Diastereoselective Synthesis of a Bis(tetrahydroindenyl)zirconocene Dichloride with “Ansa-Fused” Annulated Six-Membered Ring Systems: A Specific Solution of the Synthetic *rac-/meso*-Group 4 Bent Metallocene Problem

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1-Phenyl-1,4-pentanedione (**3**) is selectively converted to the corresponding fulvene−ketone (**4**) by treatment with cyclopentadiene in the presence of pyrrolidine. Treatment with lithium dimethylcuprate results in selective CH_3-addition at the fulvene carbon and subsequent ring-closure reaction to give **7**, which in the presence of lithium diisopropylamide is rapidly dehydrated to yield the bicyclic fulvene **8**. Its treatment with amalgamated calcium metal leads to reductive fulvene coupling and formation of the calcocene complex (**10**) of the substituted 7,7′-bi(tetrahydroindenyl) ligand. Only the respective *rac*-isomer is obtained. Hydrolysis of **10** followed by double deprotonation with butyllithium yields the corresponding 7,7′-bi(tetrahydroindenyl) dianion equivalent **16**. In tetrahydrofuran, **16** is cleaved at the 7,7′-linkage with formation of the “monomeric” disproportionation products **11**-Li and **12**-Li, and treatment of **16** with zirconium tetrachloride in THF leads back to the formation of the fulvene **8**. Transmetalation to zirconium is, however, cleanly achieved when **16** is treated with donor-ligand-free $ZrCl_4$ suspended in toluene. The corresponding diastereomerically pure *rac*-*ansa*-zirconocene dichloride **17** containing the ansa-bridge as part of the α-fused bi(tetrahydroindenyl) ligand system is obtained under these specific conditions. Complex **17** was characterized by X-ray diffraction, and the outcome of the preliminary propene polymerization experiments is reported.

Introduction

Homogeneous group 4 *ansa*-metallocene/methylalumoxane Ziegler catalysts have gained a very high importance for the formation of stereoregular α-olefin polymers. Variants of the “Brintzinger-type” *ansa*-metallocenes (**1**) and their analogues that have their indenyl or tetrahydroindenyl ligands fused at the five-membered rings, e.g., by $-CH_2-CH_2-$ or $-Si(R)_2-$ groups, have especially become of enormeous significance for practical applications.[1] Such systems contain a pair of substructures exhibiting planar chirality;[2] therefore, two diastereomeric metallocenes are possible, a *meso*- and a *rac*-form. For most practical purposes, such as the formation of isotactic polypropylene at such catalyst systems, it is required that the pure C_2-symmetric *rac*-diastereomer of the respective *ansa*-metallocene is employed, since the symmetry properties of the bent metallocene backbone are determining the stereochemistry of each carbon−carbon coupling step during the catalytic polymerization process.[3] A contamination of the catalyst system with a C_s-symmetric *meso*-metallocene would, therefore, lead to the formation of some undesired atactic α-olefin polymer.

Unfortunately, most *ansa*-metallocene syntheses lead to mixtures of the group 4 *rac*- and *meso*-metallocene diastereoisomers and, thus, require a sometimes tedious separation procedure to be carried out subsequently.[4] In some cases, especially with *ansa*-titanocene complex mixtures, a photochemical solution of this serious selectivity problem has seemed promising, as photostationary equilibria had been achieved that contained high amounts of the desired *rac*-forms.[5] However, this method could not be applied to many *ansa*-zirconocenes for practical use.

Jordan has recently reported that a variation of the σ-ligand X can be used to change the thermodynamics of some *meso*/*rac*-metallocene systems in favor of the chiral isomer. A protocol was developed to ensure formation of the respective systems under thermody-

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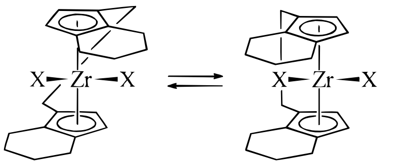


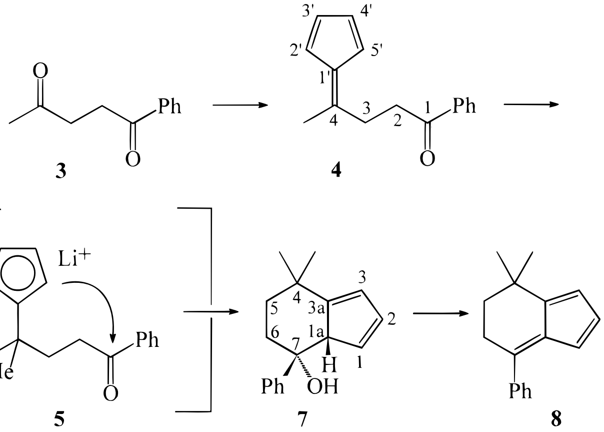
rac-**1** meso-**1**
X = -Cl, -NR$_2$

namic control starting from, e.g., Zr(NR$_2$)$_4$ and the neutral organic fused ligand system.[6] However, a detailed investigation has shown that unfortunately the desired *rac*-isomer is not in all cases thermodynamically favored.[7]

Several alternative but more special cases have been reported where persistent chiral auxiliaries were attached to the *ansa*-metallocene ligand system in order to change the diastereomeric ratios.[8] Some progress has been achieved in this way by introducing additional chirality information in the ligand-bridging moiety of the *ansa*-metallocene system.[9]

We thought that changing the position of the "ansa-bridge" could open another possibility to overcome the *meso*/*rac*-metallocene selectivity problem. Making the annulated six-membered rings of the tetrahydroindenyl systems part of the ethylene bridge would probably lead to very different overall bonding situations of the respective metallocene diastereomers and, thus, induce a sufficient energy separation between the *meso*- and *rac*-isomers to make the latter readily available under conditions of thermodynamic control on a preparative scale. We have now prepared the first representative example of such a six-membered ring-fused *ansa*-zirconocene dichloride complex and actually observed a very high preference of the occurence of the respective *rac*-metallocene diastereomer.[10] Details of a synthetic route to this class of compounds and the first structural and catalytic characterization of a specific example of such a *rac*-*ansa*-metallocene system are given in this article.

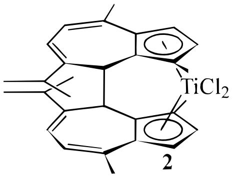
Scheme 1. Synthetic Sequence Leading to Fulvene 8[a]



[a] For reagents and reaction conditions see text and the Experimental Section.

Results and Discussion

Synthesis of the *ansa*-Metallocene Complex 17. Fulvenes can reductively be coupled to yield substituted ethylene-bridged bis(cyclopentadienide) ligand systems. This route has, in a number of cases, been used to prepare *ansa*-metallocene systems,[11] although reduction of the starting material to yield simple nonbridged alkyl-substituted Cp-systems has been a complication in several cases.[12] Fulvenes that are part of an annulated ring system have been employed in a few cases. Brintzinger has coupled guaiazulene and obtained the respective *ansa*-titanocene system (**2**) after transmetalation.[13]



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Substituted dihydropentalenes appear to favor reduction. To the best of our knowledge, reductive coupling of a fulvene that contains an annulated six-membered ring has not been reported so far.[13,14]

Our synthetic scheme, thus, requires the inital preparation of a suitably-substituted fulvene,[15] e.g., **8** (Scheme 1). This material is readily available in a three-step sequence,[16] starting from diketone **3**, that in turn is prepared by means of a cyanide-catalyzed Stetter-reaction between methyl vinyl ketone and benzaldehyde.[17] Diketone **3** is selectively transformed to the monofulvene **4** under Stone/Little-conditions[18] by reacting it with cyclopentadiene in the presence of excess

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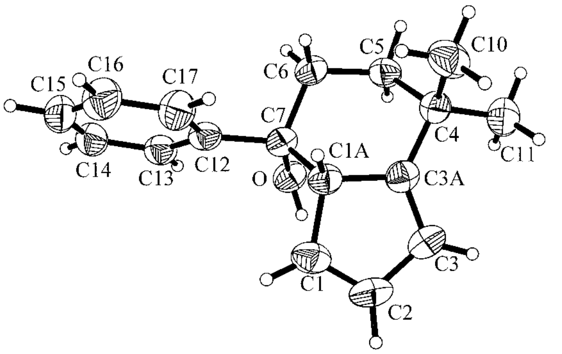
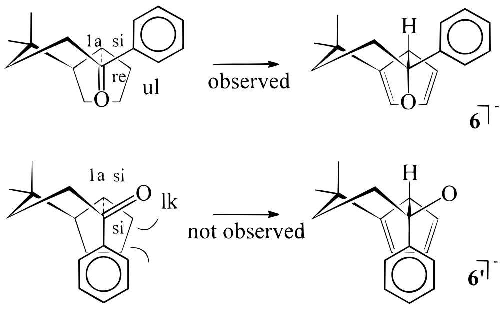


Figure 1. A view of the molecular geometry of **7**. Selected bond lengths (Å) and angles (deg): C1−C2 1.334(4), C2−C3 1.456(4), C3−C3a 1.340(3), C3a−C1a 1.514(3), C3a−C4 1.507(3), C4−C11 1.525(3), C4−C10 1.540(4), C4−C5 1.541(3), C5−C6 1.520(3), C6−C7 1.535(3), C7−O 1.431(3), C7−C12 1.522(3), C12−C13 1.392(3), C13−C14 1.386(3), C14−C15 1.371(4), C15−C16 1.387(4), C16−C17 1.385(4), C17−C12 1.388(3), C3a−C1a−C1 103.1(2), C1a−C1−C2 109.0(2), C2−C3−C3a 109.6(2), C3−C3a−C1a 108.4(2), C3a−C1a−C7 110.1(2), C1−C1a−C7 115.6(2), C1a−C7−O 109.2(2), C1a−C7−C6 108.5(2), C7−C6−C5 112.7(2), C6−C5−C4 114.5(2), C5−C4−C3a 107.1(2), C4−C3a−C1a 119.7(2).

pyrrolidine in methanol at 0 °C. Under these special reaction conditions, only the aliphatic keto-group is attacked and converted to the fulvene moiety, not the aromatic one.

Next, the fulvene must be converted to a cyclopentadienide. This can be achieved selectively by treatment of fulvene−ketone **4** with lithium dimethylcuprate reagent in ether.[19] The soft cuprate nucleophile adds a methyl anion equivalent only to the soft fulvene electrophile of **4** and leaves the aryl ketone moiety completely untouched. The thus formed intermediate **5** then undergoes an intramolecular nucleophilic attack of the Cp-anion functional group at the ketone.[16b] Subsequent hydrolysis gives the corresponding cyclized alcohol **7**. This is usually isolated as a mixture of cyclopentadiene double bond isomers, but only a single product is obtained from the cyclization reaction under kinetic control (analysis by NMR). This product is identical to the single isomer that was obtained by crystallization from ether. A single crystal was used to determine the structure by X-ray diffraction. This revealed that the stereoisomer formed contains the hydrogen atom at C1a and the hydroxy group at C7 in a trans-arrangement (see Figure 1). Consequently, this isomer contains the cyclopentadiene C=C double bonds at the C1−C2 (1.334(4) Å) and C3−C3a (1.340(3) Å) positions. The phenyl substituent at C7 is oriented almost normal to the mean tetrahydroindene plane (dihedral angles C6−C7−C12−C13 102.2(2)°, C1a−C7−C12−C17 48.7(3)°).

Scheme 2. Schematic Representation of the Diastereotopic Chair-Like Transition State Geometries of the 5 → 6/6′ Ring-Closure Reactions



The ring-closure reaction of **5** can, thus, be explained by an attack of relative topicity "unlike" (ul).[20] In a chair-shaped transition state (see Scheme 2), this mode of attack seems to be favored over the "like" (lk) alternative because of minimization of steric interference caused by the phenyl substituent. In the lk transition state geometry (Scheme 2, bottom) the bulky phenyl group would be arranged in an axial position, facing the Cp-ring system, whereas the phenyl group is located equatorially in the arrangement resulting from ul attack (Scheme 2, top).

Alcohol **7** is stable under the slightly basic reaction conditions of its formation. Treatment of **7** with lithium diisopropylamide in tetrahydrofuran at −78 °C results in a rapid dehydration.[21] The reaction mixture immediately turns to a dark red color. Fulvene **8** is isolated in almost quantitative yield as an oil from the reaction mixture after conventional aqueous workup. Red crystals of fulvene **8** were isolated in >50% yield after recrystallization from pentane.

Fulvene **8** was characterized spectroscopically (see the Experimental Section) and by an X-ray crystal structure analysis (see Figure 2). The dihydroindene six-membered ring of **8** exhibits a half-chair-like conformation. The fulvene section of the molecule is planar, as expected (double bonds between carbon atoms C1−C2 1.337(5) Å, C3−C3a 1.352(5) Å, and C1a−C7 1.349(5) Å),[22] and the plane of the phenyl substituent at C7 is rotated by ca. 43° relative to the fulvene plane.

Edelmann has recently shown that 6,6-dimethylfulvene can be reductively coupled with calcium metal to yield the corresponding tetramethylethylene-bridged calcocene (>70% yield isolated).[23] We found that a similar reaction protocol could be used to achieve the analogous coupling of fulvene system **8**.

The first coupling experiment was carried out in tetrahydrofuran-d_8. The outcome of the reaction could

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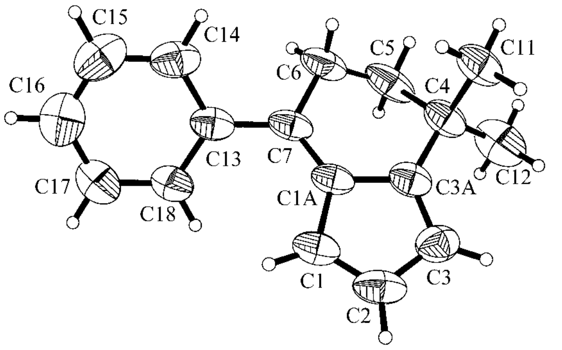
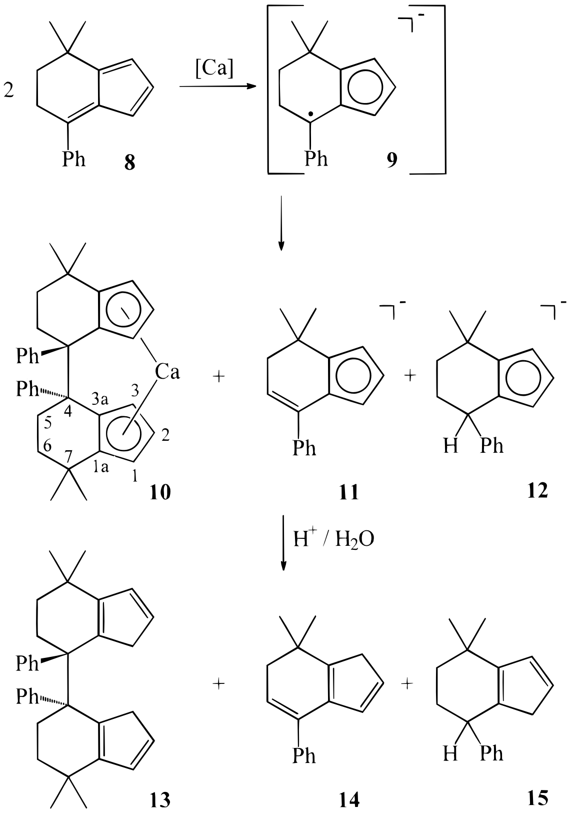


Figure 2. A view of the molecular structure of the fulvene **8**. Selected bond lengths (Å) and angles (deg): C1a−C7 1.349(5), C1a−C3a 1.471(5), C1a−C1 1.463(5), C1−C2 1.337(5), C2−C3 1.439(5), C3−C3a 1.352(5), C3a−C4 1.501(5), C4−C11 1.531(4), C4−C12 1.529(5), C4−C5 1.526(6), C5−C6 1.528(6), C6−C7 1.508(5), C7−C13 1.480(5), C13−C14 1.397(5), C14−C15 1.374(5), C15−C16 1.376(6), C16−C17 1.374(6), C17−C18 1.390(5), C18−C13 1.392(4), C13−C7−C6 116.8(3), C13−C7−C1a 124.3(3), C6−C7−C1a 118.8(3), C7−C1a−C1 131.1(4), C7−C1a−C3a 122.7(3), C3a−C1a−C1 106.2(3), C1a−C1−C2 107.7(3), C1−C2−C3 109.6(3), C2−C3−C3a 109.8(3), C3−C3a−C1a 106.6(3), C3−C3a−C4 131.7(3), C1a−C3a−C4 121.7(3).

Scheme 3



in this way be monitored by ^{1}H NMR spectroscopy in the organometallic product regime without workup. Calcium metal was activated with $HgCl_2$ in THF-d_8 overnight without stirring. To the greyish suspension, crystalline fulvene **8** was added at −10 °C, Scheme 3. The mixture turned colorless. After 2 h of stirring, the solids were allowed to precipitate and the supernatent solution was decanted and its ^{1}H NMR spectrum recorded. This revealed that a major product had been formed, to which we ascribe the structure of *ansa*-calcocene **10**.[24] Only a single diastereoisomer is formed. In view of the structure of the zirconocene complex that was derived from it (see below), it must be assumed that only the *rac*-form of the ring-fused 7,7′-bi(tetrahydroindenyl) ligand system is obtained in the calcium-mediated coupling reaction of fulvene **8**. Only a single set of ^{1}H NMR resonances is observed for the C_2-symmetric (7,7′-bi(tetrahydroindenyl))calcium complex **10** (δ 6.51, 5.82, 5.65 (m, 2 H each, cyclopentadienyl 1−3-H), 1.27 and 1.03 (s, 6 H each, *syn*- and *anti*-4-CH_3)). A few additional signals have been observed that appear to belong to the anionic ligand systems **11** and **12** (probably present here as calcium complexes). These systems are formally derived from a disproportionation reaction that was observed to take place as a reaction sequence competing with reductive coupling.[11−14] (see below)

The reductive coupling of **8** was carried out similarly on a preparative scale. In this case, the resulting calcium complex was directly hydrolyzed with an aqueous ammonium chloride solution. Conventional workup yielded the coupling product **13,** making up about half of the amount of the products formed, admixed with a 1:1 mixture of the "monomeric" disproportionation products **14** and **15**. The coupling product **13** is much less soluble in pentane/ether mixtures and could thus be obtained pure in close to 50% yield. This product consists of a single isomer; it is diastereomerically pure and contains only a single set of double bond positions inside the five-membered ring. Which of the possible double bond shift isomers is favored here could not positively be identified.

Deprotonation of **13** with butyllithium in ether gave dilithio compound **16**, which precipitated from the solution and could thus be isolated in ca. 80% yield. Surprisingly, this dilithio complex turned out to be rather labile in THF solution. In THF-d_8, it was shown to decompose during a period of 2 days rather cleanly to furnish a 1:1 mixture of the disproportionation products **11**-Li and **12**-Li. The identity of these compounds was secured by independent syntheses[25] (see Scheme 4). A spontaneous decomposition was also observed when dilithio compound **16** was treated with zirconium tetrachloride in tetrahydrofuran. Fulvene **8** was identified as a major product of the decomposition reaction of **16** under these conditions.

This rapid decomposition reaction eliminated the use of tetrahydrofuran as the commonly employed solvent for the synthesis of the group 4 metallocene complex

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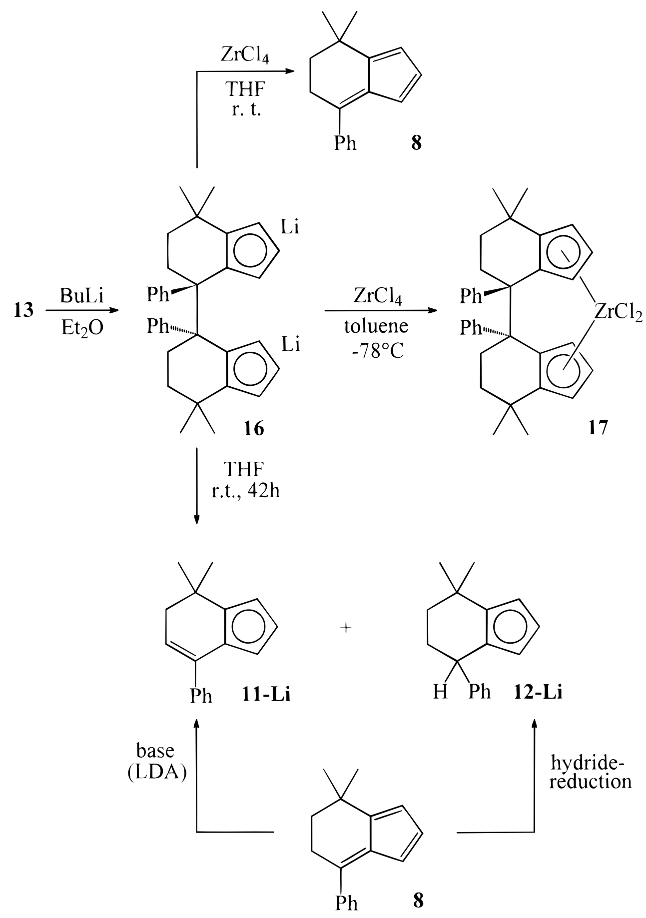
[25] (a) Knox, G. R.; Pauson, P. C. *J. Chem. Soc.* **1961**, 4610. Le Moigne, F.; Dormond, A.; Leblanc, J. C.; Moise, C.; Tirouflet, J. *J. Organomet. Chem.* **1973**, *54*, C13. Moise, C.; Leblanc, J. C.; Tirouflet, J. *J. Am. Chem. Soc.* **1975**, *97*, 6272. Leblanc, J.; Moise, C. *J. Organomet. Chem.* **1976**, *120*, 65; **1977**, *131*, 35. Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *148*, 35. Imafuku, K.; Arai, K. *Synthesis* **1989**, 501. (b) Erker, G.; Wilker, S.; Krüger, C.; Nolte, M. *Organometallics* **1993**, *12*, 2140. Erker, G.; Wilker, S.; Krüger, C.; Goddard, R. *J. Am. Chem. Soc.* **1992**, *114*, 10983.

Scheme 4



derived from **16**. However, it turned out that the unfavorable cleavage reaction could be suppressed by treatment of dilithio reagent **16** with zirconium tetrachloride in toluene. The reaction is then carried out heterogeneously. Reagent **16** was suspended in toluene, and then solid $ZrCl_4$ was added slowly in several portions at −78 °C. The mixture was warmed to ambient temperature overnight. After removal of the lithium chloride by filtration and evaporation of the solvent, an oil was obtained that contained **17** as the only identified organometallic product (a single diastereomer) aside from some unidentified apparently oligomeric material. Recrystallization from a dichloromethane/pentane mixture furnished the pure *ansa*-metallocene complex **17** crystalline in ca. 30% yield.

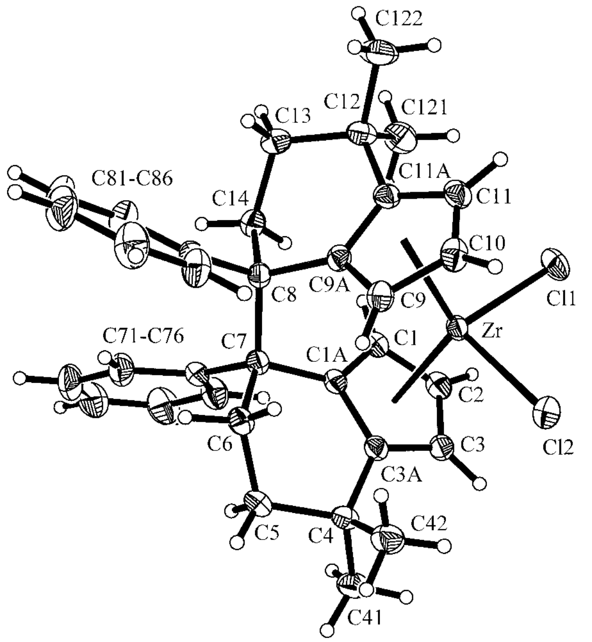


Figure 3. Projection showing the molecular geometry of *rac*-(7,7′-bi(tetrahydroindenylene))zirconium dichloride **17** (with unsystematical atom numbering scheme). Selected bond lengths (Å) and angles (deg): C9–C10 1.441(2), C10–C11 1.396(3), C11–C11a 1.424(2), C11a–C9a 1.420(2), C9a–C9 1.429(2), C1–C2 1.413(2), C2–C3 1.397(3), C3–C3a 1.426(2), C3a–C1a 1.421(2), C1a–C1 1.438(2), C1a–C7 1.537(2), C7–C6 1.549(2), C6–C5 1.522(3), C5–C4 1.537(2), C4–C3a 1.519(2), C9a–C8 1.537(2), C8–C14 1.554(2), C14–C13 1.525(2), C13–C12 1.538(3), C12–C11a 1.522(2), C12–C122 1.543(3), C12–C121 1.528(3), C4–C41 1.540(3), C4–C42 1.531(3), C7–C8 1.611(2), C8–C81 1.558(2), C7–C71 1.544(2), Cl1–Zr–Cl2 96.19(2), C1–C1a–C7 130.6(2), C1–C1a–C3a 106.4(2), C7–C1a–C3a 122.9(2), C1a–C7–C6 107.3(1), C1a–C7–C8 108.9(1), C1a–C7–C71 110.1(1), C6–C7–C71 106.9(1), C8–C7–C71 112.4(1), C6–C7–C8 111.2(1), C9a–C8–C14 106.9(1), C9a–C8–C7 109.2(1), C9a–C8–C81 108.9(1), C14–C8–C81 108.9(1), C14–C8–C7 109.1(1), C7–C8–C81 113.6(1), C8–C9a–C9 130.2(2), C8–C9a–C11a 123.3(2), C11a–C9a–C9 106.5(2).

Characterization of the *ansa*-Metallocene Complex 17. Complex **17** was characterized spectroscopically and by an X-ray crystal structure analysis. The ^1H NMR spectrum of **17** reveals the presence of a single diastereoisomer in solution, which exhibits symmetry-equivalent substructural tetrahydroindenyl moieties that are connected with each other at their 7-positions. The three Cp-hydrogens feature a separate spin-system in the ^1H NMR spectrum with resonances observed at δ 7.31, 7.09, and 6.65 (in CD_2Cl_2, coupling constants ^3J = 3.3 Hz and 3.8 Hz, ^4J = 2.3 Hz). The four diastereotopic methylene hydrogens of the tetrahydroindenyl six-membered ring give rise to four well-separated signals at δ 2.68 (6-H_{axial}), 1.95 (6-$H_{equatorial}$), 1.32 (5-H_{eq}), and 0.85 (5-H_{ax}) with a set of coupling constants (^2J = 12.2 Hz (5-H_{ax}, 5-H_{eq}), 13.8 (6-H_{ax}, 6-H_{eq}), ^3J = 1.9 Hz (5-H_{ax}, 6-H_{eq}), 12.5 (5-H_{ax}, 6-H_{ax}), 2.1 (5-H_{eq}, 6-H_{ax}), 5.0 (5-H_{eq}, 6-H_{eq})) that is characteristic for a half-chair tetrahydroindenyl conformation. In addition, the signals of the diastereotopic pairs of methyl groups are located at δ 1.34 and 1.12.

The X-ray crystal structure analysis has confirmed that the chiral *rac*-*ansa*-zirconocene dichloride **17** was formed. In the solid state, the molecule is crystallographically unsymmetric, but its deviation from an idealized molecular C_2-symmetry is very small (see Figure 3). The tetrahydroindenyl six-membered rings are connected with each other at their α-positions to the annulated Cp-ring system; this brings the substituted cyclohexene-like moieties to occupy C_2-symmetric sectors at the back-side of the bent metallocene wedge. The connecting C7–C8 bond is rather long at 1.611(2) Å. The six-membered rings each contain only one $C(sp^2)-C(sp^2)$ unsaturation (C1a–C3a 1.421(2), C9a–C11a 1.420(2) Å); therefore, they exhibit an almost ideal half-chair conformation. This leads to a clear distinction between axially and equatorially positioned methyl substituents at the ring carbon atoms C4 and C12, respectively (unsystematical atom numbering scheme as used in Figure 3). Each ring thus has one methyl substituent positioned at a lateral sector of the bent metallocene.

The phenyl substituents at the ring-junction (i.e. at the C7−C8 bond) are gauche-like oriented (dihedral angle C71−C7−C8−C81 72.2(8)°); in addition, the phenyl planes are not oriented parallel but substantially rotated relative to each other (dihedral angles C72−C71−C7−C8 117.9(2)°, C82−C81−C8−C7 84.7(2)°).

The stereochemically determined relative orientation of the annulated six-membered rings leads to an eclipsed arrangement of the five-membered ring systems (see Figure 3). The C(sp^2)−C(sp^2) bonds inside of the cyclopentadienide subunits are around an average value of 1.42 Å, with the exception of C2−C3 and its symmetry equivalent C10−C11 which are both slightly shorter at 1.397(3) and 1.396(3) Å, respectively.

The front-side of the bent metallocene is rather open. The Cp(centroid)−Zr−Cp(centroid) angle is in the typical range of strain-free *ansa*-zirconocenes at 124.7°. The zirconium−chlorine bond lengths are almost identical at 2.4406(5) and 2.4462(5) Å.[26] There is only a marginal structural shielding (C_2-symmetric) of the sectors above Cl1 and below Cl2. The respective methyl-substituent-carbon−chloride distances are 3.661 (Cl1−C121) and 3.409 Å (Cl2−C42), respectively. Nevertheless, the homogeneous Ziegler-catalyst system derived from **17** formed partially isotactic polypropylene by enantiomorphic site control, i.e., the **17**-derived catalyst system is able to transfer some of its stereochemical information onto the growing carbon chain in the course of the α-olefin polymerization process (see below).

Active metallocene Ziegler catalysts were generated from *ansa*-metallocene **17** by activation with a large excess of methylalumoxane.[27] Three preliminary propene polymerization experiments were carried out at reaction temperatures of −20, 0, and +25 °C. These experiments have shown that the novel six-membered ring-fused *ansa*-metallocene type complex, of which **17** is a representative example, is suited for being employed in the generation of active α-olefin polymerization catalyst systems.

Propene polymerization reactions were carried out in a Büchi glass autoclave in toluene solution. In all three experiments very large Al:Zr ratios were employed (−20 °C, 4300; 0 °C, 12 400; +25 °C, 1500). At the lowest temperature, only a modest catalyst activity of $a = 470$ g polypropylene/g[Zr]·h was achieved. The catalyst activities in the remaining two polymerization experiments were increased (0 °C, $a = 8600$; +25 °C, $a = 2500$). The molecular masses of the polypropylenes isolated from these two experiments were M_η 185 000 (0 °C) and 80 000 (+25 °C), respectively.

In all cases, moderately isotactic polypropylenes were obtained. The stereochemical characterization was carried out by a ^{13}C NMR methyl pentade analysis.[28] The polymers each exhibited basically only three pentade signals aside from the major *mmmm* resonance, namely the *mmmr*, *mmrr*, and *mrrm* resonances in approximately a 2:2:1 ratio. The other possible methyl pentade signals were not significantly populated. This indicates that the stereochemistry at the active catalyst is predominantly proceeding by means of enantiomorphic site control.[3] The statistical analysis revealed in all three cases this mode of stereocontrol by the chiral metallocene backbone to be >90% effective.[29] The relative intensity of the *mmmm* ^{13}C NMR methyl pentade resonance of the polymer formed at −20 °C was found to be 67%. The respective *mmmm* fractions rapidly decreased with increasing polymerization temperatures (0 °C, 52% *mmmm*; +25 °C, 33%), but also in these cases, the dominating stereocontrol remained to be by the enantiomorphic site.

Conclusions

This study has shown that a group 4 *ansa*-metallocene that has a direct connection between the 7,7′-positions of the tetrahydroindenyl moieties, i.e., exhibits the "ansa-connection" as part of the annulated six-membered rings, can very readily be prepared by means of a reductive coupling between two respective fulvene building blocks. In principle, the backbone of the resulting *ansa*-zirconocene complex **17** in some way resembles the conventional "Brintzinger *ansa*-metallocenes" as the two Cp-ring systems are connected by a (substituted) ethylene-type bridge, except that in a type of complex like **17**, this bridge is at the same time an integral part of the annulated cyclohexene structural moieties. However, this type of a construction of an *ansa*-metallocene appears to have the advantage that it may automatically provide a specific solution of the *rac*/*meso*-*ansa*-metallocene problem. The general structural motif realized with the example of *ansa*-zirconocene complex **17** seems to be much easier realized for the chiral (C_2-symmetric) *rac*-isomer than for the apparently more strained *meso*-alternative. In addition, the backbone of the six-ring fused *ansa*-metallocene **17** seems still suited for exerting a general enantiomorphic site stereocontrol leading to the formation of isotactic polypropylene at the active homogeneous metallocene/methylalumoxane Ziegler-type catalyst that is derived from it. It is likely that a similarly high degree of stereocontrol comparable to the existing Brintzinger *ansa*-metallocene types and their related systems can be achieved by attaching suitable substituents to the backbone of **17** and its analogues (e.g., at the 2- or 3-positions of the annulated Cp-rings). Convenient synthetic routes to such derivatives of **17** and related systems are currently being developed and tested in our laboratory.

Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds: Bruker AC 200 P and Varian Unity plus (^{1}H 600 MHz) NMR spectrometers; a Nicolet 5 DXC FT-IR spectrometer; a Finnigan MAT 312 mass spectrometer was used for determining the high-resolution mass spectra (HRMS) (70 eV); elemental analyses were carried

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(29) Statistical analysis, see: (a) Inoue, J.; Itabashi, Y.; Chujo, R.; Doi, Y. *Polymer* **1984**, *25*, 1640. (b) Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1989**, *101*, 642; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 628.

out with a Foss-Heraeus CHN-rapid elemental analyzer, melting points were determined by differential scanning calorimetry (2910 DSC, DuPont/STA Instruments); X-ray crystal structure analyses were done with Enraf-Nonius CAD 4 (Cu radiation) and MACH 3 (Mo radiation) diffractometers, programs used were SHELX 86, SHELX 93, XP, and SCHAKAL. Ketone **3** was prepared by the Stetter reaction according to a literature procedure.[17]

1-Phenyl-4-(2′,4′-cyclopentadienylidene)pentan-1-one, 4. Diketone **3** (35.0 g, 198 mmol) was dissolved in 2 L of absolute methanol in an inert atmosphere (argon) and cooled to 0 °C. Freshly distilled cyclopentadiene (37 mL, 31.4 g, 474 mmol) was added, and then the condensation reaction was started by adding 78 mL (70.2 g, 987 mmol) of pyrrolidine. The mixture was stirred for 14 h at 0 °C, and then the yellow suspension was poured into 1 L of ice water. The precipitated product was separated and taken into 500 mL of ether. The organic phase was washed with water and dried over magnesium sulfate. The volume was then reduced in vacuo to ca. 100 mL. A part of the product had precipitated during this procedure, and precipitation was completed at −30 °C. The bright yellow solid was collected by filtration under argon and dried at 0 °C in vacuo to yield 33.0 g (74%) of **4**, mp 83 °C (dec). ^{1}H NMR (CDCl$_3$, 200 MHz, for atom numbering see Scheme 1): δ 7.95−7.80 (m, 2 H), 7.54−7.38 (m, 3 H), 6.46 (bs, 4 H, 2′−5′-H), 3.28−3.02 (m, 2 H), 2.97−2.70 (m, 2 H, 2-H, 3-H), 2.21 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 198.5 (C-1), 151.7 (C-4), 143.1 (C-1′), 136.5 (*ipso*-C of Ph), 133.1 (*p*-C of Ph), 131.2 (double intensity, C-3′, C-4′), 128.6, 127.9 (*o*,*m*-C of Ph), 120.6, 120.1 (C-2′, C-5′), 38.2 (C-3), 30.9 (C-2), 20.9 (CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ 3065 (w), 2973 (w), 2940 (w), 2901 (w), 1690 (vs), 1637 (s), 1453 (m), 1368 (s), 1210 (m), 871 (m), 775 (m), 755 (s), 692 (m), 636 (m) cm^{-1}. Anal. Calcd for C$_{16}$H$_{16}$O (224.3): C, 85.68; H, 7.19. Found: C, 84.96; H, 7.34.

Cyclization Reaction of Fulvene−Ketone 3: Preparation of 7,7-Dimethyl-4-phenyl-4,5,6,7-tetrahydro-1a*H*-inden-4-ol, 7. A lithium dimethylcuprate solution was prepared as follows. Copper(I) iodide (60.0 g, 315 mmol) was suspended in 500 mL of absolute ether. The suspension was cooled to ca. −60 °C. During a period of 35 min, 357 mL (610 mmol) of a 1.71 M ethereal methyllithium solution was added dropwise with stirring. Initially a yellow precipitate of methylcopper was formed that redissolved toward the end of the reaction when the total volume of the methyllithium solution was added. An almost colorless dimethylcuprate solution was thus obtained. This was stirred for ca. 15 min at −50 °C and then used for the reaction with **4**. Fulvene−ketone **4** (33.0 g, 147 mmol) was dissolved in 2 L of ether at 0 °C. Into the vigorously stirred solution the cold (−30 to −50 °C) cuprate solution was added dropwise during a period of 60 min. The mixture was then allowed to warm to room temperature and stirred overnight. Water (50 mL) was then added (under argon). The copper iodide precipitate was removed by filtration. The solution was concentrated in vacuo to a volume of 300 mL, then washed with a saturated aqueous ammonium chloride solution (3 × 50 mL) and dried over magnesium sulfate. Removal of the solvent gave 33.6 g (94%) of the cyclization product as a yellow solid. The crude product consisted of a mixture of several double bond isomers. This mixture was used without further purification for preparing fulvene **8**. A ^{1}H NMR spectrum of an aliquot taken directly after workup revealed that the single isomer **7** (see Scheme 1) was formed under kinetic control. Crystallization from ether gave single crystals of the isomerically pure compound **7** that were used for the X-ray crystal structure analysis and the spectroscopic characterization. During several hours, isomerization to the mixture of double bond isomers was observed in CDCl$_3$. **7**: mp 73 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.61−7.52 (m, 2 H), 7.42−7.22 (m, 3 H), 6.48 (m, J = 5.4 Hz, 1.8 Hz, 1 H), 6.09 (m, J = 1.8, 1.3 Hz, 1 H), 5.86 (m, J = 5.4 Hz, 1.3 Hz, 1 H, C1−C3), 3.56 (bs, 1 H, OH), 2.31−2.12 (m, 1 H, 1a-H), 1.88−1.68 (m, 2 H), 1.68−1.47 (m, 2 H, 5-H, 6-H), 1.32 (s, 3 H, CH$_3$), 1.28 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 158.4 (*ipso*-C of Ph), 147.8, 135.4, 130.7, 128.2, 126.8, 124.7, 121.2 (C1, C-2, C-3, *o*,*m*,*p*-C of Ph, C-3a), 77.7, 59.5 (C-1a, C-7), 37.6, 36.6, 34.2, 28.9, 28.3 (C-4, C-5, C-6, CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ 3358 (OH, s), 3078 (w), 2961 (s), 2925 (m), 1560 (m), 1490 (m), 1446 (m), 1262 (s), 1097 (s), 1025 (s), 871 (m), 808 (s), 758 (m), 755 (m), 610 (m) cm^{-1}. HRMS: calcd for C$_{17}$H$_{20}$O, 240.1514; found, 240.1519. X-ray crystal structure analysis of **7**: formula C$_{17}$H$_{20}$O, M = 240.33, 0.4 × 0.25 × 0.1 mm, a = 8.150(1) Å, b = 8.360(1) Å, c = 10.462(1) Å, α = 100.91(1)°, β = 103.84(1)°, γ = 92.37(1)°, V = 676.8(2) Å^3, ρ_{calcd} = 1.179 g cm^{-3}, μ = 5.45 cm^{-1}, no absorption correction (0.982 ≤ C ≤ 0.999), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.541 78 Å, $\omega/2\theta$ scans, 2467 reflections collected (±h, ±k, ±l), [(sin θ)/λ]$_{\max}$ = 0.59 Å^{-1}, 2294 independent and 2067 observed reflections [$I \geq 2\ \sigma(I)$], 167 refined parameters, R = 0.062, wR^2 = 0.221, max residual electron density 0.25 (−0.27) e Å^{-3}, hydrogens calculated and riding.

Dehydrogenation of 7; Synthesis of Fulvene 8. Alcohol **7** (6.22 g, 25.9 mmol) was dissolved in 250 mL of ether and cooled to −78 °C. A cold solution (−78 °C) of lithium diisopropylamide (2.90 g, 27.1 mmol) in 150 mL of tetrahydrofuran was added dropwise with stirring. The mixture was allowed to warm to ambient temperature overnight. Water (100 mL) and then ether (100 mL) were added. The phases were separated, and the aqueous layer was extracted with ether (100 mL). Solvent was removed from the combined organic phases in vacuo, and the residue was taken up in 150 mL of ether. The ethereal solution was washed with brine (50 mL), then with water (50 mL), and then dried over magnesium sulfate. Removal of the solvent gave 5.6 g (97%) of fulvene **8** as a red oil. Recrystallization from pentane that contained a small amount of ether yielded two fractions of crystalline **8**, combined yield 3.25 g (56%), mp 54 °C. Bright red single crystals suited for the X-ray crystal structure analysis of **8** were obtained from ether at −30 °C. ^{1}H NMR (CDCl$_3$, 200.1 MHz): δ 7.48−7.33 (m, 5 H, Ph), 6.46 (m, J = 5.2, 2.3, 0.8 Hz, 1 H), 6.16 (m, J = 1.4, 2.3 Hz, 1 H), 6.14 (m, J = 5.2, 1.4 Hz, 1 H, 1−3-H), 2.82 (t, ^3J = 6.0 Hz, 2 H, 6-H), 1.80 (t, ^3J = 6.0 Hz, 2 H, 5-H), 1.18 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 149.2, 144.0, 140.7, 140.2 (C-7, C-1a, C-3a, *ipso*-C of Ph), 132.2, 129.0, 128.3, 128.1, 121.0, 118.8 (C-1, C-2, C-3, *o*,*m*,*p*-C of Ph), 39.3 (C-6), 31.4 (C-4), 29.6 (C-5), 28.5 (CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ 3059 (w), 2958 (w), 2920 (m), 2883 (s), 2878 (s), 2858 (s), 1568 (m), 1560 (s), 1472 (s), 1459 (s), 1442 (m), 1419 (s), 1379 (s), 1362 (m), 1357 (m), 1349 (s), 1341 (s), 1321 (s), 1267 (s), 1261 (s), 1213 (s), 1102 (s), 1065 (s), 1044 (s), 1028 (s), 1017 (s), 819 (m), 668 (m), 659 (s), 618 (s), 593 (s) cm^{-1}. Anal. Calcd for C$_{17}$H$_{18}$ (222.3): C, 91.84; H, 8.16. Found: C, 91.24; H, 8.15. HRMS: calcd for C$_{17}$H$_{18}$, 222.1409; found, 222.1404. X-ray crystal structure analysis of **8**: formula C$_{17}$H$_{18}$, M = 222.31, 0.4 × 0.2 × 0.1 mm, a = 15.524(1) Å, b = 20.786(4) Å, c = 7.951(1) Å, V = 2565.6(6) Å^3, ρ_{calc} = 1.151 g cm^{-3}, μ = 4.80 cm^{-1}, no absorption correction (0.978 ≤ C ≤ 0.999), Z = 8, orthorhombic, space group $Aba2$ (No. 41), λ = 1.541 78 Å, $\omega/2\theta$ scans, 1398 reflections collected (−h, −k, +l), [(sin θ)/λ]$_{\max}$ = 0.62 Å^{-1}, 1398 independent and 902 observed reflections [$I \geq 2\ \sigma(I)$], 157 refined parameters, R = 0.042, wR^2 = 0.095, max residual electron density 0.16 (−0.17) e Å^{-3}, Flack parameter x = −1(3), hydrogens calculated and riding.

(4,4-Dimethyl-7-phenyl-4,5-dihydroindenyl)lithium (11-Li) and 4,4-Dimethyl-7-phenyl-4,5-dihydro-1*H*-indene (14). A solution of fulvene **8** (3.17 g, 14.2 mmol) in 100 mL of tetrahydrofuran was added dropwise to a solution of lithium diisopropylamide (1.53 g, 14.2 mmol) in 50 mL of tetrahydrofuran at 0 °C. The mixture was stirred overnight, then the solvent was removed in vacuo. The residue was stirred in ether, and an aliquot of the solid product **11**-Li was collected by filtration and used for the spectroscopic characterization. ^{1}H NMR (tetrahydrofuran-d_8/benzene-d_6 1:1, 200.1 MHz): δ 7.75 (m, 2 H), 7.24−7.10 (m, 3 H, Ph), 6.08 (m, 1 H), 6.02 (m, 2 H, 1–3-H), 5.58 (t, ^3J = 4.7 Hz, 1 H, 6-H), 2.38 (d, ^3J = 4.7 Hz, 2 H, 5-H), 1.37 (s, 6 H, CH$_3$) ppm.

The remainder of the suspension of the lithium compound **11**-Li was poured into a saturated aqueous sodium chloride solution. Extraction with ether, drying of the organic phase, and removal of the solvent from an aliquot in vacuo gave the product **14** that was characterized spectroscopically. ^{1}H NMR (CDCl$_3$, 200.1 MHz): δ 7.50–7.00 (m, 5 H, Ph), 6.18–6.15 (m, 1 H), 6.07 (m, 1 H, 2-H, 3-H), 5.94 (t, ^3J = 4.5 Hz, 1 H, 6-H), 3.07–3.01 (m, 2 H, 1-H), 2.25 (d, ^3J = 4.5 Hz, 2 H, 5-H), 1.23 (s, 6 H, CH$_3$) ppm. IR (NaCl): $\tilde{\nu}$ 3058 (w), 3027 (w), 2959 (vs), 2925 (s), 2866 (m), 2240 (m), 1683 (s), 1600 (m), 1493 (m), 1446 (s), 1382 (m), 1358 (m), 1261 (s), 1030 (s), 910 (s), 806 (s), 737 (s), 700 (vs), 602 (vs) cm^{-1}.

4,4-Dimethyl-7-phenyl-4,5,6,7-tetrahydro-1*H*-indene (15) and (4,4-Dimethyl-7-phenyl-4,5,6,7-tetrahydroindenyl)lithium (12-Li). **15** was generated by treatment of fulvene **8** with a large excess of LiAlH$_4$ (~7×) in ether for several hours at reflux temperatures. Hydrolysis and workup with ether gave hydrocarbon **15** as an oil. An aliquot was used for characterization; a larger portion was directly used for the subsequent deprotonation reaction to give **12**-Li. **15**: ^{1}H NMR (CDCl$_3$, 200.1 MHz, mixture of double bond isomers) δ 7.35–7.05 (m, 5 H, Ph), 6.54–6.50 (m, 0.5 H), 6.28–6.17 (m, 1 H), 6.04–5.98 (m, 0.5 H, 2-H, 3-H), 3.68–3.52 (m, 1 H, 7-H), 3.04–2.95 (m, 1 H), 2.70–2.65 (m, 1 H), 2.18–1.98 (m, 1 H, CH$_2$), 1.78–1.48 (m, 3 H, 5-H, 6-H), 1.20 (s, 1.5 H, CH$_3$), 1.19 (s, 1.5 H, CH$_3$), 1.16 (s, 1.5 H, CH$_3$), 1.15 (s, 1.5 H, CH$_3$) ppm. IR (NaCl): $\tilde{\nu}$ 3070 (w), 3060 (w), 3025 (m), 2959 (s), 2928 (s), 2863 (s), 1696 (s), 1611 (m), 1491 (m), 1453 (m), 1393 (m), 1360 (m), 1260 (s), 1179 (m), 1169 (m), 1099 (m), 1077 (m), 1038 (s), 800 (s), 759 (m), 701 (s) cm^{-1}. HRMS: calcd for C$_{17}$H$_{20}$ 224.1565; found, 224.1559.

12-Li: *n*-Butyllithium (2.0 mL of a 1.7 M solution in *n*-hexane, 3.4 mmol) was added to a solution of **15** (640 mg, 2.9 mmol), dissolved in a mixture of 80 mL of pentane and 20 mL of ether, dropwise with stirring at room temperature. The resulting suspension was stirred overnight, then the volume was reduced to ca. 40 mL in vacuo. The precipitate was collected by filtration, washed with pentane, and dried in vacuo to yield 380 mg (57%) of **12**-Li, which was characterized spectroscopically. ^{1}H NMR (tetrahydrofuran-d_8/benzene-d_6 1:1, 200.1 MHz): δ 7.38–6.98 (m, 5 H, Ph), 5.78 (m, 1 H), 5.71 (m, 1 H), 5.27 (m, J = 0.5 Hz, 3.0 Hz, 1 H, 1–3-H), 3.93 (dd, ^3J = 8.6, 5.6 Hz, 1 H, 7-H), 2.13–1.87 (m, 2 H), 1.77–1.52 (m, 2 H, 5-H, 6-H), 1.40 (s, 3 H, CH$_3$), 1.35 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (APT, tetrahydrofuran-d_8/benzene-d_6 1:1, 50.3 MHz): δ 151.0 (*ipso*-C of Ph), 128.9, 127.8, 125.2 (*o,m,p*-C of Ph), 116.6 (C-1a or C-3a, the other signal is not observed), 101.6, 99.9, 97.4 (C-1, C-2, C-3), 44.4 (C-7), 40.2, 32.9 (C-5, C-6), 37.4 (C-4), 34.1 (CH$_3$), 33.3 (CH$_3$) ppm.

[*rac*-Bi[7-(7-phenyl-4,4-dimethyl-4,5,6,7-tetrahydroindenylene)]]calcium (10) and *rac*-bi[7-(7-phenyl-4,4-dimethyl-4,5,6,7-tetrahydro-1*H*-indenyl)] (13). (a) Calcocene **10** was generated in THF-d_8 for direct NMR observation. Calcium metal (10 mg, 245 μmol) was placed in a small Schlenk-tube together with 0.8 mL of tetrahydrofuran-d_8. A spatula tip of HgCl$_2$ was added, and the mixture was left for activation overnight. The mixture was then cooled to −10 °C, and 20 mg (90 μmol) of fulvene **8** was added. The mixture was stirred for 2 h at ambient temperature. The clear supernatent solution was then carefully decanted from a precipitate and used for the spectroscopic characterization of **10**. ^{1}H NMR (tetrahydrofuran-d_8, 200.1 MHz): δ 7.25–6.80 (m, 10 H, Ph), 6.54–6.48 (m, 2 H), 5.92–5.72 (m, 2 H), 5.67–5.63 (m, 2 H, 1–3-H), 3.47–3.25 (m, 2 H), 2.25–2.05 (m, 2 H), 1.50–0.95 (m, 4 H, 5-H, 6-H), 1.27 (s, 6 H, CH$_3$), 1.03 (s, 6 H, CH$_3$) ppm. (b) Reaction on a preparative scale: HgCl$_2$ (420 mg, 150 mmol) was added to 4.0 g (100 mmol) of granulated calcium metal in 20 mL of tetrahydrofuran. After the mixture was stirred overnight, a greyish suspension was obtained that contained small pieces of calcium suspended. Tetrahydrofuran (180 mL) was added, and the mixture was cooled to −78 °C. Fulvene **8** (4.60 g, 21 mmol) was added as a solid in several portions during a period of 15 min. The reaction mixture was then allowed to slowly warm to room temperature overnight with stirring. The mixture was poured into saturated aqueous ammonium chloride solution, phases were separated, and the aqueous phase was extracted several times with ether. The combined organic layers were washed with several small portions of water, then dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo yielded a yellow solid. This crude product contained the "monomeric" hydrocarbons **14** and **15**, amounting each to about 25% in addition of the desired coupling product **13**. The solid was dissolved in a mixture of 20 mL of THF, 10 mL of ether, and 80 mL of pentane. The resulting solution was concentrated at the rotary evaporator, using an aspirator vacuum, to a volume of 15 mL. Overnight at −30 °C, 1.15 g of a pale yellow solid precipitated that was recovered by filtration. The filtrate was taken up in a 1:1 mixture of ether and pentane and again concentrated to a volume of 30 mL. Pentane was added until the solution turned turbid. At −30 °C overnight, an additional fraction of 1.23 g (combined yield 51%) of **13** was obtained, mp >130 °C (dec). ^{1}H NMR (CDCl$_3$, 200.1 MHz): δ 7.48–7.02 (br m, 10 H, Ph), 6.69 (m, ^3J = 5.5 Hz, 1 H), 6.03 (d, ^3J = 5.5 Hz, 1 H, 2-H, 3-H), 2.79–2.74 (m, 2 H, 1-H), 2.18–1.85 (m, 1 H), 1.58–1.00 (m, 3 H, 5-H, 6-H), 1.15 (s, 3 H, CH$_3$), 0.83 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 148.5, 146.2, 142.6 (C-1a, C-3a, *ipso*-C of Ph), 135.5, 132.0, 127.2, 126.7, 125.4 (C-2, C-3, *o,m,p*-C of Ph), 51.0, 45.9, 38.0, 35.8, 32.7 (C-1, C-4, C-5, C-6, C-7), 31.5, 29.0 (CH$_3$) ppm. IR (KBr): $\tilde{\nu}$ 3091 (m), 3067 (m), 2955 (s), 2913 (s), 2888 (m), 2857 (m), 1599 (m), 1495 (m), 1459 (m), 1378 (m), 1356 (m), 1229 (w), 1184 (w), 1038 (w), 1012 (w), 963 (m), 778 (m), 720 (vs), 702 (vs), 659 (s) cm^{-1}. Anal. Calcd for C$_{34}$H$_{38}$ (446.7): C, 91.42; H, 8.58. Found: C, 90.41; H, 8.64. HRMS: calcd for C$_{34}$H$_{38}$, 446.2973; found, 446.2969.

[*rac*-Bi[7-(7-phenyl-4,4-dimethyl-4,5,6,7-tetrahydroindenylene]]dilithium (16). A 1.7 M solution of *n*-butyllithium in *n*-hexane (4.5 mL, 7.7 mmol) was added dropwise with stirring at 0 °C to a solution of **13** (1.64 g, 3.7 mmol) in 80 mL of ether. The resulting suspension was stirred overnight at room temperature. The volume of the reaction mixture was then concentrated to ca. 30 mL in vacuo, and 30 mL of pentane was added. The resulting precipitate was collected by filtration, washed with 30 mL of pentane, and dried in vacuo to yield 1.35 g (80%) of the dilithio compound **16** as a white powdery solid. ^{1}H NMR (tetrahydrofuran-d_8/benzene-d_6 1:5, 200.1 MHz): δ 8.15–8.07 (m, 2 H), 7.13–6.94 (m, 8 H, Ph), 6.01 (m, 2 H), 5.79 (m, 2 H), 5.72 (m, 2 H, 1–3-H), 3.00 (m, 2 H), 1.97 (m, 2 H), 1.47–1.32 (m, 4 H, 5-H, 6-H), 1.50 (s, 6 H, CH$_3$), 1.11 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (tetrahydrofuran-d_8/benzene-d_6 1:5, 50.3 MHz): δ 149.3 (*ipso*-C of Ph), 133.4, 129.0, 126.9, 126.4, 124.6 (*o,m,p*-C of Ph), 127.6, 123.0 (C-1a, C-3a), 102.4, 98.0, 97.8 (C-1, C-2, C-3), 54.7 (C-7), 38.0, 33.4, 33.1 (C-4, C-5, C-6), 34.1, 33.2 (CH$_3$) ppm. In THF-containing solvent, **16** slowly decomposes to give a 1:1 mixture of **11**-Li and **12**-Li; in pure THF-d_8, this disproportionative cleavage is complete after 42 h, in benzene-d_6/THF-d_8 5:1 the reaction takes longer.

[*rac*-Bi[7-(7-phenyl-4,4-dimethyl-4,5,6,7-tetrahydroindenylene]]dichlorozirconium (17). The dilithio compound **16** (1.30 g, 2.83 mmol) was suspended in 125 mL of toluene and cooled to −78 °C. Zirconium tetrachloride (660 mg, 2.83 mmol) was added. The mixture was slowly allowed to warm to room temperature overnight with stirring. Lithium chloride was removed by filtration. The precipitate was washed several times with toluene. Solvent was removed from the combined filtrates in vacuo. The residue was washed with pentane to yield 960 mg of crude **17**. Pentane was allowed to diffuse into a solution of 150 mg of this crude product in 2 mL of dichloromethane at room temperature. Complex **17** was obtained crystalline, yield 80 mg (30% referring to the aliquot used for purification). This material was used for the X-ray crystal structure analysis. **17**: mp > 284 °C (dec). ^{1}H NMR (dichloromethane-d_2, 599.9 MHz): δ 7.34−7.28 (m, 10 H, Ph), 7.09 (dd, $^3J = 3.3$, 3.8 Hz, 2 H, 2-H), 6.65 (dd, $^3J = 3.8$ Hz, $^4J = 2.3$ Hz, 2 H), 6.57 (dd, $^3J = 3.3$ Hz, $^4J = 2.3$ Hz, 2 H, 1-H, 3-H), 2.68 (ddd, $^3J = 12.5$ Hz, $^2J = 13.8$ Hz, $^3J = 2.1$ Hz, 2 H, 6-H$_{ax}$), 1.95 (ddd, $^3J = 5.0$ Hz, 1.9 Hz, $^2J = 13.8$ Hz, 2 H, 6-H$_{eq}$), 1.32 (ddd, $^2J = 12.2$ Hz, $^3J = 5.0$ Hz, 2.1 Hz, 2 H, 5-H$_{eq}$), 0.85 (ddd, $^2J = 12.2$ Hz, $^3J = 12.5$ Hz, 1.9 Hz, 2 H, 5-H$_{ax}$), 1.34 (s, 6 H, CH$_3$), 1.12 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (dichloromethane-d_2, 150.0 MHz): δ 142.2, 142.0, 133.2, 127.8 (double intensity), 127.2, 126.4, 121.7, 107.9 (C-1, C-1a, C-2, C-3, C-3a, *ipso*-, *o*,*m*,*p*-C of Ph), 57.1 (C-7), 35.8, 34.2, 34.1, 31.7, 30.3 (C-4, C-5, C-6, CH$_3$) ppm. Anal. Calcd for $C_{34}H_{36}ZrCl_2$ (606.8): C, 67.30; H, 5.98. Found: C, 67.94; H, 6.04. X-ray crystal structure analysis of **17**: formula $C_{34}H_{36}Cl_2Zr$, $M = 606.75$, $0.5 \times 0.3 \times 0.2$ mm, $a = 9.130(1)$ Å, $b = 10.330(1)$ Å, $c = 16.499(1)$ Å, $\alpha = 75.94(1)°$, $\beta = 85.31(1)°$, $\gamma = 66.21(1)°$, $V = 1381.0(2)$ Å^3, $\rho_{calcd} = 1.459$ g cm^{-3}, $\mu = 6.14$ cm^{-1}, empirical absorption correction via ψ-scan data ($0.939 \le C \le 0.999$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.710\,73$ Å, $\omega/2\theta$ scans, 5981 reflections collected ($-h$, $\pm k$, $\pm l$), $[(\sin \theta)/\lambda]_{max} = 0.62$ Å^{-1}, 5614 independent and 5057 observed reflections [$I \ge 2\,\sigma(I)$], 338 refined parameters, R = 0.026, wR^2 = 0.070, max residual electron density 0.48 (−0.52) e Å^{-3}, hydrogens calculated and riding.

Propene Polymerization Reactions were carried out in a 1 L thermostated Büchi autoclave system in toluene solution using a commercial methylalumoxane solution in toluene (ca. 10%). The propene polymerization reactions were carried out analogously as previously described by us.[8,30] Polymers were characterized by determining their Staudinger index; stereochemically they were characterized by ^{13}C NMR methyl pentade analysis and a statistical analysis using published procedures.[29] Three separate experiments were carried out at different temperatures yielding the polymers PP1 (−20 °C), PP2 (0 °C), and PP3 (+25 °C). In this order, the following data serve to characterize the polymerization conditions: mg **17** employed (PP1/PP2/PP3): 14.0/4.9/41.6; Al:Zr ratio: 4300/12400/1500; amount of polymer isolated (after 200 min reaction time): 2.6 g/16.8 g/41.5 g; polymerization activities $\underline{a} = 470/8600/2500$ g polypropylene/g [Zr] · h; molecular mass $\bar{M}_\eta$: (not determined)/185 000/80 000. The stereochemical characteristics (ω = fraction determined by enantiomorphic site control; α = isotacticity control) were determined by simulating the pentade intensity distribution of the ^{13}C NMR spectra analogously as previously described by us. For the polymers, the following intensities were measured (calculated) [the data are again listed in the order PP1/PP2/PP3]: *mmmm* 67.1(66.8)/52.4(52.2)/32.6(31.8), *mmmr* 11.8(11.4)/14.3(14.3)/15.8(16.1), *rmmr* 0.0(0.5)/2.1(1.1)/6.8(2.5), *mmrr* 11.6(10.7)/14.1(14.3)/15.6(16.1), *mmrm* + *rmrr* 3.2(2.7)/3.4(4.4)/11.5(9.9), *rmrm* 0.5(1.1)/3.9(2.2)/4.3(5.0), *rrrr* 0.7(0.5)/2.4(2.1)/5.1(5.5), *mrrr* 0.4(1.0)/0.0(2.2)/0.0(5.0), *mrrm* 4.8(5.4)/7.3(7.1)/8.3(8.1), ω = 93%/99%/97%; α = 92%/88%/80%; average lengths of undisturbed isotactic units $\langle m \rangle_n\alpha = 11.6/7.5/4.3$.

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Supporting Information Available: Tables of the crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates of complexes **6**, **8**, and **17** (18 pages). Ordering information is given on any current masthead page.

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