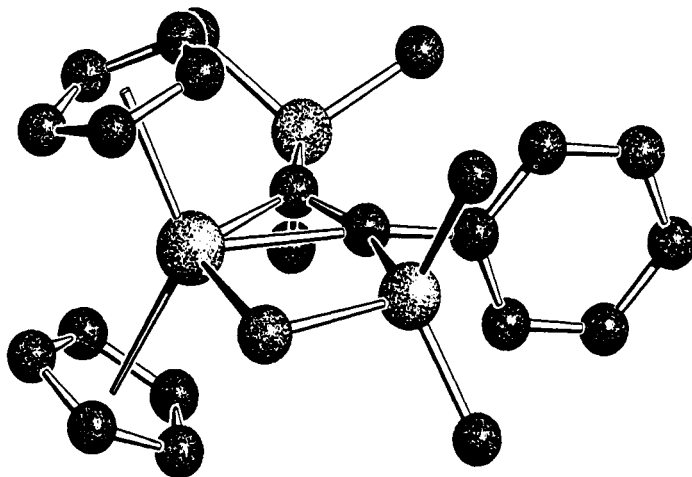
This has become evident from the X-ray crystal structure analysis of this complex. The central carbon atom [C(p)] is planar and tetracoordinate. The maximum deviation of its four substituents from the mean plane is 0.04 Å. Knowing such a stable example, it was tempting to look for reactions where planar tetracoordinate carbon might be involved e.g. as a reactive intermediate or a transition state geometry. It may be possible that this is realized in several examples of a special type of "dyotropic" rearrangement processes of d⁰-configurated bis(η-cyclopentadienyl)zirconium complexes.
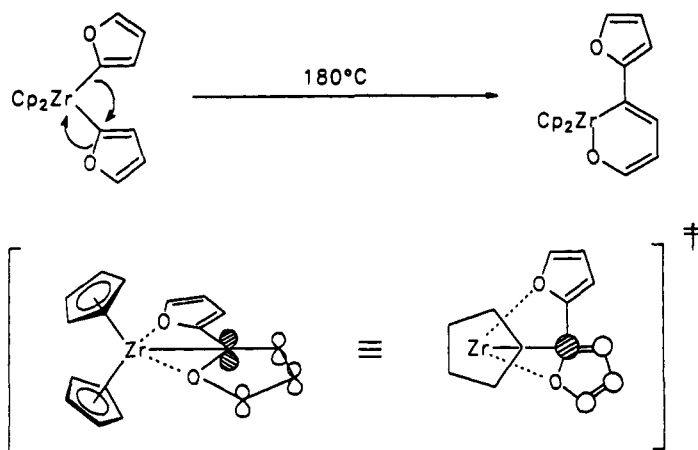

Bis(σ-furyl)zirconocene very cleanly rearranges at 180°C by means of a double σ-ligand migration to give the corresponding ring-enlarged furyl-substituted oxazirconacyclohexadiene system (ref. 4). Since the only available acceptor orbital at zirconium (which must be involved in the rearrangement in the case of a concerted reaction pathway) is extending in the σ-ligand plane, it is quite likely that a transition state geometry is involved as depicted above, featuring a central planar tetracoordinate carbon center, whose excess p-electron density is diminished by extensive π-delocalization. Phenyl as well as methyl migration is proceeding even more slowly, as would be expected for such a transition state. In contrast, the analogous reactions with trimethylsilyl migration [i.e. starting from $Cp_2Zr(SiMe_3)(\sigma\text{-furyl})$ or -(σ-thienyl)] are fast at 0°C and 40°C, respectively. Two σ-donating metal substituents probably lead to an increased stabilization of a planar tetracoordinate carbon center in the transition state of such a rearrangement process.

## ZIRCONOCENE COMPLEXES EXHIBITING PLANAR CHIRALITY (Friedrich Sosna, Roland Pfaff)

We have recently shown that (η^4-butadiene)zirconocene reacts with a variety of metal carbonyls to form metallacyclic (π-allyl)zirconoxycarbene complexes (e.g. $Cp_2Zr(C_3H_4)CH_2C[=W(CO)_5]O$ from $Cp_2Zr(C_4H_6)$ and $W(CO)_6$) (ref. 5). Such complexes cleanly add a variety of organic carbonyl compounds to the (π-allyl)Zr-terminus with formation of chiral metallacyclic nine-membered ring systems featuring a trans-C=C-double bond in the ring. Incorporation of the $O=CR^1R^2$ group of a prochiral ketone usually leads to the formation of one of the two possible diastereomers in a large excess provided the groups R^1 and R^2 are sterically sufficiently differentiated. Thus the corresponding addition of pinakolone selectively led to only the (2R*)(4,5,6-pS*) configurated diastereomer under thermodynamic control (ref. 6).


>98% (2R*)(4,5,6-pS*)

<2% (2R*)(4,5,6-pR*)
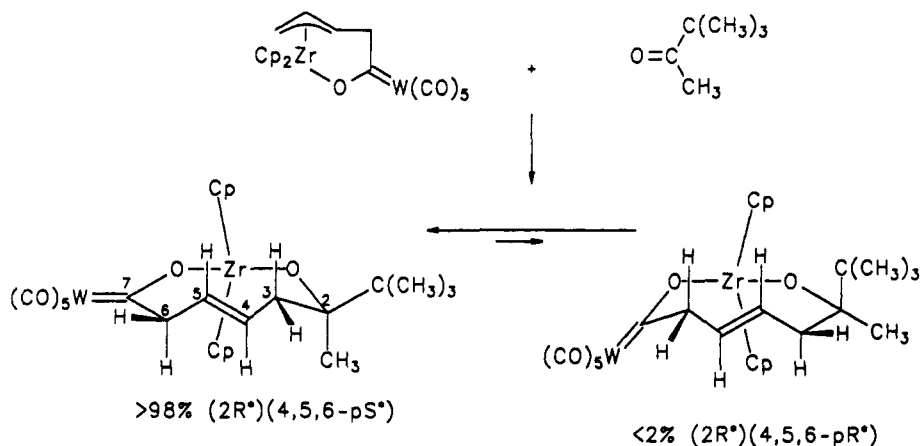
The metallacyclic zirconoxycarbene complexes can be deprotonated at the α-position to the carbene carbon atom e.g. using a phosphorous ylide as a base. We have thus prepared the corresponding salt from the (butadiene)zirconocene/W(CO)$_6$/acetone coupling product. Interestingly, the anionic metallacyclic system is still chiral. The chiral ground state conformation showed up in the low temperature limiting NMR spectra featuring signals of diastereotopic pairs of methyl groups, Cp-ligands and CH$_2$-hydrogens. The system is fluxional. Dynamic NMR spectroscopy has revealed a Gibbs activation energy of $\Delta G^{\neq}_{ent}(225K) \approx 11$ kcal/mol for the corresponding enantiomerization process which probably takes place by ring-inversion similar to the topomerization of the organic trans-cycloalkenes.

$$\Delta G^{\neq}_{ent}(225K) = 11.1 \pm 0.4 \text{ kcal/mol (THF-}d_8)$$
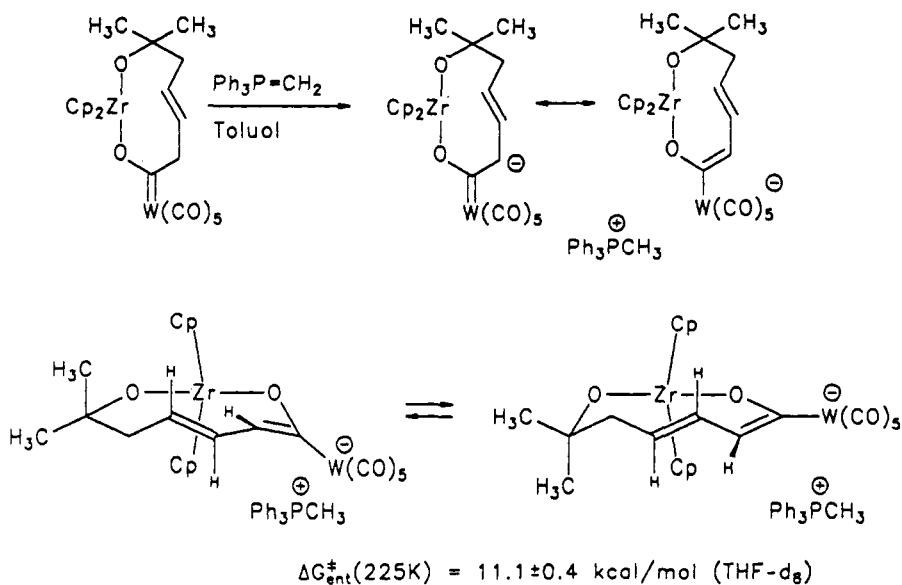
In the presence of a controlling chirality center in the ring (e.g. at C2, originating from the added ketone) the formation of the chiral zirconoxycarbene anion can be used for diastereoselective α-alkylation processes proceeding by effective stereochemical 1,5-induction. Thus, deprotonation of diastereomerically pure (racemic) (2R*)(4,5,6-pS*)-Cp$_2$ZrOCMe(CMe$_3$)CH$_2$CH=CHCH$_2$C[=W(CO)$_5$]O with Ph$_3$P=CH$_2$ followed by alkylation with methyl iodide gave a product containing three different chirality units. Of the diastereoisomers possible for such a combination the (2R*,6S*)(4,5,6-pS*) configurated isomer was obtained in >80% de. The X-ray crystal structure analysis of the major product (see below) revealed that the methyl group newly attached at carbon atom C6 was oriented cis to the smaller group at the controlling chirality center at C2. The stereochemical information in this remarkably selective 1,5-induction seems to be transferred from C2 all the way over to C6 by means of the rigid crown like conformation of the chiral metallacycle (ref. 7).
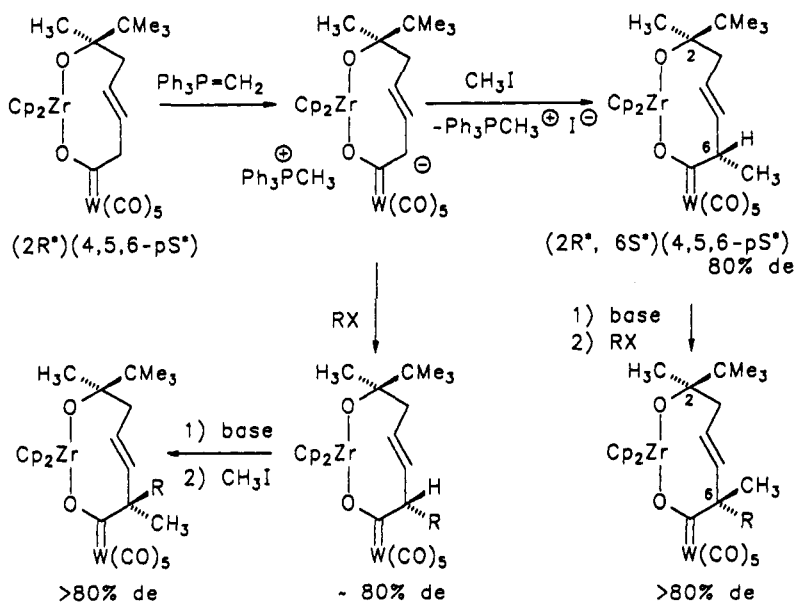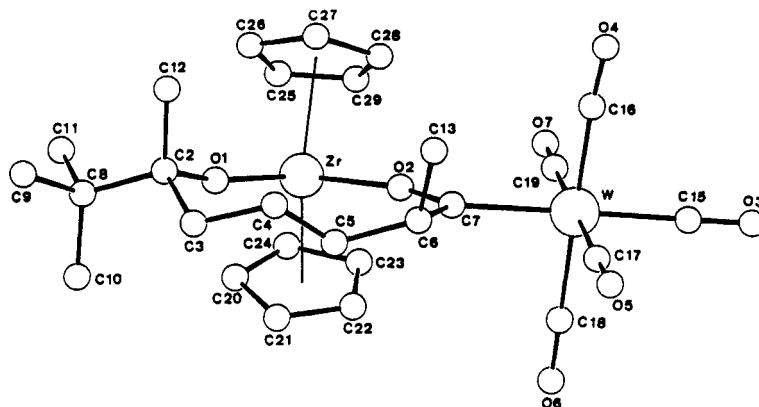
The monoalkylation product can be α-deprotonated and subsequently alkylated once more. Stereochemically, this represents a non-linear synthesis of the tert-alkylcarbene complex. Therefore, the overall induction obtained is often higher (≈90% de.) than that of the first alkylation step of the sequence. Reversal of the alkyl electrophile addition steps results in a stereochemically inverted product at carbon atom C6.
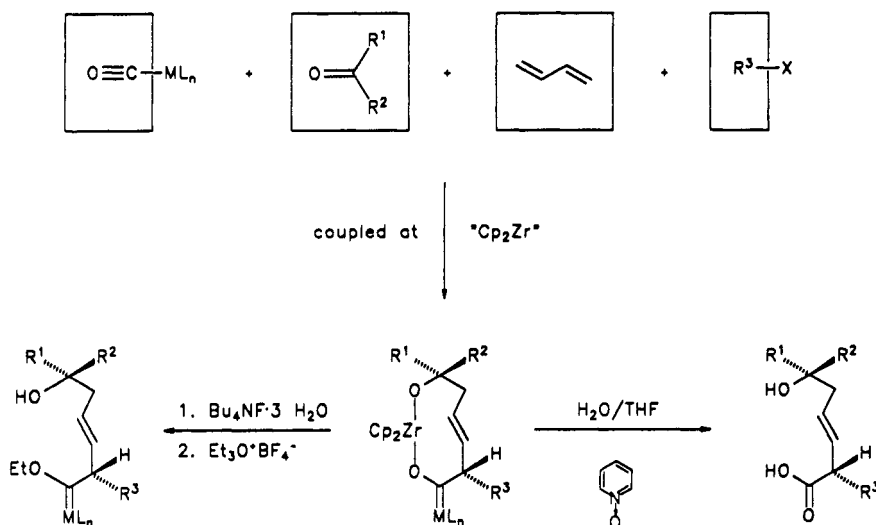

We thus have completed a stoichiometric template synthesis in the course of which a metal carbonyl, an organic carbonyl compound, a conjugated diene and one or two alkylating reagents can be stereoselectively coupled at the bent metallocene unit. The rather unreactive zirconoxycarbene complex ("protected Fischer-carbene complex") can readily be hydrolyzed and O-alkylated to give highly functionalized ordinary Fischer carbene complexes (ref. 8). Alternatively, the hydrolysis of the zirconoxycarbene complexes in the presence of reagents that react rapidly with conventional heteroatom stabilized carbene complexes directly leads to organic products in a one pot synthesis.

C_2-SYMMETRIC BENT METALLOCENES FOR STEREOSPECIFIC OLEFIN POLYMERIZATION (Rainer Nolte, Rainer Aul, Michael Aulbach, Stephan Wilker)

Cp-substituted bent metallocene moieties $(R-Cp)_2M$ with R representing hydrocarbyl units larger than primary alkyl groups tend to form preferred rotameric conformers that favour the bulky Cp-substituents antiperiplanarly oriented in the lateral sectors of the bent metallocene unit. Formally such an arrangement can be described as being derived from a helically chiral system with three directionary vectors being oriented right- or left handed helically along an arbitrary Cp-Cp connecting axis.


"h-R" (P)   "h-S" (M)
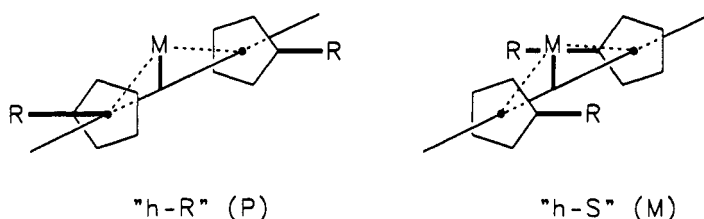
Many $(RCp)_2ZrX_2$ complexes adopt such structures in the solid state as well as in solution (ref. 9). The resulting C_2-symmetric arrangement of substituted Cp-ligands is illustrated below using as an example the [Cp-C(cyclohexyl)=CH$_2$]$_2$ZrCl$_2$ solid state structure as determined by X-ray diffraction.
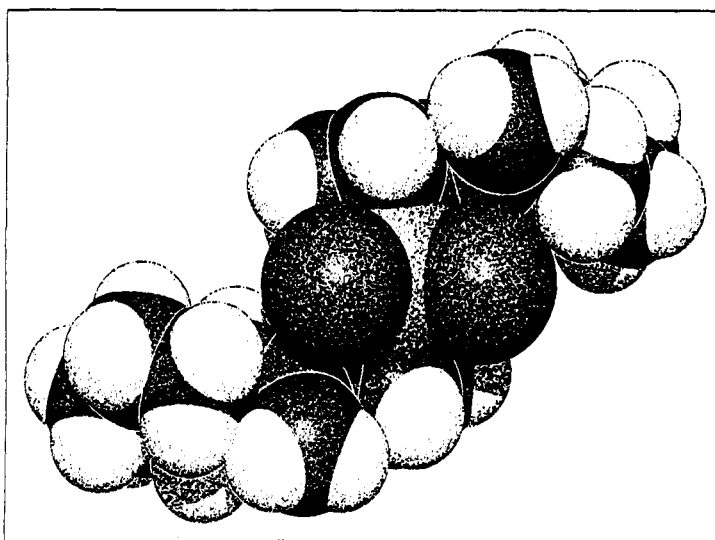

Alkylmetallocene-cations seem to represent the active principle of the very reactive $(RCp)_2MX_2$ / alkylalumoxane derived homogeneous Ziegler-type catalysts for α-olefin polymerization (ref. 10,11). Their ansa-metallocene analogues which exhibit a persistent chirality have been used very successfully for stereospecific olefin polymerization (e.g. the formation of isotactic polypropylene) (ref. 12). In principle, the above mentioned chiral open chain C_2-symmetric $(RCp)_2ZrX_2$ bent metallocenes should bear with them the necessary stereochemical information for enantioside differentiating stereospecific propene polymerization at the active cationic catalyst, could the rapid enantiomerization by means of a ring rotation pathway of a generally low activation barrier be made ineffective. One way of potentially doing that is the use of chiral R*-Cp substituents which convert the otherwise enantiomeric $(R-Cp)_2M$ rotamers into pairs of $(R*-Cp)_2M$ diastereoisomers. Sufficient energy separation of the latter should make one of these the stereochemically controlling isomer even if a still low activation barrier of diastereomeric interconversion allows for a rapid equilibration.
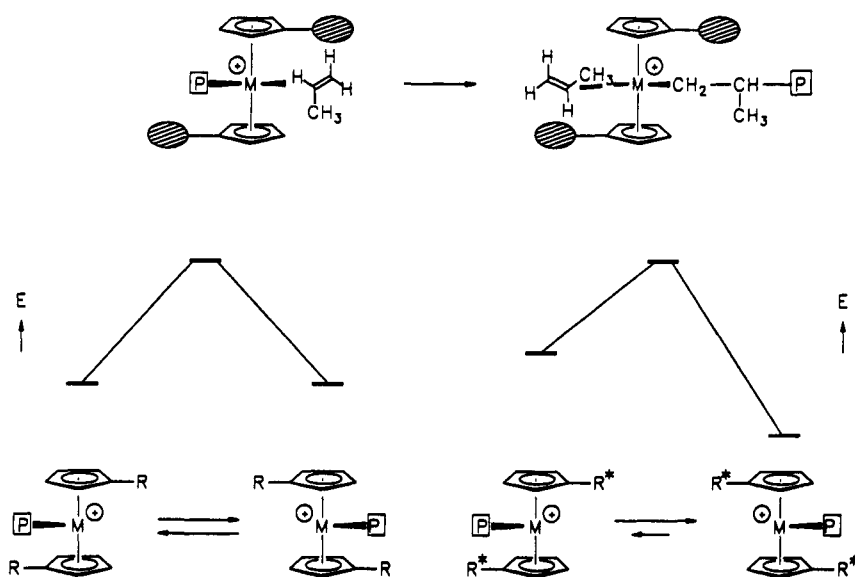
We have prepared a variety of $(R*-Cp)_2ZrCl_2$ complexes and employed them successfully as stereoselective propene polymerization catalysts. Here is a typical example which may serve to illustrate how we carried out the stereochemical analysis and description of the isotactic polypropylene obtained.
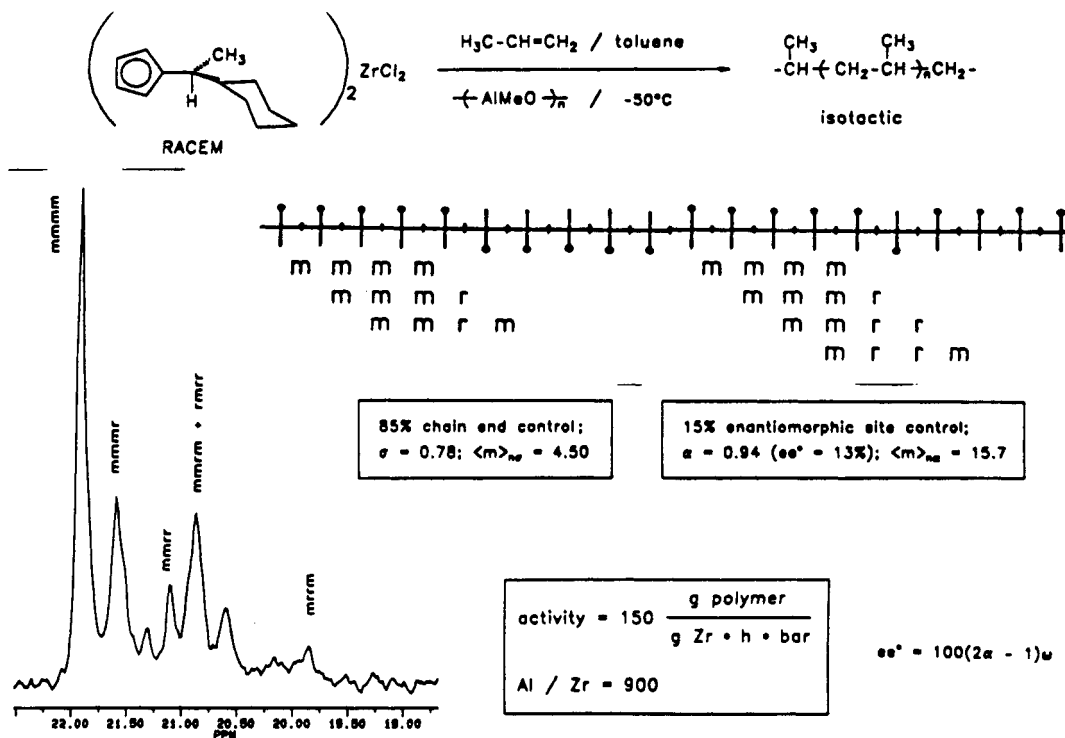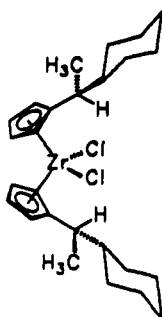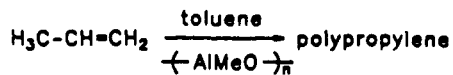
Bis(1-cyclohexylethyl-cyclopentadienyl)zirconium dichloride was obtained by reacting two molar equivalents of the corresponding racemic lithio-(Cp-R*) reagent with ZrCl₄. The obtained mixture of diastereomeric (i.e. meso and racem) (R*-Cp)₂ZrCl₂ products were separated by fractionating crystallization and the chiral racem-(Cp-CHMeCy)₂ZrCl₂ / methylalumoxane catalyst employed for polymerizing propene at our standard reaction conditions (-50°C, Al/Zr-ratio of about 1000 in a propene/toluene solvent mixture). Isotactic polypropylene was obtained with an acceptable catalyst activity. Its stereochemical analysis was carried out by means of a ¹³C NMR pentade analysis of the methyl signal region (see spectrum above). A detailed statistical analysis of the (conventionally fractionated) polymer revealed that it had to be described by a three parameter equation, containing the following descriptors for effective stereocontrol by the chiral polymer chain end (σ), the enantiomorphic site (α), and their relative statistic weight (ω for enantiomorphic site control; 1-ω for chain end control) (ref. 13). The observed spectrum could adequately be reproduced with a single set of these three parameters, namely ω = 0.15, σ = 0.78, and α = 0.94. From the numerical values of ω and α one may calculate a "relative enantioselectivity" of each active metal catalyst center (for this example ee* = 13% was calculated).
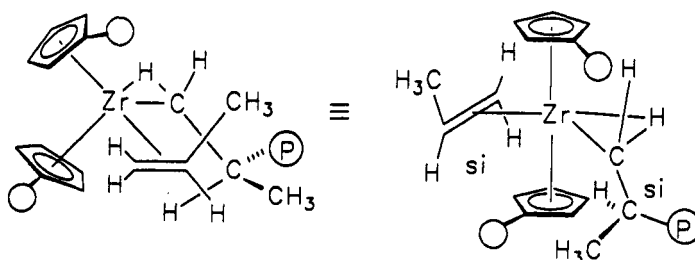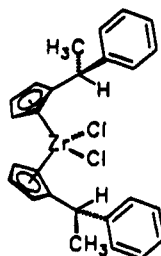

It is mechanistically reasonable that one statistical parameter alone was not sufficient to describe the stereochemical situation at the active bent metallocene catalyst for CC-coupling of the prochiral olefin with the polymer chain. Under all circumstances there are always two stereochemically relevant factors that we have to deal with, namely the chiral bent metallocene unit itself (whose stereochemical properties should remain practically unchanged throughout the reaction) and the stereogenic carbon center at the end of the growing polymer chain which is constantly being renewed with each olefin coupling reaction step. These two stereochemically controlling principles always occur combined, they are dependent of one another similar to a situation as encountered in double stereodifferentiation in conventional noncatalytic organic synthesis. So, we are left with a very difficult problem of a priori controlling the consequences of these two coupled stereochemical influences by only being able to actively alter the metallocene properties; the dependent features of the always present chiral carbon center at the β-position of the growing chain are beyond our direct means of taking control. Therefore, we considered it to be very fortunate that systematically changing the nature of the Cp-bonded auxilliary substituents has revealed some simple additivity effects which may be very useful to govern this rather complicated stereochemical situation in a rational way.
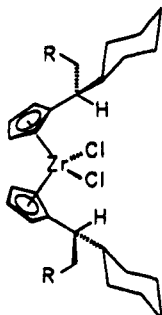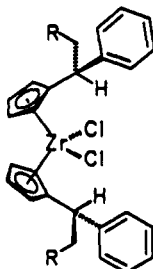
Structure / Selectivity - Relation $H_3C-CH=CH_2$ $\xrightarrow[\text{+AIMeO}\overline{}_n]{\text{toluene}}$ polypropylene


```
act.: 150
temp.: -50°C
Al/Zr = 900
ω = 0.15
α = 0.94
σ = 0.78
<m>_nα = 15.7
<m>_nσ = 4.50
ee* = 13%
```

```
act.: 28
temp.: -50°C
Al/Zr = 530
ω = 0.27
α = 0.96
σ = 0.79
<m>_nα = 24.0
<m>_nσ = 4.80
ee* = 25%
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```
act.: 135
temp.: -50°C
Al/Zr = 970
ω = 0.33
α = 0.96
σ = 0.80
<m>_nα = 24.0
<m>_nσ = 5.00
ee* = 30%
```

```
act.: 60
temp.: -50°C
Al/Zr = 1000
ω = 0.67
α = 0.95
σ = 0.92
<m>_nα = 19.1
<m>_nσ = 12.5
ee* = 60%
```

Here is an example of the outcome of a typical series of substituent variations. Let us start from the racem-[Cp-$CH(CH_3)$cyclohexyl]$_2$ZrCl$_2$ derived catalyst. As mentioned above a "relative enantioselectivity" of ee* ≈ 13% was obtained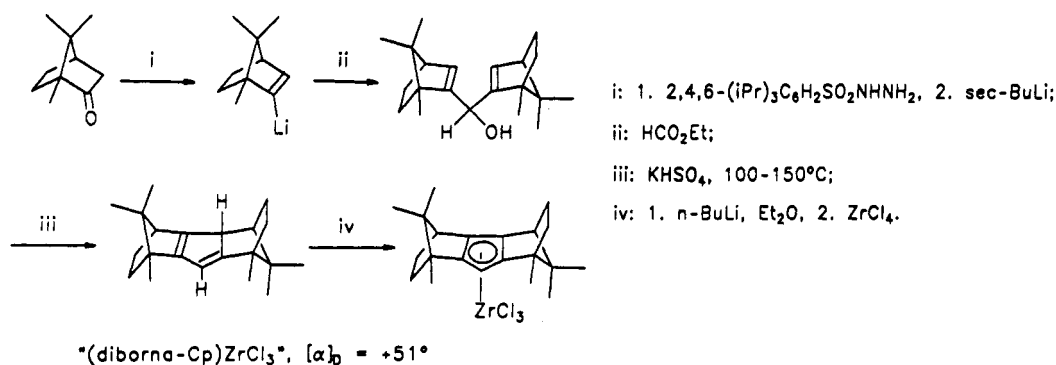 upon isotactic polypropylene formation with this methylalumoxane activated catalyst system at our standard reaction conditions. We than prepared a catalyst where the cyclohexyl rings at the Cp-substituents were replaced by phenyl groups. This catalyst resulted in a more selective CC-coupling giving an about doubled ee* of ≈ 25%. A similar result was obtained when the methyl group of the original catalyst system was replaced by a bulkier -CH_2R moiety. The racem-[Cp-$CH(CH_2R)$cyclohexyl]$_2$ZrCl$_2$ derived catalyst gave isotactic polypropylene with ee* ≈ 30%. These two observed substituent effects on the selectivity of the CC-coupling process at these reactive catalyst systems were about additive when combined in a single catalyst precursor, i.e. by using the corresponding racem-[Cp-$CH(CH_2R)$phenyl]$_2$ZrCl$_2$ / (MeAlO)$_n$ catalyst an ee* of ≈ 60% was obtained. This specific combination of substituent effects had quadrupled the effective transponation of the inherent stereochemical information at the chiral bent metallocene unit relative to our initially used catalyst system.

A NEW CHIRAL ORGANOMETALLIC LEWIS ACID (Christian Sarter, Jutta Schamberger, Adolphus A. H. van der Zeijden, Stefan Dehnicke)

Many organic reactions are catalyzed by Lewis acids. It may be advantageous to use organometallic Lewis acid catalysts as they offer much wider structural and stereoelectronic variabilities as compared to the mostly used simple inorganic systems such as AlCl$_3$, BF$_3$, TiCl$_4$ etc. We have used the organometallic Lewis acid CpZrCl$_3$ for catalyzing a variety of organic carbon carbon coupling reactions (ref. 14). A typical example is the hydroxyalkylation of 1-naphthol with ethyl pyruvate which had been carried out previously with the aid of stoichiometric amounts of e.g. AlCl$_3$ (ref. 15). Treatment of the starting components with stoichiometric (η-cyclopentadienyl)zirconium trichloride resulted in the formation of a 1:1 adduct of the CC-coupled organic reaction product and CpZrCl$_3$ with loss of one equivalent of HCl. We found that the isolated CpZrCl$_2$(OR) adduct efficiently catalyzed the naphthol + pyruvate addition reaction to yield the α-hydroxyalkylation product which is a precursor of an antiinflammatory pharmacon. We wanted to use this clean CC-coupling reaction as a test case for applying a newly developed zirconium based chiral organometallic Lewis acid system.
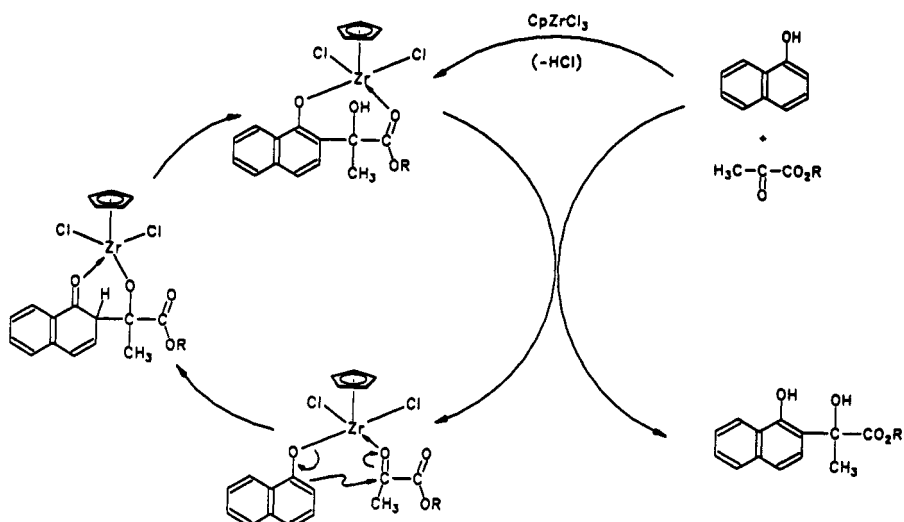
The optical active chiral organometallic Lewis acid "(diborna-Cp)zirconium trichloride" was prepared by an adaption of the pentamethylcyclopentadienyl synthesis described by J. E. Bercaw et al. (ref. 16). Our chiral pool synthesis started from enantiomerically pure (+)- or (-)camphor. This was converted to the respective bornenyllithium reagent by means of a Shapiro-reaction. Addition to formic ester followed by acid catalyzed ring closure, deprotonation and addition to zirconium tetrachloride gave the optically pure "(diborna-Cp)ZrCl₃" enantiomers (ref. 17).

i: 1. 2,4,6-(iPr)₃C₆H₂SO₂NHNH₂, 2. sec-BuLi;

ii: HCO₂Et;

iii: KHSO₄, 100-150°C;

iv: 1. n-BuLi, Et₂O, 2. ZrCl₄.

"(diborna-Cp)ZrCl₃", [α]ᴅ = +51°

"(Diborna-Cp)ZrCl₃" was employed as a catalyst for the CC-coupling reaction of 1-naphthol with ethyl pyruvate. A mixture of the two reagents and the catalyst in a 100:100:1 molar ratio at room temperature gave the hydroxyalkylation reaction product with an enantiomeric excess of 27%. Using the (+)camphor derived catalyst produced the (R)-enantiomer of the product in excess, the (-)camphor related catalyst system gave rise to the preferred formation of its enantiomer.
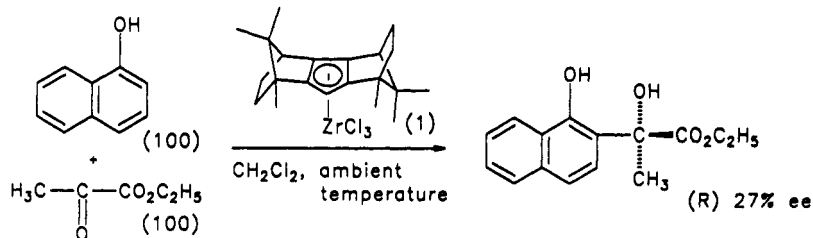
We subsequently optimized the reaction conditions for this enantioselective catalytic aldol addition type CC-coupling reaction to some extent. Lowering the temperature brought an increase to about 50% ee. Increasing the naphthol concentration had a rather adverse effect; probably the chiral catalyst system was not completely stable with regard to Cp-protonation under the rather acidic reaction conditions. Therefore, the pyruvate concentration was increased and a slightly higher catalyst concentration (5 mol%) was used to make the enantioselective catalytic reaction faster. Finally, we deliberately added a small amount of water. This was done in our continuing search for Lewis acid systems which are retaining their catalytic activity in aqueous media. This had no adverse effect on the activity of the catalytic system and, to our surprise, turned out to be advantageous for the stereochemical induction looked for. The obtained enantiomeric excess was reproducably

increased upon the addition of small quantities of water by about 10%. Under optimized conditions we prepared the 1-naphthol/ethyl pyruvate addition product on a preparative scale using separately each enantiomer of the "(diborna-Cp)ZrCl$_3$" Lewis acid catalyst. The chiral CC-coupling product was in each case isolated with a >80% excess of the respective enantiomer. We are currently investigating the synthetic potential of the "(diborna-Cp)ZrCl$_3$" catalyst system for other CC-coupling reactions in organic synthesis.

Acknowledgement

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