

Some novel structural and chemical aspects of Cp-substituted bent metallocene complexes

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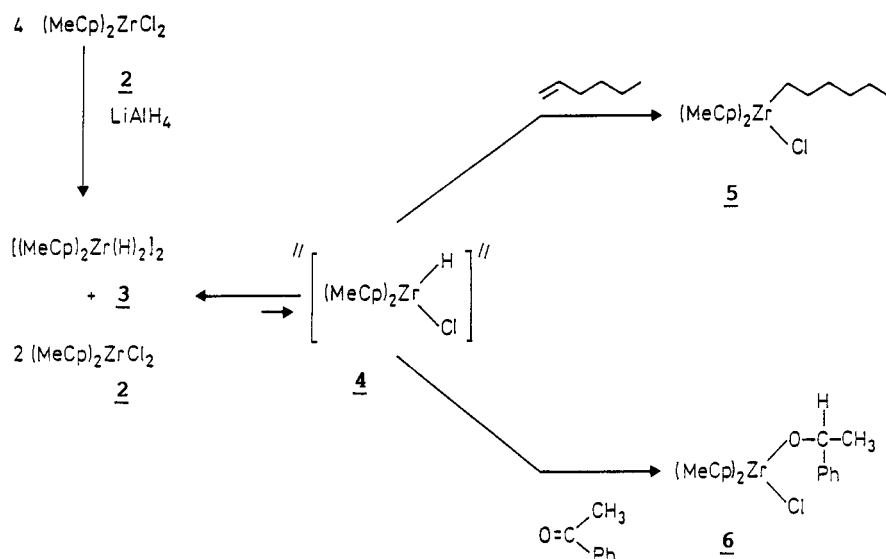
Abstract - Cp-bonded alkyl substituents may change the structural and chemical features of group 4 bent metallocene complexes considerably. Increased solubility appears to make *in situ* generated $(\text{MeCp})_2\text{Zr}(\text{H})\text{Cl}$ an improved hydrozirconation reagent. The use of methylcyclopentadienyl ring systems allows the detection of the dynamic behaviour of the doubly acetylide bridged $[(\text{MeCp})_2\text{Zr}-\text{C}\equiv\text{C}-\text{Ph}]$ -dimer. Steric interaction between bulky Cp-bonded tert-alkyl groups and the substituents at the internal carbon atoms of a conjugated diene ligand causes hindered (RCp)-metal rotation in many (diene)zirconocene and -hafnocene complexes ($\Delta G^{\ddagger}_{\text{rot}} \approx 10$ kcal/mol). Due to the preferred chiral Cp-rotameric conformation of the $(\text{Me}_3\text{C}-\text{Cp})_2\text{M}$ bent metallocene systems this dynamic feature can readily be detected in solution by NMR spectroscopy. The $(\text{Cp}-\text{CHMePh})_2\text{ZrCl}_2$ /alumoxane-system catalyzes the stereospecific polymerization of propene. Catalysts derived from rac-[(1-phenylethyl)cyclopentadienyl]-zirconocene dichloride produce isotactic polypropylene via enantiomorphic-site and chain end control.

INTRODUCTION

The chemical properties of the group 4 bent metallocene complexes Cp_2ML_n (M = Ti, Zr, Hf) can be controlled over a wide range by attaching alkyl substituents at the η -cyclopentadienyl rings. Bis(pentamethylcyclopentadienyl)zirconium and -hafnium complexes are well known examples (ref. 1). However, introducing only one alkyl substituent per cyclopentadienyl ligand is often sufficient to induce some interesting novel features. Using methyl- or tert-butylcyclopentadienyl systems may lead to reduced aggregation and enhance the solubility of e.g. zirconocene-derived reagents. The η - C_5H_4 -R ligands being of lower symmetry than their η - C_5H_5 or η - C_5Me_5 counterparts provide suitable NMR probes to detect hitherto unknown rearrangements. Bulky tert-alkyl Cp-substituents are stereochemically active, influencing the conformation of the bent metallocene unit. Additional stereochemical information is provided by using chiral substituents. In this paper several examples of zirconocene complexes bearing methyl-, tert-butyl- or (1-phenylethyl)cyclopentadienyl ligands will be presented. Each case will serve to demonstrate a particular RCp-substituent effect, influencing the reactivity, dynamic behaviour, structural, or stereochemical features of these bis(cyclopentadienyl)zirconium complexes.

AN IMPROVED HYDROZIRCONATION REAGENT

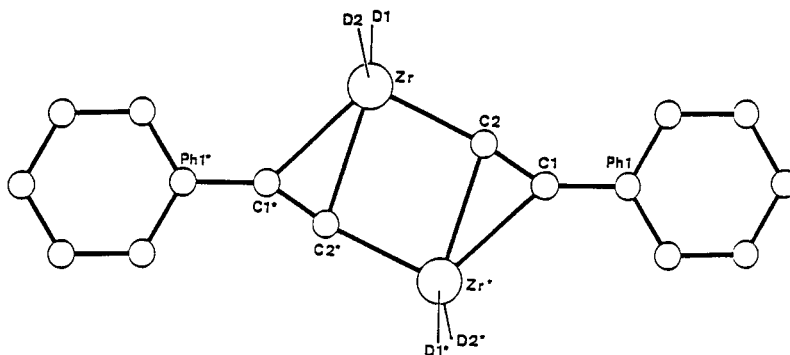
The hydrozirconation reagent $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_x$ has found many interesting applications in organic synthesis (ref. 2). It is readily available by reacting zirconocene dichloride with e.g. LiAlH_4 . In contrast, the reaction of bis(methylcyclopentadienyl)zirconium dichloride **2** with metal hydrides preferentially yields the dimeric metallocene dihydride **3** (ref. 3). We have observed that a 1:2 mixture of **3** and **2** can conveniently be used for hydrozirconation as well. Reaction of this mixture with 1-hexene cleanly produces **5** (rxn. in toluene, 97% isolated yield). Similarly, treatment of the **2/3** (2:1) mixture with acetophenone produced only $(\text{MeCp})_2\text{Zr}(\text{OCHMePh})\text{Cl}$ (**6**).



The $(\text{MeCp})_2\text{Zr}(\text{H})\text{Cl}$ hydrozirconation reagent generated *in situ* is more reactive than the commonly used oligomeric $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_x$ (**1**). In competition experiments employing excess 1-hexene or acetophenone, respectively, the hydrozirconation products containing the $(\text{MeCp})_2\text{Zr}$ -unit are formed both ca. 6-7 times faster. A hydrohafniation reagent " $(\text{MeCp})_2\text{Hf}(\text{H})\text{Cl}$ " can analogously be generated *in situ* by mixing $[(\text{MeCp})_2\text{Hf}(\text{H})_2]_2$ (**7**) and bis(methylcyclopentadienyl)hafnium dichloride (**8**) (1:2) in tetrahydrofuran. Upon addition of 1-hexene, $(\text{MeCp})_2\text{Hf}(\text{Cl})(1\text{-hexyl})$ is formed cleanly.

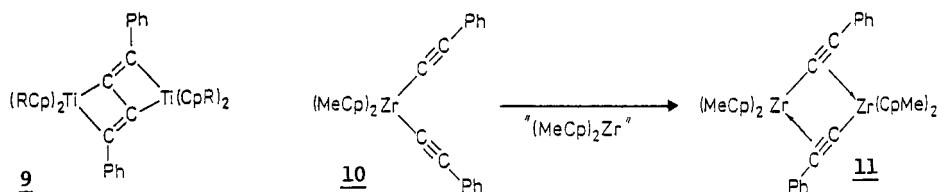
BINUCLEAR ALKYNYL-BRIDGED ZIRCONOCENE COMPLEXES

The dinuclear bis(titanocene) complex **9** was obtained from the reaction of $[(\text{RCp})_2\text{TiCl}]_2$ with phenylacetylide (ref. 4a). We have reacted $(\text{MeCp})_2\text{Zr}(-\text{C}\equiv\text{C}-\text{Ph})_2$ **10** with " $(\text{MeCp})_2\text{Zr}$ ", thermally generated *in situ* from the (*s-cis*-/*s-trans*- η^4 -butadiene) $\text{Zr}(\text{CpMe})_2$ equilibrium mixture (60:40). The doubly acetylide bridged binuclear zirconocene complex **11** is obtained whose structure (Fig. 1) is quite different from that of the bis-titanocene complex **9** (ref. 4b).

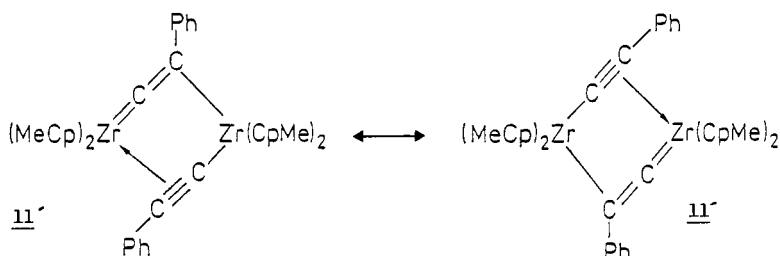


d Zr-C(2) 2.188(2) Å; C(2)-C(1) 1.261(2) Å; Zr.....Zr* 3.506(1) Å
 Zr-C(1*) 2.407(2) Å; Zr-C(2*) 2.431(2) Å; C(2).....C(2*) 3.018(2) Å
 ∠ Zr, C(2), C(1) 172.3(1)°; C(2), C(1), Ph(1) 146.8(2)°

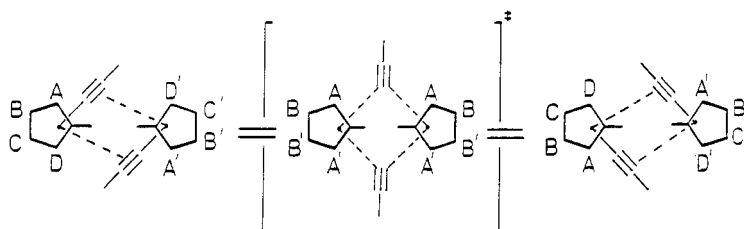
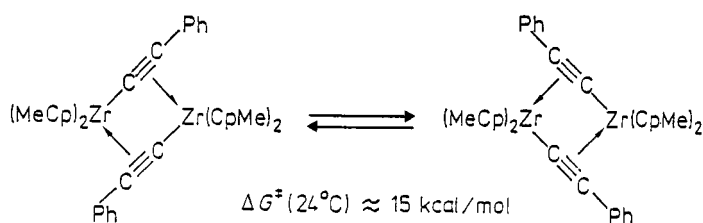
Fig. 1. A view of the central coplanar section of $[(\text{H}_3\text{CCp})_2\text{Zr}]_2(\mu\text{-C}\equiv\text{C}-\text{Ph})_2$ (**11**) as determined by X-ray diffraction. D1 and D2 denote centroids of Cp-ligands bonded to zirconium.



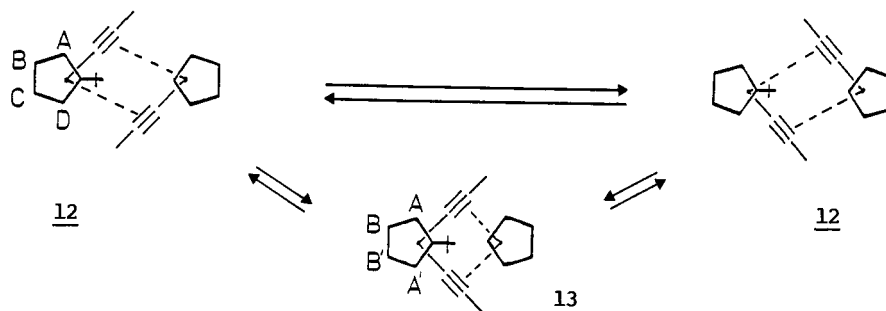
The [(MeCp)₂Zr-C≡C-Ph]-dimer **11** exhibits a C_{2h}-symmetric central framework. The large Zr...Zr* separation indicates the absence of a direct metal-metal interaction. In contrast to **9**, the phenylacetylide ligands have not undergone CC-coupling. Some metal carbene character of the Zr-C(2) linkage is indicated by the bonding parameters of the ZrCCPh moiety (see Fig. 1). The structural features of the diamagnetic [(MeCp)₂ZrCCPh]-dimer **11** can be described by equal contributions of the Zr(II),Zr(IV) resonance forms **11'**.



The use of methylcyclopentadienyl- rather than ordinary cyclopentadienyl-ligands has revealed the dynamic nature of the zirconocene acetylide dimer **11**. With increasing temperature the ¹H NMR methine resonances of the four equivalent methyl-Cp ring systems are changed from an ABCD to an AA'BB' pattern. For the coalescence temperature a Gibbs-activation energy of 15 kcal/mol has been estimated for the intramolecular exchange of μ-η¹:η²-bound alkynyl ligands.



Possibly this type of rearrangement takes place by stepwise alkynyl migration, i.e. via a C_{2v}-symmetric intermediate rather than the depicted D_{2h}-transition state geometry. This is indicated by the observation of a respective species (**13**, C_{2v}-symmetry, AA'BB'-pattern, 55%) in addition to **12** (C_s-symmetry, ABCD-pattern, 45%) in the low temperature ¹H NMR spectra of the (Me₃CCp)₂Zr(μ-C≡C-CH₃)₂ZrCp₂ system. The automerization barrier of **12** and the activation barrier of the **12** ⇌ **13** rearrangement are identical (ΔG[‡](-55°C) = 12.5 kcal/mol) within the accuracy of the dynamic NMR experiment.



HINDERED (RCp)-M ROTATION

Bis(methylcyclopentadienyl)zirconium dichloride **2** and related compounds exhibit achiral global conformational minima with eclipsed Cp-rings (ref. 5). In contrast, bis(tert-alkyl-Cp)ZrX₂ complexes usually favour chiral (C₂-symmetric) conformations (ref. 6). The bulky Cp-substituents are arranged trans to each other in the lateral sectors of the bent metallocene unit (see Fig. 2).

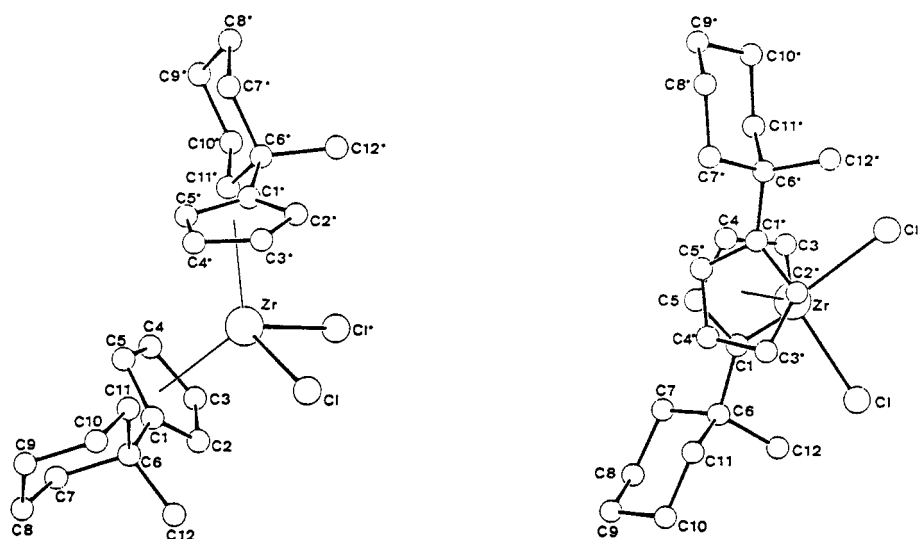
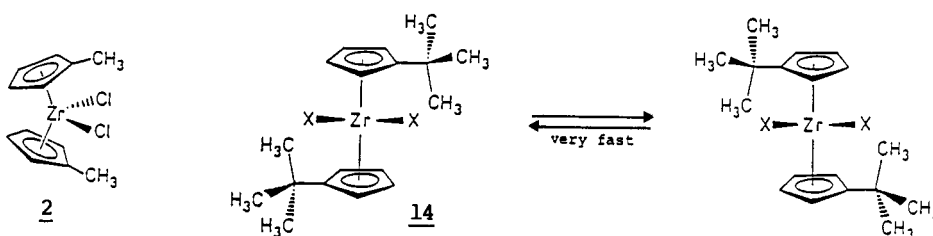


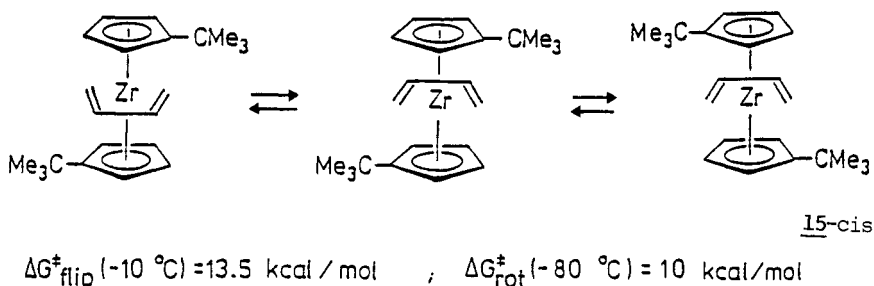
Fig. 2. Two projections of the molecular geometry of bis[(1-methylcyclohexyl)cyclopentadienyl]zirconium dichloride

However, the chiral molecular structure of e.g. bis(tert-butylcyclopentadienyl)zirconium dichloride (**14**) does not reflect itself chemically or NMR spectroscopically in solution due to extremely rapid (RCp)-M rotation.

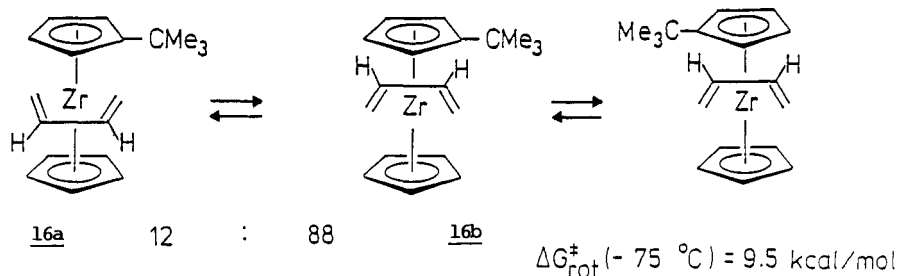


Different from suitably substituted ferrocene or uranocene derivatives (ref. 7) the direct R-Cp interligand interaction in mononuclear bent metallocene complexes $(RCp)_2MX_2$ is insufficient to induce a high (RCp)-M rotational barrier. However, in some $(RCp)_2M(\text{butadiene})$ complexes hindered (RCp)-M rotation can be detected in solution by NMR spectroscopy (ref. 8).

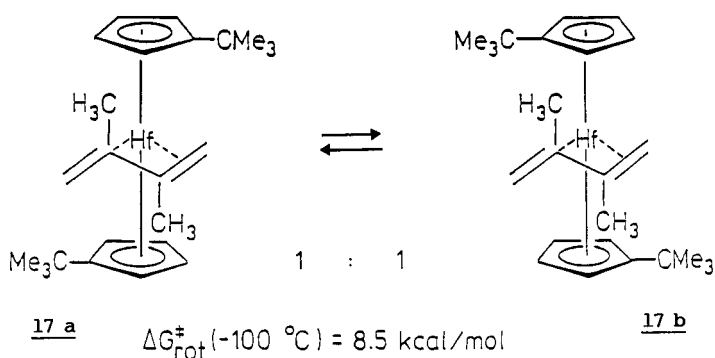
(*s*-Cis- η^4 -butadiene)bis(tert-butylcyclopentadienyl)zirconium **15-cis** exhibits 4 different ^{13}C NMR signals of the butadiene ligand and 8 methine carbon resonances due to the two inequivalent (Me_3C -Cp) ring systems at low temperature ($<-80^\circ C$). This indicates a chiral molecular structure of **15-cis** in solution. The (Me_3C Cp)-Zr rotation is "frozen" on the NMR time scale. Increasing the temperature first results in observing the (RCp)-M rotation then the usual butadiene metallocene topomerization ("ring-flip") (ref. 9) to occur. The apparent molecular symmetry as suggested from the appearance of the dynamic variable temperature NMR spectra is changed accordingly from C_1 through C_s (^{13}C : 2 butadiene, 4 RCp methine carbon signals) to C_{2v} (^{13}C : 2 RCpCH-resonances).



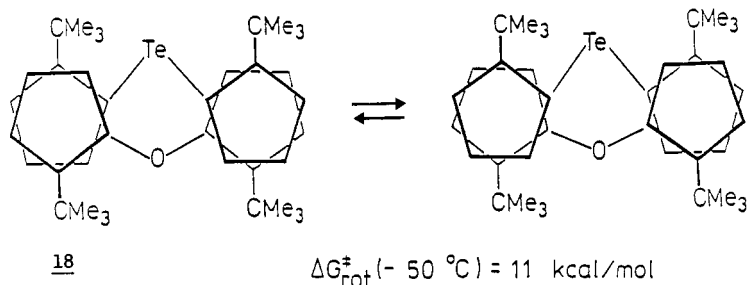
In the presence of only one tert-butyl substituted Cp-ring one can determine which intramolecular interaction is responsible for the relatively high η -cyclopentadienyl-metal rotational barrier in these butadiene metallocene complexes. Upon freezing the "ring-flip" in (*s*-cis-butadiene)Zr(Cp)(tert-butylCp) **16** one observes two diastereomers **16a** and **16b** in a 12:88 ratio by NMR spectroscopy at low temperature. According to NMR NOE measurements the *s*-cis-butadiene ligand in the major isomer (**16b**) opens itself towards the unsubstituted Cp ligand. Only this isomer shows hindered (RCp)-M rotation. Thus, it appears that unfavourable steric interaction between the bulky Cp-bonded tert-butyl group and the substituents at carbon centers C(2)/C(3) of the conjugated diene contributes significantly to the enhanced (RCp)-M rotational activation barrier in these systems.



Combination of the chiral bis(tert-alkylcyclopentadienyl)zirconium unit with a chiral metal ligand moiety leads to diastereomeric metal complexes. The (*s*-trans- η^4 -2,3-dimethylbutadiene)bis(tert-butyl-Cp)hafnium diastereoisomers **17a** and **17b** (ca. 1:1 ratio) have been observed by NMR spectroscopy at low temperature in solution. Equilibration by rapidly occurring (Me_3C Cp)-Hf rotation takes place above $-100^\circ C$ (ref. 8).



Binuclear four-membered metallacyclic chalcogen bridged bent metallocene complexes are readily available upon treatment of (butadiene) $M(\text{CpR})_2$ complexes with elemental selenium or tellurium (ref. 10). Reaction of the 95:5 equilibrium mixture of (*s-cis*/*s-trans*- η^4 -butadiene) $\text{Zr}(\text{CpCMe}_3)_2$ (**15**-*cis/trans*) with tellurium powder followed by addition of one equiv. of water gave $(\text{Me}_3\text{CCp})_2\text{Zr}(\mu\text{-Te})(\mu\text{-O})\text{Zr}(\text{CpCMe}_3)_2$ **18**. For this complex a chiral (racem.-type) geometry was found by X-ray diffraction [in contrast to the meso-type structure of $(\text{Me}_3\text{CCp})_2\text{Zr}(\mu\text{-Te})_2\text{Zr}(\text{CpCMe}_3)_2$ (ref. 11)]. Hindered (RCp)-M rotation of **18** was here detected by variable temperature ^1H NMR spectra showing coalescence of the two tert-butyl signals and the characteristic change from two to one ABCD patterns of the Me_3CCp methine hydrogen resonances.



$(\text{RCp})_2\text{ZrCl}_2$ DERIVED OLEFIN POLYMERIZATION CATALYSTS

Group 4 bent metallocene complexes have been used as transition metal components of very active homogeneous Ziegler Natta type olefin polymerization catalysts. The Cp_2MX_2 /alumoxane catalysts were introduced by Sinn, Kaminsky et al. (ref. 12). The groups of Brintzinger, Kaminsky, Ewen, Pino et al. have recently described interesting chiral variations of this catalyst system for stereospecific polymerizations and oligomerizations of α -olefins (ref. 13).

We have tested whether the chiral molecular geometry of the bis(tert-alkylcyclopentadienyl)zirconium dihalides could be utilized for stereospecific catalytic olefin carbon-carbon coupling. The $(\text{Me}_3\text{CCp})_2\text{ZrCl}_2$ /alumoxane catalyst system turned out to be sufficiently active for propene polymerization. However, even at low temperature (-60°C) it produced only atactic polypropylene (Fig. 3).

The situation is changed when bis[(1-phenylethyl)cyclopentadienyl]-zirconocene dichloride is employed as the transition metal component of the alumoxane containing catalyst system. We have prepared this specific ligand

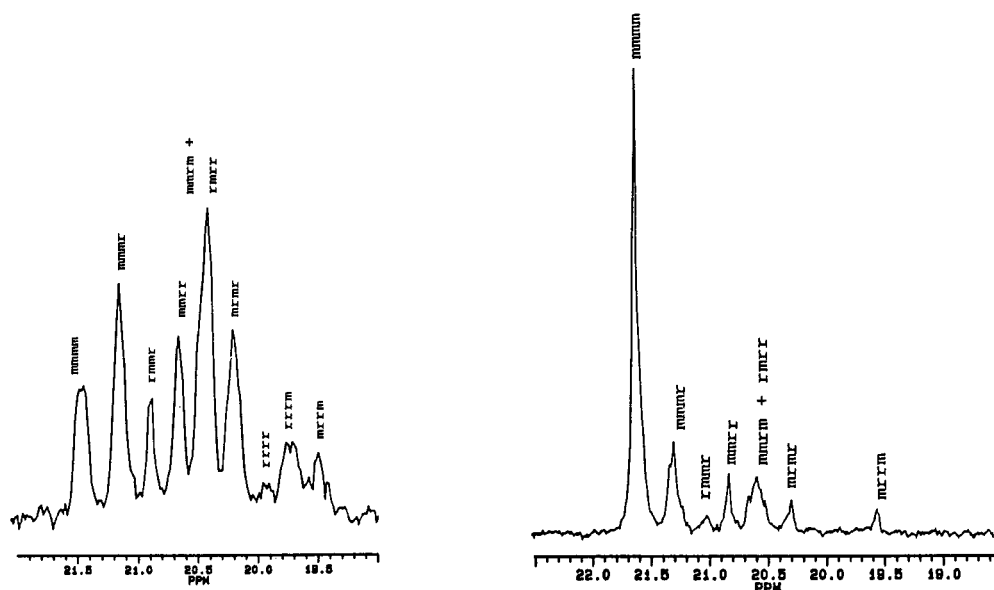


Fig. 3. ^1H decoupled ^{13}C NMR spectra (methyl-C region) of polypropylene prepared with the alumoxane/ $(\text{Cp-CMe}_3)_2\text{ZrCl}_2$ (left) or / $(\text{Cp-CHMePh})_2\text{ZrCl}_2$ (meso/racem. = 1:10) catalyst (right).

by a variation of the literature procedure (ref. 14). Treatment of 6-methyl-6-phenylfulvene with *n*-butyllithium in ether produced (1-phenylethyl)cyclopentadienyl lithium by means of hydride transfer. Subsequent reaction with zirconocene tetrachloride yielded mixtures of meso- and racem.- $(\text{Cp-CHMePh})_2\text{ZrCl}_2$ (19-meso/19-racem.) (ref. 15). Crystallization afforded several samples of this metallocene dihalide enriched in 19-racem. Crystals of pure 19-racem. were characterized by X-ray diffraction (Fig. 4).

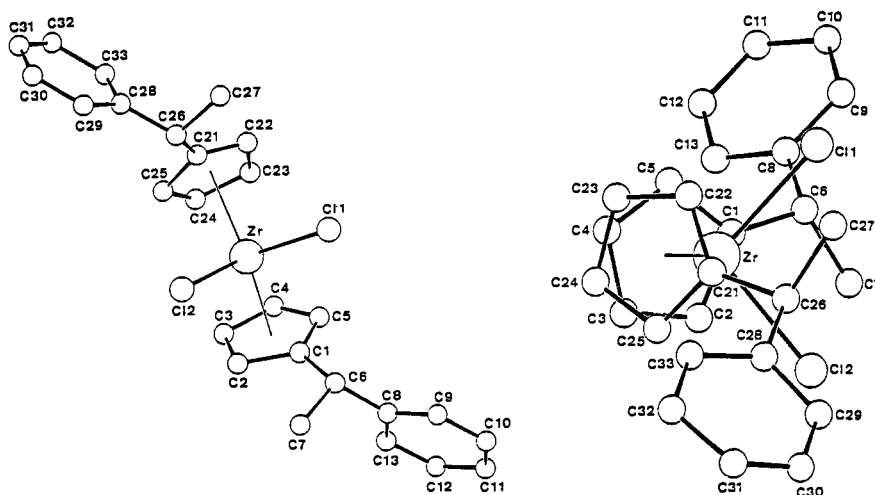


Fig. 4. Two views of the molecular geometry of racem.-bis[(1-phenylethyl)cyclopentadienyl]zirconium dichloride as determined by X-ray diffraction.

Mixtures of meso-/racem.- $(\text{Cp-CHMePh})_2\text{ZrCl}_2$ /alumoxane are active catalysts for the polymerization of propene. In a typical example, a catalyst containing 19 (meso/racem. = 1:10) and $(-\text{AlMe-O-})_n$ (Zr:Al = 1:1200) in toluene at -60°C was used for the stereospecific polymerization of propene. The stereochemical analysis of the stereoregular polypropylene obtained was carried out by ^{13}C NMR spectroscopy (resolution of the methyl region at the pentad level, see Fig. 3) with the usual statistical treatment (refs. 13a, 16). From these spectroscopic results it is suggested that a polymer is formed at this

specific catalyst containing ca. 40% of "ordinary" isotactic polypropylene (enantiomorphic-site control, $\alpha \approx 0.95$; average length of only m diad containing portions $\langle m \rangle_{n,\alpha} \approx 20$, ratio of the Me-pentads $mmmr:mmrr:mrrm = 2:2:1$). The residual material appears to have the characteristics of an isotactic block polymer (Bernoullian: $\sigma = 0.8$; $\langle m \rangle_{n,\sigma} \approx 5$, $mmmr:mrrm = 1$), similar to the polypropylene obtained by Cp_2TiPh_2 /alumoxane catalysts at low temperature (ref. 13a).

The two different types of isotactic polymers could in principle originate from the meso and racem. portions of the catalyst. However, it is well conceivable that the chiral 19-racem. derived catalyst may have produced a stereoregular block polymer containing both isotactic types, formed by a kind of double diastereoselective control (i.e. by chain end and enantiomorphic site). Additional experiments will be carried out to test the validity of this interpretation.

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