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Self-Immobilizing Precatalysts: Norbornene-Bridged Zirconium *ansa*-Metallocenes

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Abstract: We report here the synthesis of new tethered biscyclopentadienyl and bisindenyl zirconocenes, bearing one unsaturation on the interannular bridge, and their use as self-immobilizing catalysts. They proved to be active catalysts towards ethylene polymerization in solution, with activities comparable to those displayed by commercial *rac*-Et-$(Ind)_2ZrCl_2$. When tested as self-polymerization catalysts under suitable experimental conditions, they gave colored precipitates that, once reactivated with MAO, were significantly active in ethylene polymerization, although lower than those of the corresponding catalytic systems in solution. The molecular weights of the produced polymers were similar to those obtained with the same catalysts in solution, but their distribution resulted to be broader, with values typical of heterogeneous catalytic systems. From ^{13}C NMR studies we had the first spectroscopic evidence of the actual incorporation of a metallocene of this type into a polymeric chain.

Keywords: heterogeneous catalysis; immobilization; metallocenes; polymerization; Ziegler–Natta catalysis; zirconium

Introduction

In the last two decades the role of homogeneous single-center metallocene and post-metallocene organometallics as catalysts in olefin polymerization has been quite well assessed.[1] Compared to heterogeneous Ziegler–Natta catalysts they offer unique possibilities for tailoring the structure of polyolefins through rational design of the ligands coordinated to the transition metal. Furthermore, their single-center nature produces polymers with narrower molecular weight (M_w) distributions. A great number of them also exhibit greater activity and stereoselectivity. As a consequence, it is particularly intriguing to find a way to use metallocenes in existing technical process (*drop-in* technology) to replace the conventional heterogeneous catalytic systems. However, homogeneous catalysts suffer from serious drawbacks that prevent their use in already existing plants. For commercial processes only reactors for heterogeneous catalysis are used, in order to avoid the so-called "fouling" in the *slurry loop* or gas-phase reactors, when freshly formed polymer is deposited on the reactor walls, and causes problems in the cooling system, and in the continuous discharging of the produced polyolefin. Other challenges are the control of morphology and density of the polymer particles, and the production of polymers with broader molecular weight distributions for processing reasons. Furthermore, homogeneous catalysts usually require substantial volumes of organic solvents, with an increase of production and safety costs (storage, recycling, waste disposal), not counting the environmental impact. Finally, the cocatalyst (methylaluminoxane or similar compounds) is required in such an excess in homogeneous processes that it often becomes the true cost-limiting factor, even more than the metallocene itself. The most logical solution to circumvent some of these drawbacks is the immobilization of the catalysts/activator onto an inert organic (polystyrene, polysiloxane) or inorganic (silica, alumina, zeolites, $MgCl_2$) support.[2] The immobilization often requires the modification of both the catalyst and the surface to allow the formation of a covalent bond. Unfortunately, in a lot of cases, a sig-

nificant loss of activity and stereocontrol occurs in the polymerization process,[3] likely due to a reduced accessibility of the metal centers and to the interference of the solid matrix surface. One of the most elegant and innovative solutions to this problem thus far reported is the development of self-immobilizing catalysts,[4] i.e., catalysts with an unsaturated function (either on the bridge – the most efficient – or on the ligands) that can be used as a comonomer in a prepolymerization step. In practice, the catalyst is "copolymerized" in the presence of methylaluminoxane (MAO) under a low pressure of ethylene, isolated by precipitation, and reused without adding further cocatalyst.

In the framework of our research[5] on metallocene catalysts for olefin polymerization, we decided to follow the latter kind of approach. We have been looking for *ansa*-bridged complexes meeting the following requirements: i) unsaturation on the interannular bridge; ii) stereochemical versatility without the need for a redesign of the entire synthetic procedure; iii) cheap and easily retrievable starting materials and reagents; iv) versatile synthetic procedure, that could also be scaled up.

Results and Discussion

Our choice fell on a family of four new norbornene-bridged complexes (Figure 1) with π-ligands (cyclopentadienyl or indenyl) that can be prepared either with a *cis* or *trans* spatial array, starting from cyclopentadiene, simply by taking advantage of the stereochemical features of the Diels–Alder reaction. [Throughout the entire paper the Cp rings of the *cis* cyclopentadienyl derivatives will be designed outside the norbornene bridge. The authors are well aware that it is more likely that this part of the molecule is below the norbornene bridge. We have kept this design only to improve the design quality and formula readability.] Furthermore, a huge amount of literature dealing with ethylene-norbornene copolymerizations[6] is available, and can allow a more precise characterization of the immobilized catalysts.

In view of a more systematic study, we started our investigation with the *trans* bisindenyl (**1**) and the *cis* biscyclopentadienyl (**2**) zirconocenes (Figure 2), i.e., the sterically largest and smallest, respectively, of this series of metallocenes.

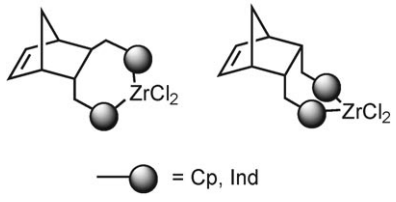


Figure 1. Family of new zirconium complexes.

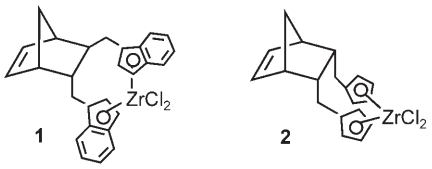


Figure 2. Complexes **1** and **2**.

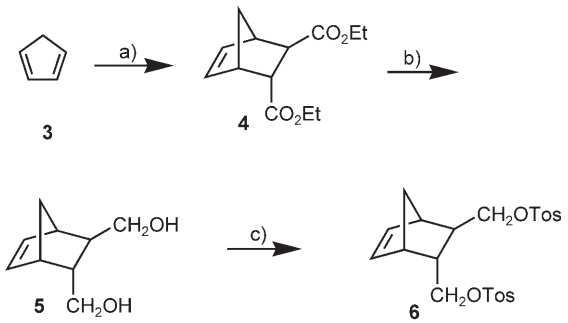
Our aim was to evaluate the influence of several factors on the immobilization procedure and polymerization activity: i) nature of the coordinated ligand; ii) mutual arrangement of the ligands with respect to the bridge; iii) sterical encumbrance of the ligands; iv) accessibility of the catalytic center.

Synthesis of the Complexes

The starting point for the synthesis of the *trans* metallocene **1** was the [2+4]cycloaddition of cyclopentadiene (**3**) with diethyl fumarate, that gave the diester **4** (Scheme 1). [As a matter of fact two enantiomers were obtained, i.e., 2-*endo*,3-*exo* and 2-*exo*,3-*endo* adducts, as confirmed by the crystal structure of the bistosyl derivative **6**. A separation of the enantiomers was not necessary, because both *rac*-metallocenes are active in polymerization.[1] For the sake of readability, the mixture of *trans* isomers will be henceforth described as a single compound.]

Reduction of **4** with $LiAlH_4$ gave the corresponding diol **5**, that was converted into the bistosyl derivative **6**, a crystalline solid that can be stored indefinitely, and produced also crystals suitable for X-ray crystallography (Figure 3).

In order to avoid the formation of spiro compounds,[8] bisindenyl **7** was prepared by reaction of **6** with indenylmagnesium bromide, instead of the more basic and commonly used indenyllithium. A great in-



Scheme 1. *Reaction conditions*: (a) Diethyl fumarate, 0 °C. (b) $LiAlH_4$, 0 °C, then reflux heating. (c) *p*-Toluenesulfonyl chloride, pyridine, −15 °C.

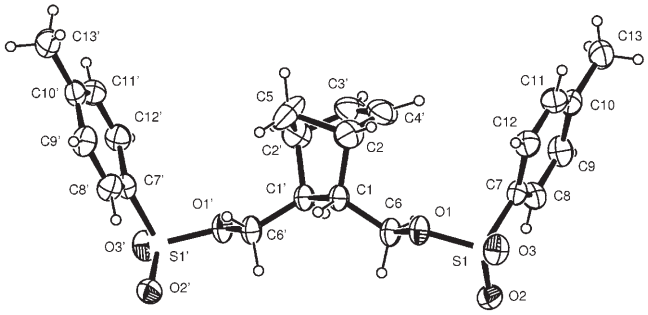


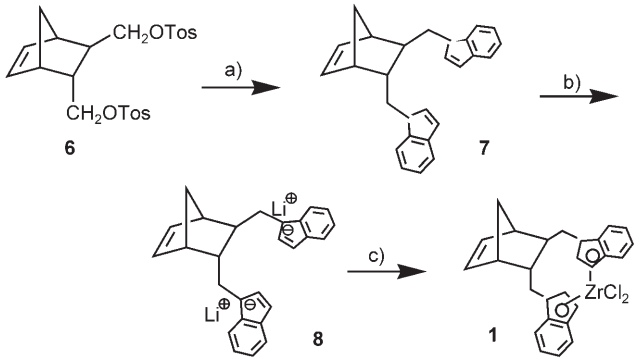
Figure 3. ORTEP[7] view of one of the enantiomers of compound **6** showing the thermal ellipsoids at 30% probability level.

crease in the reaction yields was achieved by direct deprotonation at 0 °C with *n*-butyllithium of the bisindenyl **7** still in solution, because this compound easily polymerizes at room temperature. The obtained dilithium salt **8** (indefinitely stable as a solid under an inert atmosphere), was converted into the zirconium complex **1** by reaction with $ZrCl_4$·2 THF (Scheme 2).

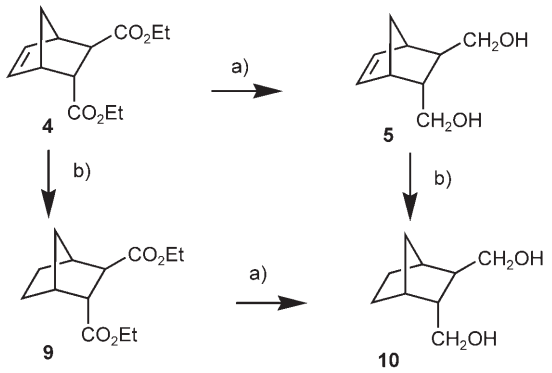
Complex **1** itself cannot be considered the best reference for the corresponding processes in the homogeneous phase, because the norbornene moiety can copolymerize too with the monomer, thus generating a complex mixture of catalysts. Therefore, we have prepared the corresponding zirconocene with a saturated bridge (**14**), to be used as a reference for the polymerizations. The double bond can be reduced either in the diester **4** or in the diol **5** (Scheme 3), but we found that the second approach makes it easier to follow the reactions progress by TLC and NMR spectroscopy, while the overall yields are comparable.

Diol **10** was converted into metallocene **14** following the same set of reactions (Scheme 4) used to prepare complex **1**.

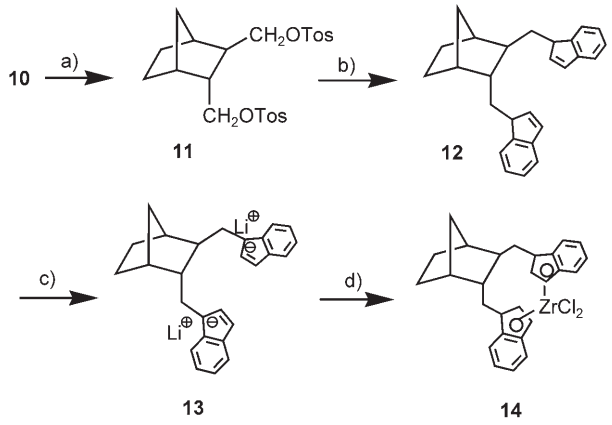
In this case, about the 80% of the complex crystallized (Figure 4). As for its parent compound **6**, because of the centrosymmetric space group, there are two enantiomers in the crystal cell.



Scheme 2. *Reaction conditions*: (a) Indenylmagnesium bromide, 0 °C. (b) *n*-BuLi, 0 °C. (c) $ZrCl_4$·2 THF.



Scheme 3. *Reaction conditions*: (a) $LiAlH_4$, 0 °C, then reflux heating. (b) H_2, Pd/C.



Scheme 4. *Reaction conditions*: (a) *p*-Toluenesulfonyl chloride, pyridine, −15 °C. (b) Indenylmagnesium bromide, 0 °C. (c) *n*-BuLi, 0 °C. (d) $ZrCl_4$·2 THF.

The Cp(centroid)-Zr distances are 2.263(2) and 2.222(2) Å, in agreement with other similar structures of bisindenylzirconium dichlorides.[9] The dihedral angle between the average planes of the indenyl moieties of 127.4(1)° and the torsion angle C14−C13/C23−C24 of 172.6(5)° define an open structure of the complex. This structure proves that most of the complex was formed by coordination to the metal center with a *trans* spatial array of the indenyl ligands, a feature not granted in the presence of a four-carbon-atom bridge, even when a structural constraint keeps the indenyl rings *trans* to each other.[10] However, since the bridge is not rigid enough to keep the zirconocene **14** in a C_{2v} symmetry, the complex seems more appropriate for ethylene polymerization than for propylene or higher olefins, where true *rac* complexes[1f] are necessary in order to produce high molecular weight polymers.

We obtained the *cis* biscyclopentadienyl derivatives by following a similar synthetic path. In this case, the starting point was the reaction between cyclopentadiene **3** and maleic anhydride to give the *endo* alde-

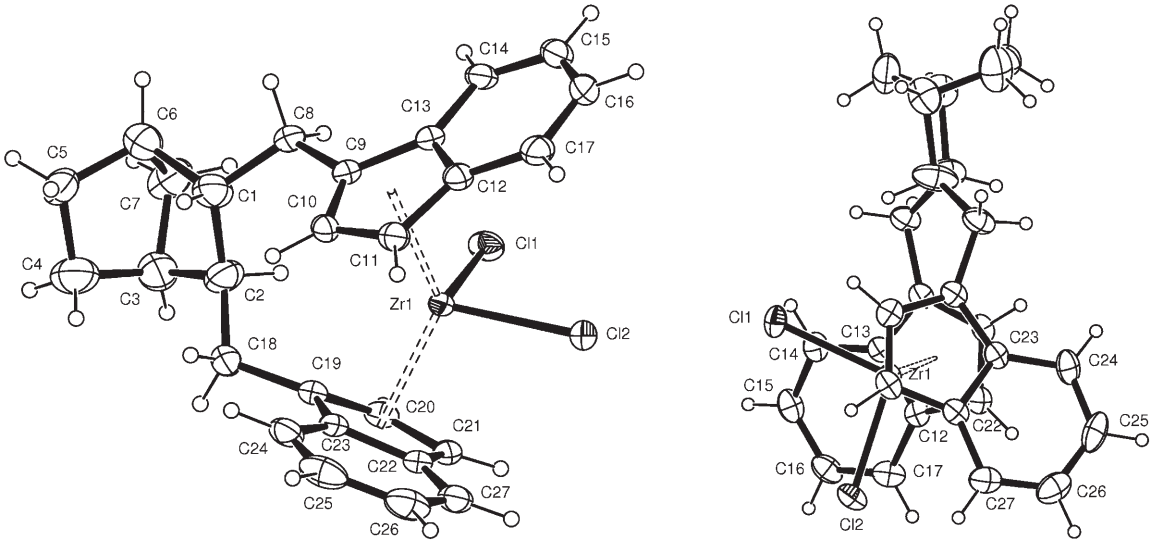
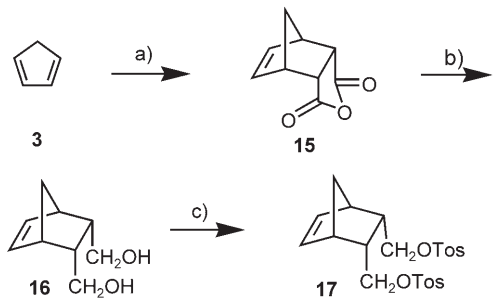


Figure 4. Front (*left*) and top (*right*) ORTEP[7] views of one of the enantiomers of compound **14** showing the thermal ellipsoids at 30% probability level. Significant bond lengths and angles: Zr1–Cp1* 2.263(2) Å; Zr1–Cp2* 2.222(2) Å; Zr1–Cl1 2.436(1) Å; Zr1–Cl2 2.439(1) Å; Cl1–Zr1–Cl2 97.76(4)°; Cl2–Zr1–Cp1 106.86(6)°; Cp1–Zr1–Cp2 128.80(8)°; Zr1,Cl1,Cl2^C9..C17 30.98(7)°; Zr1,Cl1,Cl2^C19..C27 21.63(7)°; C9..C17^C19..C27 127.4(1)°.



Scheme 5. *Reaction conditions*: (a) Maleic anhydride, −5 °C. (b) $LiAlH_4$, 0 °C, then reflux heating. (c) *p*-Toluenesulfonyl chloride, pyridine, −15 °C.

hyde **15**, that was converted into the bistosyl **17** (Scheme 5), whose structure was confirmed by X-ray crystallography (Figure 5).

Because this compound crystallizes in the non-centrosymmetric space group $P2_12_12_1$, the crystal contains only molecules of one diastereoisomer. The correct absolute configuration of the carbons (1*R*,2*S*,3*R*,4*S*, IUPAC numbering corresponding to C3, C2, C1, and C6 in Figure 5) has been confirmed by the value of the Flack parameter[11] of 0.05(8), obtained after the last cycle of refinement. The Flack parameter for the inverted absolute structure is 0.96(8).

Unfortunately, the reaction of bistosyl **17** with cyclopentadienylmagnesium bromide gave only traces of the desired biscyclopentadienyl derivative. But, after having tried different combinations of leaving groups and cyclopentadienylide counteranions, we found that the more efficient one (Scheme 6) was to react sodium cyclopentadienylide (NaCp) with the

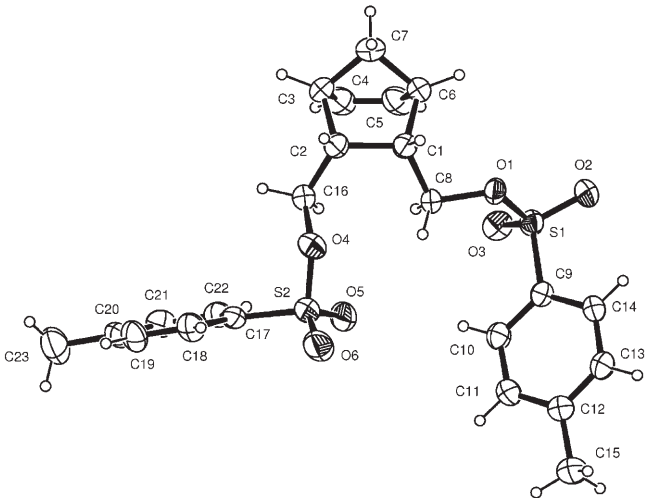
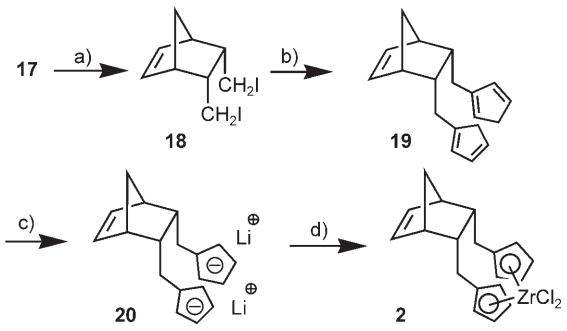


Figure 5. ORTEP[7] view of compound **17** showing the thermal ellipsoids at 30% probability level.



Scheme 6. *Reaction conditions*: (a) NaI, acetone. (b) 0 °C, NaCp. (c) *n*-BuLi, 0 °C. (d) $ZrCl_4$•2 THF.

Table 1. Polymerization results.[a]

Catalyst	P C_2H_4 [bar])	Yield [mg]	Activity[b] ($\times 10^{-3}$)	M_w	M_w/M_n
EI	1.08	2509	2323	340,456	2.88
14	1.08	2956	2788	293,383	2.99
14	0.30	478	1516	138,722	3.05
1	1.08	2480	2600	464,385	2.28
1	0.30	456	1382	277,736	3.47
2	1.08	2290	1964	476,210	3.77
2	0.30	334	1110	389,272	4.61

[a] *Polymerization conditions*: solvent = toluene (100 mL), [Zr] = 2.0–2.2 × 10^{-5} mol × L^{-1}, MAO/Zr = 3000 (molar ratio), T = 30 °C, time = 30 min.
[b] mg polymer × (mmol Zr × h × bar ethylene)$^{-1}$.

bisdiiodo derivative **18**,[12] easily obtained from the bistosyl **17**. Since the biscyclopentadienyl ligand **19** showed a strong tendency to polymerize, it was isolated only once for characterization purposes, but in the other cases it was immediately reacted at 0 °C with *n*-butyllithium to give the dilithium salt **20**, indefinitely stable in the solid state under an inert atmosphere. After deprotonation with *n*-butyllithium and metalation with $ZrCl_4 \cdot 2$ THF, the *cis* biscyclopentadienylderivative **2** was obtained.

Polymerization Activity Tests

First of all, the synthesized metallocene complexes **1**, **2**, and **14**, after activation with methylaluminoxane (MAO), were tested as homogeneous catalysts for ethylene (E) polymerization. Table 1 reports polymerization data and results of GPC analysis at two different values of ethylene pressure (1.08 and 0.3 bar). The activity of the classical and widely studied *rac*-Et-$(Ind)_2ZrCl_2$/MAO (**EI**) catalyst[13] was taken as a reference point under the same polymerization conditions. The activities observed with the novel metallocenes and **EI** were comparable. As expected, the unsaturated derivatives **1** and **2** proved to be less active in ethylene polymerization than the saturated catalyst **14**, due to the competitive coordination of the double bond of the norbornene bridge, and the biscyclopentadienyl catalyst **2** was the least reactive of all, in accord with literature data for similar complexes.[1f] The lower ethylene pressure in general did not dramatically affect the activity. The difference mainly consists in lower molecular weights and in the presence of a few chain branches in the chain, that are otherwise absent. Indeed, under starving conditions, the low propagation rate usually favors the transfer reactions and possible reinsertions of the detached chains.

Table 2. Norbornene/ethylene copolymerizations.[a]

Catalyst	Yield [mg]	Activity[b] ($\times 10^{-3}$)	Inserted[c] N mol%
1	140	152.8	2.50
2	158	139.8	2.14

[a] *Copolymerization conditions:* solvent = toluene (100 mL), P C_2H_4 = 1.08 bar (0.122 mol × L^{-1}), N = 24.8 mmol, N/E = 2.00 (molar ratio), [Zr] = 2.0 × 10^{-5} mol × L^{-1}, MAO/Zr = 3000 (molar ratio), T = 30 °C, time = 30 min.
[b] mg polymer × (mmol Zr × h × bar ethylene)$^{-1}$.
[c] Evaluated by ^{13}C NMR.

Catalysts Immobilization

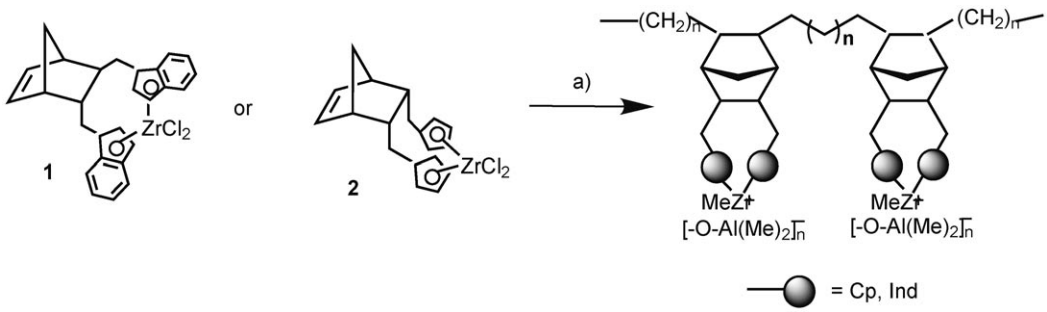
Norbornene bridged metallocenes **1** and **2** were studied as self-immobilizing catalysts in the presence of ethylene (E). First of all, the capability of **1**/MAO and **2**/MAO to produce ethylene-norbornene copolymers was verified as a necessary condition for self-copolymerization. In Table 2 are reported the copolymerization data, that show the actual possibility of insertion of a monomer as bulky as norbornene (N) with both catalysts with acceptable yields.

Catalysts **1** and **2**, activated with MAO, were then used to polymerize ethylene under conditions (low ethylene pressure and relatively high concentration of the metallocene) that can favor their incorporation as comonomers into the polymeric chain with respect to ethylene. In both cases a colored precipitate, supposed to consist of polyethylene and incorporated active catalyst (Scheme 7), was obtained (Table 3).

Since the supernatant solutions were still slightly colored, we assumed that the catalysts were only partially incorporated into the chain. It was difficult to evaluate the amount of metallocene inserted into the polyethylene chain by ^{13}C NMR analysis, because the tiny extra signals detected were below the quantitative evaluation capability of this kind of analysis. Therefore we have estimated the Zr content in the immobilized catalysts by instrumental neutron activation analysis (INAA).[14] The above experiments were repeated as before (Table 4), the solid samples washed several times with anhydrous toluene to ensure complete removal of any trace of unreacted catalyst, and dried under vacuum. The results showed that about 10–15% of the initial amount of catalyst was incorporated into the polymeric chain.

^{13}C NMR Analysis of the Immobilized Catalysts

In order to obtain direct evidence of the actual possibility that the above catalysts really insert into the polyethylene chain, we have made an experiment using **2** mainly as a comonomer in the presence of a catalytic amount of MAO-activated *rac*-Et$(Ind)_2ZrCl_2$



Scheme 7. Immobilization procedure. *Reaction conditions*: Ethylene (0.3 bar), toluene, MAO.

Table 3. Catalyst self-immobilization.[a]

Catalyst	Yield [mg]	Activity[b] ($\times 10^{-3}$)	M_w	M_w/M_n
1	73	60.2	63,464	6.53
2	80	86.6	179,954	17.58

[a] *Conditions*: solvent = toluene (35 mL), P C_2H_4 = 0.30 bar, [Zr] = 2.9×10^{-4} mol × L^{-1} (**1**), [Zr] = 2.8×10^{-4} mol × L^{-1} (**2**), MAO = 5.82–6.06 mmol (MAO/Zr = 600 molar ratio), T = 30 °C, time = 25 min.

[b] mg polymer × (mmol Zr × h × bar ethylene)$^{-1}$.

Table 4. Zr content determination.[a]

Catalyst	Immobilized catalyst[b] [mg]	% Inserted catalyst[c]
1	73.6	10.49
2	132.0	14.68

[a] *Conditions*: solvent = toluene (35 mL), P C_2H_4 = 0.30 bar, [Zr] = 2.7×10^{-4} mol × L^{-1} (**1**), [Zr] = 2.8×10^{-4} mol × L^{-1} (**2**), MAO = 5.70–5.94 mmol, (MAO/Zr = 600 molar ratio), T = 30 °C, time = 25 min.

[b] Total weight of the dried samples.

[c] Evaluated by INAA, with respect to the initial amount of catalyst.

(**EI**) catalyst. **EI** was chosen because it is able to incorporate bulky comonomers, specifically norbornene (N), in ethylene-based copolymers, while **2** was more effectively incorporated than **1** in a polyethylene chain (Table 4). Table 5 shows the copolymerization results. Our main concern was to find polymerization conditions, in particular norbornene/ethylene feed ratio, in order to attain the lowest, although quantitatively measurable, norbornene incorporation into the chain (run 1). To favor the catalyst/comonomer incorporation, a 0.1 bar ethylene pressure was used. Under the selected conditions an ethylene-norbornene copolymer with about 1.1% in mol of norbornene was obtained, an amount well above the quantitative evaluation capability of ^{13}C NMR analysis. The same conditions were then adopted with catalyst **2** (Table 5, run 2). Copolymerization time was optimized in order to insert **2** into the chain as evenly as possible, namely

Table 5. Immobilization of 2 with EI.[a]

Entry	Comonomer [mmol]	Yield [mg]	Activity[b] ($\times 10^{-3}$)	Inserted N/**2**[c] [mol%]
1	N (50)	121	302.5	1.1
2	**2** (50)	183	457.5	≈0.07

[a] *Polymerization conditions*: solvent = toluene (35 mL), catalyst = **EI** (4 micromol), comonomer/E = 0.12 (molar ratio), MAO/Zr (**EI**) = 1500 (molar ratio), P C_2H_4 = 0.1 bar (0.012 mol × L^{-1}), T = 30 °C, time = 1 h.

[b] mg polymer × (mmol Zr × h × bar ethylene)$^{-1}$. The activity is referred to **EI** concentration.

[c] Evaluated by ^{13}C NMR from the average peak areas of C7 and C2/C3.

by preparing a copolymer amount just enough for NMR analysis, without consuming all the metallocene.

In Figure 6 the aliphatic region of the ^{13}C NMR spectrum of ethylene-norbornene (a) and ethylene/**2** (b) copolymers produced by catalyst **EI** (runs 1 and 2 of Table 5, respectively) are shown. Ethylene-norbornene copolymer was used as a reference compound[6] for the assignment of several significant signals in spectrum (b).

Both spectra, in particular the second one, are rich in extra signals in addition to the expected ones. Indeed, the copolymerization conditions (low ethylene pressure, highly concentrated solutions) and the bulkiness of the comonomers reduce the propagation rate of the polymeric chain, thus favoring chain transfer processes, followed by reincorporation of the detached unsaturated oligomers. Consequently, in both cases, in addition to the signals of polyethylene chain-end groups (12.01, 21.18, 27.34, and 29.96 ppm) there are several signals (starred in the spectra) due to a variety of chain branching. This phenomenon is enhanced when **2** is used as a comonomer, because the bulky **2**/MAO complex is less easily incorporated than norbornene. The probable formation of slow propagating dormant sites can account for more frequent chain termination and branching. The complete assignment[15] of highly branched, low density polyethy-

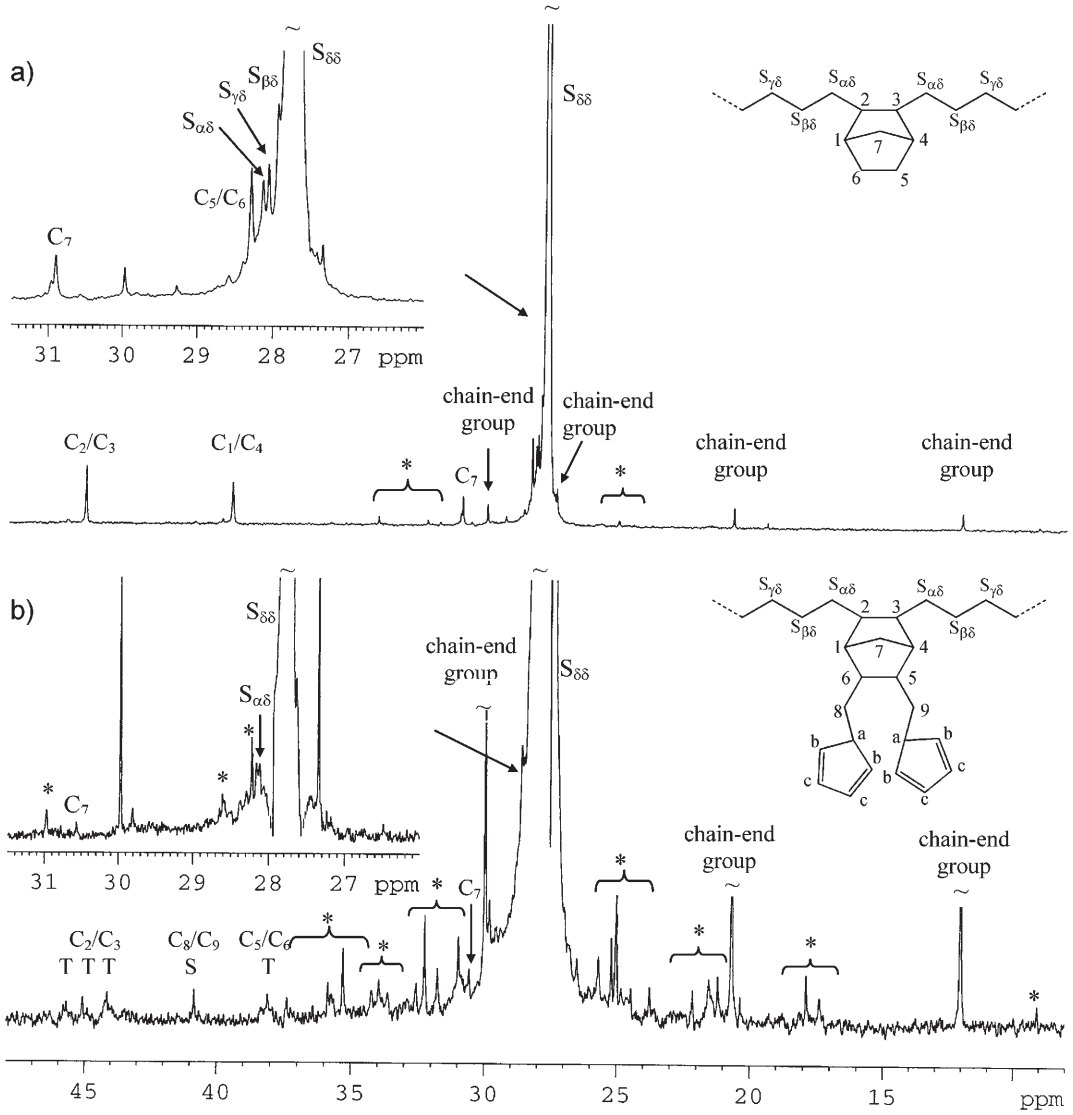


Figure 6. ^{13}C NMR spectrum of aliphatic region of: (a) ethylene-norbornene copolymer. (b) ethylene/**2** copolymer produced by catalyst **EI**. S and T refer to the secondary (methylene) and tertiary (methine) carbons of the main chain and/or of inserted **2**.

lene indicates that the signals of the ethyl branches span from 9.06 (methyl carbon) to 37.36 (methine carbon) ppm. The five small signals of similar intensities detected from 38.09 ppm downwards can be quite safely assigned to the carbons of inserted **2**. The tentative assignments of all new signals, listed in Table 6, were mainly based on DEPT analysis and previous assignments of ethylene-norbornene copolymers with isolated comonomer units.[6] S and T refer to secondary (methylene) and tertiary (methine) carbons of the main chain and/or of inserted **2**. According to Carman and Wilkes carbon terminology,[16] Greek subscripts indicate the distance of the carbon under study from the neighboring methines, where δ indicates methines farther than three bonds. Ethylene-norbornene copolymer[6] is taken as a model compound for the assignment of the methylene carbons of the chain adjacent to the inserted comonomer, of C2/C3 methines, and of C7 methylene of the same ethylene-**2**-ethylene sequence (C7 signal intensity is roughly half the intensity of the other peaks assigned to inserted **2**). The signal detected at 28.12 ppm (see the expanded spectrum of Figure 6b) is assigned to the $\alpha\delta$ methylene carbons of the chain. The next $\beta\delta$ and $\gamma\delta$ methylene carbons, well detectable in the expanded region of the ethylene-norbornene copolymer spectrum, are overlapped by the $S_{\delta\delta}$ signal of the backbone in the spectrum of ethylene-**2** copolymer (Figure 6b). Methylene signal at 40.83 ppm can be quite safely assigned to C8/C9 carbons: this is indeed the spectral region where the signals of $S_{\alpha\alpha}$ carbons of homo- and copolymers of propylene and higher α-ole-

Table 6. ^{13}C NMR chemical shift assignment for ethylene/**2** copolymer compared with ethylene/N copolymer obtained with **EI** as catalytic system.

Carbon type[a]	Assignment	Chemical shift (ppm)	
		Ethylene-**2** copolymer	Ethylene-N copolymer
CH_2	$S_{\delta\delta}$[b]	27.73	27.73
CH_2	$S_{\beta\delta}$	n.d.	27.95
CH_2	$S_{\gamma\delta}$	n.d.	28.07
CH_2	$S_{\alpha\delta}$	28.12	28.13
CH_2	C7	30.56	30.90
CH	C5/C6	38.09[b]	28.33
CH_2	C8/C9	40.83	-
CH	C1/C4	44.12–45.80[c]	39.50
CH	Ca	44.12–45.80[c]	-
CH	C2/C3	45.06	45.03
CH	Cb	125.78	-
CH	Cc	128.69	-

[a] From DEPT analysis.
[b] S refers to secondary (methylene) carbons of the main chain and/or of inserted 2.
[c] Tentative assignment.

fins are more frequently detected.[17] C5/C6 carbons are tentatively assigned on the basis of literature data reported for a copolymer of ethylene and norbornenemethanol.[18] At present we are not able to assign precisely the remaining tertiary carbons at 44.12 and 45.80 ppm to either C1/C4 or Ca. At any rate, the assignment proposed, even if not completely exhaustive, gives evidence of the occurred insertion of the metallocene comonomer into the chain.

Polymerization Activity of Immobilized Catalysts

Finally, we checked the activity of the immobilized catalysts towards ethylene polymerization, by adopting a two-step procedure (Table 7), using the same apparatus and performing the prepolymerization as before. The precipitates, filtered and carefully washed with anhydrous toluene, were reactivated with MAO, and ethylene (1.08 bar pressure) was added. The activities of the immobilized catalysts were evaluated supposing the same yields and percentages of incorporation reported in Table 4, and were, as expected, lower (about the 32–30%) than those of the corresponding catalytic systems in solution, but still acceptable. Catalyst **1**, that is less incorporated, proved to be more active than **2**, even after immobilization, thus paralleling its behavior as homogeneous catalyst. The molecular weights do not greatly differ from those obtained with the same catalysts in solution, but exhibit broader molecular weight distributions as is commonly observed with heterogeneous catalysts.

Table 7. Heterogenized catalysts: ethylene polymerization.[a]

Catalyst	Yield [mg]	Activity[b] ($\times 10^{-3}$)	M_w	M_w/M_n
1	572	848	397,429	6.73
2	579	599	301,852	11.01

[a] *Conditions*: a) *Catalyst self-immobilization*: solvent = toluene (35 mL), $[Zr] = 2.8 \times 10^{-4}$ mol $\times L^{-1}$ (**1**), $[Zr] = 2.9 \times 10^{-4}$ mol $\times L^{-1}$ (**2**), MAO = 5.88–6.12 mmol, (MAO/Zr = 600 molar ratio), $T = 30\,°C$, P $C_2H_4 = 0.30$ bar, time = 25 min. b) *Polymerization*: solvent = toluene (60 mL), MAO = 6 mmol, $T = 30\,°C$, P $C_2H_4 = 1.08$ bar, time = 30 min.
[b] mg polymer $\times$ (mmol Zr $\times$ h $\times$ bar ethylene)$^{-1}$.

Conclusions

We have prepared a series of new tethered metallocenes as self-immobilizing catalysts, following a synthetic path that has proved successful for a "tuned" synthesis of a variety of cyclopentadienyl and indenyl complexes. The syntheses used easy retrievable and relatively cheap reagents and starting materials, and allowed the preparation on a ten (or more, if desired) gram scale of the desired intermediates and metallocenes. The yields were generally good, and all of the intermediates and final complexes were purified simply by distillation or precipitation/crystallization. Among the possible compounds we have focused our studies on zirconocenes **1** and **2**, that could be considered the *steric extremes* of a series of four metallocenes, and were also representative of two classes of compounds (i.e., cyclopentadienyl and indenyl). Both complexes **1** and **2**, and the reference complex **14**, proved to be active catalysts towards ethylene polymerization in solution, with activities comparable to those displayed by commercial *rac*-Et(Ind)$_2$ZrCl$_2$. Complexes **1** and **2**, tested as self-polymerization catalysts under suitable experimental conditions, gave colored precipitates that, once reactivated with MAO, were significantly active in ethylene polymerization, although less so than the corresponding catalytic systems in solution. The molecular weights of the produced polymers were similar to those obtained with the same catalysts in solution, but their distribution was broader, with values typical of heterogeneous catalytic systems. The results are a combination of several factors: i) intrinsic activity of the metallocene (indenyl > cyclopentadienyl); ii) percentage of incorporation of the catalysts into the polymeric chain (cyclopentadienyl > indenyl); iii) accessibility of the catalytic center (indenyl > cyclopentadienyl; *trans* > *cis*). From ^{13}C NMR studies of the immobilized catalyst **2**, we also had the first spectroscopic evidence of the actual incorporation of a metallocene of this type into a polymeric chain.

The above results are encouraging, and the present work allowed the tune-up of the equipment and immobilization/polymerizations procedures. Nevertheless, the catalysts studied, although very useful for characterization purposes, suffer from steric hindrances that do not favor an optimum insertion percentage in a polyethylene chain and an easy access to the catalytic centers. In the future, they will, therefore, be converted into derivatives bearing a more open molecular structure and with a more easily polymerizable double bond.

Experimental Section

General Remarks

All manipulations of air- and/or moisture sensitive materials were carried out under inert atmospheres using dual vacuum/argon lines and standard Schlenk techniques, or in a dry-box under a nitrogen atmosphere (<10 ppm oxygen, <20 ppm water). Solvents for the synthesis and NMR characterization of air- and/or moisture-sensitive reagents were thoroughly deoxygenated and distilled under nitrogen from a suitable drying agent (pentane, petroleum ether, diethyl ether, benzene, toluene, and THF from K; C_6H_5N and C_6D_5N from KOH; CH_2Cl_2, CD_2Cl_2, and $CDCl_3$ from CaH_2), and stored under argon in Young's ampoules. Solvents and solutions were transferred, using a positive pressure of argon, through stainless-steel *cannulae* (diameter 0.5–2.0 mm), and mixtures were filtered in a similar way using modified *cannulae* which could be fitted with glass fiber filter disks (Whatman GFC). Unless otherwise specified, reagents were purchased from commercial suppliers (Aldrich, Fluka) and used without further purification. Sodium cyclopentadienylide (NaCp) was prepared by reaction at −15 °C of freshly distilled cyclopentadiene in THF with NaH, followed by filtration and storage under an inert atmosphere. $ZrCl_4 \cdot 2THF$ was prepared from $ZrCl_4$ (Strem) according to the literature procedure.[19] *rac*-Et(Ind)$_2$ZrCl$_2$ (**EI**) was provided by Witco and used without further purification. Methylaluminoxane (MAO) (Witco, 10 wt% solution in toluene) was dried under vacuum to remove solvent and unreacted trimethylaluminium, and stored under nitrogen. Nitrogen and ethylene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4 Å molecular sieves. Norbornene was dried and distilled over sodium.

Reaction courses and product mixtures were routinely monitored by thin-layer chromatography (TLC) on silica gel 60 pre-coated F_{254} plates (Fluka). Reported melting points are uncorrected. Preparative flash chromatography was performed with silica gel 60 Å (Lancaster, ASTM 230–400 mesh). Anhydrous magnesium sulfate was used in drying operations. FT-IR spectra were recorded with a Bruker IFS88 spectrometer. ^{1}H (200.13 MHz) and ^{13}C (50.32 MHz) NMR spectra of intermediates and ligands were recorded at room temperature with a Bruker AC200 spectrometer. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane ($\delta = 0$). Elemental analyses were performed using a Carlo Erba 1106 Elemental Analysis apparatus.

General remarks and pictures about the equipment used, spectroscopic and analytical data are reported in the Supporting Information file.

Synthesis of Metallocenes

Synthesis of *cis* 5-Norbornene-2,3-*endo*-dicarboxylic Anhydride (15)

Maleic anhydride (0.2 mol) was dissolved in anhydrous benzene (80 mL), and cooled to −5 °C under vigorous stirring. Freshly distilled cyclopentadiene (0.2 mol), kept at −5 °C, was added in small portions in order to control the exothermic reaction. When the addition was complete, the cooling bath was removed, the reaction mixture was allowed to reach room temperature, and stirred overnight. Cold pentane was added to complete the precipitation of the white solid product, the precipitate was isolated by filtration, washed twice with cold pentane and dried under reduced pressure. The filtered solution was concentrated on a rotary evaporator (temperature <40 °C to avoid sublimation of the compound), and another crop of crystals was collected by further precipitation with pentane, and filtration. The collected solids were dried at room temperature under high vacuum. Yield: 85%; mp 162–163 °C.

Synthesis of *trans* Diethyl Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (4)

To diethyl fumarate (0.22 mol), dissolved in anhydrous benzene (120 mL), freshly distilled cyclopentadiene (0.2 mol) was added in small portions under vigorous stirring. The reaction mixture was stirred at room temperature for two hours, then heated at 45 °C, and stirred overnight. The solvent was removed on a rotary evaporator. The diester **4** was purified by distillation at 2 mmHg (bp 102–112 °C). Yield: 80%.

Carboxylic Compound Reductions

$LiAlH_4$ (0.2 mol) was suspended under vigorous stirring in anhydrous diethyl ether (80 mL) in a two-necked, round-bottomed flask, equipped with a reflux condenser connected to a $CaCl_2$ trap, and cooled to 0 °C. The anhydride or diester (0.1 mol), dissolved in anhydrous THF (50 mL), was added dropwise at a speed such as to maintain a gentle reflux of the solvent. At the end of the addition, the cooling bath was removed, the suspension was slowly allowed to reach room temperature, and refluxed to complete the reduction. After 1 hour, the reaction, monitored by TLC (ethyl acetate/methanol = 3:1), was complete. The excess of reducing agent was decomposed by careful addition of chilled water, allowing the separation of the organic layer from the inorganic salts, which were washed with chloroform, and decanted each time (5 × 50 mL). The combined organic extracts were dried and evaporated under vacuum to give the diol in quantitative yield.

***trans*-Bicyclo[2.2.1]hept-5-ene-2,3-dimethanol (5):** Viscous colorless oil; bp 149–150 °C.

***trans* Bicyclo[2.2.1]heptane-2,3-dimethanol (10):** Viscous colorless oil; bp 119–112 °C/0.25 mmHg.

(1*R*,2*S*,3*R*,4*S*)-Bicyclo[2.2.1]hept-5-ene-2,3-dimethanol (16): White solid; mp 86 °C.

Catalytic Hydrogenations

16.4 mmol of unsaturated compound were dissolved in ethanol (150 mL) in the ampoule of a Parr hydrogenation apparatus. Palladium on charcoal (0.15 g, w/w 10%), suspended in ethanol (5 mL), was added. The flask was saturated with hydrogen (3.4 atm) and shaken under hydrogen until disappearance of the starting material. After 1 hour, the reaction, monitored by TLC (diethyl ether/petroleum ether = 1:2), was complete. The reaction mixture was filtered over Celite, and the solid repeatedly washed with ethanol. The solvent was evaporated under reduced pressure leaving a viscous colorless oil that was used without purification.

***trans*-Diethyl bicyclo[2.2.1]heptane-2,3-dicarboxylate (9):** Yield: 90%; bp 108–115 °C/2 mmHg.

***trans*-Bicyclo[2.2.1]heptane-2,3-dimethanol (10):** Yield: 95%.

Synthesis of Tosylates

A solution of the diol (8.5 mmol) in freshly distilled pyridine (40 mL) was cooled to −20 °C; *p*-toluenesulfonyl chloride (22 mmol) was added in small portions, and the suspension stirred for 30 min at −20 °C. A white solid started to precipitate. The suspension was kept overnight at −15 °C. Cold water was added until dissolution of the precipitated pyridine hydrochloride and precipitation of a new solid (the desired tosylate). Storage for a further two hours at 4–5 °C completed the precipitation of the tosylate, which was filtered and washed with cold water. The crude product was recrystallized from boiling ethanol, slowly cooled to room temperature, and left one night in the fridge (4 °C). The pure tosyl derivative was obtained after filtration and washing with cold ethanol. Another crop of crystals was obtained by concentration of the mother liquor and storing in the fridge.

***trans*-2,3-Bis(4-methylbenzensulfonate)bicyclo[2.2.1]hept-5-ene-2,3-dimethanol (6):** Yield: 75%; white needles; mp 91 °C.

***trans*-2,3-Bis(4-methylbenzensulfonate)bicyclo[2.2.1]heptane-2,3-dimethanol (11):** Yield: 79%; white needles; mp 104 °C.

(1*R*,2*S*,3*R*,4*S*)-2,3-Bis(4-methylbenzensulfonate)bicyclo-[2.2.1]hept-5-ene-2,3-dimethanol (17): Yield: 72%; white needles; mp 81–82 °C.

Synthesis of (1*R*,2*S*,3*R*,4*S*)-5,6-Bis(iodomethyl)bicyclo[2.2.1]hept-2-ene (18)

Bistosyl **17** derivative (10 mmol) was dissolved in dry acetone (80 mL), NaI (100 mmol) was added, and the reaction mixture was refluxed for 36 h in a closed Rotaflo ampoule (TLC diethyl ether/petroleum ether = 1:1). Once cooled, the reaction mixture was filtered on Celite, and the solid washed with cold acetone. The solvent was evaporated under reduced pressure (temperature < 40 °C, to prevent decomposition of the compound), water was added, and the mixture extracted with diethyl ether (3 × 30 mL). The ethereal extracts were washed with saturated sodium thiosulfate solution, water, and dried. After filtration and evaporation of the solvent under reduced pressure (T < 40 °C) a thick brownish oil, solid at −15 °C, was obtained; yield: 95%.

Synthesis of (1*R*,2*S*,3*R*,4*S*)-5,6-Bis(cyclopentadien-1-ylmethyl)bicyclo[2.2.1]hept-2-ene (19) and (1*R*,2*S*,3*R*,4*S*)-5,6-Bis(cyclopentadien-1-yl-methyl)bicyclo[2.2.1]hept-2-ene Dilithium Salt (20)

Diiodo compound **18** (4.5 mmol) was dissolved in anhydrous THF (20 mL) under an inert atmosphere, and cooled to 0 °C. A solution of NaCp (9.5 mmol) in THF (40 mL) was slowly added. The reaction mixture was allowed to stir for six hours at 0 °C, warmed to room temperature, and stirred overnight to give a cloudy solution. The solvent was pumped off to give a sticky solid that was extracted with petroleum ether 40/60 (3 × 20 mL). In one experiment the solvent was pumped off (without heating) giving the diene **19** as a yellow thick oil (a mixture of cyclopentadienyl isomers) that was used for NMR characterization. Yield: 65%.

To improve the yields, in all other experiments the petroleum ether combined extracts were only concentrated to about 20 mL, immediately cooled to 0 °C, and deprotonated by adding *n*-butyllithium (2.5 M solution in hexanes, 9 mmol). The resulting suspension was stirred at 0 °C for 30 min, then allowed to reach room temperature and stirred overnight. The lithium salt separated from the solution as a dusty solid, which was filtered *via* a *cannula* and washed twice with petroleum ether. The residual solvent was pumped off leaving the lithium salt **20** as an off-white pyrophoric powder. Yield from **18**: 57% (two steps; average yield per step: 75.5%).

Preparation of Indenyl Derivatives

A solution of bistosyl derivative (4.35 mmol) in anhydrous toluene (75 mL) was added dropwise to a cooled (0 °C) and stirred suspension of indenylmagnesium bromide (17.4 mmol) in anhydrous toluene (75 mL) under an inert atmosphere. At the end of addition, the cooling bath was removed and the reaction mixture stirred at room temperature until the disappearance of the starting material (TLC: diethyl ether/petroleum ether = 5:1). The suspension was filtered and the solid washed once with petroleum ether (30 mL). The solvent was evaporated under high vacuum, heating as little as possible. The resulting oil was extracted with petroleum ether (3 × 50 mL). Half of the solvent was evaporated, the solution cooled to 0 °C, and *n*-butyllithium (2.5 M solution in hexanes, 10 mmol) was added dropwise. The solution was stirred at 0 °C for 30 min., allowed to reach room temperature, and stirred overnight. The lithium salt separated from the solution as a dusty solid, which was filtered *via* a *cannula* and washed twice with petroleum ether. The residual solvent was pumped off leaving the lithium salt as a pyrophoric powder.

***trans*-5,6-Bis(inden-1-ylmethyl)bicyclo[2.2.1]hept-2-enyl dilithium salt (8):** Yellowish dusty solid; yield from **6**: 72.7% (two steps; average yield per step: 85%).

***trans*-5,6-Bis(inden-1-ylmethyl)bicyclo[2.2.1]heptanyl dilithium salt (13):** Yellowish dusty solid; yield over two steps: 78.2 (two steps; average yield per step: 88.5%).

Synthesis of Zirconocenes

A solution of $ZrCl_4 \cdot 2THF$ (4.5 mmol) in anhydrous THF (10 mL) was added dropwise to 4.3 mmol of the ligand dilithium salt dissolved in anhydrous THF (20 mL). The reaction mixture was stirred overnight. The solvent was removed under vacuum, the residue extracted with toluene, filtered, concentrated and layered with pentane. A dusty solid precipitated, and was isolated by filtration, washing with pentane, and evaporation of the residual solvent under high vacuum.

***trans*-5,6-Bis(inden-1-ylmethyl)bicyclo[2.2.1]hept-2-enyl-zirconium dichloride (1):** Orange-yellow microcrystalline solid; yield: 45%.

***trans*-5,6-Bis(inden-1-ylmethyl)bicyclo[2.2.1]heptanyl-zirconium dichloride (14):** Orange-yellow crystalline solid; yield: 52%.

(1*R*,2*S*,3*R*,4*S*)-5,6-Bis(cyclopentadien-1-ylmethyl)bicyclo-[2.2.1]hept-2-enylzirconium dichloride (2): Faded yellow dusty solid; yield: 64%.

X-Ray Crystallographic Studies

Crystal data of compounds **6**, **17**, and **14** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The data sets were integrated with the Denzo-SMN package[20] and corrected for Lorentz, polarization and absorption effects (SORTAV[21]). Structures were solved by direct methods (SIR97[22]) and refined anisotropically using full-matrix least-squares with all non-hydrogen atoms. Complete crystal data are reported in the Supporting Information file. In structure **6** the hydrogens were refined isotropically, except those involved in the disordered part that were included on calculated positions riding on their carrier atoms, while in structures **17** and **14** all the hydrogens were included on calculated positions riding on their carrier atoms. Compound **17** is situated on a crystallographic two-fold axis passing in between the C1–C1′ bond. Accordingly, the C3, C4 and C5 atoms, disordered around this axis, were refined over two positions with occupancies 0.5 each. All calculations were performed using SHELXL-97[23] and PARST[24] implemented in WINGX[25] system of programs. Crystallographic data (excluding structure factors) for compounds **6**, **17** and **14** have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 680030 for **6**, CCDC 680031 for **17**, and CCDC 680032 for **14**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, Union Road, Cambridge, CB2 1EZ, UK [fax: (+44)1223/336–033, e-mail: deposit@ccdc.cam.ac.uk].

Polymerizations

Polymerization Activity Tests

Ethylene polymerizations were performed at 30 °C in a 250-mL glass reactor, equipped with a magnetic stirrer, according to the following general procedure: to a solution of MAO (4.8–5.4 mmol, 10 wt% in toluene solution) in freshly distilled toluene (100 mL), after thermal equilibration, ethylene was added until saturation. Polymerization was started by adding a toluene solution (1.3 mL) of metallocene (2.0–2.2 μmol) and MAO (1.2 mmol) to the mixture *via* syringe (MAO/Zr = 3000 molar ratio). Ethylene pressure was kept constant at 1.08 or 0.3 bar throughout the experiments. Polymerizations were terminated after 30 min by adding a small amount of ethanol and dilute HCl, and polymers were precipitated by pouring the reaction mixture into a solution of concentrated HCl (5 mL) in ethanol (600 mL).

Ethylene/Norbornene Copolymerizations

Copolymerizations were performed at 30 °C in a 250-mL glass reactor, equipped with a magnetic stirrer, according to the following general procedure: norbornene (24.8 mmol) in toluene solution (3 mL) was added to a solution of MAO (4.8 mmol, 10 wt% in toluene solution) in freshly distilled toluene (100 mL). After thermal equilibration of the reactor system, ethylene was added until saturation. Polymerization was started by adding to the mixture *via* syringe a toluene solution (1.3 mL) of the metallocene (2.0 micromol) and MAO (1.2 mmol) (MAO/Zr = 3000 molar ratio). Ethylene pressure was kept constant at 1.08 bar throughout the experiments. Polymerizations were terminated and the polymers treated as previously described.

Catalyst Immobilization

Self-copolymerizations were performed at 30 °C in a 100-mL special apparatus consisting of a Schlenk tube equipped with a magnetic stirrer (see Figure S1 in Supporting Information file), according to the following general procedure: to a solution of MAO (5.7–6.4 mmol, 10 wt% in toluene solution) in freshly distilled toluene (32 mL), was added a solution of the metallocene (9.5–10.7 micromol) in toluene (3 mL) (MAO/Zr = 600 molar ratio). After thermal equilibration of the reactor system (T = 30 °C), the solution was degassed by rapid stirring for several short intervals under vacuum, and ethylene pressure brought to 0.3 bar. After 25 min, ethylene flux and stirring were stopped, and the colored precipitated polymers were allowed to settle for one hour (see Figure S2 in Supporting information). Polymerizations were terminated and the polymers treated as previously described.

Ethylene Polymerization with Heterogenized Catalysts

Self-copolymerizations were performed at 30 °C in a 100-mL apparatus as before. The solvent was filtered by suction, and the immobilized catalyst left on the frit washed (20 mL of toluene each), and filtered three times. To the solid catalyst on the frit, freshly distilled toluene (60 mL) and MAO (5.7–6.4 mmol, 10 wt% in toluene solution) were added. After thermal equilibration (T = 30 °C), ethylene was added and the pressure kept constant at 1.08 bar. Polymerizations were

terminated and the polymers treated as previously described.

NMR Analysis

^{13}C NMR spectra of the polymers were recorded in $C_2D_2Cl_4$ at 103 °C on a Bruker Avance-400 spectrometer operating at 100.58 MHz (internal chemical shift reference: 1% hexamethyldisiloxane). Conditions: 10 mm probe; 90° pulse angle; 64 K data points zero-filled to 128 K before FT; acquisition time 8.57 s; relaxation delay 20 s; 3–4 K transients. Proton broad-band decoupling was achieved using bi_waltz16_32 power-gated decoupling. In the insert of Figure 1b, the FID was processed using a Gaussian multiplication (line broadening −0.8 Hz, Gaussian broadening 0.02).

Molar Mass Determination

Gel permeation chromatographic analyses of the polymers were performed at a flow rate of 0.8 $mL \times min^{-1}$ in 1,2,4-trichlorobenzene at 145 °C using a Waters GPC 2000 instrument with a refractive index detector (Columns: 3 PL Gel Olexis + 1 F (2 μm). Molar masses were determined with reference to a polystyrene calibration curve (processing method: PS 145 Univ Lin Sep 07).

INAA (Instrumental Neutron Activation Analysis)

The samples obtained as described in Table 4 were sealed in polyethylene plastic containers under an inert atmosphere and analyzed by the INAA technique. Self-immobilized catalysts **1** and **2** contain 0.997 and 1.454 μmol of Zr, respectively.

Supporting Information

Mechanism for spiro by-product formation, complete crystallographic tables, general remarks and pictures about the equipment used, spectroscopic and analytical data for the synthesized compounds are reported in the Supporting Information file.

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