Novel Chiral Metallocenophanes Derived from [2.2]Paracyclophane and Their Use in Olefin Polymerization[‡]

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The 4-fulvenyl[2.2]paracyclophane (**1**) was transformed, by treatment with lithium aluminium hydride and methyllithium in tetrahydrofuran, to the corresponding cyclopentadienyl anions **6** and **8**, respectively. The iron complex **7** was prepared from **6**, while **8** was converted into the metal complexes **9** (Fe complex), **10** (Ti), **11** (Zr), **12** (Ti), and **13** (Zr). All new metallocene complexes were characterized by their spectroscopic data. In addition, a single crystal X-ray crystallographic analysis was performed for complex **11**. The metallacyclic zirconocene complex **15** was synthesized by the reaction of the dichloride derivative **13** with two equivalents of n-butyllithium. After activation of complexes **10**–**13** and **15** with methylalumoxane (MAO) they were used for the catalytic polymerization of ethene and propene.

Introduction

Chiral metallocene complexes are important reagents and catalysts in stereoselective synthesis of organic fine chemicals and polymers.[2] In principle, chirality may be generated in a metallocene moiety by the introduction of both achiral and chiral substituents. Whereas in the latter case the resulting metallocene unit necessarily has to be chiral, the former case is more complex. Chirality, and especially the resolution of the enantiomers of the substituted metallocene complexes, now depends on various factors, including the height of the rotational barrier and the substitution pattern. For example, a metallocene complex carrying two achiral, non-identical substituents in one cyclopentadienyl ring will always be chiral and in principle resolvable, regardless of the barrier of rotation of the five-membered rings. Placing one substituent in either ring, however, does not necessarily induce chirality. Provided the rotational barrier of this derivative is sufficiently low, one conformation having a plane of symmetry is always accessible and the metallocene complex is hence unresolvable. One of the most widely used ways of reducing conformational mobility in metallocene complexes consists of the introduction of a molecular bridge between the two "decks" of the metal organic compound.[3,4] As far as chiral substituents are concerned, we are interested in combining molecules with a chiral plane, in particular monosubstituted [2.2]paracyclophanes, with a metallocene. Because of the rigidity of the molecular framework, these cyclophanes are always chiral, regardless of the type of the substituent and its position in these bridged aromatic compounds. By condensing 1,3-cyclopentadiene and indene with 4-formyl-[2.2]paracyclophane, i.e. applying the Thiele fulvene synthesis to this aldehyde, we have recently been able to prepare a number of fulvenyl paracyclophanes.[5] In the present paper we describe the preparation of ferrocene, zirconocene, and titanocene complexes of these new chiral ligands, and we report on first polymerization experiments in which these metal complexes (in racemic form) were used as catalysts for the polymerization of olefins (ethene, propene).

Results and Discussion

Stereochemistry of Addition of Methyllithium to 4-(6-Fulvenyl)[2.2]paracyclophane (1)

The formation of cyclopentadienyl anions by addition of organolithium reagents to the 6-position of fulvenes is a

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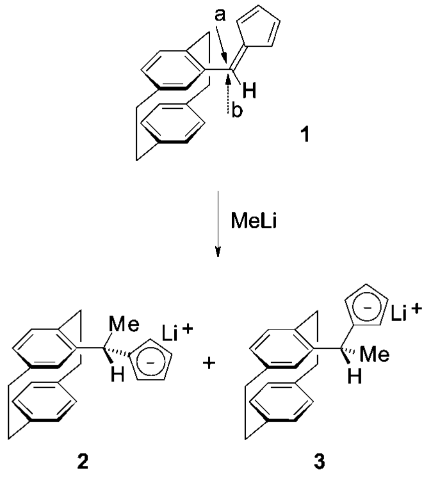
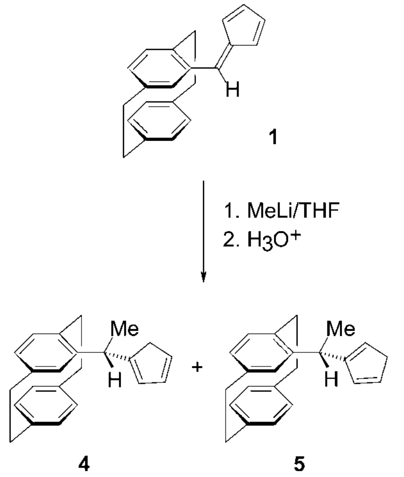


Scheme 1. Stereochemistry of addition of methyllithium to the fulvene **1**



Scheme 2. Addition of methyllithium to the fulvene **1**

well-known process for generating these species, which are necessary for subsequent metallocene formation.[6,7] To investigate the stereochemistry of this process we selected the fulvene derivative **1** (Scheme 1), which is easily available in gram quantities.[5]

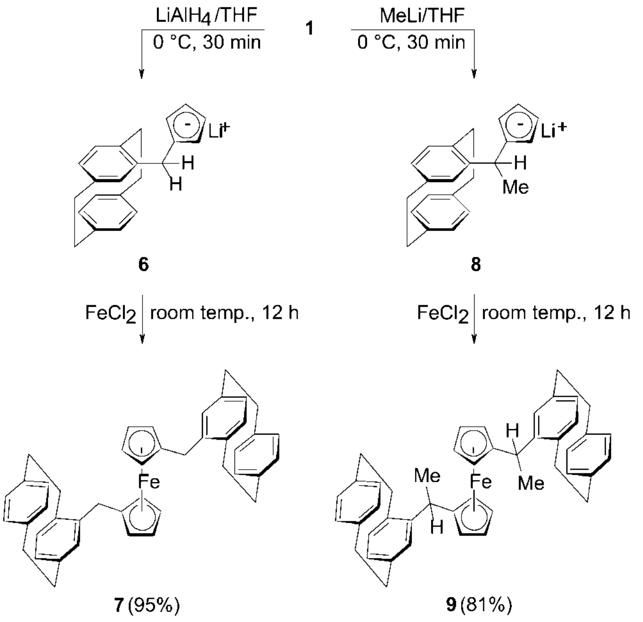
Unlike in the 4-formyl and 4-acetyl derivatives of [2.2]-paracyclophane,[8] the conformation of the substituent in 4-fulvenyl[2.2]paracyclophane (**1**) is rigid. In our earlier studies we had shown by NMR spectroscopy and X-ray crystal structure analysis[5] that the most stable conformation of **1** in solution and in the solid state is the one in which the proton at C-6 of the fulvene ring is located in the intra-annular space of the cyclophane part of the hydrocarbon, the bulky cyclopentadienyl unit pointing towards the exterior. The barrier for rotation around the C−C bond connecting the cyclophane residue and the fulvene unit is high (26 kcal·mol^{-1}). Addition of methyllithium to **1** at C-6 to provide the corresponding cyclopentadienyl anion led to the generation of a new chiral centre, and in principle a pair of diastereomeric cyclopentadienides (**2** and **3**) could be obtained, depending on the approach of the nucleophile as shown by pathways **a** and **b** in Scheme 1. However, in the former pathway the methyllithium approaches from the exterior of the cyclophane unit and it is sterically less hindered compared to pathway **b**. In this latter trajectory the approach of the metal organic reagent is sterically demanding because of hindrance by the bridge hydrogen atoms and also the unsubstituted aromatic ring of the phane unit. Both these effects essentially block one face of the C-6 position of the fulvene substituent. The approach of methyllithium via pathway **a** should hence be preferred, leading to the formation of a single diastereomer of the cyclopentadienide.

In order to verify this hypothesis, we added methyllithium to the racemic mixture of **1** and subsequently quenched the reaction mixture with acid. Careful analysis of the high-resolution ^{1}H and ^{13}C NMR spectra clearly indicated the formation of two isomeric products **4** and **5** in a nearly 2:1 ratio (Scheme 2), each one as a single diastereomer. In the ^{1}H NMR spectrum of the mixture of **4** and **5** the methine proton ($CH{-}CH_3$) appeared as overlapping quadruplets at δ_H = 3.90 and 3.87 (J = 7.1 Hz) and the methyl protons as a single doublet at δ = 1.23 (J = 7.1 Hz). In the corresponding ^{13}C NMR spectrum the methine carbon atom was registered at δ_C = 38.0 and 37.43 and the methyl carbon atom at δ_C = 23.59 and 22.92. The methylene carbon atom of the cyclopentadiene ring appeared at δ_C = 42.77 and 41.12.

Thus, we conclude that the addition of methyllithium to fulvene **1** is highly stereoselective in that the methyl group approaches from the less hindered face of the fulvene (pathway **a** in Scheme 1), leading to the formation of a single diastereomer of the cyclopentadienyl anion. This diastereomer is a crucial intermediate en route to the metallocenes. This argument is further substantiated by the X-ray crystal structure of the zirconocene dichloride **11** (to be discussed below) that clearly reveals the stereochemistry of the newly generated chiral center upon addition of methyllithium. It should be mentioned that the diastereoselectivity of the addition of organometallic reagents to the 4-formyl- and 4-acetyl derivatives of [2.2]paracyclophane is poor because of the high conformational mobility of these functional groups in comparison to the fulvenyl substituent.[7]

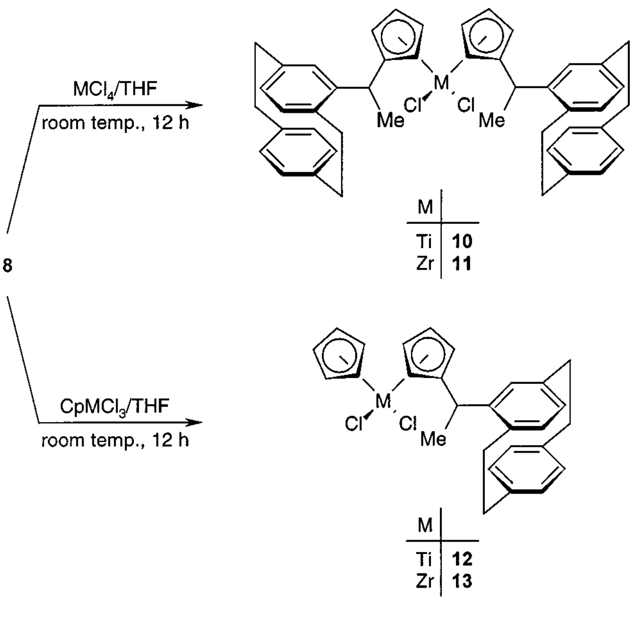
Synthesis of Metallocenes

The ferrocene derivatives **7** and **9** were prepared by reaction of the corresponding lithium cyclopentadienides **6** and **8**, respectively, with $FeCl_2$ in anhydrous tetrahydrofuran (Scheme 3). In both complexes the proton resonance signals corresponding to the cyclopentadienyl ring appeared between δ = 4.0−4.5 in the ^{1}H NMR spectra (Cp_2Fe: δ_H = 4.0−4.2). In the ^{13}C NMR spectra the corresponding carbon atoms were registered in the range δ_C = 65−70 (Cp_2Fe: δ_C = 65−67). Further, it is also evident from the NMR spectra that both **7** and **9** were produced as a 1:1 mixture of diastereomers. In the ^{1}H NMR spectrum of **9** the methyl groups produced two overlapping doublets (δ_H = 1.52 and 1.50). In the ^{13}C NMR spectrum of both compounds two sets of signals for each carbon atom were present indicating the formation of two isomers. Finally, in the mass spectra of these ferrocene derivatives the molecular ion peak appeared as the base peak, corresponding to the generation of the respective ferrocenium ions of **7** and **9**.



Scheme 3. Synthesis of the ferrocenes **7** and **9** from the fulvene **1**

The metallocene dichloride derivatives **10** and **11** were synthesized by reaction of the lithium cyclopentadienide **8** with $TiCl_4$ and $ZrCl_4$, respectively, as shown in Scheme 4. Both **10** and **11** were obtained as a 1:1 mixture of two diastereomers, as evident from the ^1H and ^{13}C NMR spectra. In the case of **10** the methine proton ($CH-CH_3$) appeared as overlapping quadruplets for the two diastereoisomers at δ = 4.52 and 4.56, and the methyl protons at δ_H = 1.35 and 1.31, each as a well-resolved doublet (J = 6.9 Hz).



Scheme 4. Synthesis of metallocene dichlorides from the fulvene **1**

The cyclopentadienyl protons were registered in the same region as the aromatic protons of the cyclophane unit between δ = 6.0 and 7.0. (Cp_2TiCl_2, δ_H = 6.59). However, in the ^{13}C NMR spectrum of **10** the carbon signals corresponding to the cyclopentadienyl unit appeared at lower δ_C values in the region of 110 to 120, in contrast to the aromatic carbon atoms, which absorbed above δ = 130. Similarly, in the case of **11** the methine proton ($CH-CH_3$) appeared as overlapping quadruplets at δ_H = 4.48 and 4.46 and the methyl protons at δ_H = 1.44 and 1.42 as two overlapping doublets (J = 6.8 Hz). In the mass spectra of **10** and **11** the molecular ions generate a cluster of peaks due to the isotopes of chlorine and the metal atom. The intensities of these peaks matched with the calculated values based on the natural isotopic abundances of chlorine and the metal atom. Finally, the structure of the zirconocene dichloride **11** was confirmed by single crystal X-ray crystallographic analysis as shown in Figure 1.

Compound **11** crystallizes with two independent half molecules and two molecules of deuteriochloroform in the asymmetric unit. The two half molecules are completed by the operation of a twofold axis. The centrosymmetric space group *Pbcn* only allows the determination of the relative configuration of the two diastereomeric molecules; both showing the same relative configuration (4*R*,17*S*). The angles between the cyclopentadiene units in the molecules amount to 54.42(11)° (C19 to C23) and 56.69(10)° (C19′ to C23′). To minimize the electronic repulsion of the π-systems, the angles between the four coplanar carbon atoms in the [2.2]paracyclophane units and the cyclopentadiene units are 78.29(10)° (C4/C5/C7/C8 to C19−C23) and 70.75(10)° (C4′/C5′/C7′/C8′ to C19′−C23′), corresponding to an approximately perpendicular arrangement. The zirconium atoms show a distorted tetrahedral coordination involving the two chlorine atoms and the centroids of the π-cyclopentadienyl units. The Zr−C bonding to the cyclopentadienyl moieties can be described as pentahapto coordinated, since the distances between the metal atoms and the coordinated carbons atoms deviate from each other negligibly: 2.483(3) to 2.561(3) Å (C19 to C23) and 2.477(3) to 2.578(3) Å (C19′ to C23′). The average Zr−C distance amounts to 2.515 Å for Zr and 2.518 Å for Zr′ and is in good agreement with the vapor-phase electron-diffraction study of the $(\pi\text{-}C_5H_5)_2ZrCl_2$ molecule:[9] 2.522(5) Å. The centroids of the cyclopentadienyl rings are separated from the heavy atoms by 2.209 Å (Zr) and 2.214 Å (Zr′). The Zr−Cl bond lengths of 2.442(1) (Zr−Cl) and 2.444(8) Å (Zr′−Cl′) are very close to the sum of Pauling radii (2.44 Å)[10] and correspond to the values found in other zirconium complexes with coordinated cyclopentadienyl groups.[11,12] The Cl−Zr−Cl angles of 95.9(4) (Zr) and 95.8(4)° (Zr′) are somewhat less than the 97.1° for $(\pi\text{-}C_5H_5)_2ZrCl_2$.[11]

The ordered deuteriochloroform molecule C99−Cl99 is stabilized by Cl···Cl interactions in the range of the double

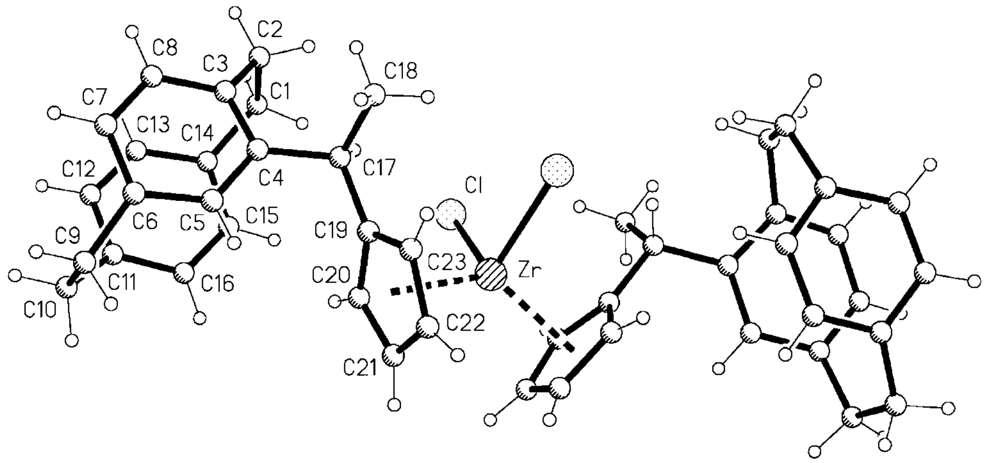


Figure 1. The structure of one independent molecule of **11** in the crystal; radii are arbitrary

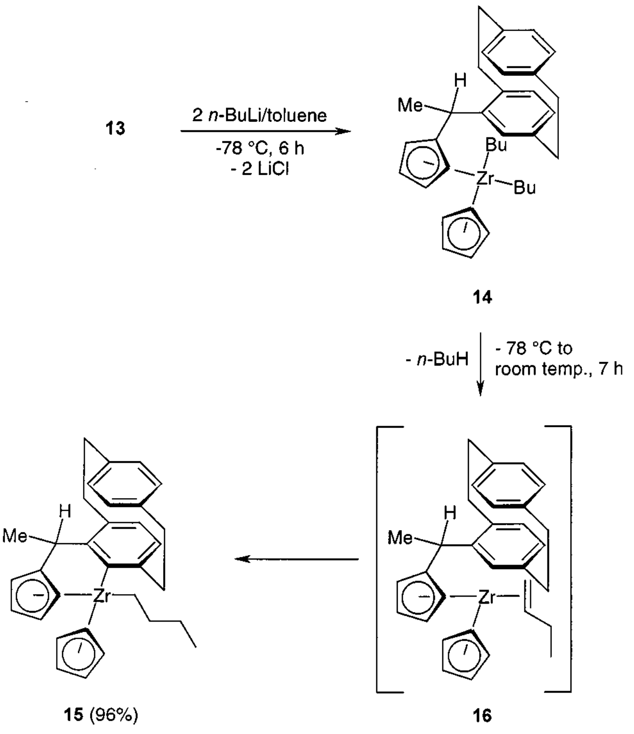
van-der-Waals radius. This molecule connects the two independent zirconocenes to another via two chlorine atoms and interacts via the third chlorine atom with the other solvent molecule: Cl′···Cl99 3.633(1) Å, Cl···Cl98 3.518(1) Å, Cl97···Cl94 3.654(7) Å.

The mixed ligand metallocene dichloride derivatives **12** and **13** were prepared by metathetic reaction of **8** with $CpTiCl_3$ and $CpZrCl_3$, respectively, in anhydrous tetrahydrofuran (Scheme 4). Both **12** and **13** formed as single diastereomers, as evident from the ^1H and ^{13}C NMR spectroscopic data. For example, the methine proton of **12** appeared as a quadruplet at $\delta_H = 4.54$ and the methyl protons absorbed as a doublet at $\delta_H = 1.30$ ($J = 7.0$ Hz). Analogously, in the case of **13** the methine proton was registered as a quadruplet $\delta_H = 4.40$ and the methyl protons appeared as a doublet at $\delta_H = 1.35$ ($J = 7.0$ Hz). In both complexes **12** and **13** the unsubstituted cyclopentadienyl ligand protons are represented by a sharp singlet at $\delta = 6.61$ and 6.52, respectively (for five proton integration) in the ^1H NMR spectra. In the ^{13}C NMR spectra the corresponding carbon atoms appear as a single resonance line at $\delta = 119.9$ and 115.8, respectively, indicating free rotation of the cyclopentadienyl ligand in these complexes.

Synthesis of a Metallacyclic Zirconocene Complex by Using a CH Bond Activation Reaction

The metallocene dichloride complex **13** is well suited as a starting material for the synthesis of metallacyclic complexes. Only a single reaction product was obtained when **13** was treated with two equivalents of *n*-butyllithium in toluene. The key reaction step in this transformation is a CH bond activation that led to cyclometallation as shown in Scheme 5.

During this reaction a zirconocene dibutyl complex **14**,[13] which was stable in solution at low temperatures (−40 °C) for several minutes, was formed as an intermediate. The unsubstituted parent compound of this complex was characterized using NMR spectroscopy.[14]



Scheme 5. Synthesis of the metallacyclic complex **15** from the metallocene dichloride complex **13**

Subsequently, **14** is proposed to lose *n*-butane[15,16] in a β-H transfer reaction, resulting in the formation of a reactive (η^2-butene) complex, **16**. "$Cp_2Zr(\eta^2$-butene)", generated as an intermediate during the reaction of Cp_2ZrCl_2 with two equivalents of *n*-butyllithium, has been stabilized with trimethylphosphane and characterized.[17−19] One phenyl moiety of the [2.2]paracyclophane group of **16** shown in Scheme 5 then reacted further to yield the corresponding metallacycle **15** by a CH bond activation and hydrogen transfer reaction.[20] The proposed structure of metallacycle **15** is based on comparison with similar phenylalkyl-substituted zirconocene complexes[21] and the steric situation at the cyclophane moiety. Within the reaction pathway only one isomer is formed (see NMR spectroscopic data) that can have either (*R*) or (*S*) configuration at the 1,1-ethylidene bridge.

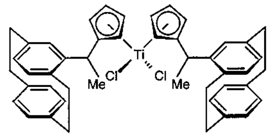
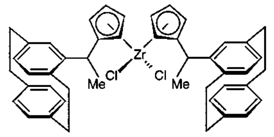
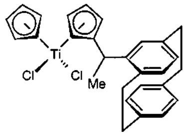
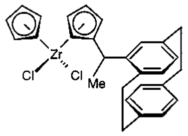
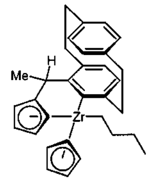
Polymerization Experiments

The resultant metallocene complexes are precursors for homogeneous ethylene and propylene polymerization. The complexes are activated by adding a 3000-fold molar excess of MAO. The formation of an active catalyst system is indicated by a colour change.

a) Ethylene Polymerization

The polymerization activities of the activated metallocene complexes, the number average of the molecular weight M_n, the weight average M_w, the centrifuge average M_z, the viscosity average M_η, and the polydispersity D of the resulting polyethylenes are listed in Table 1.

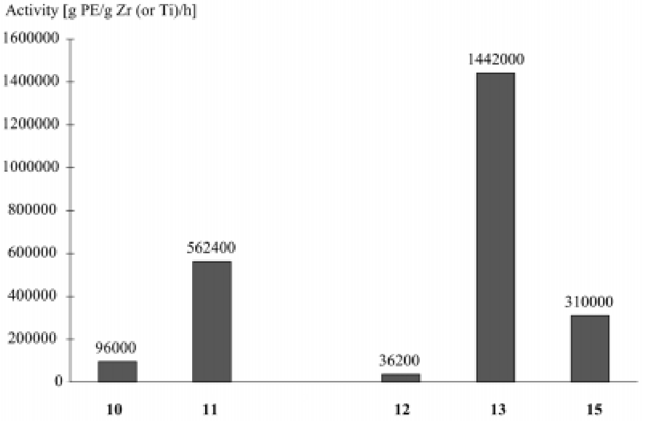
Table 1. Overview of the ethylene polymerization experiments and polymer analytical results. High temperature gel permeation chromatography (HT-GPC): M_n = number average of the molecular weight (kg/mol), M_w = weight average of the molecular weight (kg/mol), M_z = centrifuge average of the molecular weight (kg/mol), M_η = viscosity average of the molecular weight (kg/mol), D = polydispersity ($D = M_w/M_n$)

	Metallocene complex	Activity [g PE / g M / h] M = Ti, Zr	Fouling	HT-GPC M_n M_w M_z M_η D
10		96000	middle	1350 17590 395510 9770 13.0
11		562400	middle	370 4580 230360 2480 12.2
12		36200	low	280 2570 39530 1630 9.1
13		1442000	low	290 1490 8590 1220 5.2
15		310000	low	370 3240 292010 3240 8.8

The central metal has a strong influence on the polymerization behaviour of the metallocene complexes;[21] in both bis[(paracyclophanyl)ethylcyclopentadienyl]metallocene and [(paracyclophanyl)ethylcyclopentadienyl](cyclopentadienyl)metallocene complexes, the zirconium complexes $(Cp')_2ZrCl_2$ (**11**) and $Cp'CpZrCl_2$ (**13**) are much more active than the corresponding titanium complexes $(Cp')_2TiCl_2$ (**10**) and $Cp'CpTiCl_2$ (**12**). The reason for this effect is the lower thermal stability of the titanium analogues.[22]

The bulky paracyclophanyl moiety exerts two different influences on the active metal centre. On the one hand, steric crowding can have a stabilizing effect on sensitive metal centres, as in the case of the titanium complexes.[23] Therefore, the productivity of $(Cp')_2TiCl_2$ (**10**) containing two bulky moieties is higher than that of $Cp'CpTiCl_2$ (**12**) containing only one bulky group, despite the stronger blockage of the active metal centre.

On the other hand, steric crowding lowers the productivity, as in the case of the zirconium complexes. The productivity of $(Cp')_2ZrCl_2$ (**11**) is much lower than that of $Cp'CpZrCl_2$ (**13**). Similarly, steric overloading is responsible for the lower productivity of the metallacyclic zirconium complex **15** compared to the corresponding precursor **13**. After activation of the metallacycle with MAO, the ring could be expanded during the polymerization process by repeated ethylene insertion into the metal−carbon σ bond of the metallacycle.[24,25] Finally, an insoluble polymer was formed that was directly attached to one π-ligand of the active catalyst cation. The polyethylene fixed to the paracyclophanyl moiety increased the steric overloading and lowered the productivity of complex **15** significantly (Scheme 6).



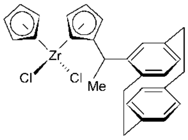
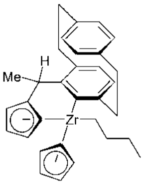
Scheme 6. Comparison of the catalytic activities of the metallocene complexes **10−13** and **15** for the polymerization of ethylene

This incorporation of the zirconium complex into the polymer backbone is an elegant and inexpensive way to inherently increase heterogeneity and form a supported and self-immobilizing catalyst for ethylene polymerization. As a result of the conversion, the polyolefins formed with the heterogeneous catalysts precipitate onto the catalyst's surface and not onto internal wall surfaces, causing reactor fouling. The conversion of a homogeneous metallocene/MAO catalyst into a heterogeneous catalyst is absolutely necessary for the "slurry loop" process.

b) Propylene Polymerization

The polymerization activities of the activated metallocene complexes, the molecular weights, and the isotacticities of the resulting polypropylenes are listed in Table 2.

Table 2. Overview of the propylene polymerization experiments and polymer analytical results.

Metallocene complex	Activity [g PP / g Zr / h]	Molecular mass[a] M$^+$ [*m*/*z*]	Tacticity (only isotactic contribution mmmm)[b] [%]
13 	49370	Low-molecular weighted oil 952[c]	4.6
15 	39350	Low-molecular weighted oil 953[c]	4.8

[a] Determined by mass spectrometry due to the low molecular weight. – [b] Determined by ^{13}C NMR spectroscopy (solvent 1,2,4-trichlorobenzene/1,1,2,2-tetrachlorodeuterioethane; 60° C). – [c] Highest peak in mass spectrum.

The synthesized metallocene complexes were activated with MAO; only the monosubstituted Cp′CpZrCl$_2$ (**13**) and the corresponding metallacycle **15** were active in the propylene polymerization with a productivity of 49370 g PP/g Zr/h (**13**) and 39350 g PP/g Zr/h (**15**). The produced polypropylenes were atactic, low-molecular weight oils with an isotactic share of only 4.6% (**13**) and 4.8% (**15**).

The comparatively low activity in propylene polymerization can be explained by the steric crowding of the active centre. The bulky paracyclophanyl group not only blocks the access of the monomer to the metal but also the growth and orientation of the polymer chain. The atactic character of the polymer is the result of random coordination of the prochiral monomer to the metal. This random coordination is probably due to the lack of a favoured configuration of the catalyst. The low-molecular weight is an indication of early termination reactions.

Experimental Section

The instrumentation used in this study has been described in the previous publications of this series.[1]

Addition of Methyllithium to Fulvene 1: Formation of 4-[1-(1-Cyclopenta-1,3-dienyl)ethyl][2.2]paracyclophane (4) and 4-[1-(2-Cyclopenta-1,3-dienyl)ethyl][2.2]paracyclophane (5): To an ice-cold solution of fulvene **1** (0.28 g, 1 mmol) in 5 mL of anhydrous THF, was added dropwise an ethereal solution of MeLi (0.65 mL of 1.6 M solution, 1.1 mmol) under N$_2$. The initially dark-red solution turned yellow. After 30 min of stirring, 10 mL of 1 N HCl was added and the mixture was extracted with dichloromethane. The organic layer was separated and washed with saturated brine solution and dried with anhydrous magnesium sulfate. Evaporation of the solvent yielded a yellow viscous oil (0.3 g, 100%) consisting of a mixture of compounds **4** and **5** in a 2:1 ratio (NMR analysis). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.23 (d, *J* = 7.1 Hz, 3 H), 2.65–3.10 (m, 9 H), 3.40 (m, 1 H), 3.87 and 3.90 (overlapping quadruplets, *J* = 7.1 Hz, 1 H), 5.85 and 6.00 (broad s, 2 × 1 H), 6.10–6.30 (m, 4 H), 6.35–6.55 (m, 4 H), 6.65 (m, 1 H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 22.8 (q), 23.5 (q), 33.2 (t), 33.3 (t), 34.7 (t), 35.1 (t), 35.2 (t), 35.3 (t), 35.3 (t), 37.3 (d), 37.9 (d), 41.0 (t), 42.7 (t), 127.4 (d), 128.5 (d), 130.1 (d), 130.3 (d), 130.5 (d), 130.9 (d), 130.9 (d), 131.3 (d), 132.1 (s), 132.3 (d), 132.5 (d), 132.6 (d), 132.6 (d), 132.9 (d), 133.0 (d), 133.7 (d), 134.4 (d), 135.4 (d), 135.4 (d), 136.9 (s), 137.0 (s), 139.3 (s), 139.4 (s), 139.4 (s), 139.5 (s), 139.7 (s), 139.7 (s), 144.5 (s), 145.3 (s), 149.6 (s), 151.8 (s). – MS (EI, 70 eV): *m*/*z* (%) = 301 (10), 300 [M$^+$] (44), 196 (30), 195 (76), 181 (42), 165 (34), 155 (12), 153 (12), 142 (11), 141 (12), 128 (16), 119 (18), 104 (14), 91 (14), 86 (18), 84 (28).

Bis[(4-[2.2]paracyclophanyl)methylcyclopentadienyl]iron(II) (7): To an ice-cold, stirred solution of fulvene **1** (0.57 g, 2 mmol) in 20 mL of anhydrous THF, was added LiAlH$_4$ (76 mg, 2 mmol) under N$_2$. The initially dark-red solution turned yellow. After stirring for 30 min at 0 °C the solution was added dropwise with a syringe to a stirred, ice-cold slurry of FeCl$_2$ (130 mg, 1 mmol) in 20 mL of anhydrous THF. After the addition was complete the solution was warmed to room temp. and stirred overnight. The reaction was quenched by dropwise addition of 20 mL of 1 N HCl. The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with water (20 mL) and dried (MgSO$_4$). Removal of the solvent yielded a brownish yellow solid (0.6 g, 95%) that was purified for analytical purposes by column chromatography on silica gel with pentane and dichloromethane (1:1, v/v) to yield ferrocene **7** as a bright yellow solid, m.p. 196–200 °C- IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1}, 2851, 1593, 1412, 716, 502. – UV/Vis (CHCl$_3$): λ_{max} (log ε) = 266 nm (3.87), 300 (3.27), 314 (3.12). – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.80 (m, 2 H), 2.93 (m, 2 H), 2.98–3.25 (m, 12 H), 3.34 (m, 2 H), 3.51 (m, 2 H), 3.89 (broad s, 4 H), 3.95 (broad s, 4 H), 6.00 (s, 2 H), 6.36 (m, 2 H), 6.40 (m, 4 H), 6.46 (m, 2 H), 6.52 (m, 2 H), 6.68 (m, 2 H). – ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 33.5 (t), 33.9 (t), 34.0 (t), 34.2 (t), 35.0 (t), 35.3 (t), 67.9 (d), 68.1 (d), 69.1 (d), 69.6 (d), 69.8 (d), 87.5 (s), 128.5 (d), 128.6 (d), 130.5 (d), 132.2 (d), 132.2 (d), 133.1 (d), 133.2 (d), 134.5 (d), 134.7 (d), 134.7 (d), 137.3 (s), 137.3 (s), 139.3 (s), 139.5 (s), 139.6 (s), 140.4 (s), 140.5 (s). – MS (EI, 70 eV): *m*/*z* (%) = 627 (50), 626 [M$^+$] (100), 522 (16), 521 (10), 405 (12), 342 (16), 341 (16), 340 (26), 300 (14), 237 (12), 181 (20), 180 (22), 179 (56), 164 (20), 104 (18). – HMRS: *m*/*z* calcd. for C$_{44}$H$_{42}$Fe: 626.2636; found 626.2627. – C$_{44}$H$_{42}$Fe (626.3): calcd. C 84.31, H 6.76; found C 84.34, H 6.69.

Bis[1-(4-[2.2]paracyclophanyl)ethylcyclopentadienyl]iron (II) (9): To an ice-cold, stirred solution of fulvene **1** (0.57 g, 2 mmol) in 20 mL of anhydrous THF, was added dropwise an ethereal solution of MeLi (1.25 mL of 1.6 M solution, 2 mmol) under N$_2$. The initially dark-red solution turned yellow. After 30 min the solution was added dropwise with a syringe to a stirred, ice-cold slurry of FeCl$_2$ (130 mg, 1 mmol) in 20 mL of anhydrous THF. After the addition the solution was stirred at room temp. overnight and worked up as described for **7** to yield a dark-red solid (0.52 g, 81%). The crude product was purified by column chromatography on silica gel with pentane and dichloromethane (1:1, v/v) to yield ferrocene **9** as a bright yellow solid, m.p. 200−202 °C; 1:1 mixture of diastereomers as inferred from the NMR spectra. − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1}, 2851, 1591, 1411, 901, 716. − UV/Vis (CHCl$_3$): λ_{max} (log ε) = 262 nm (4.05), 296 (3.42), 310 (3.36). − ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.50 and 1.52 (overlapping doublets, *J* = 7.4 Hz, 6 H), 2.75 (m, 2 H), 2.90−3.30 (m, 12 H), 3.50 (m, 2 H), 3.90 (m, 2 H), 4.18 (s, 2 H), 4.32 (d, *J* = 10.8 Hz, 2 H), 4.41 (s, 2 H), 4.50 (d, *J* = 11.4 Hz, 2 H), 5.74 (s, 1 H), 5.76 (s, 1 H), 6.25 (m, 4 H), 6.35 (m, 2 H), 6.55 (m, 4 H), 6.64 (d, *J* = 7.5 Hz, 1 H), 6.68 (d, *J* = 7.4 Hz, 1 H). − ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 23.4 (q), 23.5 (q), 33.0 (t), 33.0 (t), 34.8 (t), 34.9 (t), 35.1 (t), 35.2 (t), 36.4 (d), 36.6 (d), 67.9 (d), 68.3 (d), 68.5 (d), 68.6 (d), 69.0 (d), 69.5 (d), 69.8 (d), 92.9 (s), 93.2 (s), 130.2 (d), 130.2 (d), 130.3 (d), 130.8 (d), 130.9 (d), 132.4 (d), 132.4 (d), 132.6 (d), 132.7 (d), 132.9 (d), 132.9 (d), 135.1 (d), 135.1 (d), 136.3 (s), 136.3 (s), 139.2 (s), 139.3 (s), 139.5 (s), 139.5 (s), 139.6 (s), 139.6 (s), 146.2 (s), 146.2 (s). − MS (EI, 70 eV): *m*/*z* (%) = 655 (50), 654 [M$^+$] (100), 640 (8), 639 (10), 535 (10), 420 (12), 419 (38), 355 (20), 354 (26), 315 (20), 251 (20), 193 (52), 179 (32), 165 (22), 104 (45). − C$_{46}$H$_{46}$Fe (654.7): calcd. C 84.37, H 7.09; found C 84.32, H 7.09.

Bis{[1-(4-[2.2]paracyclophanyl)]ethylcyclopentadienyl}titanium Dichloride (10): A solution of the lithium cyclopentadienide (**8**) (2 mmol in 20 mL of anhydrous THF, prepared by the method described above for the synthesis of **9**) was added dropwise with a syringe to a stirred, ice-cold solution of TiCl$_4$ (190 mg, 1 mmol) in 20 mL of anhydrous THF. During the addition the yellowish solution turned dark red. The reaction mixture was stirred at room temp. for 12 h and worked up as described for **7** to yield a red solid (0.57 g, 83%). This solid was further purified by recrystallization by dissolving it in a minimum amount of dichloromethane and adding pentane until a slight turbidity appeared. Upon cooling the solution in the freezer (−25 °C), the titanocene dichloride **10** was obtained as a bright red solid, m.p. > 250 °C (dec.). − IR(KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2852, 1592, 1486, 824, 717. − UV/Vis (CHCl$_3$): λ_{max} (log ε) = 260 nm (4.49), 396 (3.44). − ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.31 (d, *J* = 6.9 Hz, 3 H), 1.35 (d, *J* = 7.0 Hz, 3 H), 2.65 (m, 2 H), 2.85−3.15 (m, 10 H), 3.20 (m, 2 H), 3.45 (m, 2 H), 4.52 and 4.56 (two overlapping quadruplets, 2 H, *J* = 6.9 and 7.0 Hz), 5.49 (m, 1 H), 5.53 (m, 1 H), 6.20 (m, 2 H), 6.25−6.40 (m, 6 H), 6.45−6.60 (m, 8 H), 6.58 (m, 1 H), 6.69 (m, 1 H), 6.71 (m, 1 H), 6.75 (m, 1 H), 6.86 (m, 1 H). − ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 22.2 (q), 22.3 (q), 33.3 (t), 33.3 (t), 34.9 (t), 35.0 (t), 35.2 (t), 35.3 (t), 38.5 (d), 38.6 (d), 109.8 (d), 110.8 (d), 119.9 (d), 119.9 (d), 120.8 (d), 121.0 (d), 122.2 (d), 122.2 (d), 129.6 (d), 129.7 (d), 130.6 (d), 130.7 (d). 131.5 (d), 131.5 (d), 132.1 (d), 132.6 (d), 132.6 (d), 133.1 (d), 135.9 (d), 136.0 (d), 137.0 (s), 137.1 (s), 139.3 (s), 139.3 (s), 139.7 (s), 139.8 (s), 139.8 (s), 142.3 (s), 143.0 (s), 144.9 (s), 145.0 (s). − MS (EI, 70 eV): *m*/*z* (%) = 716 [M$^+$] (3), 598 (12), 419 (8), 384 (34), 383 (22), 382 (30), 300 (16), 299 (10), 298 (22), 278 (12), 196 (20), 195 (78), 194 (18), 193 (100), 192 (12), 181 (20), 180 (18), 179 (32), 178 (34), 165 (50), 119 (42), 105 (54), 104 (30), 78 (230), 77 (12).

Bis{[1-(4-[2.2]paracyclophanyl)]ethylcyclopentadienyl}zirconium Dichloride (11): Compound **11** was prepared by the procedure described for the synthesis of **10**, using ZrCl$_4$ (230 mg, 1 mmol). The crude product was obtained as a grey solid (0.70 g, 92%). The solid was triturated with diethyl ether (20 mL) and filtered to obtain pure zirconocene dichloride **11** as a tan-coloured solid (0.37 g). Further recrystallization from dichloromethane in the freezer (−25 °C) yielded colourless crystals of **11**, m.p. 280−285 °C (dec.). The ether soluble portion was evaporated to dryness and the ^{1}H NMR spectrum of this solid (0.31 g) indicated mainly **11**, along with small amounts of **4** and **5**. − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1}, 1592, 833, 821. − UV/Vis (CHCl$_3$): λ_{max} (log ε) = 296 nm (3.52), 340 (3.27), 372 (2.85). − ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.42 and 1.44 (two overlapping doublets, 3 H each, *J* = 6.8 Hz), 2.72 (m, 2 H), 2.90−3.10 (m, 8 H), 3.15 (m, 2 H), 3.25 (m, 2 H), 3.53 (m, 2 H), 4.46 and 4.48 (two overlapping quadruplets, 1 H each, *J* = 6.8 Hz), 5.52 (d, *J* = 1.1 Hz, 1 H), 5.54 (d, *J* = 1.2 Hz, 1 H), 6.25−6.45 (m, 8 H), 6.45−6.65 (m, 8 H), 6.75 (m, 2 H), 6.82 (m, 2 H). − ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 22.6 (q), 33.3 (t), 33.3 (t), 34.9 (t), 34.9 (t), 35.2 (t), 35.3 (t), 37.6 (d), 37.7 (d), 106.5 (d), 107.1 (d), 115.1 (d), 115.2 (d), 116.9 (d), 117.4 (d), 118.0 (d), 118.4 (d), 129.5 (d), 129.6 (d), 130.3 (d), 130.4 (d), 131.4 (d), 131.4 (d), 132.1 (d), 132.6 (d), 133.1 (d), 135.8 (d), 136.9 (s), 136.9 (s), 137.9 (s), 138.3 (s), 139.3 (s), 139.3 (s), 139.7 (s), 139.8 (s), 145.2 (s), 145.2 (s). − MS (EI, 70 eV): *m*/*z* (%) = 763 (0.8), 761 (0.8), 760 (1.8), 759 (1.4), 758 (1.4) [molecular ions], 668 (46), 465 (10), 463 (16), 462 (10), 459 (22), 359 (28), 357 (38), 355 (44), 300 (62), 196 (30), 195 (100), 194 (36), 181 (56), 164 (52), 155 (16), 119 (30), 104 (28). − C$_{46}$H$_{46}$ZrCl$_2$ (761.0): calcd. C 72.4, H 6.04, Cl 9.33; found C 71.57, H 6.04, Cl 9.59.

Cyclopentadienyl[1-(4-[2.2]paracyclophanyl)ethylcyclopentadienyl]-titanium Dichloride (12): A solution of the lithium cyclopentadienide (**8**) (2.0 mmol in 20 mL of anhydrous THF) was added dropwise to a stirred, ice-cold solution of CpTiCl$_3$ (0.44 g, 2.0 mmol) in 20 mL of anhydrous THF. During the addition, the colour of the solution turned from yellow to dark red. After stirring at room temp. for 12 h, the reaction was worked up as described above to yield a dark red solid (0.9 g, 94%). Recrystallization from a mixture of dichloromethane and ether in the freezer (−25 °C) yielded the product as dark red needles (0.52 g), m.p. 208 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 3106 cm^{-1}, 2926, 2852, 1590, 856, 822. − UV/Vis (CHCl$_3$): λ_{max} (log ε) = 258 nm (4.42), 392 (3.32). − ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.30 (d, *J* = 7.0 Hz, 3 H), 2.71 (m, 1 H), 2.90−3.05 (m, 4 H), 3.14 (m, 1 H), 3.26 (m, 1 H), 3.48 (m, 1 H), 4.54 (q, *J* = 7.0 Hz, 1 H), 5.50 (d, *J* = 1.1 Hz, 1 H), 6.22 (m, 1 H), 6.30−6.45 (m, 3 H), 6.54 (m, 4 H), 6.61 (s, 5 H), 6.73 (m, 1 H), 6.90 (m, 1 H). − ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 22.3 (q), 33.2 (t), 34.9 (t), 35.1 (t), 35.3 (t), 38.4 (d), 110.2 (d), 119.9 (d), 120.3 (d), 120.4 (d), 123.7 (d), 129.6 (d), 130.5 (d), 131.5 (d), 132.1 (d), 132.6 (d), 133.1 (d), 135.9 (d), 137.0 (s), 139.3 (s), 139.7 (s), 139.7 (s), 143.3 (s), 144.8 (s). − MS (EI, 70 eV): *m*/*z* (%) = 486 (5), 485 (7), 484 (22), 483 (14), 482 (30) [molecular ions], 450 (12), 448 (16), 447 (30), 446 (18), 411 (26), 410 (60), 409 (18), 408 (22), 345 (32), 344 (26), 343 (74), 315 (28), 313 (42), 305 (32), 300 (32), 299 (100), 278 (22), 277 (26), 275 (33), 262 (28), 207 (30), 195 (90), 180 (36), 179 (50), 165 (50), 119 (100), 104 (28), 78 (10).

Cyclopentadienyl[1-(4-[2.2]paracyclophanyl)ethylcyclopentadienyl]-zirconium Dichloride (13): The complex was prepared by employing the procedure described for **12** using CpZrCl$_3$ (0.52 g, 2 mmol). The crude product was obtained as a tan-coloured solid (0.66 g, 64%) that was purified by recrystallization from a mixture of dichloromethane and diethyl ether in the freezer (−25 °C) to yield pure **13** as a colourless solid, m.p. 142−145 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1}, 1591, 835, 821, 813. − UV/Vis (CHCl$_3$): λ_{max} (log ε) = 296 nm (3.51), 330 (sh, 3.25), 378 (2.60). − ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 1.35 (d, *J* = 7.0 Hz, 3 H), 2.72 (m, 1 H), 2.90−3.30

(m, 6 H), 3.49 (m, 1 H), 4.40 (q, J = 7.0 Hz, 1 H), 5.46 (s, 1 H), 6.20 (m, 1 H), 6.28−6.35 (m, 2 H), 6.38 (m, 1 H), 6.45 (m, 2 H), 6.52 (s, 5 H), 6.55 (m, 2 H), 6.69 (m, 1 H), 6.80 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.6 (q), 33.2 (t), 34.9 (t), 35.1 (t), 35.3 (t), 37.6 (d), 103.4 (s), 106.7 (d), 115.5 (d), 115.8 (d), 117.0 (d), 119.0 (d), 129.6 (d), 130.3 (d), 131.4 (d), 132.1 (d), 132.6 (d), 133.1 (d), 135.8 (d), 136.8 (s), 138.4 (d), 139.3 (s), 139.7 (s), 139.8 (s), 145.1 (s). − MS (EI, 70 eV): *m*/*z* (%) = 530 (5), 529 (5), 528 (10), 527 (6), 526 (16), 525 (10), 524 (12) [molecular ions], 494 (20), 493 (18), 492 (54), 491 (30), 490 (76), 489 (50), 488 (100), 475 (12), 473 (12), 459 (12), 452 (16), 388 (20), 387 (20), 386 (36), 385 (36), 384 (52), 369 (14), 359 (14), 357 (28), 355 (26), 300 (24), 299 (26), 231 (40), 229 (26), 227 (38), 225 (36), 195 (72), 193 (38), 179 (76), 165 (76), 152 (12), 128 (12), 119 (40), 104 (42), 91 (12), 78 (14). − $C_{28}H_{28}ZrCl_2$ (526.7): calcd. C 63.87, H 5.38, Cl 13.35; found C 63.15, H 5.38, Cl 12.13.

X-ray Crystallography: A summary of the crystal data, data collection, and refinement parameters for the crystal structure of **11** is given in Table 3.

Table 3. X-ray structure refinement of **11**

Compound	**11**
Empirical formula	$C_{48}H_{46}Cl_8D_2Zr$
M_r	1001.69
Crystal habit	colourless tablet
Crystal size [mm]	0.35×0.31×0.13
Crystal system	Orthorhombic
Space group	*Pbcn*
Cell constants:	
a [Å]	30.6365(10)
b [Å]	14.0545(5)
c [Å]	20.9986(7)
V [Å^3]	9041.6
Z	8
D_x [Mg·m^{-3}]	1.472
μ [mm^{-1}]	0.750
Transmissions	0.73−0.93
F(000)	4032
T [°C]	−130
$2\theta_{max}$	56
No. of reflections:	
measured	127800
unique	11476
R_{int}	0.062
Parameters	554
Restraints	48
$wR(F^2$, all refl.)	0.127
$R(F, >4\sigma(F))$	0.044
S	1.01
max. Δρ [e·Å^{-3}]	1.20

Structure Determination of 11: A cut tablet was mounted on a glass fibre in inert oil and transferred to the cold gas stream of a Bruker SMART 1000 CCD diffractometer fitted with a Siemens LT-2 low-temperature attachment. Data were collected with ω- and φ-scans using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). An absorption correction was performed using the multi-scan method (program SADABS). All unique data were used for calculations (program SHELXL-97, G. M. Sheldrick, University of Göttingen). The structure was solved by direct methods and refined anisotropically by full-matrix least-squares on F^2. The deuteriochloroform molecule containing C96 is severely disordered. Two alternative positions were refined with occupancies of 0.600(3) for C96/Cl94/Cl95/Cl96 and 0.400(3) for C96′/Cl91/Cl92/Cl93, but the high residual electron density in the solvent region indicates further disorder. The hydrogen atoms were refined with a riding model or as rigid methyl groups.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-171642. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Butyl(η^5-cyclopentadienyl)[η^5:η^1-1-(4-[2.2]paracyclophanyl)ethylcyclopentadienyl]zirconium (15): *n*-Butyllithium (1.1 mL, 1.75 mmol) was added to a suspension of metallocene dichloride complex **13** (0.46 g, 0.88 mmol) in 50 mL of toluene at −78 °C under argon. After warming the reaction mixture to room temp. and stirring it for 11 h, the initially light brown suspension had turned into an orange solution. The reaction mixture was filtered through sodium sulfate. Removal of the solvent yielded a red oil (0.43 g, 96%). − ^{1}H NMR (C_6D_6, 250 MHz): δ = 0.59 (m, 1 H), 0.82 (m, 1 H), 1.05 (t, J = 14.3 Hz, 3 H), 1.12 (d, J = 7.0 Hz, 3 H), 1.39 (m, 2 H), 1.57 (m, 4 H), 2.64 (m, 2 H), 2.92 (m, 4 H), 2.97 (d, J = 7.0 Hz, 1 H), 4.97 (m, 1 H), 5.19 (m, 1 H), 5.68 (s, 5 H), 5.96 (s, 2 H), 6.35 (m, 1 H), 6.36 (m, 1 H), 6.40 (m, 1 H), 6.48 (m, 1 H), 6.83 (m, 2 H). − ^{13}C NMR (C_6D_6, 62.9 MHz): δ = 14.2 (CH_3), 21.7 (CH_3), 30.1 (CH_2), 34.3 (CH_2), 35.3 (CH_2), 35.9 (CH_2), 39.0 (CH_2), 39.6 (CH), 58.5 (CH_2), 101.3 (CH), 105.5 (CH), 110.2 (CH), 113.7 (CH), 117.8 (CH), 128.7 (CH), 130.3 (CH), 132.3 (CH), 133.3 (CH), 133.3 (CH), 133.6 (C_q), 135.5 (CH), 139.6 (C_q), 139.8 (C_q), 143.2 (C_q), 147.3 (C_q), 181.8 (C_q). − MS (EI, 70 eV): *m*/*z* (%) = 512 (10), 511 [M$^+$] (8), 457 (58), 455 (75), 453 (100), 451 (10), 352 (5), 348 (10), 347 (50), 345 (10), 321 (7), 181 (2), 165 (2), 92 (5), 91 (4).

Activation of the Metallocene Complexes with MAO: The respective metallocene complex, 10−15 mg, was activated with MAO (30% in toluene) (Zr/Al = 1:3000). A portion of the catalyst solution containing 0.5−1.5 mg metallocene complex was used within 1 h for the homo-polymerization of the olefin.

Homo-Polymerization of Ethylene: *n*-Pentane (500 mL) and the catalyst solution were placed in a 1-L Büchi laboratory autoclave. The autoclave was thermostated at 60 °C. An ethylene pressure of 10 bar (99.98% ethylene) was applied after an internal temperature of 50 °C had been reached. The mixture was stirred for 1 h at 60 (±2) °C. The reaction was terminated by releasing the pressure from the reactor. The obtained polymer was dried in vacuo.

Homo-Polymerization of Propylene in Bulk: The catalyst solution was placed in a 1-L Büchi laboratory autoclave followed by the condensation of 500 mL of propylene (polymerization grade). The autoclave was thermostated at 60 °C and the mixture was stirred for 1 h at 60 (±2) °C. The reaction was terminated by releasing the pressure from the reactor.

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