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Synthesis and characterization of new one-carbon-bridged titanocene and zirconocene derivatives

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Abstract

A variety of new chiral one-carbon-bridged metallocene derivatives of titanium and zirconium has been prepared. Addition of the anions of cyclopentadiene, indene and fluorene to 6-t-butylfulvene produced the ligands t-BuCH(C_5H_5)R (R = C_5H_5, **8**; C_9H_7, **9**; $C_{13}H_9$,**10**). The reaction of the ligands **8–10** with n-BuLi produced the corresponding bis-anions, which were reacted with titanium or zirconium tetrachloride at low temperature (−78°C), to produce the complexes t-BuCH(η^5-C_5H_4)(R)MCl_2 (R = η^5-C_5H_4, M = Ti, **11**; R = η^5-C_5H_4, M = Zr, **12**, R = η^5-C_9H_6, M = Ti, **14**; R = η^5-C_9H_6, M = Zr, **15**; R = η^5-$C_{13}H_8$, M = Zr, **16**). The chlorine atoms in complexes **11** and **16** can be easily replaced by methyl groups producing the corresponding dimethyl derivatives **13** and **17**.

Keywords: Titanium; Zirconium; Metallocenes

1. Introduction

In recent years, great interest has been focused on the use of Group 4 metallocenes as homogeneous Ziegler-Natta catalysts. The symmetry of the complex was found to have a decisive effect in the process of stereoregulation. The achiral systems, bis(cyclopentadienyl)titanium dichloride (**1**) and its zirconium analog (**2**) produce only atactic polypropylene in low yields [1]. The racemic form of Et(Ind)$_2$TiCl$_2$ (**3**) produces isotactic polypropylene [2] and its zirconium analog shows extremely high activities [3]. The complex Me$_2$C(Cp)-(Flu)HfCl$_2$ (**4**) and its zirconium analog (**5**) produce highly syndiotactic polypropylene with high activities [4]. The mechanism of polymerization is proposed to involve the alternating coordination of both prochiral faces of the monomer [4,5]. Other bridging systems containing silicon have also been succesfully used [6]. The asymmetric system, *anti*-MeCH(C_5Me_4)(Ind)TiCl$_2$ (**6**) produces a partially crystalline polymer with thermoplastic elastomeric behavior [7].

In order to better understand the role played by the symmetry of the metallocene catalyst precursor in the polymerization of α-olefins, we have undertaken the synthesis of a variety of metallocene derivatives of titanium and zirconium with systematic changes of the symmetry, the bridge, and the cyclopentadienyl ring. As a continuation of a previous communication [8], we wish to report here the complete synthesis and characterization of new ansa-metallocenes with asymmetric bridges.

2. Results and discussion

One of the limitations in studying two-carbon-bridged metallocenes is the difficult synthesis of mixed cyclopentadienyl systems and asymmetric chiral bridges. These problems could be overcome with the synthesis of one-carbon-bridges, with variations of the symmetry in the bridge. The addition of anions to fulvenes is an excellent route for the synthesis of cyclopentadienyl-one-carbon-bridged metallocenes. The choice of substituents in the 6-position of the fulvene and the appropriate anion generates a variety of possibilities.

Starting with 6-t-butylfulvene (**7**) and either cyclopentadienyl, indenyl or fluorenyl anions, the ligands

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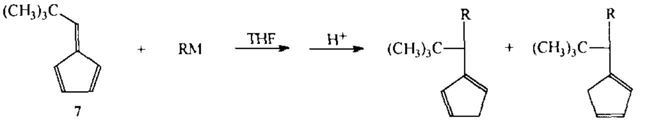
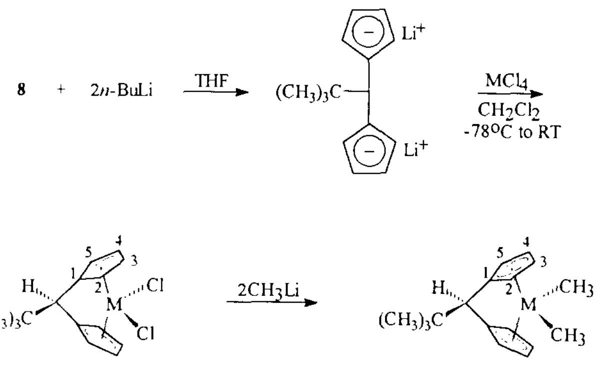
8, **9** and **10** were obtained as a mixture of isomers (as observed by ^{1}H NMR) after hydrolysis and work-up. Compounds **9** and **10** contain an asymmetric center on the bridging carbon (the isomers of compound **8** in which the the two cyclopentadienyl rings have different arrangements of the diene, are also chiral). In all cases the addition reaction aromatizes the cyclopentadienyl ring originally forming the fulvene. After hydrolysis and extraction with diethyl ether, the products were purified by chromatography on a small silica gel column to afford reasonably pure materials. CpLi was not reactive enough towards the addition to the hindered fulvene **7**. It was then necessary to use CpNa or CpK in THF in order to obtain a reasonable yield of **8**. All organic compounds synthesized were heat- and light-sensitive to produce insoluble materials that were not characterized, but could correspond to products of successive dimerization and polymerization. Attempts to vacuum distill **8** and **9** produced considerable decomposition.



M = K for R = C_5H_5;
Li for R = C_9H_7, $C_{13}H_9$

R = C_5H_5, **8**; C_9H_7, **9**;
$C_{13}H_9$, **10**.

The synthesis of the ansa-metallocenes followed the usual procedure using methylene chloride as a solvent, which in our hands gave better results than the widely used THF method. The organic ligands **8**–**10** were treated with two equivalents of n-butyllithium to produce the corresponding dilithium salts, which were reacted with titanium or zirconium tetrachloride at low temperature in methylene chloride. Starting with ligand **8**, the titanium complex **11** and the zirconium derivative **12** were obtained. Compound **11** was characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry and elemental analysis. The ^{1}H NMR spectrum of **11** shows a sharp singlet at 1.33 ppm assigned to the t-butyl group. The singlet at 3.83 ppm is due to the proton on the bridge. There are four multiplets between 5.49 and 7.05 ppm that correspond to the four non-equivalent protons on the cyclopentadienyl rings. Due to their inclination, each cyclopentadienyl group produces an anisotropic shielding for the protons on the other ring. The distal protons (H-3 and H-4) are more influenced than the proximals (H-2 and H-5) because of their proximity to the central axis of the opposite ring, producing two sets of signals. At the same time, the t-butyl group shields the protons located on its side of the framework (confirmed by NOE experiment). As a result, the multiplets at 5.49, 5.74, 6.85 and 7.05 correspond to H-3, H-4, H-2 and H-5, respectively. The zirconium analog **12** displayed similar spectroscopic behavior.



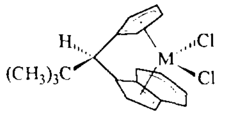
M = Ti, **11**;
Zr, **12**.

M = Ti, **13**

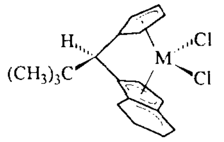
The synthesis of methylated derivatives of metallocenes has been an important instrument in the formation of cationic species, which have been demonstrated to be the real catalyst precursors for the polymerization of ethylene and propylene [5,9].

Compound **11** undergoes easy exchange of the chlorine atoms by reaction with two equivalents of methyllithium in diethyl ether to yield the dimethyl derivative **13**. The ^{1}H NMR spectrum of **13** exhibits two upfield singlets at -0.05 and 0.02 ppm, which correspond to the two non-equivalent methyl groups on the titanium atom. The singlets at 1.12 and 2.89 ppm are assigned to the t-butyl group and the proton on the bridge, respectively, and they are upfield relative to the dichloride **11**. The multiplets at 5.08 and 5.21 ppm correspond to the distal protons on the cyclopentadienyl groups and are upfield relative to the dichloride **11**. Surprisingly, the multiplets for the proximal protons on the cyclopentadienyl group (6.97 and 7.09 ppm) are slightly downfield relative to the dichloride **11**.

By using ligand **9**, the corresponding titanium (**14**) and zirconium (**15**) complexes were obtained. Compounds **14** and **15** can be produced with different arrangements of the groups due to the complete asymmetry of the organic ligand. In the case of compound **14**, the indenyl benzo ring can be positioned on the opposite side of the t-butyl group to produce the *anti*-arrangement **14a**; or the two groups can be located on the same side of the framework, resulting in a *syn*-arrangement **14b**. Both arrangements, *syn*- and *anti*-, are chiral, producing enantiomeric mixtures. The ^{1}H NMR spectrum of **14**, after purification by size exclusion chromatography [10], reveals the presence of the two diasteromers. The t-butyl group in the *syn*-isomer is more deshielded (1.52 ppm) by the anisotropic effect of the benzo ring in the indenyl substituent than the t-butyl group in the anti-isomer (1.43 ppm). The ratio of *syn*- versus *anti*-isomers varies and depends on many factors. From the ^{1}H NMR spectrum of the crude material, it is observed that the *anti*-isomer predominates, as expected for steric reasons, while the crystallized product favors the *syn*-isomer. The more symmetric distribution of the groups in the *anti*-isomer imparts a different solubility behavior to that of the *syn*-isomer. This feature was taken into consideration and the *anti*-isomer **14a**, being more soluble, could be separated from the mixture by repeated recrystallizations from hexane.



M = Ti, **14a**;
Zr, **15a**.

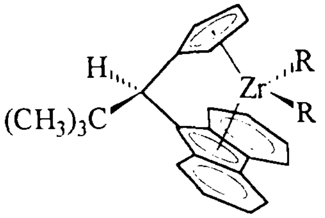


M = Ti, **14b**;
Zr, **15b**.

Compound **15** displayed similar behavior to **14**. Several attempts to purify **15** crystallization or by size-exclusion chromatography failed. Compound **15** is very sensitive in solution to air and moisture, and it was always mixed with impurities that appeared in the ^{1}H NMR spectrum as broad signals between 0.5 and 1.4 ppm. Analysis of the mass spectrum of **15** reveals the presence of high molecular weight materials besides the desired complex. The highest peak corresponds to a structure with two organic ligands on one zirconium atom (L_2ZrCl_2) with a consistent fragmentation pattern ($[L_2ZrCl_2]^+$, m/e 660; $[L_2ZrCl_2-Cl]^+$, m/e 625; $[L_2ZrCl_2-C_4H_9]^+$, m/e 603; $[L_2ZrCl_2-C_4H_9-Cl]^+$, m/e 568). The rest of the spectrum fits the structure of **15** ($[M]^+$, m/e 410).

The synthesis of metallocenes with bridged ligands could lead in theory to multiple side reactions like the formation of oligomers. This would result in poor yields of the desired ansa-metallocenes. When the organic ligand contains different cyclopentadienyl derivatives (cyclopentadienyl and indenyl, compound **9**; cyclopentadienyl and fluorenyl, compound **10**) the situation becomes more complicated due probably to the favored complexation of the cyclopentadienyl moiety. The impurities accompanying compound **15** could then correspond to a metallocene derivative with two organic ligands linked to a zirconium atom through the cyclopentadienyl rings.

From the ligand **10**, the zirconocene derivative **16** was obtained. The red-orange product was obtained in a relatively highly yield (33%) compared to the other metallocenes of the same family synthesized in this work. The ^{1}H NMR spectrum of **16** exhibits a sharp singlet at 1.52 ppm, which is assigned to the t-butyl group. The proton on the bridge is found at 4.64 ppm. Multiplets at 5.44, 5.87 and 6.20, 6.33 ppm correspond to the distal and proximal protons on the cyclopentadienyl group, respectively. Multiplets between 7.23 and 8.30 ppm are due to the aromatic protons of the fluorenyl group.



R = Cl, **16**; CH_3, **17**.

The chlorine atoms in compound **16** can be replaced with methyl groups. The treatment of **16** with two equivalents of methyllithium in toluene solution gave the dimethyl derivative **17**. Complex **17** was identified by ^{1}H NMR spectroscopy. The two non-equivalent methyl groups on the zirconium display signals at very high field (−1.62 and −1.58 ppm) due to the anisotropy of the fluorenyl group. The t-butyl group and the proton on the bridge appear at 1.39 and 4.12 ppm, respectively, both at higher field relative to the dichloride **16**.

The fluorenyl derivatives **16** and **17** are active catalyst precursors for the syndioselective polymerization of propylene and the results will be described elsewhere [11].

3. Experimental section

3.1. General laboratory material and equipment

All operations were carried out under an argon atmosphere using standard Schlenk, vacuum or glove box techniques [12]. The argon was deoxygenated with BTS catalyst and dried with molecular sieves and P_2O_5. Diethyl ether and THF were predried over sodium wire, and distilled under argon from sodium/potassium alloy. Pentane, hexane, benzene and toluene were distilled under argon directly from sodium/potassium alloy. Methylene chloride was distilled under argon from calcium hydride.

Celite was obtained from Fischer Scientific Co. and used with no pretreatment. Cyclopentadiene was obtained from the cracking of its dimer over boiling decalin. Indene (Fluka) was purified by vacuum distillation from calcium hydride. Fluorene (Fluka) was purified by recrystallization from pentane. Titanium tetrachloride, obtained from Alfa, was distilled under argon and stored over copper wire. Zirconium tetrachloride was obtained from Aldrich. Silica was obtained from M. Woelm and used without any pretreatment. Bio-beads S-X2 were obtained from Bio-Rad and swollen in benzene. 6-t-Butylfulvene was prepared following the literature procedure [13].

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution unless otherwise noted using a Jeol FX-90Q, Varian XL-200 or XL-300 NMR spectrometers using tetramethylsilane (TMS) or the residual solvent signals as reference. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, MA. Electron impact mass spectra were obtained at 70 eV on a Varian CH7 mass spectrometer at the Universität Bayreuth.

3.2. Syntheses

3.2.1. 1,1-bis(cyclopentadienyl)-2,2-dimethylpropane (8)

A solution of cyclopentadiene (2.96 g, 44.8 mmol) in 80 ml of THF was reacted at 0°C with 1.75 g (44.8 mmol) of potassium metal. After stirring at room temperature for 4 h all the metal was consumed and a white suspension of CpK was formed. A solution of 6-t-butylfulvene (6.00 g, 44.8 mmol) in 20 ml of THF was added dropwise at 0°C to the CpK suspension and allowed to warm to room temperature. The mixture was stirred for 10 h and refluxed for another 30 min to produce a dark red solution. The mixture was then hydrolyzed with 200 ml of saturated aqueous ammonium chloride and extracted with 150 ml of diethyl ether. The solvent was removed in vacuo from the organic phase and the remaining brown yellow oil was dissolved in pentane, dried over anhydrous sodium sulfate, and passed through a silica gel plug. Washing with 100 ml of pentane afforded a light yellow solution. The solvent was removed under reduced pressure to produce 6.97 g (77%) of **8** as a pale yellow oil.

^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.95 (s, 9H, $(CH_3)_3C$); 2.91, 3.00 (m, 4H, C_5H_5-saturated); 3.47 (s, 1H, CH-bridge); 6.0–6.7 (m, 6H, C_5H_5-olefinic). MS: m/e 200 $(M)^+$; 155 $(M-3CH_3)^+$; 143 $(M-C_4H_9)^+$; 128 $(C_5H_4{=}C_5H_4)^+$; 57 $(C_4H_9)^+$.

3.2.2. 1-Cyclopentadienyl-1-indenyl-2,2-dimethylpropane (9)

A solution of indene (2.63 ml, 22.4 mmol) in 50 ml of THF was reacted at −20°C with 14.0 ml of n-butyllithium (1.6 M). The temperature was allowed to rise and the solution was stirred for 4 h to produce a dark yellow solution. A solution of 3.00 g (22.4 mmol) of 6-t-butylfulvene in 20 ml of THF was added dropwise at 0°C and stirred at room temperature for 24 h. The reaction mixture was worked-up as for **8** to produce 4.80 g (85.5%) of **9** as a light yellow oil.

^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.11 (s, 9H, $(CH_3)_3C$); 2.97, 3.08 (m, 2H, C_5H_5-saturated); 3.43 (m, 2H, C_9H_7-saturated); 3.88 (m, 1H, CH-bridge); 5.52, 6.0–6.8 (m, 4H, C_5H_5 and C_9H_7-olefinic); 7.1–7.6 (m, 4H, C_9H_7-aromatic). MS: m/e 250 $(M)^+$; 193 $(M-C_4H_9)^+$; 178 $(C_5H_4{=}C_9H_6)^+$; 135 $(M-C_9H_7)^+$; 115 $(C_9H_7)^+$; 65 $(C_5H_5)^+$; 57 $(C_4H_9)^+$.

3.2.3. 1-Cyclopentadienyl-1-fluorenyl-2,2-dimethylpropane (10)

A solution of fluorene (3.72 g, 22.4 mmol) in 50 ml of THF was reacted at 0°C with 14 ml of n-butyllithium (1.6 M). The mixture was stirred at room temperature for 4 h to produce a cherry red solution. A solution of 6-t-butylfulvene (3.00 g, 22.4 mmol) was added dropwise at 0°C and stirred at room temperature for 20 h. The reaction mixture was worked-up as for **8** and the pentane solution (ca. 100 ml) was cooled to −20°C. A white crystalline solid (mp. 61–64°C) was obtained (4.36 g, 65%).

Elemental Analysis for $C_{23}H_{24}$: Calcd: C, 91.95; H, 8.05; Found: C, 91.63; H, 8.08%. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.27 (s, 9H, $(CH_3)_3C$); 2.23, 2.48 (m, 2H, C_5H_5-saturated); 3.34 (m, 1H, $C_{13}H_9$-saturated); 4.34 (bs, 1H, CH-bridge); 5.52–6.10 (m, 3H, C_5H_5-olefinic); 7.2–7.8 (m, 8H, $C_{13}H_9$-aromatic). MS: m/e 300 $(M)^+$; 243 $(M-C_4H_9)^+$; 165 $(C_{13}H_9)^+$; 135 $(M-C_{13}H_9)^+$.

3.2.4. 2,2-Dimethylpropylidene-1,1-bis-(η^5-cyclopentadienyl)titanium dichloride (11)

A solution of the ligand **8** (2.00 g, 9.98 mmol) in 100 ml of THF was cooled to −20°C and reacted with 12.48 ml of 1.6 M n-butyllithium. Upon addition the solution turned dark yellow. The mixture was allowed to warm to room temperature and stirred for 4 h to produce a brown-red solution. The solvent was removed under reduced pressure to produce a yellow solid that was cooled to −78°C and dissolved in 150 ml of cooled methylene chloride. A solution of $TiCl_4$ (1.89 g, 9.98 mmol) in 150 ml of CH_2Cl_2 was cooled to −78°C and then added dropwise to the bis-anion solution via cannula. Upon addition, the color changed to dark brown. The mixture was slowly allowed to warm to room temperature and stirred for 10 h. The solvent was removed under reduced pressure and the remaining brown solid was extracted three times with 150 ml portions of warm hexane. The resulting red solution was evaporated to one-third of its original volume and cooled to −20°C. Dark red crystals of the product were formed (0.16 g, 5%).

Compound **11** can also be prepared in THF. A solution of 5.0 mmol of the bis-anion in 150 ml of THF (from 1.0 g (5 mmol) of ligand **8** and 6.3 ml of 1.6 M n-butyllithium) at −20°C was slowly treated with a solution of $TiCl_4$. 2THF (1.67 g, 5 mmol) in 150 ml of THF. The reaction mixture turned dark brown. Warming to room temperature and stirring for 24 h produced a black mixture. The solvent was evaporated under reduced pressure and the black residue was extracted with hexane and crystallized as in the CH_2Cl_2 method to produce 0.03 g of **11** (2%).

Elemental Analysis for $C_{15}H_{18}Cl_2Ti$: Calcd.: C, 56.82; H, 5.72; Found: C, 56.87; H, 5.94%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.33 (s, 9H, $(CH_3)_3C$); 3.83 (s, 1H, C*H*-bridge); 5.49 (m, 2H, H-3); 5.74 (m, 2H, H-4); 6.85 (m, 2H, H-2); 7.05 (m, 2H, H-5). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.0 ($(CH_3)_3C$); 33.8 ($(CH_3)_3C$); 53.3 (*C*H-bridge); 109.9 (C_5H_4-*ipso*); 110.6; 117.3; 127.7; 134.3 (C_5H_4). MS: *m/e* 316 $(M)^+$; 281 $(M-Cl)^+$; 259 $(M-C_4H_9)^+$; 246 $(M-2Cl)^+$; 223 $(M-C_4H_9-Cl)^+$.

3.2.5. 2,2-Dimethylpropylidene-1,1-bis-(η^5-cyclopentadienyl)dimethyltitatium (13)

A solution of 0.10 g (0.32 mmol) of compound **11** in 50 ml of hexane was cooled to −20°C and 0.50 ml of 1.4 M methyllithium was added dropwise. The color changed immediately from dark-red to orange and a precipitate was observed. The reaction mixture was warmed to room temperature stirred for 1 h and filtered over Celite. The resulting yellow-orange solution was evaporated to one-third of its original volume and cooled to −50°C. Yellow crystals of **13** were formed (0.07 g, 80%).

Elemental Analysis for $C_{17}H_{24}Ti$: Calcd: C, 73.91; H, 8.76; Found: C, 73.81; H, 8.83%. ^1H NMR ($CDCl_3$, 300 MHz): δ −0.05 (s, 3H, CH_3); 0.02 (s, 3H, CH_3); 1.12 (s, 9H, $(CH_3)_3C$); 2.89 (s, 1H, C*H*-bridge); 5.08 (m, 2H, H-3); 5.21 (m, 2H, H-4); 6.97 (m, 2H, H-2); 7.09 (m, 2H, H-5).

3.2.6. 2,2-Dimethylpropylidene-bis-(η^5-cyclopentadienyl) zirconium dichloride (12)

A solution of the ligand **8** (2.00 g, 9.98 mmol) in THF was treated with 12.48 ml of 1.6 M n-butyllithium at −20°C and stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the resulting yellow solid was cooled to −78°C and suspended in 150 ml of cooled CH_2Cl_2. A suspension of $ZrCl_4$ (2.33 g, 10 mmol) in 150 ml of CH_2Cl_2 was cooled to −78°C and added dropwise via cannula to the bis-anion solution. The mixture was slowly allowed to warm to room temperature and the color changed to dark gray. After stirring for 10 h, the solvent was evaporated and the dark residue was extracted three times with 150 ml portions of warm hexane. The solvent was reduced to ca. 50 ml and the light yellow solution was cooled to −20°C. The product crystallized as an off-white solid (0.25 g, 7%).

Compound **12** can also be prepared in THF. To a solution of 10 mmol of the bis-anion in 200 ml of THF (from 2.0 g (10 mmol) of ligand **8** and 12.5 ml of 1.6 n-butyllithium) at −20°C, was added dropwise 200 ml of a THF solution of 3.77 g (10 mmol) of $ZrCl_4.2THF$. The color changed to yellow and after warming to room temperature and stirring for 24 h, the reaction mixture appeared dark gray. The solvent was evaporated under reduced pressure and the dark residue was extracted with hexane and crystallized as in the CH_2Cl_2 method to produce 0.05 g (1.4%) of product.

Elemental Analysis for $C_{15}H_{18}Cl_2Zr$: Calcd: C, 49.99; H, 5.03; Found: C, 49.88; H, 5.03%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.30 (s, 9H, $(CH_3)_3C$); 3.84 (s, 1H, C*H*-bridge); 5.67 (m, 2H, H-3); 5.82 (m, 2H, H-4); 6.53 (m, 2H, H-2); 6.75 (m, 2H, H-5). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.0 ($(CH_3)_3C$); 34.2 ($(CH_3)_3C$); 54.1 (*C*H-bridge); 106.3; 113.3 (C_5H_4); 116.3 (C_5H_4-*ipso*); 119.3; 125.9 (C_5H_4). MS: *m/e* 360 $(M)^+$; 303 $(M-C_4H_9)^+$; 265 $(M-C_4H_9-Cl)^+$; 229 $(M-C_4H_9-2Cl)^+$.

3.2.7. 2,2-Dimethylpropylidene-(η^5-cyclopentadienyl)-(η^5-indenyl)titanium dichloride (14)

A solution of the ligand **9** (2.00 g, 7.99 mmol) in 50 ml of THF was reacted at −20°C with 10.0 ml of n-butyllithium (1.6 M) and stirred at room temperature for 4 h to yield a dark yellow solution. The solvent was removed under reduced pressure and the resulting tan brownish solid was cooled to −78°C and suspended in 150 ml of cooled CH_2Cl_2. A solution of $TiCl_4$ (1.52 ml, 7.99 mmol) in 150 ml of CH_2Cl_2 was cooled to −78°C and added dropwise via cannula to the bis-anion. Upon addition the color changed to dark brown. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The solvent was evaporated and the dark brown residue was extracted with warm hexane until no more green product was observed in solution. The solvent was removed and the remaining green solid was eluted with benzene in a 30 × 2 cm Bio-Beads column. The green product came down after a wide red brown band. The solvent was removed and the solid was recrystallized from toluene-hexane 1:3 at −20°C. The product was obtained as a dark green crystalline solid (0.10 g, 3.4%). Two diastereomers, *anti*-(**14a**) and *syn*-(**14b**), are observed by ^1H NMR. The *anti*-enantiomeric pair **14a** could be separated from the mixture by repeated recrystallizations from hexane.

Elemental Analysis for $C_{19}H_{20}Cl_2Ti$: Calcd.: C, 62.15; H, 5.49; Found: C, 62.37; H, 5.67%. ^1H NMR ($CDCl_3$, 300 MHz): *Anti*-isomer: δ 1.43 (s, 9H, $(CH_3)_3C$); 4.32 (s, 1H, C*H*-bridge); 5.27 (m, 1H), 5.69 (m, 1H) (H-3, H-4); 5.91 (d, 3 Hz, 1H, C_9H_6); 6.65 (m, 1H), 6.76 (m, 1H) (H-2, H-5); 7.02–7.22 (m, 2H, C_9H_6-aromatic); 7.33 (d, 3 Hz, 1H, C_9H_6); 7.46–7.68 (m, 2H, C_9H_6-aromatic). *Syn*-isomer: δ 1.52 (s, 9H, $(CH_3)_3C$); 4.27 (s, 1H, C*H*-bridge); 5.50 (m, 1H), 5.57 (m, 1H) (H-3, H-4); 5.63 (d, 3 Hz, 1H, C_9H_6); 6.62 (m, 1H), 6.76 (m, 1H) (H-2, H-5); 7.09 (d, 3 Hz, 1H, C_9H_6); 7.02–7.22 (m, 2H), 7.46–7.68 (m, 2H) (C_9H_6-aromatic). MS: *m/e* 366 $(M)^+$; 351 $(M-CH_3)^+$; 336 $(M-2CH_3)^+$; 321 $(M-3CH_3)^+$; 309 $(M-C_4H_9)^+$; 274 $(M-C_5H_4-2CH_3)^+$; 237 $(M-C_5H_4-2CH_3-Cl)^+$; 115 $(C_9H_8)^+$.

3.2.8. 2,2-Dimethylpropylidene-(η^5-cyclopentadienyl)-(η^5-indenyl)zirconium dichloride (15)

A solution of the ligand **9** (2.00 g, 7.99 mmol) in 50 ml of THF was reacted at −20°C with 10.0 ml of n-butyllithium (1.6 M) and stirred at room temperature for 4 h to yield a dark yellow solution. The solvent was removed under reduced pressure and the resulting tan brownish solid was cooled to −78°C and suspended in 150 ml of CH_2Cl_2. A suspension of $ZrCl_4$ (1.86 g, 7.99 mmol) in 150 ml of CH_2Cl_2 was cooled to −78°C and slowly added via cannula to the bis-anion. Upon addition the color changed to light yellow. The reaction mixture was slowly warmed to room temperature and stirred for 12 h. At this point, a bright yellow solution with a white solid in suspension was observed. The solvent was evaporated and the residue was extracted with three 150 ml portions of warm hexane. The solvent was removed to leave a bright yellow solid (0.22 g, 6.7%). Purification was attempted by size exclusion chromatography on Bio-Beads and by recrystallization from hydrocarbon solvents but it was impossible to separate the complex from polymeric material. Hence, an analytically pure sample could not be obtained. The complex was unusually sensitive to small amounts of air and moisture to produce a pale yellow insoluble solid. Two diastereomers, *anti*-(**15a**) and *syn*-(**15b**), are observed by ^1H NMR.

^1H NMR ($CDCl_3$, 300 MHz): *Anti*-isomer: δ 1.40 (s, 9H, $(CH_3)_3C$); 4.23 (s, 1H, CH-bridge); 5.54 (m, 1H), 5.81 (m, 1H) (H-3, H-4); 6.22 (d, 4 Hz, 1H, C_9H_6); 6.38 (m, 1H), 6.58 (m, 1H) (H-2, H-5); 6.93 (d, 4 Hz, 1H, C_9H_6); 7.0–7.7 (m, 4H, C_9H_6-aromatic). *Syn*-isomer: δ 1.43 (s, 9H, $(CH_3)_3C$); 4.26 (s, 1H, CH-bridge); 5.64 (m, 1H), 5.85 (m, 1H) (H-3, H-4); 6.03 (d, 4 Hz, 1H, C_9H_6); 6.37 (m, 1H), 6.53 (m, 1H) (H-2, H-5); 6.74 (d, 4 Hz, 1H, C_9H_6); 7.0–7.7 (m, 4H, C_9H_6-aromatic). MS: *m/e* 410 $(M)^+$; 385 $(M-CH_3)^+$; 375 $(M-Cl)^+$; 283 $(M-C_4H_9-2Cl)^+$; 275 $(C_9H_7ZrCl_2)^+$; 115 $(C_9H_7)^+$.

3.2.9. 2,2-Dimethylpropylidene-(η^5-cyclopentadienyl)-(η^5-fluorenyl)zirconium dichloride (16)

A solution of 3.00 g (10.0 mmol) of the ligand **10** in 100 ml of THF was treated at −20°C with 12.5 ml of n-butyllithium (1.6 M). The temperature was allowed to rise and the mixture was stirred at room temperature for 4 h. The resulting dark red solution was evaporated under reduced pressure to produce a pink yellow pyrophoric solid, which was cooled to −78°C and suspended in 150 ml of cooled CH_2Cl_2. A suspension of $ZrCl_4$ (2.33 g, 10.0 mmol) in 150 ml of methylene chloride was cooled to −78°C and added dropwise via cannula to the bis-anion suspension. After the addition was completed, the reaction mixture was slowly allowed to warm to room temperature to produce a bright orange solution with a white solid in suspension. The mixture was filtered over Celite and the solvent was removed under reduced pressure to produce a red orange solid which was washed three times with 100 ml portions of pentane and crystallized from toluene at −50°C. Red-orange crystals were obtained (1.5 g, 33%).

Elemental Analysis for $C_{23}H_{22}Cl_2Zr$: Calcd.: C, 59.98; H, 4.82; Found: C, 60.60; H, 4.97%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.52 (s, 9H, $(CH_3)_3C$); 4.64 (s, 1H, CH-bridge); 5.44 (m, 1H, H-3); 5.87 (m, 1H, H-4); 6.20 (m, 1H, H-2); 6.33 (m, 1H, H-5); 7.23–8.30 (m, 8H, $C_{13}H_8$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 30.1 ($(CH_3)_3C$); 34.8 ($(CH_3)_3C$); 51.1 (CH-bridge); 102.8, 108.0, 108.9, 115.8, 119.8, 120.3, 122.0, 122.4, 123.2, 123.9, 124.7, 125.1, 125.2, 125.7, 126.0, 128.7, 129.5 (only 17 signals are observed for C_5H_4 and $C_{13}H_8$). MS: *m/e* 461 $(M)^+$; 426 $(M-Cl)^+$; 404 $(M-C_4H_9)^+$; 331 $(M-C_4H_9-2Cl)^+$; 295 $(M-C_{13}H_{10})^+$; 243 $(M-C_{13}H_8-C_4H_9)^+$;165 $(C_{13}H_9)^+$.

3.2.10. 2,2-Dimethylpropylidene-(η^5-cyclopentadienyl)-(η^5-fluorenyl)dimethylzirconium (17)

A solution of 0.25 g (0.54 mmol) of **16** in 50 ml of toluene was cooled to −20°C and 0.80 ml of 1.4 M methyllithium was added dropwise. The reaction mixture was stirred for 1 h and slowly changed from red-orange to yellow with a white precipitate in suspension. The mixture was warmed to room temperature, stirred for another hour and filtered over Celite. The resulting orange solution was evaporated to one-half of its original volume and cooled to −20°C. Yellow crystals of **17** were formed (0.07 g, 31%).

^1H NMR ($CDCl_3$, 300 MHz): δ −1.62 (s, 3H, CH_3); −1.58 (s, 3H, CH_3); 1.39 (s, 9H, $(CH_3)_3C$); 4.12 (s, 1H, CH-bridge); 5.30 (m, 1H, H-3); 5.60 (m, 1H, H-4); 6.14 (m, 1H, H-2); 6.25 (m, 1H, H-5); 7.18–7.40 (m, 4H, $C_{13}H_8$); 7.58 (d, 2H, $C_{13}H_8$); 8.20 (dd, 2H, $C_{13}H_8$).

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References

[1] H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, *18* (1980) 99.

[2] J.E. Ewen, *J. Am. Chem. Soc.*, *106* (1984) 6355.

[3] W. Kaminsky, K. Külper, H.H. Brintzinger and F.R.W.P. Wild, *Angew. Chem. Int. Ed. Engl.*, *24* (1985) 507.

[4] J.A. Ewen, R.L. Jones, A. Razavi and J. Ferrara, *J. Am. Chem. Soc.*, *110* (1988) 6255.

[5] A. Razavi and J. Ferrara, *J. Organomet. Chem.*, *435* (1992) 299.

[6] W.A. Herrmann, J. Rohrmann, E. Herdtweck, W. Spaleck and A. Winter, *Angew. Chem. Int. Ed. Engl.*, *28* (1989) 1511; W.

Spaleck, M. Antberg, J. Rohrmann, A. Winter, B. Bachmann, P. Kiprof, J. Behm and W.A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, *31* (1992) 1347.

[7] D.T. Mallin, M.D. Rausch, Y. Lin, S. Dong and J.W.C. Chien, *J. Am. Chem. Soc.*, *112* (1990) 2030.

[8] G.S. Herrmann, H.G. Alt and M.D. Rausch, *J. Organomet. Chem.*, *401* (1991) C5.

[9] W.M. Tsai, M.D. Rausch and J.C.W. Chien, *Appl. Organomet. Chem.*, *7* (1993) 71.

10] Size exclusion chromatography have been used in the purification of oxophilic complexes. See: S. Collins, Y. Hong, R. Ramachandran and N.J. Taylor, *Organometallics*, *10* (1991) 2349; Y. Chen, M.D. Rausch and J.C.W. Chien, *Organometallics*, *13* (1994) 748.

[11] R. Fierro, Z. Yu, M.D. Rausch, S. Dong, D. Alvares and J.C.W. Chien, *J. Polym. Sci.*, in press.

[12] D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*, Mc-Graw-Hill, New York, 1969.

[13] K.J. Stone and R.D. Little, *J. Org. Chem.*, *49* (1984) 1849.