DOI: 10.1002/ejic.200700918

Heterocycle-Substituted Indenes as Precursors for Supported Zirconocene Catalysts

Pedro J. Aragón Sáez,[a] Fernando Carrillo-Hermosilla,*[a] Elena Villaseñor,[a]
Antonio Otero,*[a] Antonio Antiñolo,[a] and Ana M. Rodríguez[a]

Keywords: Metallocenes / Zirconium / Heterocycles / Polymerization

The indene ligands {1-C_9H_7R} [R = $C_2H_4(C_4H_7O_2)$ (**1**), $C_2H_4(C_3H_5O_2)$ (**2**), $CH_2(C_5H_9O)$ (**3**)] were prepared by alkylation of indene and used to prepare the $SiMe_2$-bridged indenylcyclopentadiene ligands {$Me_2Si(3-C_9H_6R)(C_5Me_4H)$} [R = $C_2H_4(C_4H_7O_2)$ (**4**), $CH_2(C_5H_9O)$ (**5**)]. Bis(indenyl)- and *ansa*-indenylcyclopentadienyl zirconocenes [Zr{1-η^5-C_9H_6R}$_2Cl_2$] {R = $C_2H_4(C_4H_7O_2)$ (**6**), $C_2H_4(C_3H_5O_2)$ (**7**), $CH_2(C_5H_9O)$ (**8**)} and [Zr{$Me_2Si(3-\eta^5-C_9H_5R)(\eta^5-C_5Me_4)$}$Cl_2$] {R = $C_2H_4(C_4H_7O_2)$ (**9**), $CH_2(C_5H_9O)$ (**10**)} were prepared by the reaction of $ZrCl_4$ with the appropriate mono- or dilithium salts of **1**–**5**. The molecular structure of [Zr{$Me_2Si(3-\eta^5-C_9H_5C_2H_4(C_4H_7O_2))(\eta^5-C_5Me_4)$}$Cl_2$] (**9**) was determined by single-crystal X-ray diffraction studies. Indenylzirconium complexes **6**–**10** were immobilized on thf-modified $MgCl_2$, and these supported systems were used to polymerize ethylene in the presence of methylaluminoxane. The catalytic activity of these complexes in both homogeneous and supported polymerization reactions is discussed.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

A large number of supported metallocene catalysts for olefin polymerization have been prepared during the last few decades.[1] These catalysts need to be immobilized on a support in order to be used in gas-phase and slurry reactors with existing procedures. Relative to the homogeneous systems, supported catalysts produce polymers with improved particle morphologies and avoid reactor fouling. In addition, immobilized metallocenes can be activated with relatively lower amounts of methylaluminoxane (MAO). In most cases, silica gel is the preferred inorganic support.[2–4] In contrast, magnesium chloride, which is widely used to support conventional Ziegler–Natta catalysts, has been studied to a lesser extent as a carrier for single-site catalysts.[1,5] Soga and coworkers used the Lewis acidity of $MgCl_2$ to fix the *ansa*-metallocene complex $Cl_2Si(Ind)_2ZrCl_2$ through the $SiCl_2$ Lewis basic bridge. When activated by MAO or Al(*i*Bu)$_3$, this catalyst polymerizes propylene to give isotactic polypropylene, but with an activity about 100 times less than that of $Me_2Si(Ind)_2ZrCl_2$–MAO.[6]

One of the proposed methods to obtain supported catalysts[5,7–9] involves the reaction between a pendant group and specific sites of the solid surface. As part of our continued interest in this field,[10–12] this approach was applied here to obtain several supported bis(indenyl)- and *ansa*-indenylcyclopentadienyl zirconocenes bearing heterocyclic rings containing potential oxygen donor atoms, which are capable of bonding to acidic sites on the surface of magnesium chloride.

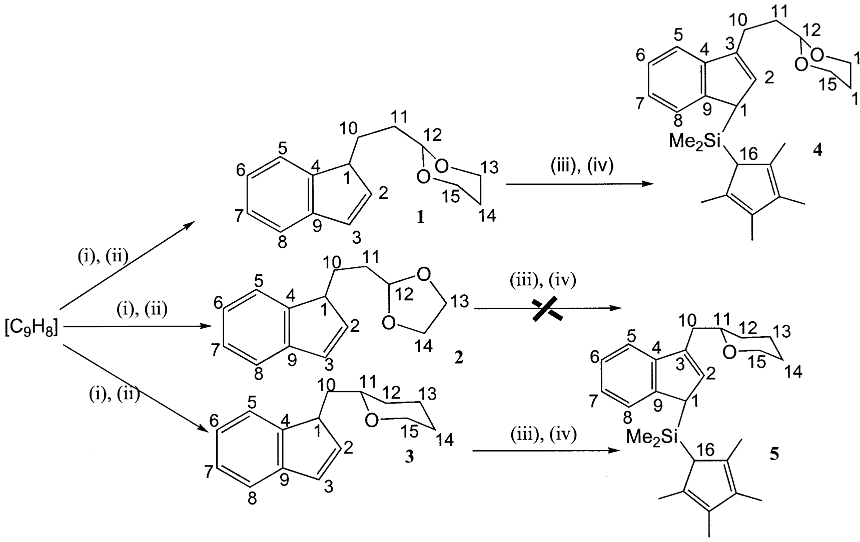
Results and Discussion

The preparation of the substituted indene precursors {1-C_9H_7R} [R = $C_2H_4(C_4H_7O_2)$ (**1**), $C_2H_4(C_3H_5O_2)$ (**2**), $CH_2(C_5H_9O)$ (**3**)] was achieved by the reaction of RBr [R = $C_2H_4(C_4H_7O_2)$, $C_2H_4(C_3H_5O_2)$, $CH_2(C_5H_9O)$] and indenyllithium (Scheme 1). ^{1}H NMR spectroscopy showed isolated products **1**–**3** to be virtually exclusively the 1-isomers. The 1-H signal for **1**–**3** was observed at δ = 3–4 ppm as a multiplet corresponding to one proton. Protons 2-H and 3-H appear as two multiplets in the region δ = 6–7 ppm, and each correspond to two protons. Compound **3** appears as a 3:1 mixture of diastereoisomers.

The bridged indenylcyclopentadiene compounds {$Me_2Si(3-C_9H_6R)(C_5Me_4H)$} [R = $C_2H_4(C_4H_7O_2)$ (**4**), $CH_2(C_5H_9O)$ (**5**)] were obtained by reaction of the lithium salt of the appropriately substituted indene and $ClSiMe_2(C_5Me_4H)$ (Scheme 1). Unfortunately, the corresponding bridged compound bearing the ethyldioxolane group could not be obtained in a satisfactory manner. ^{1}H NMR spectroscopy showed that isolated products **4** and **5** were mainly the isomers bearing the $SiMe_2$ bridge at the 1-position of both the indenyl and cyclopentadienyl moieties. In addition, compound **5**, which contains two stereogenic centers, was

---

[a] Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha,
Campus Universitario de Ciudad Real, 13071 Ciudad Real, Spain
E-mail: Antonio.Otero@uclm.es;
Fernando.Carrillo@uclm.es



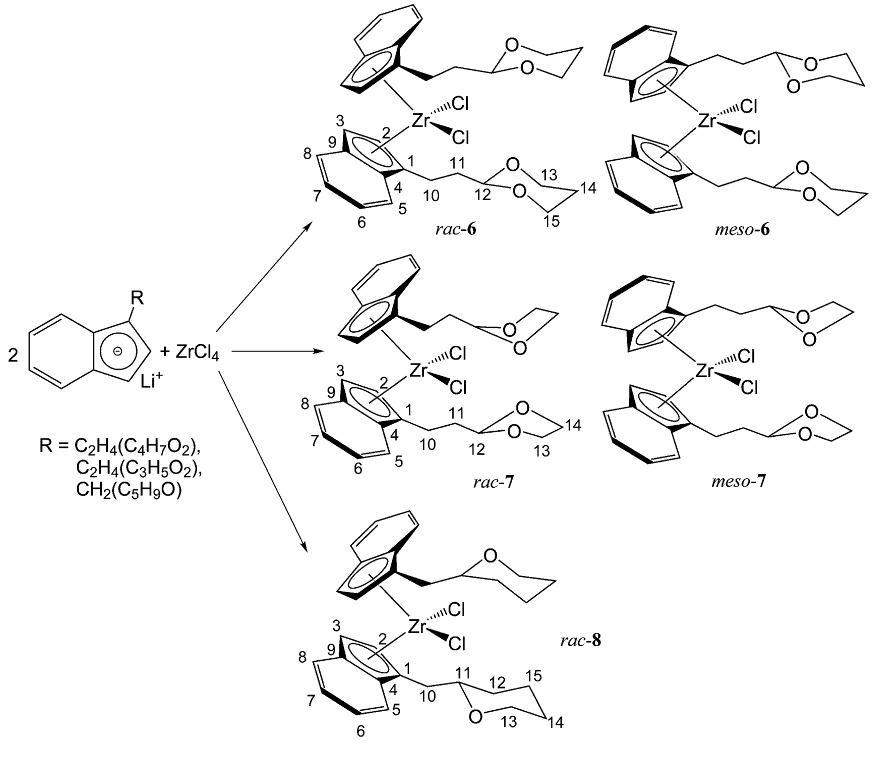
Scheme 1. (i) *n*BuLi; (ii) RBr [R = $C_2H_4(C_4H_7O_2)$, $C_2H_4(C_3H_5O_2)$, $CH_2(C_5H_9O)$]; (iii) *n*BuLi; (iv) $ClSiMe_2(C_5Me_4H)$.

obtained as a 2.5:1 mixture of diastereoisomers of the 1-$SiMe_2$-bridged isomer.

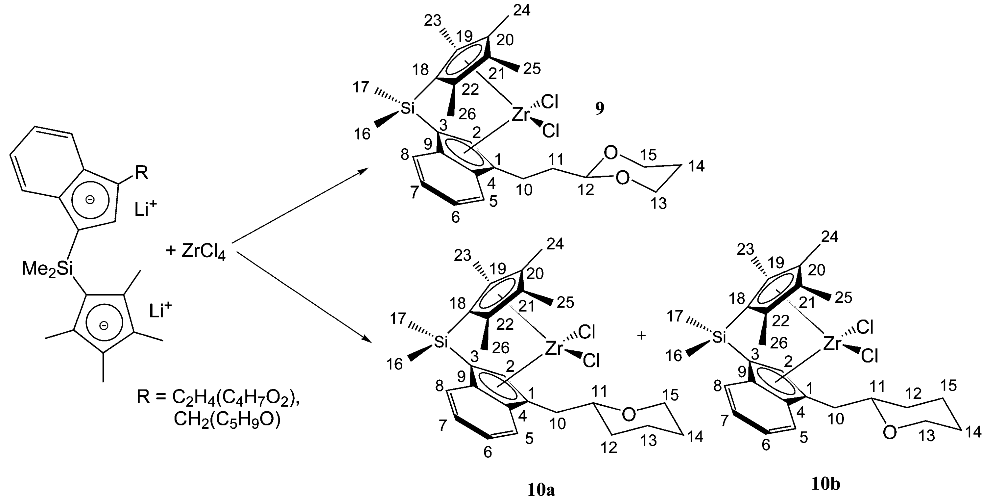
The bis(indenyl) zirconocenes were obtained as yellow solids by treatment of two equivalents of the lithium salt of the corresponding substituted indene with $ZrCl_4$ in toluene (Scheme 2). Complexes **6** and **7** were obtained as 1:1 and 1:0.6 mixtures of *rac* and *meso* diastereoisomers, respectively, as evidenced by NMR spectroscopy. The ^{1}H NMR spectra of **6** and **7** exhibit two clear sets of signals corresponding to the 2-H and 3-H protons at δ = 5.6–6.3 ppm, and the "inner" two doublet signals can be assigned to the *rac* isomer and the "outer" ones to the *meso* isomer, as established by NOESY NMR experiments.

It is noteworthy that complex **8** was only obtained as the *rac* isomer. In this case, only two doublets corresponding to the 2-H and 3-H protons were observed in the ^{1}H NMR spectra.

The *ansa*-indenylcyclopentadienyl metallocenes were obtained in a similar way as yellow solids from the dilithium salts of the corresponding ligands and $ZrCl_4$ in toluene (Scheme 3). The ^{1}H NMR spectra of complex **9** show a lack of symmetry of these chiral complexes, and four signals can



Scheme 2.



Scheme 3.

be assigned to the cyclopentadienyl methyl groups, a singlet for the 2-H proton of the indenyl group, and four multiplets due to the protons on the C_6 ring of the indenyl moiety.

Compound **9** crystallized on cooling a concentrated solution in toluene at –30 °C. The molecular structure was solved by X-ray diffraction studies (Figure 1). The results show a mononuclear zirconium complex that crystallizes in the space group $Pca2_1$ in the orthorhombic system. Selected bond lengths and angles and crystallographic parameters are presented in Tables 1 and 4, respectively. The overall geometry of **9** is similar to that found in the parent complex $[Zr\{Me_2Si(\eta^5\text{-}C_9H_6)(\eta^5\text{-}C_5H_4)\}Cl_2]$ and other similar complexes,[13,14] adopting a distorted tetrahedral coordination in which the Cl–Zr–Cl bond angle is 97.46(9)° and the Cent(indenyl)–Zr1–Cent($CpMe_4$) angle is 128.52(3)° (Cent = ring centroid). The Zr–Cl bond lengths are 2.438(4) and 2.402(4) Å. The Zr–Cent(Cp) and Zr–Cent(Ind) lengths are 2.264(8) and 1.841(9) Å, respectively. The C1–Si–C16 angle is 94.78(15)°. The dihedral angle between the cyclopentadienyl and the indenyl rings is 62.3(1)°. The substituent is oriented in the lateral sector in the opposite direction to the six-membered ring of the indenyl ligand. In the solid state, the heterocyclic group is located far from the metal atom and the molecule has a chair conformation. An analogous separated disposition was found for the benzyl group of the substituted complex $[Zr\{Me_2C(3\text{-}\eta^5\text{-}(C_6H_5CH_2)C_9H_6)(\eta^5\text{-}C_5H_4)\}Cl_2]$.[14]

In addition to the conformational chirality of compound **10**, the presence of a chiral center at C-11 of the heterocyclic pendant group leads to the formation of a 1:1 mixture of diastereoisomers. Indeed, two sets of signals were obtained for all the protons in the ^1H NMR spectra. Unfortunately, we were unable to distinguish between the two isomers.

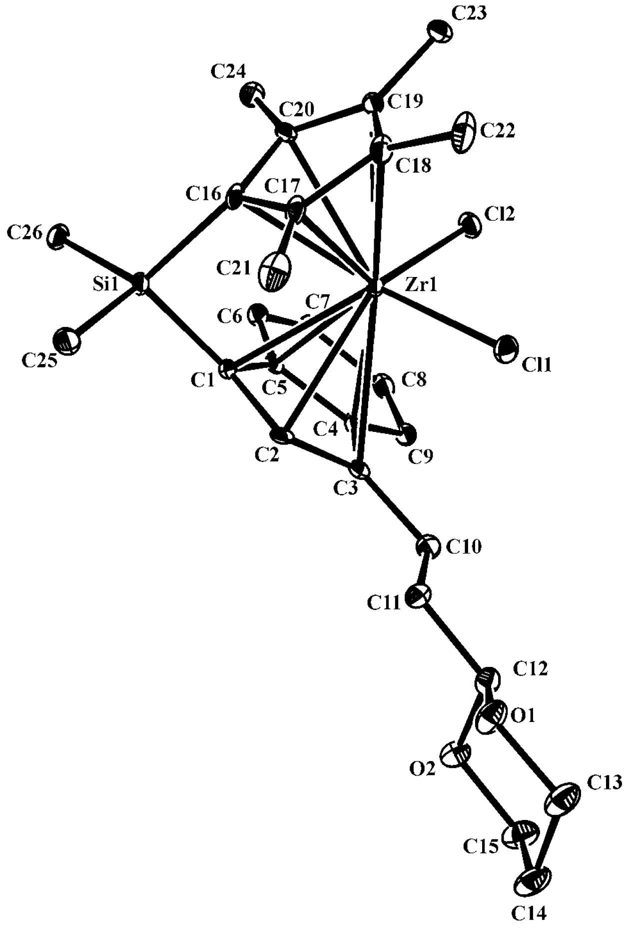


Figure 1. ORTEP view of complex **9**.

The polymerization of ethylene under homogeneous conditions was carried out by using **6**–**10** as the catalyst precursors and MAO as a cocatalyst with different Al/Zr ratios. The polymerization experiments were carried out at 343 K and at an olefin pressure of 1.2 bar. The results of the different experiments are given in Table 2. Unsubstituted analogs $[Zr\{\eta^5\text{-}C_9H_7\}_2Cl_2]$[15] (**11**) and $[Zr\{Me_2Si(\eta^5\text{-}C_9H_6)(\eta^5\text{-}C_5Me_4)\}Cl_2]$[16] (**12**) were used as reference precatalysts.

In all cases, as expected, higher activities were found for the higher Al/Zr ratios. In the case of bis(indenyl) zirconocenes and for complex **10**, the new complexes showed lower

Table 1. Selected bond lengths and angles for **9**; Cent(indenyl) is the centroid of C1–C5; Cent($CpMe_4$) is the centroid of C16–C20.

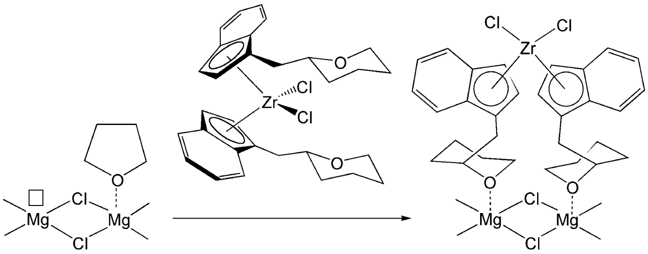
Bond lengths [Å]	
Zr1–Cl1	2.438(4)
Zr1–Cl2	2.402(4)
Zr1–Cent(indenyl)	2.264(8)
Zr1–Cent($CpMe_4$)	1.841(9)
Bond angles [°]	
Cent(indenyl)–Zr1–Cent($CpMe_4$)	128.52(3)
Si1–C1–Cent(indenyl)	164.53(4)
Si1–C16–Cent($CpMe_4$)	144.98(5)
Cl1–Zr1–Cent(indenyl)	106.23(6)
Cl1–Zr1–Cent($CpMe_4$)	106.98(7)
Cl2–Zr1–Cent(indenyl)	106.96(5)
Cl2–Zr1–Cent($CpMe_4$)	106.20(7)
Cl1–Zr1–Cl2	97.46(9)
C1–Si–C16	94.78(15)

Table 2. Catalytic activities in ethylene polymerization at different Al/Zr ratios. Polymerization conditions: 343 K, 1.2 bar monomer pressure, toluene (15 mL), Zr (6 µmol), t_{Pol} = 30 min.

Al/Zr	Catalyst activity [$kg_{PE}\,mol_{Zr}^{-1}\,h^{-1}$]						
ratio	**6**	**7**	**8**	**11**	**9**	**10**	**12**
50	121	89	59	88	281	67	240
100	177	114	143	137	367	128	371
200	217	142	186	210	487	185	457
500	276	203	262	420	586	304	582
1000	363	282	369	652	689	392	687
2000	522	380	543	763	864	523	834

Table 3. Catalytic activities in ethylene polymerization for the different supported catalysts. Polymerization conditions: 343 K, 1.2 bar monomer pressure, toluene (100 mL), Zr (6 µmol), MAO (Al/Zr, 200), t_{Pol} = 30 min.

Complex	%Zr	Activity [$kg_{PE}\,mol_{Zr}^{-1}\,h^{-1}$)
6	0.52	315
7	0.95	173
8	0.36	503
11	0.12	traces
9	0.27	596
10	0.44	411
12	0.05	traces



Scheme 4. Proposed interaction between the modified complexes and support surface.

activities than that of the reference compounds. This behavior can be explained in terms of possible contacts between donor oxygen atoms and the cationic zirconium center in the active species. Similar interactions were proposed for a methyltetrahydrofuryl-substituted bis(cyclopentadienyl) metallocene and were thought to be responsible for the lack of activity of that complex.[17] In contrast with these results, complex **9** has a similar catalytic activity to unsubstituted analog **12**. This observation can be explained if the molecular structure found in the solid state of **9** is to a large extent maintained in solution, where the heterocyclic moiety is far from the active center.

Complexes **6**–**12** were supported on thf-modified $MgCl_2$. This support was prepared by allowing the product to precipitate from a solution of anhydrous $MgCl_2$ in thf. This solid was impregnated with a zirconocene solution in toluene. The product was washed and dried, and the amount of supported metallocene was verified by elemental analysis (Zr). The average results of several samples are summarized in Table 3.

Supported substituted complexes **6**–**10** show a higher metal content than the unsubstituted analogs, which is consistent with the proposed influence of the presence of the heterocyclic group in the supporting process (Scheme 4).

The supported complexes were treated with MAO in order to obtain a 200:1 Al/Zr ratio, and these materials were employed as heterogeneous catalysts in the polymerization of ethylene under identical conditions to those described above for the homogeneous experiments. The activities found are given in Table 3. As a result of the improved supporting process for the heterocycle-substituted metallocenes, higher activities were found for these catalysts than those obtained from "conventional" unsubstituted complexes. Samples from the different catalysts were treated with MAO for 15 min and then filtered off. The obtained solutions were contacted with ethylene in similar conditions to the supported catalysts, and no reaction was found from the samples corresponding to heterocycle-substituted metallocenes. In contrast, traces of polyethylene were produced when samples coming from the reference complexes were used, which thus indicates the strong fixation of modified complexes on the surface.

In addition, it is noteworthy that supported complexes **6**–**10** show higher activities than their corresponding homogeneous catalysts (for a 200:1 Al/Zr ratio). This can be explained in terms of a fixation of these complexes on the $MgCl_2$ surface through the donor oxygen atoms, a process that precludes interaction with the active center during the polymerization process (Scheme 4).

In contrast with previous reported results,[6] no activity was found when TIBA was used as the cocatalyst in the absence of MAO.

Conclusions

The synthesis of several bis(indenyl)- and *ansa*-indenylcyclopentadienyl zirconocenes with pendant heterocyclic groups was achieved. These compounds are capable of interacting with the acidic surface of $MgCl_2$. This process gives rise to well-supported catalysts in comparison with the use of unsubstituted analogs. The activities of these supported catalysts were tested in the polymerization of ethylene, and better results were obtained with these catalysts than for the reference unsubstituted complexes.

Experimental Section

General Remarks: All reactions were carried out by using standard Schlenk tube and glove-box techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. $ZrCl_4$, neat indene, $BrC_2H_4(C_4H_7O_2)$, $BrC_2H_4(C_3H_5O_2)$, $BrCH_2(C_5H_9O)$, $ClSiMe_2(C_5Me_4H)$, MAO (10 wt.-% MAO, in toluene), TIBA (1.0 M in hexane), and anhydrous $MgCl_2$ were purchased from Aldrich and used directly.

^{1}H and ^{13}C spectra were recorded with a Varian INNOVA FT-500 spectrometer and referenced to the residual deuterated solvent. The different peaks were assigned by means of 2D COSY, NOESY, and g-HSQC experiments. C and H microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer. Metal content was determined at the Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany).

{1-$C_9H_7C_2H_4(C_4H_7O_2)$} (1): *n*BuLi (1.60 M in hexane, 9.60 mL, 15.43 mmol) was added over 15 min to a cooled (–78 °C) solution of [C_9H_8] (2.00 mL, 15.43 mmol) in Et_2O (50 mL). At the end of the addition, the solution was allowed to reach room temperature and stirred for 4 h, cooled again to –78 °C, and 2-(2-bromoethyl)-1,3-dioxane (2.10 mL, 15.43 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred for 16 h. The solvent was removed in vacuo and hexane (100 mL) was added. Water (200 mL) was added, the organic product was extracted with hexane, the aqueous layer was washed with hexane (3 × 50 mL), and the organic layers were combined, dried with $MgSO_4$ and filtered. The solvent was removed from the filtrate under reduced pressure to yield the title compound as a white solid. Yield: 2.91 g (82%). ^{1}H NMR (500 MHz, $CDCl_3$, predominant isomer): δ = 1.33 (m, 1 H, 14-H_{eq}), 1.66 (m, 3 H, 10-H, 11-H, 11′-H), 2.06 (m, 2 H, 10′-H, 14-H_{ax}), 3.49 (m, 1 H, 1-H), 3.72 (m, 2 H, 13-H_{ax}, 15-H_{ax}), 4.09 (m, 2 H, 13-H_{eq}, 15-H_{eq}), 4.49 (t, *J* = 4.8 Hz, 1 H, 12-H), 6.52 (m, 1 H, 2-H), 6.81 (m, 1 H, 3-H), 7.18 and 7.24 (2 t, *J* = 7 Hz, 1 H each, 6-H, 7-H), 7.33 and 7.43 (2 d, *J* = 7 Hz, 1 H each, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, predominant isomer): δ = 25.87 (C-11), 26.15 (C-14), 32.98 (C-10), 50.13 (C-1), 67.09 (C-13, C-15), 102.36 (C-12), 121.09 (C-5), 123.01 (C-8), 124.79 (C-6), 126.54 (C-7), 131, 24, 138.94 (C-2, C-3), 144.38 (C-4), 144.70 (C-9) ppm. $C_{15}H_{18}O_2$ (230.30): calcd. C 78.23, H 7.88; found C 78.33, H 7.91.

{1-$C_9H_7C_2H_4(C_3H_5O_2)$} (2): The synthesis of **2** was carried out in an identical manner to that of **1**. [C_9H_8] (2.00 mL, 15.43 mmol), *n*BuLi (1.60 M in hexane, 9.6 mL, 15.43 mmol), and 2-(2-bromoethyl)-1,3-dioxolane (1.90 mL, 15.43 mmol). Yield: 2.07 g (62%). ^{1}H NMR (500 MHz, $CDCl_3$, predominant isomer): δ = 1.59 (m, 3 H, 10-H, 11-H, 11′-H), 1.97 (m, 1 H, 10′-H), 3.43 (m, 1 H, 1-H), 3.73 (m, 2 H, 13-H_{syn}, 14-H_{syn}), 3.84 (m, 2 H, 13-H_{anti}, 14-H_{anti}), 4.76 (t, *J* = 4.4 Hz, 1 H, 12-H), 6.43 (dd, J^2 = 2.0 Hz, J^2 = 5.4 Hz, 1 H, 2-H), 6.72 (dd, J^4 = 1.5 Hz, J^2 = 5.4 Hz, 1 H, 3-H), 7.09 (m, 1 H, 6-H), 7.15 (m, 1 H, 7-H), 7.25 (d, *J* = 7.3 Hz, 1 H, 5-H), 7.34 (d, *J* = 7.3 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, predominant isomer): δ = 25.66 (C-10), 31.44 (C-11), 50.08 (C-1), 65.13 (C-13), 65.16 (C-14), 104.72 (C-12), 121.30 (C-5), 123.16 (C-8), 125.03 (C-6), 126.79 (C-7), 131.54 (C-3), 139.07 (C-2), 144.62 (C-4), 147.62 (C-9) ppm. $C_{14}H_{16}O_2$ (216.28): calcd. C 77.75, H 7.46; found C 77.82, H 7.49.

{1-$C_9H_7CH_2(C_5H_9O)$} (3): The synthesis of **3** was carried out in an identical manner to that of **1**. [C_9H_8] (2.00 mL, 15.43 mmol), *n*BuLi (1.60 M in hexane, 9.6 mL, 15.43 mmol), and 2-(bromomethyl)tetrahydro-2*H*-pyran (2.0 mL, 15.43 mmol). Toluene (100 mL) was used instead of hexane to extract the crude product. Yield: 2.81 g (85%). ^{1}H NMR (500 MHz, $CDCl_3$, predominant isomer): δ = 1.34 (m, 2 H, 10-H, 12-H_{ax}), 1.56 (m, 3 H, 12-H_{eq}, 13-H_{ax}, 14-H), 1.67 (m, 1 H, 14′-H), 1.87 (m, 1 H, 13-H_{eq}), 2.24 (m, 1 H, 10′-H), 3.48 (m, 1 H, 1-H), 3.50 (m, 1 H, 15-H_{ax}), 3.78 (m, 1 H, 11-H), 4.11 (m, 1 H, 15-H_{eq}), 6.68 (m, 1 H, 2-H), 6.85 (m, 1 H, 3-H), 7.22 (t, *J* = 7 Hz, 1 H, 6-H), 7.28 (t, *J* = 7 Hz, 1 H, 7-H), 7.38 (t, *J* = 7 Hz, 1 H, 5-H), 7.45 (t, *J* = 7 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, predominant isomer): δ = 23.90 (C-12), 26.52 (C-13), 32.98 (C-14), 39.11 (C-10), 47.12 (C-1), 68.87 (C-15), 77.07 (C-11), 121.28 (C-5), 123.12 (C-8), 125.04 (C-6), 126.68 (C-7), 131.12 (C-3), 139.24 (C-2), 144.40 (C-4), 148.64 (C-9) ppm. $C_{15}H_{18}O$ (214.30): calcd. C 84.07, H 8.47; found C 84.16, H 8.50.

[$SiMe_2${1-$C_9H_6C_2H_4(C_4H_7O_2)$}{C_5HMe_4}] (4): *n*BuLi (1.60 M in hexane, 5.40 mL, 8.68 mmol) was added over 15 min to a cooled (–78 °C) solution of **1** (2.00 g, 8.68 mmol) in Et_2O (50 mL). At the end of the addition, the solution was allowed to reach room temperature and stirred for 4 h, cooled again to –78 °C, and (C_5HMe_4)-$SiMe_2Cl$ (2.00 mL, 8.68 mmol) in Et_2O (50 mL) was added. The reaction mixture was warmed up to room temperature and stirred for 15 h. The solvent was removed in vacuo, and hexane (100 mL) was added to the resulting yellow oil. The mixture was filtered, and the solvent was removed from the filtrate under reduced pressure to yield the title compound as a yellow oil. Yield: 2.13 g (60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.48, –0.21 [2 s, 3 H each, Si(CH_3)$_2$], 1.31 (m, 1 H, 14-H_{eq}), 1.79, 1.83, 1.96, 1.98 [4s, 3 H each, C_5(CH_3)$_4$], 2.08 (m, 3 H, 14-H_{ax}, 11-H, 11′-H), 2.68 (m, 2 H, 10-H, 10′-H), 3.01 (s, 1 H, 1-H), 3.49 (s, 1 H, 16-H), 3.74 (m, 2 H, 13-H_{ax}, 15-H_{ax}), 4.10 (m, 2 H, 13-H_{eq}, 15-H_{eq}), 4.59 (m, 1 H, 12-H), 6.21 (m, 1 H, 2-H), 7.14 (m, 1 H, 6-H), 7.22 (m, 1 H, 7-H), 7.38 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.62, –4.72 [Si(CH_3)$_2$], 11.27, 11.31, 14.72, 14.80 [C_5(CH_3)$_4$], 25.66 (C-11), 26.31 (C-14), 31.52 (C-10), 42.69 (C-1), 54.06 (C-16), 67.82 (C-13), 67.91 (C-15), 104.61 (C-12), 121.31 (C-5), 123.31 (C-8), 125.03 (C-6), 126.86 (C-7), 127.90 (C-2), 119.01 (C-3), 120.12 (C-4), 122.05 (C-9), 124.09, 124.98, 126.02, 129.63 [C_5(CH_3)$_4$] ppm. $C_{26}H_{36}O_2Si$ (408.65): calcd. C 76.42, H 8.88; found C 76.39, H 8.92.

[$SiMe_2${1-$C_9H_6CH_2(C_5H_9O)$}{C_5HMe_4}] (5): The synthesis of **5** was carried out in an identical manner to that of **4**. Compound **2** (2.00 g, 9.33 mmol), *n*BuLi (5.83 mL, 9.33 mmol), and (C_5HMe_4)-$SiMe_2Cl$ (2.1 mL, 9.33 mmol). Yield: 2.31 g (63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.38, –0.08 [2 s, 3 H each, Si(CH_3)$_2$], 1.57 (m, 6 H, 12-H_{ax}, 12-H_{eq}, 13-H_{ax}, 13-H_{eq}, 14-H_{ax}, 14-H_{eq}), 1.92, 1.93, 2.05, 2.08 [4 s, 3 H each, C_5(CH_3)$_4$], 2.72 (m, 1 H, 10-H), 2.92 (m, 1 H, 10′-H), 3.12 (s, 1 H, 1-H), 3.39 (s, 1 H, 16-H), 3.51 (m, 1 H, 15-H_{ax}), 3.69 (m, 1 H, 11-H), 4.06 (m, 1 H, 15-H_{eq}), 6.34 (m, 1 H, 2-H), 7.23 (m, 1 H, 6-H), 7.32 (m, 1 H, 7-H), 7.48 (m, 2 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.26, –4.36 [Si(CH_3)$_2$], 11.47, 11.60, 15.01, 15.10 [C_5(CH_3)$_4$], 23.87 (C-12), 26.39 (C-13), 32.23 (C-14), 35.42 (C-10), 43.08 (C-1), 55.05 (C-16), 68.91 (C-15), 77.37 (C-11), 132.30 (C-2), 123.91 (C-5), 124.95 (C-8), 119.46 (C-6), 123.29 (C-7), 119.37 (C-3), 120.22 (C-4), 125.11 (C-9), 123.99, 124.12, 125.22, 126.02 [C_5(CH_3)$_4$] ppm. $C_{26}H_{36}OSi$ (392.65): calcd. C 79.53, H 9.24; found C 79.63, H 9.21.

[Zr{η^5-$C_9H_6C_2H_4(C_4H_7O_2)$}$_2$$Cl_2$] (6): A cooled (–78 °C) slurry of [$ZrCl_4$] (1.01 g, 4.34 mmol) in toluene (80 mL) was rapidly added to a cooled (–78 °C) solution of $Li_2\{1\text{-}C_9H_7C_2H_4(C_4H_7O_2)\}$ in Et_2O (80 mL), which was obtained by treatment of **1** (2.00 g, 8.68 mmol) with *n*BuLi (5.4 mL, 8.68 mmol). The reaction mixture was stirred for 30 min at –20 °C and then overnight at room temperature. The solvent was removed in vacuo and toluene (60 mL) was added. The yellow suspension was filtered through a G4 frit with Celite. The filtrate was evaporated to dryness under reduced pressure to yield a yellowish product. The product was washed with hexane (40 mL), and the residue was dried to give a yellow solid. Yield: 0.83 g (31%), *rac*/*meso*, 50:50. ^{1}H NMR (500 MHz, CD_2Cl_2, *rac* isomer): δ = 1.30 (m, 2 H, 14-H_{eq}), 1.80 (m, 4 H, 11-H, 11′-H), 2.18 (m, 2 H, 14-H_{ax}), 2.78 (m, 2 H, 10-H), 3.02 (m, 2 H, 10′-H), 3.68 (m, 4 H, 13-H_{ax}, 15-H_{ax}), 4.09 (m, 4 H, 13-H_{eq}, 15-H_{eq}), 4.41 (t, *J* = 4.5 Hz, 2 H, 12-H), 5.80 (d, *J* = 3.1 Hz, 2 H, 3-H), 6.07 (d, *J* = 3.1 Hz, 2 H, 2-H), 7.23 (m, 2 H, 6-H), 7.27 (m, 2 H, 7-H), 7.60 (m, 4 H, 5-H, 8-H) ppm. ^{1}H NMR (500 MHz, CD_2Cl_2, *meso* isomer): δ = 1.32 (m, 2 H, 14-H_{eq}), 1.84 (m, 4 H, 11-H, 11′-H), 2.07 (m, 2 H, 14-H_{ax}), 2.85 (m, 2 H, 10-H), 3.06 (m, 2 H, 10′-H), 3.70 (m, 4 H, 13-H_{ax}, 15-H_{ax}), 4.08 (m, 4 H, 13-H_{eq}, 15-H_{eq}), 4.45 (t, *J* = 4.4 Hz, 2 H, 12-H), 5.68 (d, *J* = 3.3 Hz, 2 H, 3-H), 6.28 (d, *J* = 3.3 Hz, 2 H, 2-H), 7.22 (m, 4 H, 6-H, 7-H), 7.44 (m, 2 H, 5-H), 7.60 (m, 2 H, 8-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, *rac*/*meso* mixture): δ = 22.36 (C-10, *meso*), 22.61 (C-10, *rac*), 25.75 (C-14, *rac* and *meso*), 35.30 (C-11, *rac* and *meso*), 66.79 (C-13, *rac* and *meso*), 66.87 (C-15, *rac* and *meso*), 99.30 (C-3, *meso*), 99.46 (C-3, *rac*), 101.39 (C-12, *rac*), 101.40 (C-12, *meso*), 120.38 (C-2, *meso*), 122.29 (C-2, *rac*), 123.88–127.25 (C-5, C-6, C-7, C-8, *rac* and *meso*), 131.14 (C-1, *rac*), 137.85–138.86 (C-4, C-9, *rac* and *meso*) ppm. $C_{30}H_{34}Cl_2O_4Zr$ (620.72): calcd. C 58.05, H 5.52; found C 58.10, H 5.49.

[Zr{η^5-$C_9H_6C_2H_4(C_3H_5O_2)$}$_2$Cl$_2$] (7): The synthesis of **7** was carried out in an identical manner to that of **6**. Compound **2** (2.00 g, 9.25 mmol), *n*BuLi (5.7 mL, 9.25 mmol), and [$ZrCl_4$] (1.08 g, 4.62 mmol). Yield: 0.71 g (26%), *rac*/*meso*, 63:37. ^{1}H NMR (500 MHz, CD_2Cl_2, *rac* isomer): δ = 1.82 (m, 4 H, 11-H, 11′-H), 2.78 (m, 2 H, 10-H), 2.98 (m, 2 H, 10′-H), 3.79 (m, 4 H, 13-H_{syn}, 14-H_{syn}), 3.92 (m, 4 H, 13-H_{anti}, 14-H_{anti}), 4.78 (t, *J* = 4.6 Hz, 2 H, 12-H), 5.75 (d, *J* = 3.1 Hz, 2 H, 3-H), 6.01 (d, *J* = 3.1 Hz, 2 H, 2-H), 7.20 (m, 4 H, 6-H, 7-H), 7.39, 7.53 (2 d, *J* = 8.8 Hz, 2 H each, 5-H, 8-H) ppm. ^{1}H NMR (500 MHz, CD_2Cl_2, *meso* isomer): δ = 1.83 (m, 4 H, 11-H, 11′-H), 2.86, 3.09 (2 m, 2 H each, 10-H, 10′-H), 3.79 (m, 4 H, 13-H_{syn}, 14-H_{syn}), 3.90 (m, 4 H, 13-H_{anti}, 14-H_{anti}), 4.81 (t, *J* = 4.6 Hz, 2 H, 12-H), 5.64 (d, *J* = 3.1 Hz, 2 H, 3-H), 6.21 (d, *J* = 3.1 Hz, 2 H, 2-H), 7.22 (m, 4 H, 6-H, 7-H), 7.56, 7.60 (2 d, *J* = 8.8 Hz, 2 H each, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, *rac*/*meso* mixture): δ = 22.23 (C-10, *meso*), 22.53 (C-10, *rac*), 33.82–33.91 (C-11, *rac* and *meso*), 64.92–64.95 (C-13, C-14, *rac* and *meso*), 99.18 (C-3, *meso*), 99.27 (C-3, *rac*), 103.72 (C-12, *rac*), 104.01 (C-12, *meso*), 120.34 (C-2, *rac*), 121.95 (C-2, *meso*), 123.84, 125.65 (C-5, C-8, *meso*), 125.53, 126.26 (C-6, C-7, *meso*), 124.54, 126.10 (C-5, C-8, *rac*), 126.00, 126.34 (C-6, C-7, *rac*), 127.32 (C-1, *meso*), 127.78 (C-1, *rac*), 131.25–138.79 (C-4, C-9, *rac* and *meso*) ppm. $C_{28}H_{30}Cl_2O_4Zr$ (592.67): calcd. C 56.74, H 5.10; found C 56.81, H 5.14.

[Zr{η^5-$C_9H_6CH_2(C_5H_9O)$}$_2$Cl$_2$] (8): The synthesis of **8** was carried out in an identical manner to that of **6**. Compound **3** (2.00 g, 9.33 mmol), *n*BuLi (5.8 mL, 9.33 mmol), and [$ZrCl_4$] (1.09 g, 4.66 mmol). Yield: 0.77 g (28%). ^{1}H NMR (500 MHz, CD_2Cl_2, *rac* isomer): δ = 1.22 (m, 2 H, 12-H_{ax}), 1.35 (m, 2 H, 12-H_{eq}), 1.41 (m, 2 H, 14-H_{ax}), 1.43 (m, 2 H, 14-H_{eq}), 1.45 (m, 2 H, 13-H_{ax}), 2.61 (dd, *J* = 14.6 Hz, *J* = 8.4 Hz, 2 H, 10-H), 3.00 (dd, *J* = 14.6 Hz, *J* = 8.4 Hz, 2 H, 10′-H), 3.18 (m, 2 H, 15-H_{ax}), 3.26 (m, 2 H, 11-H), 3.81 (m, 2 H, 15-H_{eq}), 5.80 (d, *J* = 3.0 Hz, 2 H, 3-H), 6.19 (d, *J* = 3.0 Hz, 2 H, 2-H), 7.19 (m, 4 H, 6-H, 7-H), 7.52 (m, 4 H, 5-H, 8-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 23.43 (C-13), 25.90 (C-12), 32.07 (C-14), 35.26 (C-10), 68.42 (C-15), 77.89 (C-11), 100.11 (C-3), 118.70 (C-1), 123.05 (C-2), 123.83 (C-5), 125.77 (C-8), 125.50 (C-6), 125.99 (C-7), 126.38, 126.61 (C-4, C-9) ppm. $C_{30}H_{34}Cl_2O_2Zr$ (620.72): calcd. C 61.20, H 5.82; found C 61.10, H 5.79.

[Zr{Me_2Si(3-η^5-$C_9H_5C_2H_4(C_4H_7O_2)$)(η^5-C_5Me_4)}Cl$_2$] (9): A cooled (–78 °C) slurry of [$ZrCl_4$] (1.14 g, 4.89 mmol) in toluene (80 mL) was rapidly added to a cooled (–78 °C) solution of $Li_2[\{C_9H_6C_2H_4(C_3H_5O_2)\}\{C_5Me_4\}SiMe_2]$ in Et_2O (80 mL), which was obtained by treatment of **4** (2.00 g, 4.89 mmol) with *n*BuLi (6.1 mL, 9.78 mmol). The reaction mixture was stirred for 30 min at –20 °C and then overnight at room temperature. The solvent was removed in vacuo and toluene (60 mL) was added. The yellow suspension was filtered through a G4 frit with Celite. The filtrate was evaporated to dryness under reduced pressure to yield a yellowish product. The product was washed with hexane (40 mL), and the residue was dried to give a yellow solid. Yield: 0.61 g (22%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.93, 1.34 [2 s, 3 H each, Si(CH_3)$_2$], 1.34 (d, *J* = 13.7 Hz, 1 H, 14-H_{eq}), 1.90, 1.90, 1.95, 2.01 [4 s, 3 H each, C_5(CH_3)$_4$], 2.09 (m, 1 H, 14-H_{ax}), 2.11 (m, 2 H, 11-H, 11′-H), 3.04 (m, 2 H, 10-H, 10′-H), 3.74 (m, 2 H, 13-H_{ax}, 15-H_{ax}), 4.11 (m, 2 H, 13-H_{eq}, 15-H_{eq}), 4.51 (t, *J* = 5.1 Hz, 1 H, 12-H), 5.60 (s, 1 H, 2-H), 7.06 (dd, *J* = 8.1 Hz, *J* = 4.1 Hz, 1 H, 6-H), 7.34 (dd, *J* = 8.1 Hz, *J* = 4.1 Hz, 1 H, 7-H), 7.46 (d, *J* = 8.1 Hz, 1 H, 5-H), 7.60 (d, *J* = 8.1 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 1.09, 1.40 [Si(CH_3)$_2$], 12.15, 12.48, 14.67, 15.29 [C_5(CH_3)$_4$], 23.19 (C-10), 25.81 (C-14), 35.27 (C-11), 66.86, 66.88 (C-13, C-15), 84.61 (C-3), 95.74 (C-18), 101.70 (C-12), 116.30 (C-2), 124.03 (C-1), 124.40 (C-5), 125.42 (C-8), 126.18, 126.30 (C-6, C-7), 127.86 (C-6), 126.30 (C-7), 127.86–13.80 (C-19, C-20, C-21, C-22), 134.92, 135.34 (C-4, C-9) ppm. $C_{26}H_{34}Cl_2O_2SiZr\cdot C_7H_8$ (660.90): calcd. C 59.97, H 6.41; found C 59.95, H 6.45.

[Zr{Me_2Si(3-η^5-$C_9H_5CH_2(C_5H_9O)$)(η^5-C_5Me_4)}Cl$_2$] (10): The synthesis of **10** was carried out in an identical manner to that of **9**. Compound **5** (2.00 g, 5.09 mmol), *n*BuLi (6.4 mL, 10.18 mmol), and [$ZrCl_4$] (1.19 g, 5.09 mmol). Yield: 0.65 g (23%). Diastereoisomer **10a** or **10b**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.95, 1.18 [2 s, 3 H each, Si(CH_3)$_2$], 1.48 (m, 5 H, 12-H_{ax}, 12-H_{eq}, 13-H_{ax}, 14-H_{ax}, 14-H_{eq}), 1.87 (m, 1 H, 13-H_{eq}), 1.89, 1.91, 1.94, 2.01 [4s, 3 H each, C_5(CH_3)$_4$], 2.98 (m, 1 H, 10-H), 3.17 (m, 1 H, 10′-H), 3.35 (m, 1 H, 15-H_{ax}), 3.52 (m, 1 H, 11-H), 3.91 (m, 1 H, 15-H_{eq}), 5.69 (s, 1 H, 2-H), 7.05 (m, 1 H, 6-H), 7.33 (m, 1 H, 7-H), 7.48 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.62 (d, *J* = 8.8 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.22, 0.53 [Si(CH_3)$_2$], 11.26, 11.58, 13.74, 14.38 [C_5(CH_3)$_4$], 22.64 (C-13), 25.08, 31.71 (C-12, C-14), 35.47 (C-10), 67.67 (C-15), 76.84 (C-11), 94.81, 94.83 (C-3, C-18), 117.52 (C-2), 123.31–128.14 (C-1, C-5, C-6, C-7, C-8, C-19, C-20, C-21, C-22), 131.75–134.46 (C-4, C-9) ppm. Diastereoisomer **10b** or **10a**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.94, 1.17 [2 s, 3 H each, Si(CH_3)$_2$], 1.48 (m, 5 H, 12-H_{ax}, 12-H_{eq}, 13-H_{ax}, 14-H_{ax}, 14-H_{eq}), 1.81 (m, 1 H, 13-H_{eq}), 1.88, 1.90, 1.94, 2.00 [4 s, 3 H each, C_5(CH_3)$_4$], 2.98 (m, 1 H, 10-H), 3.11 (m, 1 H, 10′-H), 3.27 (m, 1 H, 15-H_{ax}), 3.45 (m, 1 H, 11-H), 3.91 (m, 1 H, 15-H_{eq}), 5.62 (s, 1 H, 2-H), 7.05 (m, 1 H, 6-H), 7.33 (m, 1 H, 7-H), 7.48 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.52 (d, *J* = 8.8 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.10, 0.55 [Si(CH_3)$_2$], 11.38, 11.47, 13.79, 13.97 [C_5(CH_3)$_4$], 22.57 (C-13), 25.05, 30.98 (C-12, C-14), 35.93 (C-10), 67.58 (C-15), 76.82 (C-11), 94.71, 94.73 (C-3, C-18), 117.52 (C-2), 123.31–128.14 (C-1, C-5, C-6, C-7, C-8, C-19, C-20, C-21, C-22), 131.75–134.46 (C-4, C-9) ppm. $C_{26}H_{34}Cl_2OSiZr$ (552.76): calcd. 56.49, H 6.20; found C 56.61, H 6.22.

thf-Modified $MgCl_2$ Support: Anhydrous magnesium chloride, dried for 2 h at 393 K, was mixed with tetrahydrofuran for 24 h at room temperature with a thf/$MgCl_2$ molar ratio of 20. The $MgCl_2(thf)_2$ complex was precipitated by the addition of purified *n*-hexane. The solid was filtered off, washed thoroughly with *n*-hexane, and dried in vacuo at 333 K. The support wt.-% content of Mg and C was determined by atomic absorption spectrometry (AAS), which gave results consistent with the empirical formula $MgCl_2(thf)_{1.25}$. FTIR analysis revealed a band due to tetrahydrofuran bound to magnesium chloride at 1033 cm^{-1}, whereas a band due to free thf at 1080 cm^{-1} was not observed.

X-ray Crystal Structure Determination of 9: A summary of the crystallographic data for **9**·C_7H_8 is given in Table 4. The single crystal was mounted on a glass fiber and transferred to a Bruker X8 APEX II CCD-based diffractometer, at $T = 100$ K, equipped with a graphite-monochromated Mo-K_α radiation source ($\lambda = 0.71073$ Å) and using 0.3° ω-scan frames covering a complete sphere of the reciprocal space up to $\theta_{max} = 28$. Data were integrated by using SAINT[18] and an absorption correction was performed with the program SADABS.[19] The software package SHELXTL version 6.12[20] was used for space group determination, structure solution, and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed with a "riding model" and included in the refinement at calculated positions. CCDC-652041 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystal data and structure refinement for **9**·C_7H_8.

Empirical formula	$C_{34}H_{42}Cl_2O_2SiZr$
Formula weight	660.88
Temperature [K]	100(2)
λ [Å]	0.71073
Crystal system	Orthorhombic
Space group	$Pca2_1$
a [Å]	10.676(1)
b [Å]	12.278(1)
c [Å]	23.589(2)
V [Å^3]	3091.9(5)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.420
μ [mm^{-1}]	0.596
F(000)	1376
Crystal size [mm^3]	0.34 × 0.22 × 0.19
θ range for data collection [°]	1.73 to 27.91
Index ranges	$-13 \le h \le 13$
	$-15 \le k \le 16$
	$-31 \le l \le 30$
Reflections collected	20285
Independent reflections	7088 [$R_{int} = 0.0510$]
Data/restraints/parameters	7088/1/359
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0446$, $wR_2 = 0.0995$
R indices (all data)	$R_1 = 0.0670$, $wR_2 = 0.1141$
Absolute structure parameter	–0.05(5)
Largest diff. peak and hole [e Å^{-3}]	1.267 and –1.057

Polymerization Experiments: Polymerizations (three runs per catalyst) for soluble catalysts were carried out in a RADLEYS CAROUSEL multireactor, equipped with pressurized 25-mL glass vials with toluene as a solvent. This kind of reactor allowed comparative preliminary catalytic studies to be performed with the use of minimal amounts of reagents and solvents, and minimization of the waste products. Catalysts (6 µmol) were treated with the appropriate quantity of a commercial solution of MAO in toluene for 15 min. Toluene, $Al(iBu)_3$ scavenger (1 mL), and activated catalyst were introduced in this order (total volume 15 mL) into the reactor, and the temperature was maintained at 343 K. The nitrogen atmosphere was removed and a continuous flow of ethylene (1.2 bar) was introduced over 30 min.

For supported catalysts, a similar procedure was followed by using a 250-mL glass reactor. The corresponding solid containing near 6 µmol of supported complex (approx. 100 mg), was suspended in toluene (10 mL) and treated with a commercial solution of MAO in toluene (0.8 mL, Al/Zr ca. 200) for 15 min. Toluene, $Al(iBu)_3$ scavenger (1 mL), and activated catalyst were introduced in this order (total volume 100 mL) into the reactor, and the temperature was maintained at 343 K. The nitrogen atmosphere was removed and a continuous flow of ethylene (1.2 bar) was introduced over 30 min.

In both cases, the reaction mixture was then quenched by the addition of acidified methanol. The polymer was collected by filtration, washed with methanol, and dried under vacuum at room temperature for 24 h.

No activity was detected in absence of MAO with TIBA as a cocatalyst.

Acknowledgments

We gratefully acknowledge financial support from the Ministerio de Educación y Ciencia, Spain (Grant No. CTQ2006-11845), and the Junta de Comunidades de Castilla-La Mancha (Grant No. PBI-05-029).

---

[1] a) G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347–1376; b) M. R. Ribeiro, A. Deffieux, M. F. Portela, *Ind. Eng. Chem. Res.* **1997**, *36*, 1224–1237.
[2] W. Kaminsky, D. Arrowsmith, C. Strübel, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2959–2968.
[3] R. Goertzki, G. Fink, B. Tesche, B. Steinmetz, R. Rieger, W. Uzick, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 677–682.
[4] P. Roos, G. G. Meier, J. J. C. Samson, G. Weicker, K. R. Westerterp, *Macromol. Rapid Commun.* **1997**, *18*, 319–324.
[5] J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* **2005**, *105*, 4073–4147.
[6] K. Soga, T. Arai, T. Uozumi, *Polymer* **1997**, *38*, 4993–4995.
[7] J. P. McNally, U.S. Patent 5,698,487, **1997**.
[8] M. W. Holtkamp, U.S. Patent 6,147,173, **2000**.
[9] V. Busico, M. Guardasole, R. Cipullo, L. Resconi, G. Morini, *PCT Int. Appl. WO 2004078804*, **2004**.
[10] C. Alonso-Moreno, A. Antiñolo, F. Carrillo-Hermosilla, P. Carrión, I. López-Solera, A. Otero, S. Prashar, J. Sancho, *Eur. J. Inorg. Chem.* **2005**, 2924–2934.
[11] C. Alonso-Moreno, A. Antiñolo, F. Carrillo-Hermosilla, P. Carrión, A. Otero, J. Sancho, E. Villaseñor, *J. Mol. Catal. A* **2004**, *220*, 285–295.
[12] P. Carrión, F. Carrillo-Hermosilla, C. Alonso-Moreno, A. Otero, A. Antiñolo, J. Sancho, E. Villaseñor, *J. Mol. Catal. A* **2006**, *258*, 236–245.
[13] S. C. Yoon, T. K. Han, B. W. Woo, H. Song, S. I. Woo, J. T. Park, *J. Organomet. Chem.* **1997**, *534*, 81–87.
[14] H. G. Alt, M. Jung, W. Milius, *J. Organomet. Chem.* **1998**, *558*, 111–121.
[15] E. Samuel, M. D. Rausch, *J. Am. Chem. Soc.* **1973**, *95*, 6263–6267.
[16] P. Beagly, P. Davies, H. Adams, C. White, *Can. J. Chem.* **2001**, *79*, 731–741.

[17] E. A. H. Griffiths, I. R. Gould, S. Ramdas, *Chem. Commun.* **1998**, 2177–2178.
[18] *SAINT+: Area-Detector Integration Program (v7.12a)*, Bruker-Nonius AXS, Madison, Wisconsin, USA, **2004**.
[19] G. M. Sheldrick, *SADABS: A Program for Empirical Absorption Correction (v.2004/1)*, University of Göttingen, Göttingen, Germany, **2004**.
[20] *SHELXTL-NT: Structure Determination Package (v.6.12)*, Bruker-Nonius AXS, Madison, Wisconsin, USA, **2001**.

Received: September 4, 2007