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Ethylene Bis(2-indenyl) Zirconocenes: A New Class of Diastereomeric Metallocenes for the (Co)Polymerization of α-Olefins

Colin J. Schaverien,*,† René Ernst,† Peter Schut,† and Tiziano Dall'Occo‡

Shell Research and Technology Centre Amsterdam, Postbus 38000,
1030 BN Amsterdam, The Netherlands, and Basell Polyolefins, Centro Ricerche G. Natta,
P.le G. Donegani 12, 44100 Ferrara, Italy

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Sequential additions of NaOEt and benzyl chloride (BzCl) to diethyl adipate in THF afforded $EtOOCCH(Bz)CH_2CH_2CH(Bz)COOEt$ (**3**) in high yield via successive Dieckmann condensations. This was converted to CH_2CH_2(2-indene)$_2$ (**2**) using standard synthetic methodology, from which 436 g of CH_2CH_2(2-indenyl)$_2ZrCl_2$ (**1**) was prepared. Incorporation of a 1-alkyl substituent gave *rac* and *meso* isomers CH_2CH_2(1-R-2-indenyl)$_2ZrCl_2$ (R = Me, **12r**, **12m**; R = Et, **14r**, **14m**). Methylation gave *rac*- and *meso*-CH_2CH_2(1-Me-2-indenyl)$_2$-$ZrMe_2$ (**15r**, **15m**) and CH_2CH_2(2-indenyl)$_2ZrMe_2$ (**16**). CH_2CH_2(4-Ph-2-indene)$_2$ (**20**) was prepared similarly to **2** using 2-phenyl benzylbromide and diethyladipate/NaOEt, from which *rac*- and *meso*-CH_2CH_2(4-Ph-2-indenyl)$_2ZrCl_2$ (**19r** and **19m**) were prepared. Alkylation of **19m** gave *meso*-CH_2CH_2(4-Ph-2-indenyl)$_2ZrMe_2$ (**23m**). The 4-phenyl metallocenes *rac*- and *meso*-CH_2CH_2(1-Me-4-Ph-2-indenyl)$_2ZrCl_2$ (**25r** and **25m**) were prepared via **20**. C_2-symmetric CH_2CH_2(1,3-Me_2-2-indenyl)$_2ZrCl_2$ (**29**) was prepared to compare its polymerization behavior with **1**. These zirconocenes displayed activities of up to 4320 kg PE/(g Zr·h) for the polymerization of ethylene (9.6 bar, 80 °C, hexane) to linear PE. The activity was much lower (2−20 kg/(g Zr·h); liquid propylene, 50 °C) for the polymerization of propylene to low molecular weight atactic polypropylene. Alkyl groups in the 1- and/or 3-positions led to a significant reduction of 2,1-insertions from 9.4% in the polymer from **1**/MAO, and 9.9% from **19**/MAO, to 0.1−0.4%. Attempts to prepare an isospecific catalyst were unsuccessful; substituent variation i.e., 4-phenyl in **19**, did not provide effective enantiomorphic site control. Addition of H_2 has a dramatic activation effect (>100-fold) in propylene polymerization and afforded saturated propylene oligomers with activities up to 6240 kg/(g Zr·h). The low polymer molecular weights allowed detailed NMR analysis of the end groups, which enabled the chain transfer and metallocene activation mechanisms to be identified. Copolymerization of ethylene and propylene (in liquid propylene at 50 °C with 6 mol % ethylene) afforded copolymers with activities of 1300−12500 kg/(g Zr·h). Reactivity ratios ($r_E = 41-98$, $r_P = 0.0025-0.0084$, $r_Er_P = 0.1-0.7$) indicate a very high preference for sequential ethylene insertions. Copolymerization of ethylene and 1-hexene (4.4 bar ethylene, heptane, 70 °C) gave copolymers with activities of up to 1100 kg/(g Zr·h) using **12r**/MAO. The copolymer microstructure showed highly preferential sequential ethylene incorporation: r_E = ca. 200, $r_H = 0.004$.

Introduction

Unbridged zirconocene dichlorides,[1] when activated by a cocatalyst, particularly methylaluminoxane (MAO), are very efficient catalysts for the polymerization of ethylene. By linking two indenyl ligands Brintzinger[2] and Ewen[3] showed that the resulting chiral bridged metallocenes could exercise enantiomorphic site control in the polymerization of propylene and afford isotactic polypropylene (i-PP).[4] Extensive investigation of substituent effects has resulted in highly active, highly stereospecific homogeneous catalysts for the polymerization of propylene to high molecular weight, highly

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* To whom correspondence should be addressed. E-mail: Colin.J.Schaverien@opc.shell.com.

† Shell Research and Technology Centre Amsterdam.

‡ Basell Polyolefins.

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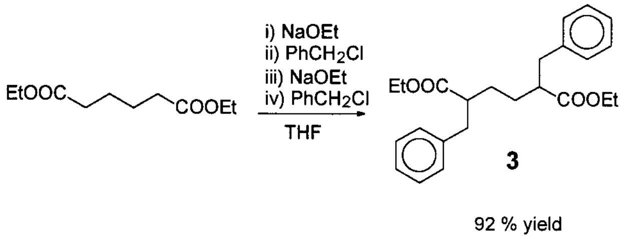
isotactic PP.[4] These metallocenes[5] usually contain two indenyl groups with a bridge (normally CH_2CH_2, $SiMe_2$, or CMe_2) linking the 1,1′-positions. Ligand modifications, with retention of a bridged bis(cyclopentadienyl)-type framework, have afforded catalysts for syndiotactic-PP,[6] hemiisotactic-PP,[7] and atactic-PP,[8] whereas unbridged 2-arylindenyl zirconocenes have yielded elastomeric-PP.[9] Increasing attention is also being paid to variations in the bridge position in the conventional bis(1-indenyl) ligand framework.[10]

Halterman[11a] and Bosnich[11b] first prepared chiral titanocenes with bis(indenyl) ligands bridged at the 2-position. They devised a conceptually elegant way to obtain a single metallocene diasteromer by using rigid, intrinsically chiral binaphthyl and 6,6′-dimethylbiphenyl bridges, while Nantz[12] has focused on ethylene-bridged bis(2-indenyl) titanocenes. Recently, Nantz has reported[12c] the $TiCl_4$-mediated reductive coupling of 2-(hydroxymethyl)indenes for the preparation of a range of such ethylene-bridged bis(2-indenes), from which the corresponding titanocenes were prepared. The parent titanocene CH_2CH_2(2-indenyl)$_2TiCl_2$, as well as *rac*- and *meso*-CH_2CH_2(1-R-2-indenyl)$_2TiCl_2$ (R = Me,[12b] benzyl[12b]), were prepared and the X-ray crystal structures of *rac*-CH_2CH_2(1-R-2-indenyl)$_2TiCl_2$ (R = Me,[12b] i-Bu,[12c] i-Pr[12c]), CH_2CH_2(2-tetrahydroindenyl)$_2TiCl_2$,[12b] and CH_2CH_2(5-Me-2-tetrahydroindenyl)$_2TiCl_2$[12c] determined. These titanocenes were used as catalysts for the epoxidation of substituted olefins.[12]

We report here a family of chiral ethylene-bridged bis(2-indenyl) zirconocenes for the polymerization of ethylene, of propylene, and for the highly efficient copolymerization of ethylene/propylene and ethylene/1-hexene. Some preliminary results have been reported in patent applications.[13]

Scheme 1



Results and Discussion

The reported synthesis of CH_2CH_2(2-indene)$_2$ (**2**) was of low yield (15%)[12a] and, although convenient to perform, only suitable for preparing small quantities (ca. 5 g) of **2**. We have developed three new routes to **2** from which ethylene-bridged bis(2-indenes) can be prepared. Two are described[14] in the Supporting Information. Although synthetically viable, they are, however, only suitable for preparing a maximum of 10 g (route 1) or 50 g (route 2) of **2**. A new, simple, and efficient route was devised that uses inexpensive starting materials. Sequential addition[15] of NaOEt, benzyl chloride (BzCl), NaOEt, and benzyl chloride to diethyl adipate in THF, then washing with water to remove NaCl, and subsequent removal of excess BzCl and BzOEt (from the reaction of BzCl with NaOEt) under vacuum afforded ca. 95% pure dibenzyl ester **3** in 92% yield. **3** was isolated as a viscous yellow-brown oil, which solidifies on standing for several weeks at 20 °C to a light beige powder (Scheme 1). For the exact methodology, see the Experimental Section.

The impurities are typically 2−3% of **4** and <1% of the cyclopentanone **5**. This approach relies on successive Dieckmann condensations. Although the Dieckmann reaction is well established[16] and has been used for preparing alkyl-substituted cyclopentanones,[17] we are not aware of other examples of its use to prepare 2,5-dialkyladipates. A proposed mechanism is shown in Scheme 2.

De-esterification of **3** with KOH (3 equivs) in MeOH/H_2O (4:1 vol/vol) at 90 °C for 3 h afforded the dicar-

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(9) Hauptman, E.; Waymouth, R. M.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 11586. Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1242.

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(11) (a) Halterman, R. L.; Ramsey, T. M. *Organometallics* **1993**, *12*, 2879. (b) Ellis, W. E.; Hollis, T. K.; Odenkirk, W.; Whelan, J.; Ostrander, R.; Rheingold, A. L.; Bosnich, B. *Organometallics* **1993**, *12*, 4391.

(12) (a) Nantz, M. H.; Hitchcock, S. R.; Sutton, S. C.; Smith, M. D. *Organometallics* **1993**, *12*, 5012. (b) Hitchcock, S. R.; Situ, J. J.; Covel, J. A.; Olmstead, M. M.; Nantz, M. H. *Organometallics* **1995**, *14*, 3732. (c) Palandoken, H.; Wyatt, J. K.; Hitchcock, S. R.; Olmstead, M. M.; Nantz, M. H. *J. Organomet. Chem.* **1999**, *579*, 338.

(13) Schaverien, C. J.; Ernst, R.; van Loon, J. D.; Dall'Occo, T. Eur. Patent Appl. 941997 to Montell Technology Company, priority date March 9, 1998. Dall'Occo, T.; Baruzzi, G.; Schaverien, C. J. Eur. Patent Appl. 942011 to Montell Technology Company, priority date March 9, 1998.

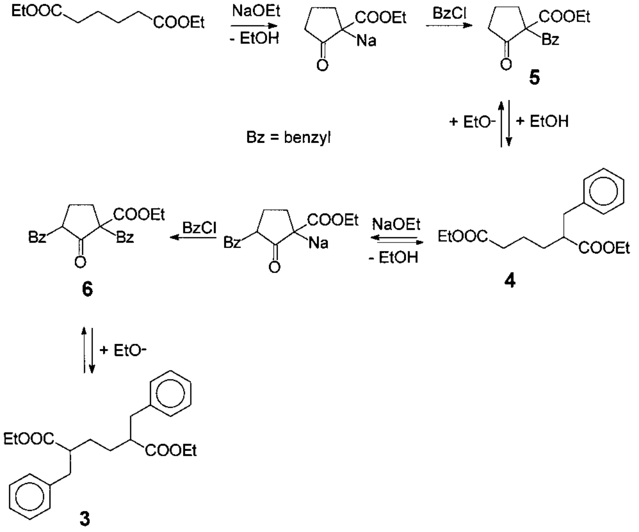
(14) Route 1: Reaction of the diGrignard of *o*-$C_6H_4(CH_2Cl)_2$ with 0.5 equiv of diethylsuccinimate gave the diol in 65−75% yield. However, the diGrignard has to be prepared in dilute solution. See: Lappert, M. F.; Martin, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1959. Similar methodology has been used previously to afford 2-indenes. See ref 11b as well as Eur. Patent Appl. 727446 to Idemitsu priority date Oct 26, 1993, and Witte, P.; Lal, T. K.; Waymouth, R. M. *Organometallics* **1999**, *18*, 4147. Dehydration with *p*-toluenesulphonic acid in refluxing toluene yielded **2** (36%), 1,1′,4,4′-bis(indanyl)furan (38%), and a double bond isomer of **2**, C_6H_4-$(CH_2)_2C{=}CHCH_2$(2-indene) (2%). Route 2: Treatment of 300 g of $PhCH_2CH(COOEt)_2$ with NaH at 50 °C for 2 h gave Na[$PhCH_2C(COOEt)_2$], which was quenched with 2 equiv, 450 g of 1,2-dibromoethane to afford $PhCH_2C(COOEt)_2CH_2CH_2Br$. This was isolated and reacted with an additional 1 equiv of Na[$PhCH_2C(COOEt)_2$] to yield 307 g, 49% of the tetraester as a white powder. De-esterification, then decarboxylation at 180 °C afforded **7**. See Supporting Information for full experimental details.

(15) Direct reaction of diethyladipate with 2 equiv of NaH in the presence of 2 equiv of $PhCH_2Cl$ afforded a complex mixture of products, including **3**. NB: Benzyl chloride does not react with NaH. See: Cristol, S. J.; Ragsdale, J. W.; Meek, J. S. *J. Am. Chem. Soc.* **1949**, *71*, 1863.

(16) (a) *Vogel's Textbook of Practical Organic Chemistry,* 5th ed.; Longman Scientific & Technical: Harlow, U.K., 1989; p 1095. March, J. *Advanced Organic Chemistry,* 4th ed.; John Wiley & Sons: New York, 1992; p 492.

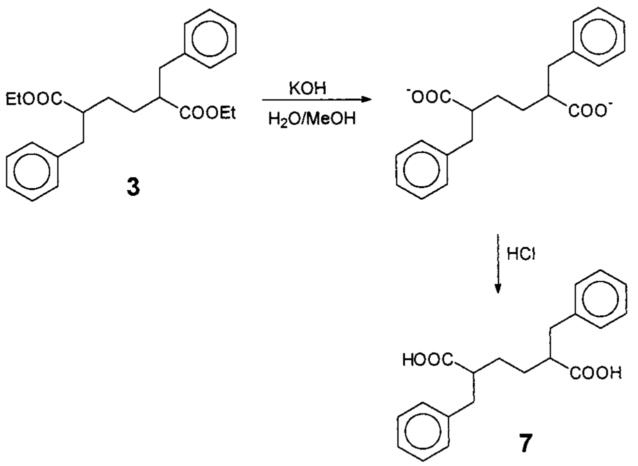
(17) Ring opening of the cyclopentanone ring has been shown to give monoalkyl adipic esters in good yield. Nicole, L.; Berlinguet, L. *Can. J. Chem.* **1962**, *40*, 353.

Scheme 2



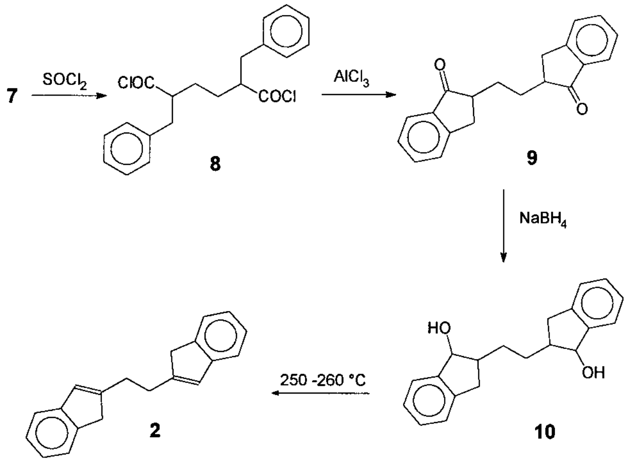
boxylate dianion. After evaporation of MeOH, the colorless aqueous solution was washed with ether to remove the organic impurities formed in the synthesis of **3** (Scheme 3). Acidification of **3** with concentrated HCl in water at 10 °C precipitated **7** as a white powder, which was conveniently isolated by filtration and washing with water. After drying to constant weight **7** was isolated in 95% yield.

Scheme 3



Treatment of **7** with excess $SOCl_2$ (55 °C, 8 h) gave acid chloride **8** as a viscous light brown oil. This was used directly in the Friedel–Crafts reaction (2.6 equiv $AlCl_3$ in CH_2Cl_2 at 20 °C). After stirring for 16 h at 20 °C, the reaction mixture was carefully poured onto crushed ice. This afforded bis(indanone) **9** as a white powder in 90% overall yield from **7**. Reduction of **9** with $NaBH_4$ (1.1 equiv) at 10 °C under air in THF/MeOH afforded diol **10**. Many different acid/solvent combinations were investigated for the dehydration of **10** to **2**. No reaction occurred on refluxing **10** in toluene with *p*-toluene sulfonic acid under Dean–Stark conditions (as determined by NMR spectroscopy), although two products were observed by GC(MS) of the reaction mixture, both with mass 258, indicating dehydration on the GC column. This suggested that thermolysis of **10** might be an efficient dehydration method. Indeed, thermolysis

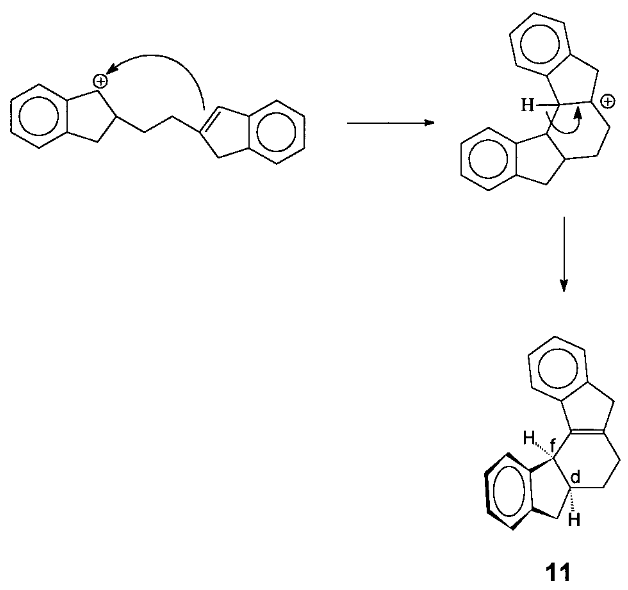
Scheme 4



of **10** at 250–260 °C (melt) gave **2**[12] in moderate yield (42%) (Scheme 4).

In the thermolysis of **10**, a byproduct was formed. On the basis of mass spectrometry, $^1H-^1H$ COSY, $^{13}C-^1H$ HETCOR, and $^{13}C-^{13}C$ INADEQUATE 2D NMR techniques, this was identified as **11**. Only one (double bond) regioisomer is present. Instead of eliminating a proton to form **2**,[12] intramolecular electrophilic attack of the formed double bond on the transitory positive charge occurs (Scheme 5).

Scheme 5



UFF molecular modeling[18] shows **11** is in the lowest energy configuration, i.e., with the protons attached to carbons d and f in a *cis* conformation. Bis(indene) **2**[12] could be separated from **11** by washing with CH_2Cl_2.

Deprotonation of **2** with 2 equiv of n-BuLi in ether at −5 °C cleanly afforded $Li_2[CH_2CH_2(2\text{-indenyl})_2]$. Addition of $Li_2[CH_2CH_2(2\text{-indenyl})_2]$ in ether, cooled to −78 °C, to $ZrCl_4$ in CH_2Cl_2, also cooled to −78 °C, and then warming to 20 °C afforded **1**, which was separated from LiCl, and any polymeric products, by Soxhlet extraction

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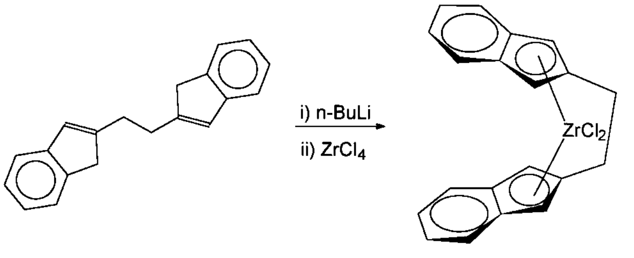
[18] Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024. Castonguay, L. A.; Rappé, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 5832. Rappé, A. K.; Goddard, W. A., III. *J. Phys. Chem.* **1991**, *95*, 3358.

Scheme 6



2 **1**

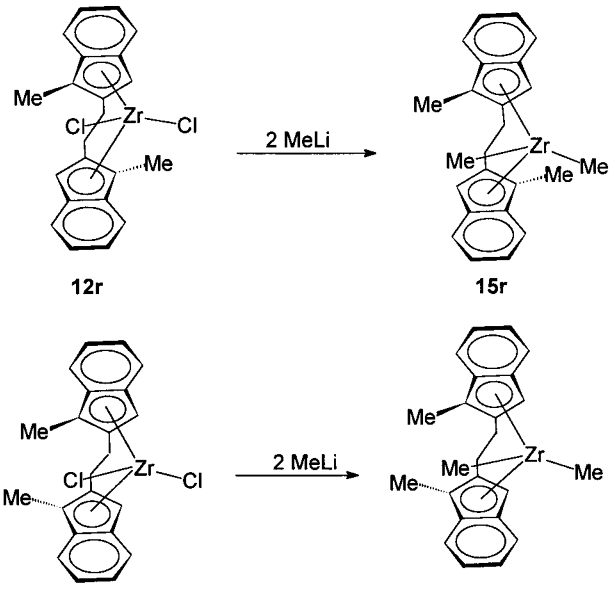
with CH_2Cl_2. This afforded 436 g of zirconocene **1**[19] as a bright yellow powder in 75% yield (Scheme 6). As expected, the ^1H NMR spectrum in CD_2Cl_2 of **1** displays equivalent cyclopentadienyl protons at δ 6.41 ppm, and the ethylene bridge protons are a singlet at δ 3.31 ppm. In the ^{13}C NMR spectrum, these resonate at δ 103.1 and 31.1 ppm, respectively.

This route uses inexpensive starting materials and concentrated solutions allowing the use of ordinary laboratory glassware. No crystallization or distillation purification steps are involved, and workup can be performed under air. Only the treatment of **8** with $AlCl_3$, and conversion of **2** to **1**, must be performed under an inert atmosphere.

Metallocene **1** is achiral, possesses C_2-symmetry,[20] and would not be expected to exert enantiomorphic site control in the polymerization of α-olefins. As exemplified crystallographically by Nantz,[12] and in contrast to the *rac* and *meso* isomers of ethylene-bridged bis(1-indenyl) metallocenes, the spatial environment of the bis(2-indenyl) framework remained almost identical in both the *rac* and *meso* titanocene isomers.[12] To induce enantiomorphic site control, a difference in energy between the two diastereomers ($\Delta\Delta G$) is required to allow effective discrimination between the two propylene enantiofaces. This enables the substituent effect (size and position) in the CH_2CH_2(2-indenyl)$_2$ framework to be separated from the intrinsic influence of different *rac* and *meso* ligand spatial environments, found in bridged bis(1-indenyl)$_2$ metallocenes, in inducing enantiomorphic site control in α-olefin polymerization. To prepare *rac* and *meso* isomers, two approaches were used: (i) alkyl substitution in the cyclopentadienyl ring. This was achieved by either deprotonation of **2** and RX quench or, preferably, reaction of **9** with RMgX followed by dehydration and (ii) substitution in the benzene ring. This was achieved by successive Dieckmann condensations of diethyladipate with the appropriately substituted benzyl halide.

Bis(indene) CH_2CH_2(1-Me-2-indene)$_2$ (**13**)[12] was prepared by deprotonation of **2** with n-BuLi and quenching with MeI and was isolated as a mixture of the three double bond isomers. As shown by Nantz for titanocenes,[12] the prochiral ligands CH_2CH_2(1-R-2-indene)$_2$ afford a mixture of *rac* and *meso* diastereomers in the corresponding zirconocenes. From **13**, *rac*- and *meso*-CH_2CH_2(1-Me-2-indenyl)$_2ZrCl_2$ (**12r** and **12m**) were prepared. In **12r**, the indenyl 3-H proton resonates at δ 6.16 ppm (^1H NMR) and the indenyl 3-carbon at δ 97.9 ppm (^{13}C NMR). In **12m**, these resonances are at δ 6.71 and 101.0 ppm, respectively. The 1-ethyl derivatives *rac*- and *meso*-CH_2CH_2(1-Et-2-indenyl)$_2ZrCl_2$ (**14r** and **14m**) were prepared in an analogous fashion. See the Experimental Section. The *rac* and *meso* metallocene isomers **12r**, **12m** and **14r**, **14m** could be completely separated by crystallization.

Scheme 7



12r **15r**

12m **15m**

Due to the absence of a suitable stereochemical probe, these metallocene dichlorides could not be unequivocally distinguished as the *rac* and *meso* isomers. Therefore *rac*- and *meso*-CH_2CH_2(1-Me-2-indenyl)$_2ZrMe_2$ (**15r** and **15m**) were prepared by addition of MeLi to **12r** and to **12m**, respectively. As expected, **15r** has a single Zr-*Me* resonance at δ −1.02 ppm (^1H) and at δ 40.1 ppm (^{13}C). In contrast, **15m** gives rise to two equal intensity Zr-*Me* signals, at δ −0.38 and −1.82 ppm (^1H), and at δ 44.1 and 37.0 ppm (^{13}C). See Scheme 7. As is commonly observed in metallocene chemistry, the numerical average of the *meso* isomer resonances is very close to that of the single resonance of the *rac* isomer in both the ^1H and ^{13}C NMR spectra and to that in CH_2CH_2(2-indenyl)$_2$-$ZrMe_2$ (**16**) (Zr-*Me* at δ −1.02 ppm).

4-Phenyl-substituted CH_2CH_2(4-Ph-2-indenyl)$_2ZrCl_2$ (**19**) was prepared, an analogue of the archetypal catalyst for isospecific propylene polymerization *rac*-Me_2Si(2-Me-4-Ph indenyl)$_2ZrCl_2$.[4c] 2,5-Di(2-phenylbenzyl)diethyladipate (**18**) was prepared similarly to **2**. Addition of NaOEt to diethyladipate in THF, followed by 2-phenylbenzyl bromide, afforded 2-(2-phenylbenzyl)-diethyladipate (**17**) in 92% yield (GC) as a viscous oil. This was used directly to prepare **18** in another NaOEt/2-phenylbenzylbromide cycle (Scheme 8). De-esterification of **18** using KOH in MeOH/H_2O (in 73% overall

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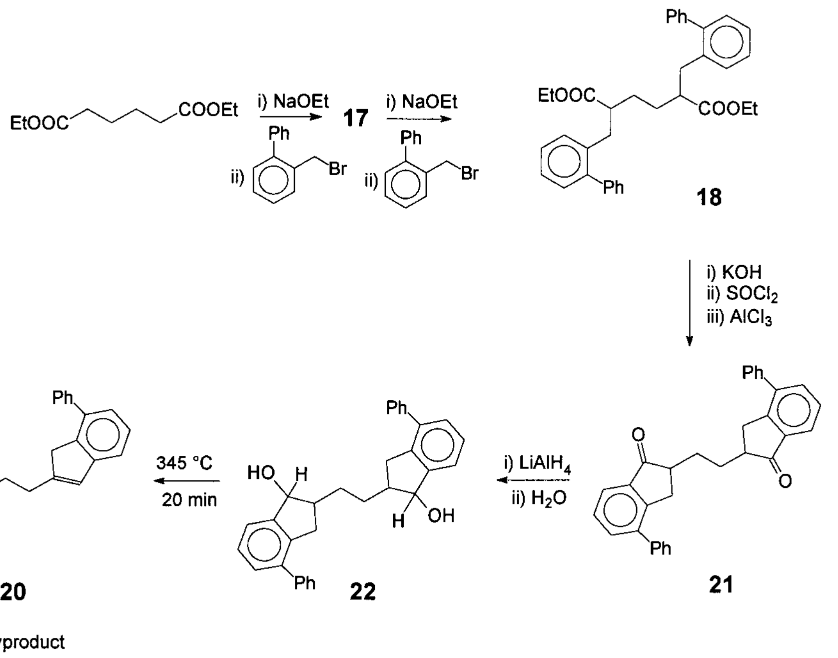
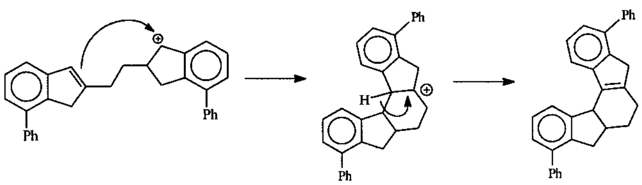
(19) **Caution**: The mutagenic potential of **1** was determined by its effects on two histidine-requiring strains of *Salmonella typhimurium* (TA 98 and TA 100) in the absence, and presence, of a rat liver metabolizing system (S9 mix) using the plate-incorporation method ("Ames test"). This showed **1** to be moderately mutagenic (>5-fold increase in mean number of revertant colonies (at dosages > 556 μg/plate)) compared to the spontaneous reversion rate observed in DMSO. Ames, B. N.; McCann, J.; Yamasaki, E. *Mutat. Res.* **1975**, *31*, 347. Maron, D. M.; Ames, B. N. *Mutat. Res.* **1983**, *113*, 173. We speculate that the flat indenyl rings allow intercalation.

(20) Zirconocenes **1**, **16**, and **29** have C_2-symmetry due to the zigzag conformation of the ethylene bridge. The X-ray crystal structure of CH_2-CH_2(2-tetrahydroindenyl)$_2TiCl_2$ showed slight distortion from idealized C_2-symmetry.[12b]

Scheme 8



Scheme 9



yield from diethyl adipate), preparation of the acid chloride with excess $SOCl_2$ (100% yield), and intramolecular Friedel−Crafts acylation with $AlCl_3$ afforded **21** in 89% isolated yield. ^{13}C NMR data (see Experimental Section) of the diacid, acid chlorides, **21** and **22** in Scheme 8 indicated two diastereomers for each compound. The ortho-phenyl substitution pattern in **18** allowed formation of only one (regio)isomer of bis(indanone) **21** after Friedel−Crafts ring closure. In principle, this synthetic methodology could be extended to other (ortho-)substituted benzyl halides in order to prepare other ethylene-bridged bis(2-indenes) from diethyladipate.

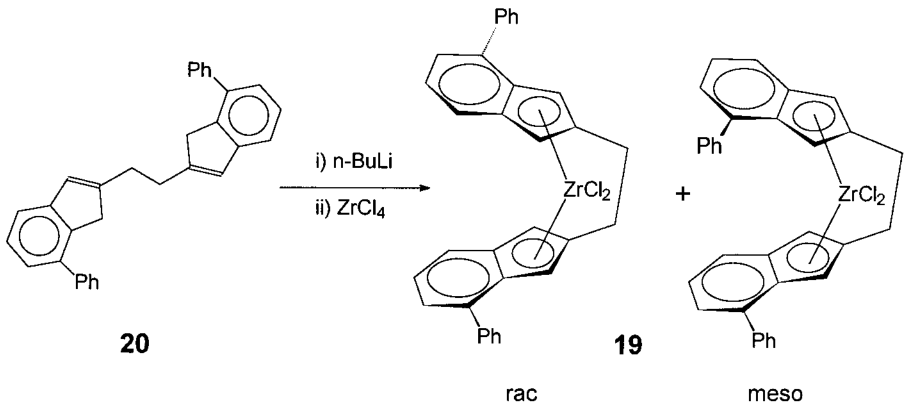
Reduction of **21** with $LiAlH_4$ gave diol **22** in 91% yield. Thermolysis of **22** for 20 min at 345 °C was found to be the best method for the formation of **20** (in 87% yield), which consists of two double bond isomers. A byproduct was consistently observed. On the basis of the similarity of its ^{1}H NMR spectrum to that of **11**, it was tentatively identified as the multicyclic molecule in Scheme 9. **20** was further purified by column chromatography. This also allowed separation of the double bond isomers.

Treatment of **20** with 2 equiv of n-BuLi in ether gave the dianion, which was reacted with $ZrCl_4$ in toluene. Workup afforded **19** as a 1:1 mixture of *rac* and *meso* isomers (Scheme 10).

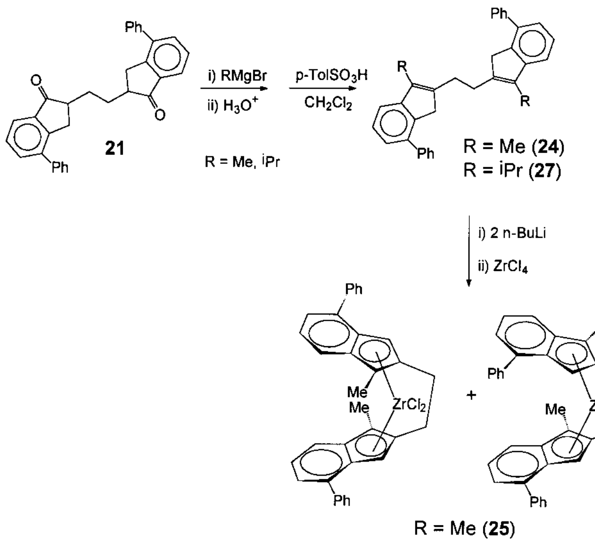
The *meso* isomer **19m** could be completely separated from **19r** by selective crystallization. However, the best separation achieved for **19r** was a 4:1 mixture of *rac* and *meso* isomers. The assignment of **19m** as the *meso* isomer was confirmed by reacting **19m** with MeLi to afford *meso*-CH_2CH_2(4-Ph-2-indenyl)$_2$ZrMe_2 (**23m**). ^{1}H NMR spectroscopy showed two equal intensity Zr-*Me* resonances at δ −1.83 and 0.11 ppm.

Bis(indene) **24** was prepared straightforwardly in 69% isolated yield from bis(indanone) **21** by reaction with MeMgBr in a ether/THF mixture and dehydration with p-$MeC_6H_4SO_3H$ at 20 °C. This facile dehydration is in marked contrast to the dehydration of **10** or **22**, which required elevated temperatures. It is probable that the

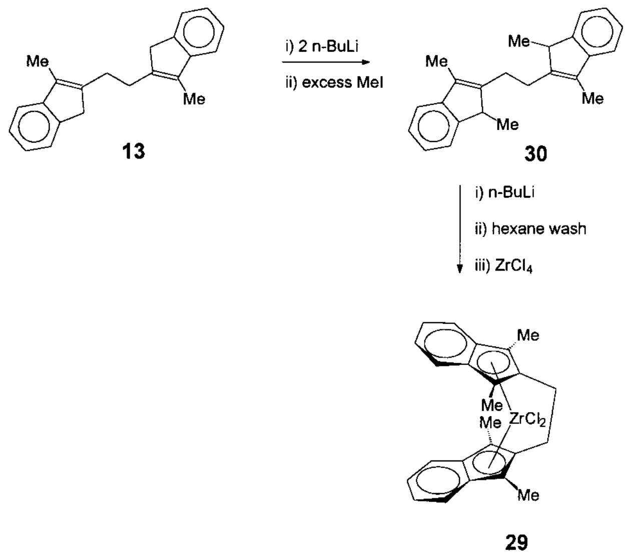
Scheme 10



Scheme 11



Scheme 12



1-alkyl group stabilizes the formed cation. The absence of multicyclic byproducts, as was observed for dehydration of **10** and **22**, can be ascribed to steric hindrance, which inhibits intramolecular attack of the formed double bond on the transient carbocation. The route described here to give **24** and **27** (vide infra) is much preferred over the alternative deprotonation of **20**/RX quench, which would lead to various mutual orientations of 1-R and 4-Ph groups (Scheme 11).

CH_2CH_2(1-Me-4-Ph-2-indenyl)$_2$$ZrCl_2$ (**25**) was formed as a 1:1 ratio of *rac* and *meso* isomers. Although **25m** could be completely separated from the *rac* isomer, total separation of **25r** by crystallization was unsuccessful. The best result, obtained by extraction with and crystallization from hexane, was a 4:1 **25r**:**25m** ratio.

The steric bulk of the alkyl groups in the 1- (or 3-) position (R = H, **19**; R = Me, **25**) has no discernible effect on the *rac*:*meso* ratio. In contrast, Nantz observed[12] that the diastereomeric ratios in the titanocenes CH_2CH_2(1-R-2-indenyl)$_2$$TiCl_2$ (R = Me, *rac*:*meso* = 1.1:1; R = benzyl, *rac*:*meso* = 3.6:1) and in their hydrogenated counterparts CH_2CH_2(1-R-2-tetrahydroindenyl)$_2$$TiCl_2$ (R = i-Bu, *rac*:*meso* = 4:1; R = i-Pr, *rac*:*meso* = 2:1; R = Ph, *rac*:*meso* = 4.3:1) were much more sensitive to the steric bulk of the substituent. This is presumably due to the enhanced mutual repulsion of these 1- or 3-substituents in the *meso* form of the compacter titanocenes.

CH_2CH_2(1,3-Me_2-2-indenyl)$_2$$ZrCl_2$ (**29**) is expected to be more active in the polymerization of propylene because of the anticipated suppression of 2,1-insertions, as determined by UFF molecular modeling[18] (Scheme 12).

Deprotonation of **13** with 2 equiv of n-BuLi and subsequent quenching with MeI gave bis(indene) **30** as mixture of double bond isomers as well as 1,1-*gem*-dialkylated product(s). Purification was accomplished by reaction of **30** with n-BuLi to afford Li_2[**30**], followed by washing with hexane to remove the more soluble *gem*-dimethylated impurities, in which the (di)anion cannot be formed. This gave **30** in 24% isolated yield. Deprotonation of **30** with n-BuLi afforded Li_2[**30**], which reacted with $ZrCl_4$ in toluene to give **29** as an orange powder in 10% isolated yield.

Given the close congruence of these metallocenes with known titanocenes,[12] and our emphasis on (co)polymerization, (co)polymer characterization, end group analysis, and structure–property relationships (vide infra), many of these zirconocenes were not characterized by elemental analysis. In lieu, ^{1}H NMR spectra are reproduced in the Supporting Information.

Polymerization Results

1. Ethylene. Activation of these 2,2′-bridged metallocenes with excess MAO or the aluminoxane of triisobutylaluminum (TIBA) or trisooctylaluminum (TIOA)[21] afforded highly active catalysts for the polymerization of ethylene. Methylene-bridged CH_2(2-indenyl)$_2$$ZrCl_2$ (**33**)[22] was also evaluated for comparison purposes, as well as the archetypal C_2-symmetry metallocene *rac*-CH_2CH_2(1-indenyl)$_2$$ZrCl_2$ (*rac*-EBIZrCl$_2$). For conditions and details see Table 1. Aluminoxanes tetraisobutylaluminoxane (TIBAO) and tetraisooctylaluminoxane (TIOAO) (freshly prepared from TIBA or TIOA with 0.5 equiv of water at 0 °C in hexane) afford catalysts at least as active as those obtained with MAO as cocatalyst.

The activity of **1** and **12r** are higher than, and the activity of **12m** is similar to, that of *rac*-EBIZrCl$_2$ (entries 13, 14), and much higher than that of **33** (entries 11, 12). Low molecular weight polyethylene (LVN = 0.2–0.7 dL/g) is produced with a relatively narrow molecular weight distribution, M_w/M_n = ca. 2.5. The presence of a 1-Me group provides *rac* and *meso* metallocene isomers with different behavior. Precatalyst **12m** is less active and affords a polymer of lower molecular weight than either **1** or **12r**. The use of TIOAO as cocatalyst, instead of MAO, gives a further increase in molecular weight (see entries 1 and 2 for **1** and entries 5 and 7 for **12r**) and an increase in activity.

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[21] Dall'Occo, T.; Galimberti, M.; Resconi, L.; Albizzati, E.; Pennini, G. WO Patent Appl. 96/2580 to Montell Technology Company, priority date July 20, 1994.

[22] Van Beek, J. A. M.; de Vries, J.; Arts, H. J.; Persad, R.; van Doremaele, G. H. J. WO 94/11406 to DSM, priority date November 11, 1992. van Doremaele, G. H. J.; van Beek, J. A. M.; Postema, R. A. J. WO 95/10546 to DSM, priority date October 11, 1993. See also: Resconi, L. WO 00/29415 to Montell Technology Company, priority date November 18, 1998.

Table 1. Ethylene Polymerization Parameters and Polymer Characterization[a]

entry	metallocene	amount (μmol)	cocatalyst	yield (g)	activity (kg/(g Zr·h))	LVN (dL/g)	$M_w \times 10^{-3}$ (g/mol)[f]	M_w/M_n[f]
1[b]	**1**	0.24	MAO	2.88	530	0.42		
2	**1**	0.25	TIOAO	3.25	860	0.54		
3[c]	**1**	0.48	TIOAO	94	4320	0.56	23	2.6
4[d]	**1**	0.48	TIOAO	64	1470	0.47		
5	**12r**	0.22	MAO	2.75	810	0.46		
6	**12r**	0.22	TIBAO	3.66	1070	0.59		
7	**12r**	0.22	TIOAO	4.61	1350	0.67	32	2.3
8	**12m**	0.22	MAO	1.92	560	0.36		
9	**12m**	0.22	TIBAO	1.28	380	0.36		
10	**12m**	0.22	TIOAO	1.57	460	0.37	18	2.5
11	**33**	0.74	MAO	1.51	130	0.17		
12[e]	**33**	1.20	TIOAO	1.54	27	0.2		
13	*rac*-EBIZrCl_2	0.21	MAO	1.31	410	1.38		
14	*rac*-EBIZrCl_2	0.21	TIOAO	1.18	370	1.60		

[a] Polymerization conditions: 200 mL glass autoclave, 100 mL of hexane with Al/Zr molar ratio of 1000:1. 10 min at 80 °C under 4.6 bar ethylene. [b]Polymerization time 15 min. [c]In 1 L of hexane in a 2.3 L autoclave for 30 min, 9.6 bar ethylene. Al/Zr molar ratio 2000 [d]In 1 L of hexane in a 2.3 L autoclave for 60 min, 9.6 bar ethylene under 0.2 bar H_2. Al/Zr = 2000. [e]Polymerization time 30 min. [f]GPC data.

This increase is most pronounced for **1**/TIOAO (entry 3) compared to **1**/MAO (entry 1) and **12r**/TIOAO (entry 7), compared to **12r**/MAO (entry 5). Addition of H_2 (0.2 bar) leads to a decrease in activity[23] and the expected decrease in polymer molecular weight (compare entries 3 and 4, Table 1). This H_2-induced reduction of activity in ethylene polymerizations has been previously observed in both Ti-based Ziegler–Natta catalysts[24a,b] and metallocenes.[24c] The exact reason for this has, however, not been unequivocally established, although it has been attributed[24b] to slow chain reinitiation after chain transfer to hydrogen caused by M–Et being stabilized by a relatively strong β-agostic interaction. Single-component ethylene polymerization catalysts with β-agostic stabilized M–Et[24d,e] have been isolated, and the observed[24d] rates of ethylene insertion into $(C_5Me_5)_2Sc{-}R$ followed $Sc{-}H \gg Sc{-}n\text{-}Pr > Sc{-}Me > Sc{-}Et$.

The polyethylene obtained is essentially linear, as given by DSC measurements (mp (T_{m2}) = 133 °C and enthalpy of fusion of 233 J/g, for **1**/MAO). Due to the low molecular weight and relatively narrow molecular weight distribution of the polyethylene produced, metallocene **1**, in conjunction with a Ziegler–Natta catalyst, has been used to prepare broad molecular weight distribution HDPE having a very low xylene soluble polymer content.[13]

2. Propylene. These zirconocenes were also tested for the polymerization of propylene (liquid propylene, 50 °C, with and without H_2). The results are given in Table 2, as well as the characterization of the resulting polymers and end group analysis. Metallocene **1**, when activated by methylaluminoxane (MAO), exhibited very low activity (1.9 kg/(g Zr·h)) for the polymerization of propylene to low molecular weight (presumably)[25] atactic-PP. An unusually high percentage (9.4%) of 2,1-insertions was observed. Similarly, CH_2CH_2(4-Ph-2-indenyl)$_2$ZrCl_2 (**19**) also showed a very low activity (5 kg/(g Zr·h)) and gave (presumably)[25] atactic-PP possessing 9.9% 2,1-insertions. Alkyl substitution in either the 1- and/or 3-positions suppresses propylene 2,1-insertions. The 1-alkyl-substituted metallocenes **12r**/MAO, **12m**/MAO, and **14m**/MAO polymerize propylene with activities of 16, 15, and 11 kg polymer/(g Zr·h), respectively, to afford essentially a-PP having fewer 2,1-insertions (2.7, 0.4, and 0.9%, respectively). The effect of alkyl groups in the 1- and/or 3-positions is exemplified by 1,3-dimethyl-substituted **29**, activated by MAO, which afforded a-PP with only 0.2% 2,1-insertions and a higher activity (60 kg/(g Zr·h)).

Both *rac* and *meso* isomers of **12**, **14**, **19**, and **25** polymerize propylene to give essentially a-PP, as reflected by the triad distributions in Table 2. A 1-alkyl substituent, although inhibiting 2,1-insertions, provides insufficient steric bulk to afford enantiomorphic site control. Slightly enhanced polymer isotacticity (mm = 62%) was achieved in the polymerization with **19r**/MAO/H_2, although it is uncertain if this is energetically or statistically significant. Given the suppression of 2,1-insertions by 1- and/or 3-alkyl substituents (vide supra), the combination of a 1-methyl and a 4-phenyl group in CH_2CH_2(1-Me-4-Ph-2-Ind)$_2$ZrCl_2 (**25r**) gave a synergetic effect with an increase of activity to 1350 kg/(g Zr·h). **25m**/MAO gave atactic-PP with moderate activity (280 kg/(g Zr·h)).

To compare the effect of bridge length, the known bridged (2-indenyl)metallocenes 1,1′-biphenyl(2-indenyl)$_2$-ZrCl_2[11] (**31**), S(2-indenyl)$_2$ZrCl_2[22] (**32**), and CH_2(2-indenyl)$_2$ZrCl_2[22] (**33**) were prepared. These 2-indenyl metallocenes were much less active than their ethylene-bridged counterparts. See Table 2.

Saturated End Groups. The formation of a low molecular weight polymer allowed comprehensive identification of the end groups, providing information on the chain transfer mechanisms. As well as *n*-propyl and vinylidene end groups characteristic of 1,2-insertion into Zr-H/β-H elimination to the metal or β-H transfer to monomer, strong signals corresponding to isobutyl end groups were also observed, indicating that a major termination pathway is chain transfer to Al, particularly in the absence of H_2. This is commensurate with the high Al:Zr ratio and the low activity. Thus, even in the

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(23) The polymerization time of entry 3 was 30 min, while that of entry 4 was 60 min. We cannot rule out that the apparent reduction in activity is due to a nonlinear polymerization activity/decay profile.

(24) (a) Kissin, Y. V. *J. Mol. Catal.* **1989**, *56*, 220 (b) Kissin, Y. V.; Mink, R. I.; Nowlin, T. E.; Brandolini, A. J. *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlach: Berlin, 1999; p 60. (c) Reddy, S. S.; Sivaram, S. *Prog. Polym. Sci.* **1995**, *20*, 309. (d) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566. (e) Tanner, M. J.; Brookhart, M.; DeSimone, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 7617.

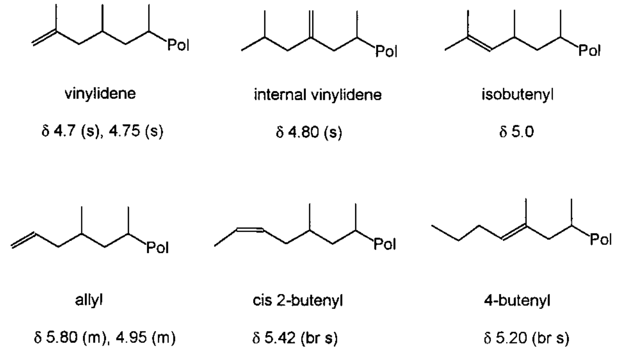
(25) We assume the polypropylene is atactic, although the high level of 2,1-regioerrors rendered accurate triad analysis meaningless in the polymer from **1**/MAO and **19**/MAO.

Table 2. Propylene Polymerization Data, Polymer Microstructure, and End Group Analysis[a]

polymerization conditions						polymer regio- and steroeoregularity				polymer end groups[c]								
compd	amt Zr (μmol)	Al/Zr ratio	activity (kg/(g Zr·h))	H$_2$ (mol %)	M_n[b]	2,1- (mol %)	mm (mol %)	mr (mol %)	rr (mol %)	*n*-propyl	*n*-butyl	i-Bu	DMB[g]	vinylidene	allyl	4-butenyl	*cis*/*trans* 2-butenyl	internal vinylidene
1	4.0	1000	1.9	0.0	3200	9.4	*d*	*d*	*d*	0.42	0.0	1.25	0.00	0.056	0.07	0.14	0.06	0.00
1	2.0	10000	530	2−3	400	0.3	n.d.	n.d.	n.d.	0.89	0.9	0.2	0.00	0.01	0.00	0.00	0.00	0.00
12r	3.75	5400	16	0.0	2700	2.7	20	49.1	30.9	0.34	0.32	1.17	0.00	0.17	0.00	0.00	0.00	0.00
12r	0.5	40200	6240	2−3	850	n.d.	n.d.	n.d.	n.d.	0.82	0.57	0.5	trace	0.11	0.00	0.00	0.00	0.00
12m	4.0	5000	15	0.0	3600	0.4	18.9	49.9	31.2	0.2	0.0	1.2	n.d	0.6	0.00	0.00	0.00	0.00
12m	0.5	40200	4160	2.5−3.1	1800	0.3	22.0	46.0	32.0	0.83	0.18	0.89	trace	0.09	0.01	0.00	0.00	0.00
14r	4.0	5000	7	0.0		insufficient polymer sample				insufficient polymer sample								
14r	0.5	40000	1320	2.4−3.6	1600	0.5	36	38	26	0.78	0.48	0.70	trace	0.03	0.01	0.00	0.00	0.00
14m	4.0	5000	11	0.0	3300	0.9	17	51	32	0.20	0.01	1.25	0.22	0.3	0.02	0.00	0.00	0.01
14m	0.5	40000	5080	2.0−2.5	1700	0.3	23	46	31	0.82	0.13	0.81	0.08	0.12	0.00	0.01	0.03	0.00
19r[e]	4	5000	5	0	3200	9.9	*d*	*d*	*d*	0.60	0.25	0.47	0.29	0.03	0.05	0.20	0.09	0.02
19r[e]	0.5	40000	330	2.7	1100	0.2	62.2	21.6	16.2	0.95	0.68	0.26	0.07	0.04	0.003	0.00	0.00	0.00
25r[e]	4	5000	1350[f]	0.0	15500	0.4	21.1	47.4	31.6	0.35	0.03	0.74	0.00	0.24	0.15	0.05	0.01	0.43
25r[e]	0.5	40000	1080	2.7	1000	0.1	27.8	44.3	27.9	0.94	0.03	0.73	0.00	0.28	0.02	0.00	0.00	0.00
25m	4	5000	280	0.0	15100	<0.1	21.9	49.2	28.9	0.38	0.04	1.13	0.00	0.11	0.14	0.00	0.00	0.21
25m	0.5	40000	900	2.7	1000	0.2	26.3	46.6	27.1	0.93	0.04	0.91	trace	0.09	0.03	0.00	0.00	0.00
29	4	5000	60	0.0	5500	0.2	19.0	51.8	29.2	0.0	0.0	1.91	0.00	0.06	0.03	0.00	0.006	0.003
29	0.5	40000	5040	2.7	1900	0.5	40.3	36.8	22.8	0.8	0.05	1.14	trace	0.01	0.002	0.00	0.00	0.00
31	4.0	5000	31	0.0	12000	1.4	84.1	10.7	5.1	0.6	0.5	0.9	n.d.	0.00	0.00	n.d.	n.d.	n.d.
31	0.5	40195	114	2−4	1700	1.2	44.2	33.9	21.9	0.9	0.2	1.2	n.d.	0.00	0.00	n.d.	n.d.	n.d.
33	4.0	5000	27	0.0	800	2.0	12	49	39	0.97	0.05	0.19	0.00	0.77	0.02	0.00	0.00	0.00
33	2.0	10000	400	2−3	700	1.2	13	45	42	1.04	0.04	0.19	0.00	0.73	0.00	0.00	0.00	0.00

[a] Performed in a 5 L reactor containing 1.6 kg of liquid propylene at 50 °C for 1 h unless otherwise stated, cocatalyst = MAO. Total amount of MAO kept constant at 20 mmol in each experiment except in the first entry. [b] From ^{1}H NMR. [c] Sum of end groups normalized to 2. [d] The high percentage of 2,1-regiodefects renders triad analysis meaningless. [e] Polymerizations performed with 4:1 *rac*:*meso* ratio. [f] Polymerization time = 30 min. [g] DMB = 2,3-dimethylbutyl. Under the conditions used, S(2-indenyl)$_2$ZrCl$_2$ (**32**)/MAO was inactive.

Scheme 13. Unsaturated End Groups; ^{1}H NMR Chemical Shifts Relative to Lowest Field Signal of 1,2,4-Trichlorobenzene at δ 7.32 ppm



absence of external H_2, the majority of the end groups are saturated (Table 2). The high percentage of 2,1-regioerrors in the polymer obtained from **1**/MAO and **19**/MAO has consequences for the end group analysis. A small amount of *n*-butyl end groups are observed (in the absence of external H_2). These arise from 2,1- (1,3-) insertion, then transfer to Al or, alternatively, by consumption of in-situ-generated H_2 (vide infra). Transfer to Al would be consistent with the large Al:Zr ratio. Resonances due to the 2,3-dimethylbutyl end group[26] were also observed (2,1-insertion into Zr−H followed by 1,2-insertion into Zr−i-Pr).

Unsaturated End Groups. A variety of unsaturated end groups were observed. Small amounts of allyl end groups (from β-Me elimination) were observed throughout. No resonances due to an isobutenyl end group (δ 5.0 ppm) were observed.[27] The resonance is also obscured by that of the higher field allyl multiplet. Relatively high levels of *cis* or *trans* (we assume *cis*) 2-butenyl end groups were observed. These are formed by β-H transfer to monomer after a 2,1-insertion.[28] As previously described by Resconi,[29d,30a] the broad singlet[31] at δ 5.20 ppm (^{1}H NMR) and ascribed to the 4-butenyl end group[29d] is only observed in conjunction with the broad singlet at δ 5.42 ppm (2-butenyl), indicating that it, too, is associated with 2,1-insertions. Indeed, inspection of Table 2 shows that both end groups are most prevalent from **1**/MAO and **19**/MAO (Scheme 13).

Effect of Added Hydrogen. Kinetic data[32] has indicated that chain propagation after a 2,1-regiodefect is strongly inhibited due to the higher steric hindrance of a Zr−CHMeCH$_2$−P moiety, compared to Zr−CH$_2$-CHMe−P. The dosing of hydrogen in the polymerization of propylene by both Ziegler−Natta[32] and metallocene[33] catalysts leads to an activity enhancement due to the reactivation of these dormant sites. For the polymerization of propylene by *rac*-EBIZrCl$_2$[33a] and *rac*-Me$_2$Si-(2-Me-4-Ph-indenyl)$_2$ZrCl$_2$,[33b] dosing of H_2 resulted in an increase of activity by 3-fold and 10-fold, respectively.

Notably, when the polymerization of propylene is performed under H_2 (2−3 mol % in the autoclave gas cap as determined by on-line monitoring), a dramatic increase (100−1000-fold) in catalyst activity was observed. This afforded saturated propylene oligomers with activities of 6−10 tons/(g Zr·h). In addition, the polymer derived from **1**/MAO/H_2 and **19**/MAO/H_2 showed a marked reduction in embedded 2,1-insertions: from 9.4% to 0.3% and from 9.9% to 0.2%, respectively. As well as *n*-propyl (from 1,2-insertion into Zr−H initiator) and isobutyl (from chain transfer to H_2 after a 1,2-insertion) end groups, the other significant chain termination pathway is chain transfer to H_2 after a 2,1-insertion giving rise to *n*-butyl end groups.

In-Situ Hydrogen Generation and Consumption. In some of these polymerizations performed with added H_2, obvious discrepancies between isolated and calculated[34] polymer yields were observed. In these instances, we attribute the higher calculated yield to the hydrogenation of propylene to propane[34] (determined and quantified by on-line GC sampling) concomitant with the polymerization of propylene. This indicates that in polymerizations performed without added H_2 this is a viable pathway for low equilibrium levels of hydrogen generated in-situ (determined and quantified by on-line GC sampling) by allylic activation to be consumed by propylene hydrogenation. An alternative pathway for H_2 consumption is chain transfer to H_2 (i.e., detection of n-Bu end groups (vide supra) in the absence of external hydrogen (see Table 2).

Hydrogen evolution has been observed during olefin polymerizations[29] and is supported theoretically.[29e] Propylene insertion into a Zr−allyl species has been recently studied,[35] and propylene oligomerization by [(C$_5$Me$_5$)$_2$MMe(THT)]BPh$_4$ (M = Zr, Hf; THT = tetrahydrothiophene)[36] showed slow deactivation by formation

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[26] Randall, J. C.; Ruff, C. J.; Vizzini, J. C.; Speca, A. N.; Burkhardt, T. J. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999; p 601. Moscardi, G.; Piemontesi, F.; Resconi, L. *Organometallics* **1999**, *18*, 5264.

[27] Spectra measured in 1,2,4-trichlorobenzene. In $C_2D_2Cl_4$, which can contain acidic impurities, isomerization to the isobutenyl end group has been observed.[30a]

[28] Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Ziegler, R. *Macromolecules* **1995**, *28*, 8, 6667.

[29] (a) Horton, A. D.; Van Baar, J. F. Personal communication. (b) Karol, F. J.; Kao, S.; Wasserman, E. P.; Brady, R. C. *New. J. Chem.* **1997**, *21*, 797. (c) Wasserman, E.; Hsi, E.; Young, W.-T. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1998**, *39*, 425. (d) Resconi, L.; Piemontesi, F.; Camurati, I,; Sudmeijer, O.; Nifant'ev, I. E.; Ivchenko, P. V.; Kuz'mina, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 2308. (e) Margl, P. M.; Woo, T. K.; Blöchl, P. E.; Ziegler, T. *J. Am. Chem. Soc.* **1998**, *120*, 2174.

[30] (a) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145. (b) Resconi, L. *J. Mol. Catal. A: Chem.* **1999**, *146*, 167 (c) Sacchi, M. C.; Carvill, A.; Forlini, F.; Tritto, I.; Locatelli, P. *Recent Res. Dev. Macromol. Res.* **1999**, *4*, 57.

[31] In $C_2D_2Cl_4$, this resonance appears as a triplet at δ 5.21 ppm.[29d]

[32] Ziegler−Natta: Chadwick, J. C.; Morini, G.; Albizzati, E.; Balbontin, G.; Mingozzi, I.; Christofori, A.; Sudmeijer, O.; van Kessel, G. M. M. *Macromol. Chem. Phys.* **1996**, *197*, 250.

[33] Metallocenes: (a) Tsutsui, T.; Kashiwa, N.; Mizuno, A. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 565. (b) Aulbach, M.; Bachmann, B.; Küber, F.; Spaleck, W.; Winter, A. *Proceeding of Metallocenes '95*; April 1995 in Brussels, Belgium; Schotland: Skillman, NJ; p 321. (c) Busico, V.; Corradini, P.; Cipullo, R. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 97. (d) Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538. (e) Spaleck, W.; Küber, F.; Bachmann, B.; Fritze, C.; Winter, A. *J. Mol. Catal.* **1998**, *128*, 279. (f) Carvill, A.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromolecules* **1997**, *30*, 7056. (g) Lin, S.; Kravchenko, R.; Waymouth, R. M. *J. Mol. Catal.* **2000**, *158*, 423.

[34] During propylene polymerizations the gas cap was sampled and analyzed by on-line GC at 1 min intervals. The propane/propylene ratio was determined, making use of the natural abundance (typically 0.3 mol %) of propane in the propylene feed. From the change in propane/propylene ratio as a function of time propylene conversion could be determined. The calculated polypropylene yield is therefore given by propylene intake × $(1 - R_0/R_t)$ where R_0 = propane/propylene ratio at $t = 0$; R_t = propane/propylene ratio at time t during the polymerization. The calculated yield is compared with the actual weight of polymer isolated from the autoclave. A calculated yield significantly larger than the actual yield is ascribed to propane formation by hydrogenation of propylene during the polymerization.

[35] Lieber, S.; Prosenc, M.-H.; Brintzinger, H.-H.*Organometallics* **2000**, *19*, 377.

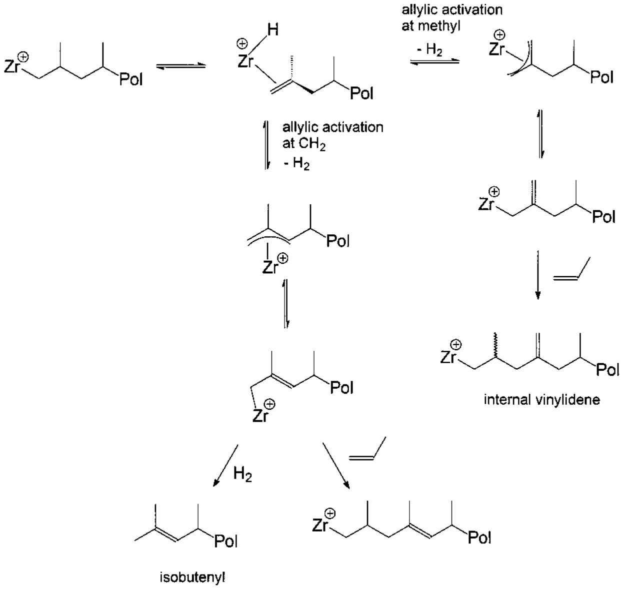
Table 3. Ethylene/Propylene Copolymerization Parameters and Copolymer Characterization[a]

metallocene	amt Zr (μmol)	Al/Zr ratio	polym time (min)	yield (g)	activity (kg/(g Zr·h))	LVN (dL/g)	propylene incorp (mol %)
1	0.5	40000	45	44.5	1300	0.47	13.8
12r	0.94	21500	17	260	10 660	0.71	17.9
12m	1.0	20400	33	250	4992	0.53	24.1
14r	0.5	40180	65	316	6400	0.93	26.9
14m	0.5	40230	60	570	12 500	0.63	23.3
31	0.5	40450	60	6.3	138	2.22	52.9
32	0.97	21000		~1			45

[a] EP copolymerizations were performed at 50 °C in a 25 L reactor containing 7.5 kg of liquid propylene and with 5.5−6.2 mol % ethylene as measured in the liquid phase. Total amount of MAO cocatalyst was kept constant at 20 mmol in each experiment.

of meth(allyl) species. Addition of H_2 restored catalyst activity. As suggested by others,[29,30] hydrogen formation can be ascribed to formation of internal unsaturations (internal vinylidene at δ 4.80 ppm) in the polymer. See Table 2. The mechanism of allylic activation and H_2 evolution has been previously reported,[29b,30a,b] as well as end group characterization. This suggests propylene insertion into a Zr(η^1-allyl) initiator generated by allylic activation of methyl, rather than methylene groups, with liberation of H_2[30] (Scheme 14). Indeed, we did not detect isobutenyl end groups (Table 2).

Scheme 14. Proposed Mechanism for Internal Vinylidene Formation



As found for *rac*-Me_2C(3-t-Bu-indenyl)$_2ZrCl_2$/MAO[30] and observed here for various 2,2′-bridged metallocenes (Table 2), addition of external H_2 suppresses the formation of both internal vinylidene and 2- and/or 4-butenyl end groups.

Field desorption MS analysis of the low molecular weight polymers from **19r**/MAO and **29**/MAO showed peaks corresponding to saturated polymer as well as masses corresponding to significant amounts of mono and double unsaturations. The polymer from **29**/MAO/H_2, measured as a reference for the invasiveness of the technique, showed, as expected for a polymerization performed under hydrogen, only masses attributable to saturated polymer.

Copolymerization Results

Ethylene/Propylene. Copolymerization of ethylene and propylene (liquid propylene, 50 °C, ca. 6 mol % ethylene) afforded low molecular weight (LVNs = 0.47−0.93 dL/g) EP copolymers with very high activities (1300−12 500 kg/(g Zr·h)). For conditions see Table 3. The activities are also higher than those obtained in the polymerization of ethylene. This increase in activity, the "positive comonomer effect",[24c,33g,37] is often observed in copolymerizations of ethylene and another α-olefin (often propylene or 1-hexene), compared to the ethylene polymerization activity, despite reactivity ratio $r_E \gg r_{\alpha-\text{olefin}}$ (vide infra). This phenomenon is not completely understood. It has been postulated[37] that this may be due to easier monomer diffusion in the copolymer, with respect to the more crystalline polyethylene, or to changes in rate constants for ethylene insertion in the presence of α-olefin, or to an increase in the number of active sites.

The EP copolymers were analyzed by ^{1}H and ^{13}C NMR spectroscopy. Despite these copolymerizations being performed in liquid propylene (>10 M), with ca. 6 mol % ethylene, much more ethylene (73.1−86.1 mol %) than propylene is incorporated. This is also reflected in their ethylene and propylene reactivity ratios (vide infra). There is also little variation in copolymer "blockiness" (Table 4). Analysis of the saturated end groups by ^{13}C NMR spectroscopy showed only sequences of *n*-hexyl (and possibly longer)[38] of the initiating alkyl group. This suggests that initiation occurs exclusively by sequential ethylene insertion. Given the much higher activities observed for EP copolymerization compared to propylene polymerization, ethylene seems to fulfill a similar activating role to H_2 in the polymerization of propylene. One possibility is insertion into a transient Zr−allyl species to reinitiate propagation, although we have no evidence to support this. The unsaturated end groups were predominantly vinyl with relatively little vinylidene (^{1}H NMR), indicating that chain transfer to monomer occurs mainly after ethylene insertion. As in the polymerization of ethylene and propylene, the EP (co)polymer molecular weights are all low (LVN < 1 dL/

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[36] Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362.

[37] (a) Chien, J. C. W.; Nozaki, T.*J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 227. (b) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.* **1993**, *194*, 3167. (c) Lehtinen, C.; Löfgren, B. *Eur. Polym J.* **1997**, *33*, 115. (d) Naga, N.; Ohbayashi, Y.; Mizunuma, K. *Makromol. Rapid Commun.* **1997**, *18*, 837. (e) Koivumäki, J.; Fink, G.; Seppälä, J. V. *Macromolecules* **1994**, *27*, 6254. (f) Lehmus, P.; Härkki, O.; Leino, R.; Luttikhedde, H. J. G.; Näsman, J. H.; Seppälä, J. V. *Macromol. Chem. Phys.* **1998**, *199*, 1965. (g) Spitz, R.; Pasquet, V.; Joly, J. F. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 95. (h) Soga, K.; Yanagihara, H.; Lee, D. *Makromol. Chem.* **1989**, *190*, 995.

[38] *n*-Alkyl end groups longer than *n*-hexyl cannot be differentiated from each other by NMR spectroscopy.

Table 4. Distribution of Ethylene and Propylene Blocks in EP Copolymer[a]

entry	metallocene	E	P	PP	PE	EE	PPP	PPE	EPE	PEP	PEE	EEE	r_E	r_P	$r_E r_P$
1	**1**	86.1	13.8	2.0	23.4	74.3	0.2	3.7	10.3	2.3	21.2	61.9	98.1	0.0068	0.67
2	**12r**	82.1	17.9	4.0	27.7	68.3	2.2	5.7	11.4	2.4	22.3	56.0	78.1	0.0084	0.66
3	**12m**[b]	75.9	24.0	2.1	43.6	54.1	0.4	3.7	19.6	6.6	30.2	39.1	41.6	0.0025	0.104
4	**31**[c]	46.7	52.9	37.7	30.0	31.4	28.0	18.8	4.7	5.3	19.1	22.7	43.4	0.237	10.29
5	**32**	55.0	45.0										11.8	0.026	0.31

[a] All percentages in mol %. [b] 0.1 mol % 2,1-regiodefects present, hence % E + % P $\neq$ 100%. [c] 0.4 mol % 2,1-regiodefects present, hence % E + % P $\neq$ 100%.

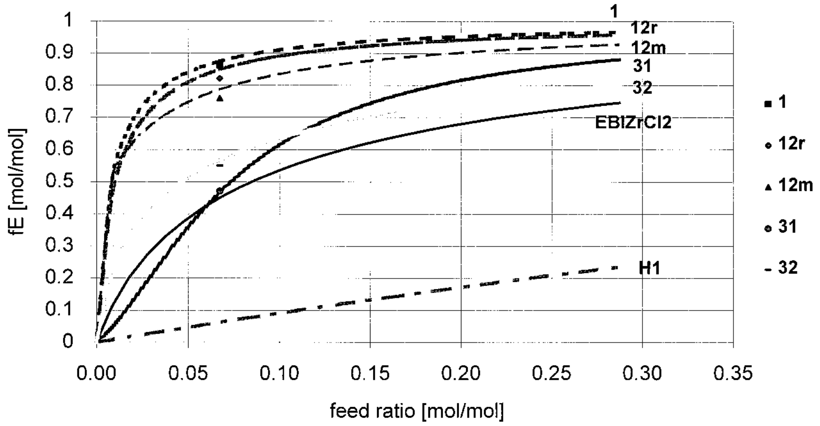

Figure 1. Ethylene content in copolymer as a function of the feed ratio in liquid propylene at 50 °C. H1 = *rac*-Me_2Si(2-Me-4-Ph-indenyl)$_2ZrCl_2$/MAO.

g). There does not appear to be a correlation of activity with the percentage of incorporated ethylene or with copolymer molecular weight. An increase in EP copolymer molecular weight with increasing ethylene incorporation has been previously reported for *rac*-$EBIZrCl_2$[39a] and *rac*-Me_2Si(1-tetrahydroindenyl)$_2ZrCl_2$/MAO.[39b]

1,1′-Biphenyl(2-indenyl)$_2ZrCl_2$[11] (**31**) gave a higher molecular weight EP copolymer with significantly more (52.9 mol %) propylene incorporation than the ethylene-bridged bis(2-indenyl) zirconocenes (Table 3). S(2-indenyl)$_2ZrCl_2$[22] (**32**) was much less active and gave only traces (<1 g) of copolymer, but also with higher propylene incorporation (45 mol %) than the ethylene-bridged zirconocenes.

The ethylene and propylene distributions, as well as the reactivity ratios, are given in Table 4.

Ethylene (r_E) and propylene (r_p) reactivity ratios[40] were calculated[41] for the EP copolymers from **1**, **12r**, and **12m** and are compared with **31**, **32**, and *rac*-$EBIZrCl_2$ by fitting normalized experimental ^{13}C NMR peak areas to a single-site first-order Markov model. The single-site Markov model is completely defined by the ethylene and propylene reactivity ratios r_E and r_p, respectively. Each of the 2,2′-bridged metallocenes has a clear preference for ethylene with $r_E \gg 1$ and $r_P \ll 1$. In comparison, *rac*-$EBIZrCl_2$[39a] and *rac*-Me_2Si(1-indenyl)$_2$-$ZrCl_2$[37c,d] have a much smaller preference for ethylene over propylene with $r_E = 6.61$, $r_P = 0.06$ and $r_E = 4.23$, $r_P = 0.12$, respectively. The highly isospecific and sterically encumbered metallocene *rac*-Me_2Si(2-Me-4-Ph-indenyl)$_2ZrCl_2$[4c] gives high levels of α-olefin incorporation even at relatively low α-olefin concentrations.[42] In contrast, sterically hindered $(C_5Me_5)_2ZrCl_2$/MAO[42] shows a very high preference for consecutive ethylene insertions with $r_E = 250$.

The data in Table 4 are also given in Figure 1, in which the ethylene content (f_E) of the EP copolymer is displayed as a function of the feed (ethylene/propylene in mol %) ratio (F_E) and of the ethylene and propylene reactivity ratios (r_E, r_P). The lines give f_E as a function of F_E as calculated according to the Mayo–Lewis copolymerization equation,[44] and the displayed points in Figure 1 give f_E as determined directly by ^{13}C NMR spectroscopy.

Ethylene/1-Hexene. Copolymerizations were also performed with 1-hexene as α-olefin in heptane at 70 °C under 4.4 bar ethylene to form LLDPE. The details are shown in Table 5. As expected, the incorporation of 1-hexene increases with increasing [1-hexene], and there is a commensurate decrease in both copolymer crystallinity, as given by ΔH_{fusion}, and melting point, entries 1–5. Using **1**/TIOAO as catalyst and a 50:50 vol/vol 1-hexene:heptane ratio, a maximum of 9.9 wt %

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[39] (a) Drögemuller, H.; Heiland, K.; Kaminsky, W. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W.; Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 303. (b) Sugano, T.; Endo, J.; Takahama, T. In *Science and Technology in Catalysis*; Izumi, Y., Arai, H., Iwamoto, M., Eds.; Elsevier: New York, 1994; p 371.

[40] Odian, G. In *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991.

[41] The reactivity ratios were determined by using a first-order Markov model (single site) with the Levenspiel Marquadt algorithm. See: Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes in Pascal. The Art of Scientific Computing*; Cambridge University Press: Cambridge, 1990.

[42] Miri, M.; Hetzer, D.; Miles, A.; Pecak, M.; Riscili, B. In *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999; p 509.

[43] Ewen, J. A. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodansha: Tokyo, 1986; p 271. Zambelli, A.; Grassi, A.; Galimberti, M.; Mazzocchi, R.; Piemontesi, F. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 523.

[44] Mayo-Lewis equation: $f_E = F_E(1 - F_E) + r_E F_E^2/\{r_E F_E^2 + 2F_E(1 - F_E) + r_P(1 - F_E)^2\}$ where $F_E = x/1+ x$ where f_E = ethylene mole fraction in EP copolymer, F_E = ethylene mole fraction in the reaction medium ($\cong x/1 + x$), r_E = ethylene reactivity ratio, r_p = propylene reactivity ratio, x = feed ratio (mol/mol), i.e., molar ratio of ethylene to propylene ($x \cong$ [E]/[P]). Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.

Table 5. Ethylene/1-Hexene Copolymerization Parameters and Copolymer Characterization[a]

entry	metallocene	amount (μmol)	1-hexene (mL)	time (min)	yield (g)	activity (kg/(g Zr·h))	LVN (dL/g)	1-hexene incorp (wt %)	ΔH_{fusion} (J/g)	mp (°C)
1	**1**	0.18	0	15	1.65	396	0.60	0.0	233	132.9
2	**1**	0.20	5	15	2.25	497	0.54	1.7	188	124.2
3	**1**	0.18	10	15	2.62	653	0.60	2.9	162	120.9
4	**1**	0.20	15	15	3.18	703	0.57	4.0	152	118.4
5	**1**	0.24	50	30	3.88	356	0.49[b]	9.9	86	116.0
6	**12r**	0.11	15	20	3.72	1093	0.59	5.4	154	116.7
7	**12r**	0.11	50	30	5.60	1097	0.58[c]	16.4	90	95.3
8	**12m**	0.22	15	20	3.20	470	0.30[d]	9.9	139	108.9
9	**12m**	0.44	50	30	6.46	316	0.33	31.2	amorphous	
10	*rac*-EBIZrCl$_2$	0.25	15	20	3.2	440	1.03	28.2	44	68.0

[a] Cocatalyst was TIOA/H$_2$O in all cases. Al:Zr = 1000. Polymerizations in heptane, total volume = 100 mL, ethylene pressure 4.4 bar. [b] M_w = 22 000, M_w/M_n = 2.6. [c] M_w = 33 000, M_w/M_n = 2.2. [d] M_w = 18 000, M_w/M_n = 2.3.

Table 6. Distribution of Ethylene and Hexene Blocks in EH Copolymer[a]

entry	metallocene	E	H	HH	HE	EE	HHH	HHE	EHE	HEH	HEE	EEE	n_E	r_E	r_H	r_Er_H
4	**1**	98.63	1.37	0.00	2.80	97.2	0.00	0.00	1.37	0.00	2.90	95.73	70.4	182	*b*	*b*
5	**1**	96.47	3.53	0.00	7.10	92.9	0.00	0.00	3.53	0.00	7.05	89.42	27.2	235	*b*	*b*
6	**12r**	98.1	1.9	0.00	3.5	96.5	0.00	0.00	1.7	0.00	3.7	94.6	56.1	144	*b*	*b*
7	**12r**	93.8	6.2	0.2	12.3	87.5	0.00	0.4	5.9	0.6	11.2	81.9	15.2	128	0.004	0.51
8	**12m**	96.5	3.5	0.00	6.8	93.2	0.00	0.00	3.3	0.1	6.8	89.8	28.4	72	*b*	*b*
9	**12m**	86.8	13.2	0.4	25.7	73.9	0.00	0.8	12.3	2.1	21.8	63.9	6.75	52	0.004	0.21
10	*rac*-EBIZrCl$_2$	88.4	11.6	0.5	22.2	77.3	0.00	1.0	10.6	1.7	18.8	67.9	7.97	18	0.018	0.32

[a] All percentages in mol %. [E] = [EEE] + [HEE] + [HEH]; [H] = [HHH] + [HHE] + [EHE]. [b] Due to the total absence of adjacent hexene units ([HH] = 0), r_H and hence the product r_Er_H could not be calculated.

1-hexene incorporation was obtained. The ethylene/1-hexene copolymer is low molecular weight (LVN = 0.49−0.60 dL/g for **1**/TIOAO), which is practically independent of the level of 1-hexene incorporation. GPC analysis confirms that the copolymer is of low molecular weight (M_w = 18−33 000) and shows a narrow molecular weight distribution, with M_w/M_n = 2.2−2.6. Notably both **12r**/TIOAO and **12m**/TIOAO afford copolymers with significantly higher 1-hexene incorporation than **1**/TIOAO, reaching 31.2 wt % (entry 9, Table 5). The copolymerization activity of this class of metallocenes is higher than *rac*-EBIZrCl$_2$ for both ethylene polymerization and ethylene/1-hexene copolymerization. The reactivity toward α-olefins is, however, less, as reflected by their respective reactivity ratios (Tables 4−6). *rac*-EBIZrCl$_2$ (entry 10, Table 5) affords copolymers with ca. 3−7 times higher comonomer content.

The diad and triad distributions in ethylene/1-hexene copolymerization were determined for entries 4−10 of Table 5. These are shown in Table 6.

The reactivity ratios r_E and r_H for ethylene/1-hexene copolymerization were determined from the peak intensities in the copolymer ^{13}C NMR spectrum and calculated using the equations[45] $r_E = 2[EE]/[EH]X$ and $r_H = 2[HH]X/[EH]$, where [EE], [HE], [HH] are the intensities of the diad sequences and X is the concentration ratio of ethylene to hexene in the reactor. This yields r_E = 182 (entry 4) and 235 (entry 5). These high r_E values evidence the high reactivity of **1** toward ethylene compared to 1-hexene and the difficulties in inserting high amounts of comonomer. Lower r_E values, but of the same order of magnitude, are obtained with 1-methyl-substituted **12r** and **12m**. The presence of a substituent in the 1-position of the indenyl ligand, particularly in **12m**, presumably for steric reasons, facilitates approach of the α-olefin to the active site compared to **1**. These reactivity ratios suggest that the 2,2′-bridged metallocenes are less open than *rac*-EBIZrCl$_2$ (r_E = 18; r_H = 0.018) (entry 10, Table 6), which incorporates more 1-hexene. With both the 2,2′-bridged metallocenes and *rac*-EBIZrCl$_2$, the comonomer distribution, evaluated on the basis of r_Er_H is in the range 0.2−0.5, indicating a tendency to an alternate distribution.

Summary

A robust and convenient synthetic route to ethylene-bridged bis(2-indenyl) zirconocenes has been developed. This proceeded via successive Dieckmann condensations to afford 2,5-dibenzyl-substituted adipates **3** and **18** as the key intermediates. Incorporation of 1-alkyl and/or 4-phenyl substituents provided *rac* and *meso* metallocene isomers.

After activation with excess MAO, TIBAO, or TIOAO, they were highly active for the polymerization of ethylene to low molecular weight linear PE (activities up to 4320 kg PE/(g Zr·h)) and for the copolymerization of ethylene with either propylene (activities of 1.3−12.5 tons copolymer/(g Zr·h)) or 1-hexene (activities up to 1100 kg/(g Zr·h)). The preference for ethylene incorporation was reflected in the high ethylene ($r_E \gg 1$) and the very low propylene (r_P) or 1-hexene (r_H) reactivity ratios with r_P = 0.002−0.008 and r_H = 0.004. In contrast, they displayed poor activity (10−20 kg PP/(g Zr·h)) for the polymerization of propylene. The low activity was (partially) attributed to the uncommonly high percentage 2,1-insertions from **1** (9.4%) and from **19** (9.9%) and to consumption of the in-situ-generated hydrogen from allylic activation. Analogous to adding ethylene, performing the polymerization of propylene under H$_2$ led to a >100-fold increase in activity and afforded saturated propylene oligomers with activities up to 6240 kg/(g Zr·h).

Experimental Section

General Procedures. 1,1′-Biphenyl(2-indenyl)$_2$ZrCl$_2$[11] (**31**) and S(2-indenyl)$_2$ZrCl$_2$[22] (**32**) were prepared according to the literature, and CH$_2$(2-indenyl)$_2$ZrCl$_2$[22] (**33**) was prepared by

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(45) Cheng, H. C. *Polym. Bull.* **1991**, *26*, 325.

modification[46] of the reported synthesis. Tris(2,4,4-trimethylpentyl)aluminum (TIOA) and tris(2-methylpropyl)aluminum (TIBA) were purchased from WITCO and used as a 1 M solution in heptane. Diethyl adipate and 2-phenylbenzyl bromide were purchased from Aldrich and used as received. Claisen alkali solution was prepared by slowly adding 1050 g (18.75 mol) of KOH pellets to 750 mL of water in a 3 L Erlenmeyer flask with stirring. **Caution**: Solution becomes hot. After allowing the aqueous KOH solution to cool, it was diluted with MeOH to a total volume of 3 L. Elemental analyses were performed at Analytische Laboratorien, Lindlar, Germany. Given the close congruence of these zirconocenes with related titanocenes,[12] only a limited number of elemental analysis were performed. ^{1}H NMR spectra of the zirconocenes are given in the Supporting Information.

NMR. The ligands and metallocenes were characterized using a Varian Gemini 300 (^{1}H NMR at 300 MHz, ^{13}C at 75.4 MHz) unless otherwise stated. The solvents are as indicated, and the measurements were performed at 25 °C. Polypropylene and the EP copolymers were characterized by ^{13}C NMR at 125.4 MHz on a Bruker 500. The samples were dissolved in 1,2,4-trichlorobenzene with some 1,4-$C_6D_4Cl_2$ added as lock in 5 mm NMR tubes. The measurements were at 130 °C with a 70° pulse and a relaxation delay of 15 s. ^{1}H NMR spectra were determined at 120 °C in 1,2,4-trichlorobenzene/1,4-$C_6D_4Cl_2$ on the Bruker 500 (512 scans, 5 s delay) and the chemical shifts of the end groups referenced to the lowest field signal of 1,2,4-trichlorobenzene at δ 7.32 ppm. The 1-hexene units in the ethylene/1-hexene copolymers were determined at 120 °C on a Bruker AC-200 spectrometer operating at 50 MHz. The powder polymer samples were dissolved in $C_2D_2Cl_4$ to give an 8% w/v solution. Peak assignments and composition calculations were according to Cheng.[45] The triad and diad distributions as well as the kinetic parameters r_E and $r_{P\text{ or }H}$ were calculated from ^{13}C NMR analysis.[47] Ethylene/propylene copolymer limiting viscosity numbers (LVNs) were measured at 135 °C in decalin, which was inhibited with 2,6-di-*tert*-butyl-4-methylphenol (1 g/L). Polyethylene and ethylene/1-hexene copolymers were measured at 135 °C in tetrahydronaphthalene in the presence of 0.5 wt % 2,6-di-*tert*-butyl-4-methylphenol. The polymer viscosity-averaged molecular weights (M_v) can be obtained from the experimentally determined LVN using the correlations reported.[48]

Polymerization Methodology. Ethylene polymerizations were performed in a 200 mL glass autoclave equipped with magnetic stirrer, temperature indicator, and ethylene-feed line. The autoclave was flushed with ethylene, and 90 mL of hexane was then added at 20 °C. The catalyst premix was prepared by adding to 10 mL of hexane in the following order: the cocatalyst, then in the case of TIOA or TIBA 0.48 equiv of H_2O, and finally after 5 min stirring the appropriate metallocene dissolved in the minimum amount of toluene. After another 5 min stirring, this premix was introduced into the autoclave. The temperature was increased to 80 °C and kept constant throughout the polymerization. The autoclave was pressurized to 4.6 bar and the total pressure kept constant by supplying ethylene on demand. After the time indicated the polymerization was interrupted by removing from the heating bath, immediately venting the reactor, and adding 1 mL of MeOH. The thus obtained polymer was washed with acidic methanol, then with methanol, and dried at 60 °C under vacuum. Propylene (gas, 9 bar) was purified by passing it over a BTS column containing a copper catalyst (BASF R3-11), as well as a column containing a mixed bed of molecular sieves (3 Å (bottom), 4 Å (mid part), and 13X (top)) to remove oxygen and water, respectively (O_2 level ~0.3 ppm, H_2O level 0.5 ppm). Each column is ca. 3 m × 15 cm. Nitrogen and propylene feedstreams were continuously monitored at ppm level. AMS and Systech analyzers were used to determine the oxygen content. MCM analyzers were used to determine the water content. RGA3 (reduction gas analyzer; Trace Analytical) was used to determine the CO content (ppb range). The propane/propylene ratio in the gas cap was determined at 1 min intervals using an Interscience GC. Hydrogen was measured by an Orbisphere hydrogen analyzer at 15 s intervals during the polymerizations.

Propylene polymerizations were performed in a 5 L jacket-cooled steel autoclave equipped with mechanical stirrer and loaded with 1.6 kg of liquid propylene. In the premix (in toluene), 500 molar equiv of MAO was used and the premix stirred in a drybox at 20 °C for a known time, between 1.5 h and overnight. The scavenger MAO was injected into the autoclave containing the liquid propylene, and subsequently (5 min later) the premix added. The reactor was held at 30 °C for 1 min and then the temperature raised with a temperature gradient of 4 °C/min to 50 °C (pressure 19.5 bar). Polymerization was continued for a further 60 min at 50 °C and then stopped by rapidly venting the excess propylene to the incinerator.

Ethylene/propylene copolymerizations were performed in a 25 L reactor loaded with 7.5 kg of liquid propylene and with an ethylene/propylene feed ratio in the range 5.5−6.1 mol % ethylene (liquid phase) depending on the copolymerization. The feed ratio was kept constant throughout the polymerization by adding ethylene on demand. The total amount of MAO was kept constant at 20 mmol (11.0 g of a 4.84 wt % Al solution in toluene). The premix was with a Zr:MAO ratio of 1:500. The scavenger MAO was injected into the autoclave and 5 min later the premix added at 50 °C. The copolymerizations were essentially isothermal, with typical initial reactor exotherms of 1−5 °C being observed. The copolymerization was continued at 50 °C for the time stated and then killed by the injection of 2.5 mL of MeOH. The excess ethylene and propylene were vented to the incinerator, and the copolymer was isolated. Monomer distributions were calculated as described.[49]

Ethylene/1-hexene copolymerizations were performed at 70 °C similar to that described for ethylene polymerization except that heptane was used as solvent. The total volume was 100 mL, and the amount of 1-hexene, in the feed, is given in Table 5.

Preparation of 3 from Diethyl Adipate. NaOEt (487 g, 6.87 mol) was suspended in 3.54 kg of THF in a 10 L cylindrical double-walled glass reactor equipped with overhead stirrer and oil heating/cooling bath. This suspension was heated to 60 °C, whereupon 1170 g (5.73 mol) of diethyl adipate was added during 1 h. The reaction mixture was stirred for 16 h at 60 °C, and 820 g (6.41 mol, 1.12 equiv) of benzyl chloride was added during 3.75 h. This was stirred for another 3.5 h at 60 °C and then allowed to cool. At 23 °C, 487 g (6.87 mol) of NaOEt was added during 2 h and the reaction then slowly warmed to 60 °C and stirred for 16 h. Then 879 g (6.87 mol) of benzyl chloride was added during 1.75 h. The reaction mixture was stirred at 65 °C for 6 h and then cooled to 30 °C, whereupon an extra 100 g of NaOEt was added to effect complete conversion of dibenzyl-substituted cyclopentanone **6** to **3**. After 5 h at 60 °C, 207 g (1.62 mol) of benzyl chloride was added during 1.75 h to convert unreacted NaOEt to $PhCH_2OEt$. After 2 h at 60 °C, 224 g of EtOH was added. The reaction mixture was allowed to cool to 25 °C and 2.8 L of dilute HCl (pH = 2) added to neutralize the bases. Toluene (1.5 L) was added, and the organic and aqueous layers were separated by draining out of the base of the reactor. The solvents were removed on a rotary evaporator and excess benzyl chloride and benzyl ethyl ether removed on a Schlenk

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[46] See Supporting Information for the synthesis of **33**.

[47] Uozumi, T.; Soga, K. *Macromol. Chem.* **1992**, *193*, 823.

[48] For PE, $[\eta] = 3.8 \times 10^{-4} M_v^{0.725}$; for a-PP, $[\eta] = 1.85 \times 10^{-4} M_v^{0.74}$; for i-PP, $[\eta] = 1.93 \times 10^{-4} M_v^{0.74}$. Moraglio, G.; Gianotti, G.; Bonicello, U. *Eur. Polym. J.* **1973**, *9*, 623. Pearson, D. S.; Fetters, L. J.; Younghouse, L. B.; Mays, J. W. *Macromolecules* **1988**, *21*, 478.

[49] Doi, Y.; Ohnishi, R.; Soga, K.*Makromol. Chem. Rapid Commun.* **1983**, *4*, 169.

line at 100 °C. This gave 2035 g (92% yield based on diethyladipate) of ca. 95% pure **3** as a viscous oil that solidifies on prolonged standing. The impurities are ca. 3% **4** and cyclopentanone **5**.

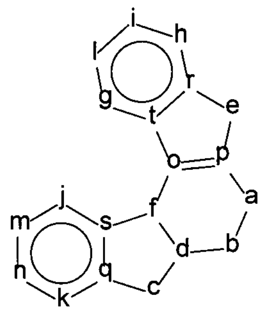
De-esterification of 3 to Diacid 7. Compound **3** was divided into three batches: 680 g (1.78 mol) of **3** was added to a 3 L three-necked round-bottom flask equipped with an overhead stirrer; 3 equiv (5.34 mol, 850 mL) of Claisen alkali solution was added and the mixture heated to 90 °C. After 3 h GC shows that complete conversion had occurred. The mixture was cooled and the MeOH removed under vacuum. The aqueous solution was then washed with 800 mL ether to remove organic impurities (from the synthesis of **3**). The viscous aqueous dicarboxylate solution was poured into a 5 L beaker, diluted with an additional 1 L of water, and cooled to 10 °C. Concentrated HCl was slowly added until pH 1−2 was reached. Diacid **7** precipitated and was isolated by filtration and washed with 300 mL of water. Drying in a vacuum oven at 70 °C to constant weight gave 546 g, 94% of diacid **7**. ^{1}H NMR (CD_3OD): δ 7.10 (m, 10H), 2.90 (m, 2H), 2.70 (m, 4H), 1.60 (m, 4H) ppm.

Preparation of Acid Chloride 8. To 546 g (1.674 mol) of diacid **7** in a 2 L pear-shaped flask was added 13.75 mol (1004 mL) of $SOCl_2$. The resulting suspension was stirred for 16 h at 20 °C. Gas evolution was rapid, but controlled. After heating to 60 °C for 4 h, a homogeneous solution was obtained. ^{1}H NMR spectroscopy showed complete conversion. The $SOCl_2$ was removed under vacuum to afford a viscous oil. This was dissolved in 300 mL of toluene and then the toluene removed under vacuum at 50 °C, to ensure complete removal of residual $SOCl_2$. This afforded **8** as a viscous light brown oil. ^{1}H NMR ($CDCl_3$): δ 7.4−7.2 (m, 10H), 3.14 (m, 4H), 2.87 (m, 2H), 1.80 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 176.1 (C=O), 137.1 (C), 129.1 (CH), 128.9 (CH) 127.3 (CH), 58.5 (CH), 58.4 (CH), 37.7 (CH_2), 37.5 (CH_2), 28.3 (CH_2), 28.23 (CH_2) ppm. Two (diastereo)isomers were observed.

Preparation of Bis(indanone) 9. To 537 g (4.02 mol, 30% excess) of $AlCl_3$ suspended in 700 mL of CH_2Cl_2 in a 3 L three-necked flask equipped with a large dropping funnel and kept under nitrogen was slowly (during 3 h) added 571 g of **8** (prepared from 508 g of **7**) dissolved in 1050 mL of CH_2Cl_2. There was no significant temperature rise. **Caution**: Copious HCl evolution. After stirring for 16 h at 20 °C an orange suspension was obtained. This was carefully poured onto crushed ice. The yellow CH_2Cl_2 layer was separated and the water layer extracted with 4 × 250 mL of CH_2Cl_2. Upon drying with anhydrous $MgSO_4$ a clear red-orange solution was obtained. This was filtered and the solvent removed in a vacuum to afford a slightly sticky white solid. This was washed with 500 mL of pentane to give 420 g, 93% of **9** as a white powder. ^{1}H NMR ($CDCl_3$): δ 7.7−7.3 (m, 8H), 3.3 (dd, J = 17.4, 8.1, 2H), 2.85 (m, 2H), 2.63 (m, 2H), 2.1 (m, 2H), 1.60 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 208.6 (C=O), 153.8, 136.7, 134.8, 127.4 (CH), 126.6 (CH), 123.9, 47.5 (CH), 32.7 (CH_2), 29.3 (CH_2) ppm. Two (diastereo)isomers in ca. 1:1 ratio were observed by GC and ^{13}C NMR spectroscopy.

Preparation of Diol 10. 9 (414 g, 1.427 mol) was suspended in 2.5 L of THF and 1 L of MeOH in a 5 L beaker. This was cooled in an ice bath to 10 °C. $NaBH_4$ (60 g, 1.58 mol) was added slowly during 3 h to this stirred suspension, resulting in immediate gas evolution. This was stirred for 16 h at 20 °C, and then THF and MeOH were removed on a rotary evaporator to give a viscous beige slurry. Water (2 L) was added and the solution acidified using dilute HCl to pH 3 to give a beige powder that was isolated by filtration. Drying to constant weight in a vacuum oven at 60 °C gave 413 g of **10**. ^{1}H NMR ($CDCl_3$): δ 7.4−7.05 (m, 8H), [5.13 (m), 5.05 (m), 4.87 (m), total 2H], 3.1 (m, 1H), 2.9 (m, 1H), 2.75 (m, 1H), 2.5 (m, 1H), 2.4−1.4 (m, total 8H) ppm.

Preparation of CH_2CH_2(2-indene)$_2$ (2). Quantities (64, 110, 234, 308, 300 g) of **10** were placed (separately) in a 1 L three-necked round-bottom flask in a heating mantel. These were heated to 250−265 °C with a N_2 purge to flush away the evolved water. The diol melts at 180−200 °C. Each thermolysis was monitored regularly by GC. The thermolysis was stopped when conversion of **10** was complete. This was typically after 2−3 h and gave a melted “glass”. The best conversions were, as determined by GC, a **2**:**11** ratio of 3:1, in which **2** was 60% of the total products. After thermolysis, the five fractions were combined by adding ca. 500 mL of CH_2Cl_2 to each 1 L flask with stirring and scratching to solubilize the melted glass. The CH_2Cl_2-insolubles were isolated by filtration and were, surprisingly, **2** by GC analysis. These were washed with a little pentane to give 114 g of 98.95% pure (by GC) **2** as a white powder. The CH_2Cl_2 was removed under vacuum from the CH_2Cl_2-soluble fraction to give a slightly oily orange powder. This was washed with pentane to give 252 g of **2** as a 96.0% pure, light beige, powder. Total = 366 g, 42% yield. **2**: ^{1}H NMR ($CDCl_3$): δ 7.5−7.1 (m, 8H), 6.63 (s, 2H), 3.39 (s, 4H, CH_2), 2.86 (s, 4H, CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ 150.1, 145.9, 143.4, 127.1, 126.7, 124.2, 123.8, 120.5, 41.5 (CH_2), 31.0 (CH_2) ppm. **11**: ^{1}H NMR (C_6D_6, 400 MHz): δ 7.50 (t, 7.43 Hz, 2H), 7.27 (t, 2H), 7.12 (t, 2H), 7.03 (t, 7.43 Hz, 1H), 6.93 (t, 7.43 Hz, 1H), 3.97 (d, 5.4 Hz, 1H, **f**), 2.99 (dd, 6.60, 8.76 Hz, 1H, **c**), 2.87 (s, 2H, **e**), 2.40 (d, 15.37 Hz, 1H, **c′**), 2.26 (m, 1H, **d**), 1.98 (m, 2H, **a**), 1.35 (m, 2H, **b**) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8 (C_a), 25.5 (C_b), 38.0 (C_c), 38.3 (C_d), 40.1 (C_e), 42.9 (C_f), 118.3 (C_g), 123.1 (C_h), 123.4 (C_i), 124.6 (C_j), 124.7 (C_k), 125.7 (C_l), 125.8 (C_m), 125.8 (C_n), 136.3 (C_o), 141.9 (C_p), 142.1 (C_q), 142.6 (C_r), 145.0 (C_s), 146.3 (C_t) ppm. Assignments were from ^{13}C−^{1}H HETCOR and ^{13}C−^{13}C INADEQUATE 2D NMR spectra.



Preparation of CH_2CH_2(2-indenyl)$_2$ZrCl$_2$ (1). To 146 g, 0.566 mol of **2** in a 2 L three-necked round-bottom flask under N_2 was added 1 L of ether, and the mixture was cooled to −5 °C. Then 475 mL of a 2.5 M n-BuLi solution in hexane (2.1 equiv) was added over 2.5 h. A beige slurry of dianion was obtained. The internal solution temperature rose to and was maintained at 2−4 °C, by adjusting the rate of addition. **Caution**: ca. 1.2 mol (ca. 25 L) butane (bp −0.5 °C) is liberated. After the addition was complete, the reaction was stirred for a further 30 min. ^{1}H NMR spectroscopy (THF-d_8) showed clean conversion to Li_2[CH_2CH_2(2-indenyl)$_2$]. The solution was reduced to ca. 1 L and cooled to −78 °C. A suspension of 132 g (0.566 mol) of $ZrCl_4$ in 500 mL of CH_2Cl_2 in a 2 L three-neck round-bottom flask, also cooled to −78 °C, was added to the solution of the cooled dianion. This rapidly gave a bright yellow suspension with considerable heat evolution. The reaction mixture was allowed to warm slowly to 20 °C and stirred for a further 16 h at 20 °C. All solvents were then removed under vacuum to give a light yellow powder. Pure **1** was separated from LiCl, and possible polymeric products were separated by Soxhlet extraction with CH_2Cl_2. This gave 197 g, 83% yield of **1**. In a separate reaction, a further 210 g of **2** was converted into 239 g of **1** (70% yield). A total of 436 g of **1** was prepared from 356 g of **2**. Li_2[CH_2CH_2(2-indenyl)$_2$]: ^{1}H NMR (THF-d_8): δ 7.00 (dd, J = 5.7, 3, 4H), 6.20 (dd, J = 5.7, 3, 4H), 5.70 (s, 4H), 3.22 (s, 4H) ppm. **1**: ^{1}H

NMR (C_6D_6): δ 7.5 (dd, 4H), 6.95 (dd, 4H), 5.85 (s, 4H), 2.52 (s, 4H) ppm. ^{1}H NMR (CD_2Cl_2): δ 7.5 (dd, *J* = 9.7, 4.8, 4H), 7.17 (dd, *J* = 9.7, 4.8, 4H), 6.41 (s, 4H), 3.31 (s, 4H) ppm. ^{13}C NMR (CD_2Cl_2): δ 140.6 (2C), 129.4 (4C), 126.1 (4CH), 125.5 (4CH), 103.1 (4CH), 31.1 (2 CH_2) ppm. Anal. Calcd for $C_{20}H_{16}ZrCl_2$: C, 57.40; H, 3.85. Found: C, 57.29; H, 4.00.

Preparation of CH_2CH_2(1-Me-2-indene)$_2$ (13). To a suspension of 10 g (38.7 mmol) of **2** in 100 mL of THF was added 32 mL of n-BuLi (2.5 M in hexane) in 15 min at 0 °C. After stirring for 30 min at 20 °C the red-brown solution was cooled to 0 °C, and a solution of 6.0 mL of MeI in 50 mL of THF (also cooled to 0 °C) was added. The reaction mixture was stirred for 2 h at 20 °C and then the solvent was removed in vacuo. The sticky yellow-orange solid was dissolved in 200 mL of ether and extracted three times with saturated $NaHCO_3$ and saturated NaCl. The ether was removed in vacuo to afford **13** as a mixture of two double bond isomers in a ca. 10:1 ratio. Yield: 9.7 g, 88%. NMR data for major double bond isomer. ^{1}H NMR ($CDCl_3$): δ 7.45−7.10 (m, 8H), 6.53 (s, 2H), 3.43−3.30 (m, 2H, C*H*Me), 2.90−2.60 (m, 4H, CH_2-bridge), 1.36 (d, 7.5 Hz, 6H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ 154.7 (C), 148.8 (C), 144.0 (C), 126.5 (CH), 124.8 (CH), 123.9 (CH), 122.5 (CH), 120.0 (═CH), 46.2 and 46.0 (*C*HMe), 28.1 (CH_2-bridge), 15.8 (Me) ppm.

Synthesis of *rac*- and *meso*-CH_2CH_2(1-Me-2-indenyl)$_2$-$ZrCl_2$ (12r and 12m). A 2.5 M n-BuLi hexane solution (4.1 mL) was added to 1.4 g of **13** in 50 mL of ether cooled to 0 °C. After 45 min the ether was removed in a vacuum and the dianion suspended in 80 mL of toluene at 20 °C in the drybox. $ZrCl_4$ (1.15 g, 4.93 mmol) as a slurry in 10 mL of toluene was added, whereupon the reaction mixture changed from yellow to dark brown. After stirring for 21 h at 20 °C, the toluene solution was separated by centrifugation and the remaining solid extracted with 3 × 25 mL of toluene. The toluene extracts were combined, concentrated, and crystallized at −35 °C to afford 300 mg of the *rac* isomer (**12r**). The toluene-insoluble precipitate from the reaction mixture was extracted with CH_2Cl_2, and the CH_2Cl_2 removed in a vacuum to give a yellow powder. This was washed with 2 × 5 mL of pentane to afford 230 mg of pure *meso* isomer (**12m**). **12r**: ^{1}H NMR (CD_2Cl_2): δ 7.54−7.34 (m, 4H), 7.21−7.10 (m, 4H), 6.16 (s, 2H, ═CH), 3.63−3.45 (m, 2H, CH_2 bridge), 3.20−3.03 (m, 2H, CH_2 bridge), 2.48 (s, 6H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ 137.7 (C), 129.8 (C), 128.9 (C), 126.2 (CH), 125.6 (CH), 125.3 (CH), 123.5 (CH), 116.3 (*C*-Me), 97.9 (CH), 27.5 (*C*H_2-bridge), 11.8 (Me) ppm. Anal. Calcd for $C_{22}H_{20}ZrCl_2$: C, 59.18; H, 4.51. Found: C, 58.94; H, 4.57. **12m**: ^{1}H NMR (CD_2Cl_2): δ 7.50 (m, 2H), 7.38 (m, 2H), 7.24−7.06 (m, 4H), 6.71 (s, 2H, ═CH), 3.55−3.25 (m, 4H, CH_2 bridge), 2.44 (s, 6H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ 137.1 (C), 130.3 (C), 128.1 (C), 126.3 (CH), 125.8 (CH), 125.3 (CH), 123.6 (CH), 116.6 (*C*-Me), 101.0 (CH), 28.9 (*C*H_2-bridge), 11.79 (Me) ppm.

Preparation of CH_2CH_2(1-Et-2-indene)$_2$. **2** (1.36 g, 5.26 mmol) was dissolved in 25 mL of THF and cooled to −10 °C. n-BuLi (5.5 mL) was added and the orange-brown solution stirred for 2 h at 20 °C. This was added via a cannula to a solution of EtI (1.1 mL, 7.1 mmol) dissolved in 10 mL of THF at −10 °C. After 2 h the THF was removed under vacuum, and ether added. This ether solution was washed three times with saturated $NaHCO_3$ and with saturated NaCl. After drying over $MgSO_4$, 1.46 g of CH_2CH_2(1-Et-2-indene)$_2$ was obtained as a yellow oil. ^{1}H NMR and GC spectroscopy showed the three possible double bond isomers.

Synthesis of *rac*- and *meso*-CH_2CH_2(1-Et-2-indenyl)$_2$-$ZrCl_2$ (14r and 14m). n-BuLi (4.5 mL, 7.2 mmol) was added to 1.16 g (3.5 mmol) of CH_2CH_2(1-Et-2-indene)$_2$ suspended in 50 mL of ether at −10 °C. After 45 min the ether was removed under vacuum and the dianion suspended in 80 mL of toluene at 20 °C. $ZrCl_4$ (1.16 g, 4.93 mmol) as a slurry in 10 mL of toluene was added, whereupon the reaction mixture changed from yellow to dark brown. After stirring for 21 h at 20 °C, the toluene solution was separated by centrifugation and the remaining solid extracted with 3 × 25 mL of toluene. The toluene extracts were combined, concentrated, and crystallized at −35 °C to afford 72 mg of **14r**. The toluene-insoluble precipitate from the reaction mixture was extracted with CH_2Cl_2, and the CH_2Cl_2 removed in a vacuum to give a yellow powder. This was washed with 2 × 5 mL of pentane to afford 300 mg of **14m**.

$Li_2[CH_2CH_2$(1-Et-2-indenyl)$_2]$: ^{1}H NMR (THF-*d*$_8$): δ 7.09 (dd, *J* = 4.8, 4.2, 2H), 6.99 (dd, *J* = 4.8, 4.2, 2H), 6.23 (m, 4H), 5.65 (s, 2H), 3.28 (s, 4H, CH_2), 2.96 (q, *J* = 7.5, 4H, C*H*$_2$Me), 1.29 (t, 7.5, 6H, CH_2*Me*) ppm. **14r**: ^{1}H NMR (C_6D_6): δ 7.43 (d, *J* = 9, 4H), 6.97 (t, *J* = 6.6, 2H), 6.86 (t, *J* = 6.6, 2H), 5.65 (s, 2H, ═CH), 3.01 (dq, *J* = 14.7, 7.5, 2H), 2.77 (d, *J* = 9, 2H), 2.45 (dq, *J* = 14.7, 7.5, 2H), 2.35 (d, *J* = 8.4, 2H), 0.95 (t, *J* = 7.5, 6H) ppm. ^{13}C NMR (THF-*d*$_8$): δ 137.3 (C), 130.84 (C), 128.75 (C), 127.0 (CH), 126.0 (CH), 125.5 (CH), 124.0 (CH), 122.75 (*C*-Me), 98.5 (CH), 27.4 (CH_2), 20.7 (CH_2), 16.1 (Me) ppm. **14m**: ^{1}H NMR (CD_2Cl_2): δ 7.51 (m, 2H), 7.37 (m, 2H), 7.20−7.07 (m, 4H), 6.73 (s, 2H, ═CH), 3.50−3.28 (m, 4H, CH_2 bridge), 3.05 (dq, *J* = 14.7, 7.5, 2H), 2.80 (dq, *J* = 14.7, 7.5, 2H) 1.14 (t, *J* = 7.5, 6H) ppm. ^{13}C NMR (CD_2Cl_2): δ 135.0 (C), 129.9 (C), 125.6 (C), 125.0 (CH), 124.3 (CH), 123.0 (CH), 122.9 (CH), 122.1 (*C*-Me), 100.8 (CH), 28.1 (*C*H_2-bridge), 20.0 (CH_2), 14.8 (Me) ppm.

Synthesis *rac*- and *meso*-CH_2CH_2(1-Me-2-indenyl)$_2ZrMe_2$ (15r and 15m). Zirconocenes **12r** and **12m** (ca. 20 mg) were suspended in C_6D_6 in different NMR tubes. MeLi, as a white powder, made by removing the ether from a MeLi solution, was added to each NMR tube in the drybox. Occasional shaking of the NMR tube gave within 2 h clean conversion to **15r** and **15m**, respectively. **15r**: ^{1}H NMR (C_6D_6): δ 7.37 (m, 4H), 6.95 (m, 4H), 5.50 (s, 2H, ═CH), 2.63−2.3 (m, 4H, CH_2 bridge), 2.09 (s, 6H, Me), −1.02 (s, 6H, Zr-*Me*) ppm. ^{13}C NMR (C_6D_6): δ 129.6 (C), 125.2 (CH), 124.8 (C), 123.4 (CH), 122.6 (CH), 110.0 (5 ring *C*-Me), 97.6 (5-ring *C*H), 40.1 (Zr-*Me*), 26.8 (*C*H_2-bridge), 10.8 (Me) ppm. **15m**: ^{1}H NMR (C_6D_6): δ 7.42 (d, 2H), 7.30 (d, 2H), 7.04 (t, 2H), 6.9 (t, 2H), 5.93 (s, 2H, ═CH), 2.6−2.3 (m, 4H, CH_2 bridge), 2.03 (s, 6H, Me), −0.38 (s, 3H, Zr-*Me*), −1.82 (s, 3H, Zr-*Me*) ppm. ^{13}C NMR (C_6D_6): δ 129.2, 127.4, 125.6, 125.0, 123.7, 123.2, 121.9, 108.6 (5 ring *C*-Me), 97.8 (5 ring *C*H), 44.1 (Zr-*Me*), 37.0 (Zr-*Me*), 27.5 (*C*H_2-bridge), 11.6 (Me) ppm.

Synthesis of CH_2CH_2(2-indenyl)$_2ZrMe_2$ (16). Zirconocene **1** was suspended in toluene and cooled to −78 °C. Two equivalents of solid MeLi was added and the reaction mixture allowed to warm to room temperature. Filtration and removing the toluene in vacuo gave **16**. ^{1}H NMR (C_6D_6): δ 7.33 (m, 4H), 6.8 (m, 4H), 5.73 (s, 4H, ═CH), 2.29 (m, 4H, CH_2 bridge), −1.02 (s, 6H, Zr-*Me*) ppm.

Synthesis of 2,5-Di(2-phenylbenzyl)hexane Diacid (18). A solution of 43.8 mL (0.22 mol) of diethyladipate in 220 mL of THF was added to a three-neck flask equipped with water cooler. NaOEt (16.3 g, 0.24 mol) was added in small portions at 20 °C. The reaction mixture was stirred at 60 °C for 16 h. After cooling to 20 °C, 48.6 g (0.20 mol) of 2-(bromomethyl)-biphenyl was added dropwise. This was stirred at 60 °C for 16 h to give 92% (by GC) of 2-(2-phenylbenzyl)diethyladipate (**17**) as a viscous oil. NaOEt (14.9 g, 0.22 mol) and 2-(bromomethyl)biphenyl (44.4 g, 0.18 mol) were then added successively. Workup involved adding dilute HCl to neutralize the base, and the THF was separated from the aqueous layer. The aqueous layer was extracted three times with CH_2Cl_2. The combined THF and CH_2Cl_2 extracts were evaporated to dryness to give 2,5-di(2-phenylbenzyl)diethyladipate (**18**) as a very viscous oil. KOH (180 mL of 6.25 M) in H_2O/MeOH was added and the reaction mixture refluxed for 16 h. The methanol was removed on the rotary evaporator and the aqueous layer washed with 2 × 200 mL of ether. The alkaline aqueous layer was acidified at 0 °C with 37% HCl to pH 1. A white/yellow powder precipitated, which was filtered off and washed with water and a little hexane. It was thoroughly dried to afford 77.0 g, 73% yield.

2-(2-Phenylbenzyl)diethyladipate (17). ^{1}H NMR (CDCl$_3$): δ 7.48−7.16 (m, 18H), 4.08 (q, 2H, CH$_2$), 3.97 (q, 2H, CH$_2$), 2.85 (d, 2H, CH$_2$), 2.37 (m, 1H, CH), 2.11 (t, 2H, CH$_2$), 1.45−1.28 (q, 2H, CH$_2$ and m, 2H, CH$_2$), 1.21 (t, 3H, Me), 1.08 (t, 3H, Me) ppm. ^{13}C NMR (CDCl$_3$): δ 175.2 (*C*O$_2$Et), 173.1 (*C*O$_2$Et), 142.2 (C), 141.6 (C), 136.6 (C), 130.1 (CH), 129.7 (CH), 129.1 (CH), 128.1 (CH), 127.2 (CH), 126.9 (CH), 126.3 (CH), 60.14 (*C*H$_2$Me), 60.0 (*C*H$_2$Me), 46.0 (CH$_2$), 35.6 (CH$_2$), 33.8 (CH$_2$), 31.4 (CH$_2$), 22.4 (CH$_2$), 14.2 (CH$_2$*Me*), 14.05 (CH$_2$*Me*) ppm.

2,5-Di(2-phenylbenzyl)hexane Diacid. ^{1}H NMR (THF-d_8): δ 10.45 (s, 2H, O*H*), 7.39−7.05 (m, 18H), 2.76 (m, 2H, CH$_2$), 2.60 (m, 2H, CH$_2$), 2.22 (m, 2H, CH), 1.30−1.00 (m, 4H, CH$_2$) ppm. ^{13}C NMR (THF-d_8): δ 176.5 (*C*O$_2$H), 143.7 (C), 143.2 (C), 138.5 (C), 131.0 (CH), 130.8 (CH), 130.4 (2 × CH), 129.1 (2 × CH), 128.2 (CH), 127.9 (CH), 127.0 (CH), 47.2 and 47.0 (CH), 36.3 and 36.2 (CH$_2$), 30.8 (CH$_2$) ppm. Two isomers were observed.

2,5-Di(2-phenylbenzyl)hexanoyl Dichloride. To 77.0 g (0.16 mol) of 2,5-di(2-phenylbenzyl)hexane diacid in a 1 L flask equipped with a reflux condenser was added 150 mL (2.06 mol) of SOCl$_2$. The white suspension was warmed to 50 °C and became a yellow solution with concomitant evolution of HCl and SO$_2$. After gas evolution had finished, excess thionyl chloride was removed under vacuum. Toluene (100 mL) was then added, and this was removed under vacuum to ensure complete removal of SOCl$_2$. The acid chloride was isolated as a viscous beige oil. Yield: 82.9 g, 100%. ^{1}H NMR (CDCl$_3$): δ 7.55−7.20 (m, 18H), 3.07 (m, 2H, CH$_2$), 2.85 (dd, 2H, CH$_2$, J = 15 Hz), 2.64 (m, 2H, CH), 1.36 (m, 2H, CH$_2$), 1.17 (m, 2H, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ 175.9 (*C*OCl), 142.3 (C), 141.1 (C), 134.6 (C), 130.5 (CH), 129.9 (CH), 129.1 (2 x CH), 128.6 (2 x CH), 127.8 (CH), 127.4 (CH), 127.2 (CH), 57.25 and 57.08 (CH), 34.9 (CH$_2$), 28.2 (CH$_2$) ppm. Two isomers were observed.

Synthesis of 1,2-Di(4-phenyl-2-indanoyl)ethane (21). To a suspension of 56.0 g (0.42 mol) of AlCl$_3$ in 40 mL of CH$_2$Cl$_2$ was added 82.9 g (0.16 mol) of 2,5-di(2-phenylbenzyl)hexanoyl dichloride in 250 mL of CH$_2$Cl$_2$ at 20 °C. The reaction mixture was poured onto ice 5 min after addition was complete. The CH$_2$Cl$_2$ layer was separated from the water layer and the water layer extracted with 2 × 200 mL of CH$_2$Cl$_2$. The combined CH$_2$Cl$_2$ layers were washed with saturated NaHCO$_3$. The CH$_2$Cl$_2$ was removed in vacuo and the resulting powder washed with ca. 50 mL of hexane. This afforded 63.3 g, 89% yield of **21**. ^{1}H NMR (CDCl$_3$): δ 7.86−7.10 (m, 16H), 3.36 (dd, 2H), 2.86 (m, 2H, CH), 2.63 (m, 2H, CH$_2$), 2.07 (m, 2H, CH$_2$), 1.55 (m, 2H, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ 208.3 (*C*=O), 151.0 (C), 140.3 (C), 139.0 (C), 137.1 (C), 134.9 (CH), 128.6 (2 x CH), 128.4 (2 × CH), 128.0 (CH), 127.7 (CH), 122.8 (CH), 47.8 and 47.2 (CH), 32.7 and 32.4 (CH$_2$), 29.5 and 28.6 (CH$_2$) ppm. Two isomers were observed.

Synthesis of 1,2-Di(4-phenyl-2-indanol)ethane (22). 21 (20.0 g, 45.2 mmol) in 310 mL of THF was slowly added during 20 min via a cannula to a suspension of 1.85 g (48.7 mmol) of LiAlH$_4$ (1.09 equiv) in 80 mL of THF in a 1 L flask cooled to 0 °C. After the addition was complete, the reaction mixture was stirred for 45 min at 20 °C. THF was removed in vacuo, ice and dilute HCl were added, and the suspension was acidified to pH 1. The suspension was filtered, washed with water, and dried to give 18.3 g of **22** as an off-white powder. Yield: 91%. ^{1}H NMR (CDCl$_3$): δ 7.50−7.10 (16H), 4.85 (m, 2H, C*H*-OH), 3.11 (dd, J = 18, 2H, CH$_2$), 2.55 (m, 2H, CH), 2.22−1.40 (m, 8H, 3 × CH$_2$, 2 × OH) ppm. ^{13}C NMR (THF-d_8): δ 149.0 (C), 142.3 (C), 140.1 (C), 139.2 (C), 129.6 (2 × CH), 129.3 (2 × CH), 128.4 (CH), 127.8 (2 × CH), 123.8 (CH), 81.9 (*C*-OH), 56.9 and 52.6 (CH), 37.0 (CH$_2$), 33.4 and 33.2 (CH$_2$) ppm. Two isomers were observed.

Synthesis of CH$_2$CH$_2$(4-Ph-2-indene)$_2$ (20). 22 (11.0 g, 24.6 mmol) was added to a 1 L three-neck flask. This was heated to 345 °C for 20 min under a slow stream of N$_2$. After cooling, this afforded **20** as a yellow glass, which was isolated as a yellow powder by dissolving in CH$_2$Cl$_2$ and removing the CH$_2$Cl$_2$ in vacuo. Yield: 8.8 g, 87%. The product was isolated as a mixture of two double bond isomers in a ca. 1:1 ratio. Column chromatography on silica was used for additional purification. Double bond isomer **1**: ^{1}H NMR (CDCl$_3$): δ 7.59−7.14 (m, 16H), 6.64 (s, 2H, CH), 3.46 (s, 4H, CH$_2$), 2.82 (s, 4H, CH$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ 149.9 (C), 146.0 (C), 141.2 (C), 140.5 (C), 137.5 (C), 128.4 (2 × CH), 127.0 (2 × CH), 126.7 (CH), 124.5 (CH), 119.2 (CH), 41.1 (CH$_2$), 30.6 (CH$_2$) ppm. The other double bond isomer has an olefinic CH at δ 6.76 ppm.

Synthesis of *rac*/*meso*-CH$_2$CH$_2$(4-Ph-2-indenyl)$_2$ZrCl$_2$ (19r, 19m). To a solution of 465 mg (1.13 mmol) of **20** in 20 mL of ether was added dropwise 0.95 mL of n-BuLi (2.5 M in hexane) at −78 °C. The reaction mixture was allowed to warm to 20 °C. The ether was removed in vacuo to afford the dianion as a light yellow powder. The dianion was suspended in toluene and cooled to −20 °C, and 0.28 g of ZrCl$_4$ was added. After stirring for 16 h at 20 °C, the reaction mixture was centrifuged. The remaining powder was washed once more with toluene (20 mL) and extracted with CH$_2$Cl$_2$ to separate the product from LiCl. This afforded a mixture of *rac* and *meso* isomers as a yellow powder. By crystallization from toluene, **19m** could be completely separated from **19r**. Isolated **19r** was contaminated with 20% **19m**. Li$_2$[**20**]: ^{1}H NMR (THF-d_8): δ 7.74 (d, J = 7.2, 4H), 7.28 (t, J = 7.8, 4H), 7.10 (t, J = 7.2, 2H), 7.05 (d, J = 7.2, 2H), 6.35 (m, 4H), 6.08 (d, J = 2, 2H, CH), 5.85 (d, J = 2, 2H, CH), 3.22 (s, 4H, CH$_2$) ppm. **19r**: ^{1}H NMR (C$_6$D$_6$): δ 7.70−6.90 (m, 16H), 6.37 (d, J = 2.1, 2H, CH), 5.53 (d, J = 2.1, 2H, CH), 2.48 (br s, 4H, CH$_2$-bridge) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.76−7.22 (m, 16H), 6.70 (d, J = 2.1, 2H, CH), 6.35 (d, J = 2.1, 2H, CH), 3.39 (m, 4H, CH$_2$-bridge) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ 140.5, 140.4, 139.6, 130.3, 129.1, 128.5, 127.6, 126.2, 125.9, 124.5, 103.9 (CH), 100.4 (CH), 30.8 (CH$_2$) ppm. **19m**: ^{1}H NMR (C$_6$D$_6$): δ 7.62−6.85 (m, 16H), 6.39 (d, J = 2.1, 2H, CH), 5.95 (d, J = 2.1, 2H, CH), 2.41 (m, 4H, CH$_2$-bridge) ppm. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.64−7.19 (m, 16H), 6.78 (d, J = 2.1, 2H, CH), 6.41 (s, J = 2.1, 2H, CH), 3.37 (s, 4H, CH$_2$-bridge) ppm.

Synthesis of *meso*-CH$_2$CH$_2$(4-Ph-indenyl)$_2$ZrMe$_2$ (23m). Excess MeLi was added to 30 mg of **19m** in C$_6$D$_6$ to cleanly afford **23m** after 1 h at 20 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.48−6.89 (m, 16H), 6.24 (d, J = 2.1, 2H, CH), 5.90 (d, J = 2.1, 2H, CH), 2.28 (m, 4H, CH$_2$), 0.11 (s, 3H, Zr-Me), −1.83 (s, 3H, Zr-Me) ppm.

Preparation of CH$_2$CH$_2$(1-Me-4-Ph-2-indene)$_2$ (24). To a solution of 67.8 mL of MeMgBr (3 M in ether) in 100 mL of ether cooled to 0 °C was added 15 g (33.9 mmol) of **21** in 150 mL of THF in 45 min. A white/beige precipitate formed. The reaction mixture stirred for 2 h at 20 °C and then was poured onto ice, acidified to pH 1, and extracted with ether. The organic layer was washed with saturated NaCl solution and the solvent removed in vacuo. The diol was dissolved in CH$_2$Cl$_2$, *p*-toluene sulfonic acid was added, and the mixture was stirred overnight at 20 °C. The solution was dried over MgSO$_4$ and filtered, and the solvent was removed in vacuo. Yield: 13.1 g, 69%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.6−7.2 (m, 16H), 3.43 (d, 4H, CH$_2$, 5-ring), 2.69 (s, 4H, CH$_2$ bridge), 2.08 (s, 6H, CH$_3$) ppm.

Preparation of CH$_2$CH$_2$(1-Me-4-Ph-2-indenyl)$_2$ZrCl$_2$ (25). To a solution of 0.54 g (1.23 mmol) of **24** in 20 mL of ether was added 1.1 mL of n-BuLi (2.5 M in hexane) at −78 °C. The reaction mixture was allowed to warm to 20 °C and the color changed to orange-red. The reaction mixture was stirred for 2 h at 20 °C, after which the solvent was removed in vacuo. The sticky product was washed with hexane, and the orange dianion was used without further purification. To a suspension of the dianion in 10 mL of toluene cooled to −30 °C was added 0.29 g of ZrCl$_4$. The reaction mixture was stirred for 16 h at 20 °C. The orange suspension was filtered and the filtrate concentrated. ^{1}H NMR spectroscopy showed a 1:1 ratio of *rac*/

meso isomers. Washing with hexane gave a small quantity of **25r**, albeit in a 4:1 *rac*:*meso* ratio. Crystallization from a CH_2Cl_2/hexane mixture gave 94% **25m**. **25r**: ^1H NMR (CD_2Cl_2): δ 7.7−7.1 (m, 16H), 6.44 (s, 2H, CH), 3.59−3.14 (m, 4H, CH_2 bridge), 2.34 (s, 6H, Me) ppm. **25m**: ^1H NMR (CD_2Cl_2): δ 7.7−7.1 (m, 16H), 6.90 (s, 2H, CH), 3.50−3.20 (m, 4H, CH_2 bridge), 2.48 (s, 6H, Me) ppm. *rac* and *meso* assignments were based on comparison with the cyclopentadienyl C*H* shift in **12r** and **12m** and the characteristic CH_2CH_2 bridge pattern for the *rac* and *meso* isomers.

Preparation of CH_2CH_2(1-i-Pr-4-Ph-2-indene)$_2$ (27). In a 250 mL flask containing 40 mL of a 2.0 M (9 equiv) i-PrMgCl in ether solution and cooled to 0 °C was added dropwise during 15−20 min a solution of 4.0 g (9.04 mmol) of **21** in 80 mL of THF. This was stirred for 90 min and then poured onto ice. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were washed with a saturated NaCl solution and then dried over $MgSO_4$ to give the diol. This was dehydrated by adding 1.5 g of *p*-toluene sulfonic acid to a CH_2Cl_2 solution and stirring for 20 h at 20 °C. This was dried with $MgSO_4$ to give a clear yellow solution, which was filtered through a plug of silica to give 290 mg of **27**. The low yield is due to the large excess of *p*-TsOH inadvertently used. ^1H NMR ($CDCl_3$): δ 7.52−7.13 (m, 16H), 3.36 (s, 4H, CH_2), 3.18 (septet, 2H, CH), 2.67 (s, 4H, CH_2-bridge), 1.36 (d, 12H, Me) ppm. ^{13}C NMR ($CDCl_3$): δ 145.5, 142.7 (C), 141.4 (C), 141.0 (C), 140.6 (C), 137.6, 128.5 (2 × CH), 128.3 (2 × CH), 126.9 (CH), 126.5 (CH), 124.2 (CH), 119.5 (CH), 40.4 (CH_2), 26.7 (CH), 21.1 (Me) ppm.

Preparation of CH_2CH_2(1,3-Me$_2$-2-indene)$_2$ (30). To a suspension of 9.7 g (33.9 mmol) of **13** in 100 mL of THF was added 28.5 mL of n-BuLi (2.5 M in hexane) in 10 min at 0 °C. After stirring for 90 min at 20 °C the red-brown solution was cooled to 0 °C and 5.3 mL of MeI in 50 mL of THF (also cooled to 0 °C) was added. The reaction mixture was stirred for 2 h at 20 °C. Subsequently the solvent was removed in vacuo and the sticky yellow-orange solid dissolved in 200 mL of ether and extracted three times with saturated $NaHCO_3$ and saturated NaCl. The ether was removed in vacuo and the yellow sticky solid washed with hexane to extract the *gem*-disubstituted bis(indene). Isolated yield of **30** was 2.3 g, 24%.

Preparation of CH_2CH_2(1,3-Me$_2$-2-indenyl)$_2$ZrCl$_2$ (29). To 1.47 g (4.68 mmol) of **30** in 30 mL of ether at −78 °C was added 3.9 mL of n-BuLi (2.5 M in hexane). After 30 min the reaction mixture was allowed to warm to 20 °C. The orange-brown reaction mixture was filtered and the resulting powder washed with hexane to give Li_2[**30**]. To a suspension of light yellow Li_2[**30**] in 30 mL of toluene and cooled to −30 °C was added a suspension of 0.95 g (4.08 mmol) of $ZrCl_4$ in 10 mL of toluene. The reaction mixture was allowed to warm to 20 °C, whereupon the color changed to orange. The mixture was stirred overnight and filtered, and the precipitate was extracted with 3 × 10 mL of toluene. The solvent was evaporated in vacuo, and the solid was washed with hexane to afford 206 mg, 10.5% of **29** as an orange powder. Li_2[**30**]: ^1H NMR (THF-d_8): δ 7.03 (dd, 4H), 6.25 (dd, 4H), 3.01 (s, 4H, CH_2 bridge), 2.43 (s, 12H, CH_3) ppm. **29**: ^1H NMR (CD_2Cl_2): δ 7.45 (dd, 4H), 7.16 (dd, 4H), 3.50 (s, 4H, CH_2 bridge), 2.59 (s, 12H, CH_3) ppm.

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Supporting Information Available: Experimental details for the two alternative synthetic routes to **1**, modified synthesis of **33**, and ^1H NMR spectra of the zirconocenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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