# Some New *exo,exo*-Bis(isodicyclopentadienyl)titanium and -zirconium Dichloride Derivatives: Synthesis, Characterization, and Evaluation as Propene Polymerization Catalysts

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Exo,exo derivatives of the efficient catalyst precursors (diisodicyclopentadienyl)titanium and -zirconium dichloride substituted at the central position have been synthesized. These compounds have been characterized by solution NMR measurements, which also permitted the calculation of rotational barriers. The solid-state structures of *exo,exo*-bis(3-diphenylphosphinoisodicyclopentadienyl)titanium and -zirconium dichloride were determined by X-ray crystallography. Unfortunately, after activation by methylalumoxane, these complexes are shown to serve as poor catalysts for the polymerization of propene.

## Introduction

Homogeneous group 4 metallocene/methylalumoxane Ziegler catalysts have played a very important role in the formation of stereoregular α-olefin polymers.[1] The most common ligands found in titanocene and zirconocene complexes have planar structures as, for example, the $\eta^5$-cyclopentadienyl or indenyl systems. For the isodicyclopentadienyl ligand, group 4 metals can be selectively coordinated to the diastereotopic exo or endo faces, respectively, by carefully selecting the experimental conditions.[2] In the presence of methylalumoxane, some of these complexes exhibit interesting activity and selectivity as homogeneous Ziegler−Natta catalysts.[3] It was demonstrated by dynamic NMR spectroscopy[3] that *exo,exo*-bis(isodicyclopentadienyl)titanium dichloride exhibits a chiral $C_2$-symmetric structure in solution that is characterized by a bislateral (anti) orientation of the annulated bicyclo[2.2.1]heptene moieties at the bent-metallocene wedge. The activation energy for the conformational inversion of that complex is $\Delta G^{\ddagger}_{\rm rot}(198\ {\rm K}) = 9.8 \pm 0.4$ kcal mol$^{-1}$. The rotational barrier of the analogous zirconium dichloride complex is much lower (~6 kcal mol$^{-1}$). This low energy may be the underlying reason for the lack of stereoselectivity (even at low temperature) exhibited by this catalyst in propene polymerization.

Since the preparation of ansa metallocenes derived from isodicyclopentadienyl ligands has not been successful, it was of interest to synthesize *exo,exo*-bis(isodicyclopentadienyl)titanium or -zirconium dichlorides substituted in the central position and to make the complexes as stereorigid as possible to enhance their rotational barriers.

## Results and Discussion

Isodicyclopentadienide anion (**1**) was obtained by conventional reaction of isodicyclopentadiene and *n*-butyllithium in ether at −80 °C.[4] When exposed to various electrophilic reagents in THF solution, **1** gave in each case a mixture of exo and endo isomers **2** and **2′**[5] as defined by NMR analysis. The 3-substituted isodicyclopentadienide anions, generated by subsequent treatment of **2** and **2′** with *n*-butyllithium in tetrahydrofuran, gave rise to metallocenes **4**−**9** in totally

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**Table 1. Comparative 200 MHz $^1H$ NMR Spectral Data for 4−9 (d ppm/TMS; $CDCl_3$ Solution at 298 K)**

| compound | peripheral | bridgehead | exo-ethano bridge | endo-ethano bridge | syn-methano bridge | anti-methano bridge | *R* |
|---|---|---|---|---|---|---|---|
| **4** | 5.82 (s) | 3.29 (s) | 1.80 (d; $J = 7.3$ Hz) | 1.06 (d; $J = 7.3$ Hz) | 1.25 (d; $J = 9.3$ Hz) | 0.82 (d; $J = 9.3$ Hz) | 2.15 (s) |
| **5** | 5.65 (s) | 3.30 (s) | 1.80 (d; $J = 6.8$ Hz) | 1.05 (dd; $J = 7.3$ Hz; $J = 2.4$ Hz) | 1.38 (d; $J = 8.9$ Hz | 1.05 (d; $J = 9.8$ Hz) | 2.16 (s) |
| **6** | 6.05 (s) | 3.30 (s) | 1.82 (d; $J = 7.3$ Hz) | 1.02 (d; $J = 7.3$ Hz) | | 1.35 (s) | 0.17 (s) |
| **7** | 5.93 (s) | 3.32 (s) | 1.81 (d; $J = 6.8$ Hz) | 0.99 (dd; $J = 1.9$ Hz; $J = 7.3$ Hz) | 1.54 (d; $J = 9.3$ Hz) | 1.43 (d; $J = 9.3$ Hz) | 0.17 (s) |
| **8** | 5.97 (s) | 3.34 (s) | 1.89 (d; $J = 7.8$ Hz) | 1.17 (d; $J = 6.3$ Hz) | 1.50 (s) | 1.32 (d; $J = 9.8$ Hz) | 7.24−7.35 (m) |
| **9** | 5.82 (s) | 3.34 (s) | 1.88 (d; $J = 7.3$ Hz) | 1.15 (d; $J = 7.3$ Hz) | 1.58 (d; $J = 9.3$ Hz) | 1.35 (d; $J = 9.8$ Hz) | 7.25−7.36 (m) |

**Table 2. Comparative 50 MHz $^{13}C$ NMR Spectral Data for 4−9 ($\delta$ ppm/TMS; $CDCl_3$ Solution at 298 K)**

| compound | quaternary | ipso cyclopentadienide | peripheral | bridge-head | ethano bridge | methano bridge | *R* |
|---|---|---|---|---|---|---|---|
| **4** | 146.6 | 146.3 | 109.4 | 42.4 | 28.7 | 46.1 | 18.7 |
| **5** | 138.7 | 141.2 | 104.3 | 41.8 | 28.9 | 47.8 | 17.5 |
| **6** | 149.2 | 150.1 | 112.3 | 41.7 | 28.6 | 47.7 | 0.6 |
| **7** | 146.4 | 140.0 | 109.3 | 41.2 | 28.8 | 48.9 | 0.5 |
| **8** | not visible | 149.5 (d; $^1J_{C-P}$ =14.0 Hz) | 111.6 (s l) | 42.6 | 28.6 | 46.6 (d; $J = 11.6$ Hz) | ipso: 137.9 (d; $^1J_{C-P}$ =13.4 Hz)<br>ortho: 134.7 (d; $^2J_{C-P} = 21.4$ Hz)<br>méta: 128.5 (d; $^3J_{C-P} = 7.3$ Hz)<br>para: 129.0 (s) |
| **9** | 144.5 | 138.4 (d; $^1J_{C-P} = 15.9$Hz) | 108.1 (d; $^2J_{C-P} = 9.8$Hz) | 41.9 | 29.0 | 48.1 (d; $J = 7.9$ Hz) | ipso: 137.9 (d; $^1J_{C-P} = 13.4$ Hz)<br>ortho: 134.5 (d; $^2J_{C-P} = 21.3$Hz)<br>méta: 128.4 (d; $^3J_{C-P} = 7.9$Hz)<br>para: 129.0 (s) |

stereoselective $\pi$ complexation processes when reacted with the appropriate metal tri- or tetrahalide.

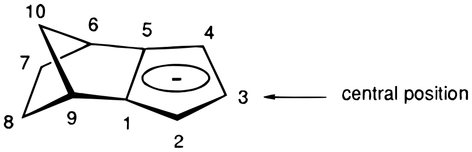
The $^1H$ and $^{13}C$ NMR parameters determined for **4−9** at ambient temperature are compiled in Tables 1 and 2. Assignment of signals to individual protons has been facilitated by reference to similar molecules already published.[6] With regard to the $^{13}C$ NMR spectra, the reported values were obtained by the *J*-modulated spin−echo program and the chemical shifts were identified by comparison to data for other known metallocene dichlorides.[6,7] In accord with our earlier results,[2] $^1H$ and $^{13}C$ NMR chemical shifts of the aliphatic fragment are characteristic of exo isomers. Those signals due to the methano and ethano bridges are particularly well resolved between 0.8 and 1.9 ppm.

As expected, the $^{13}C$ chemical shifts are influenced by the nature of the transition metal. For example, when passing from the titanium complex to its zirconium analogue, the carbons of the Cp ring are shielded on the order of 2.8−11.1 ppm because of decreased electronegativity on the part of the metal. For the ethano and methano bridge carbons, the effect is reversed and is most important for the methano bridge.

In the case of suitably substituted group 4 metallocenes, three different favored conformations may be observed in solution.[8] In the case of the diisodicyclopentadienyltitanium and -zirconium complexes,[3] these could be described as follows: the rotamer characterized by the localization of the two norbornyl groups outside of the Cl−M−Cl angle is termed the bis-lateral (anti) conformation and exhibits $C_2$ symmetry. The bis-central (syn) conformation with $C_{2v}$ symmetry is adopted when each norbornane segment is inside of the Cl−M−Cl angle. The last conformation of $C_1$ symmetry, characterized by a norbornyl group centered on the Cl−M−Cl angle and the other one localized outside of this region, is named lateral-central (gauche-like).

Although all three conformations (Scheme 3) might be present simultaneously in solution at room temperature, the $^1H$ and $^{13}C$ NMR spectra of complexes **4−9** are in accord with an apparent $C_{2v}$-symmetric situation.

**Scheme 1**



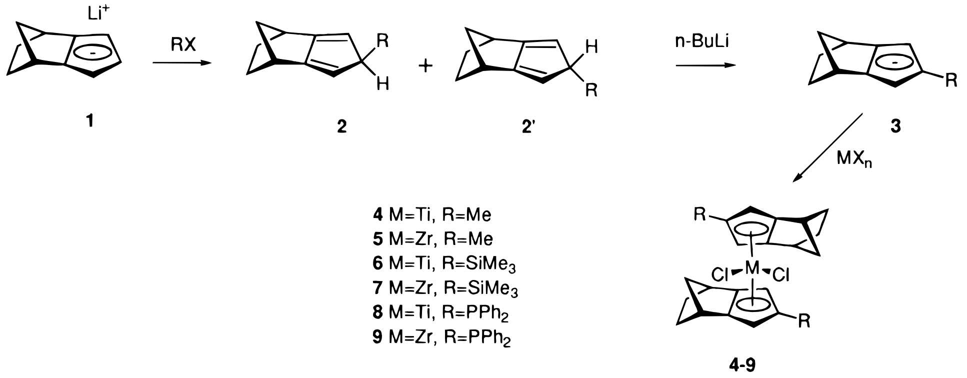
However, this is likely to be the result of a fast equilibrium between metallocene conformers of lower symmetry on the NMR time scale. Decreasing the temperature causes the respective diastereotopic pairs of NMR signals of the less congested anti conformation to separate in the $^1H$ NMR spectrum below their coalescence temperatures. In Table 3 are compiled the results obtained from dynamic NMR experiments. It is noteworthy that the rotational barrier of the substituted titanium complexes is approximately 2 kcal $mol^{-1}$ higher than those of the corresponding bis(isodicyclopentadienyl)titanium dichlorides. The rapid equilibration of conformations of complex **7** cannot be arrested on the $^1H$ NMR time scale.

The molecular structures of **8** and **9** were determined by X-ray diffraction. Two ORTEP representations of **9** are shown in Figure 1. No drawing of the Ti complex is displayed since **8** and **9** are isostructural. Selected bond lengths and angles are reported in Tables 4 and 5. The labeling schemes used for both structures are the same.

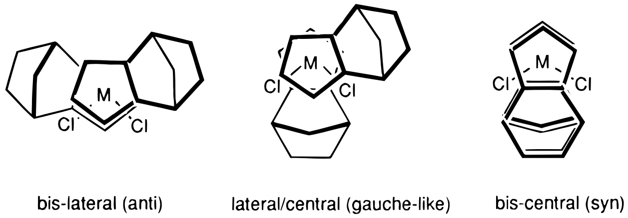
The molecular structures of **8** and **9** correspond to the anti bent-metallocene conformer, which was observed previously for the analogous *exo,exo*-bis(isodicyclopentadienyl)titanium and -zirconium dichlorides.[6] A projection of the substituted isodicyclopentadienyl ligands onto the $MCl_2$ plane shows a bis-lateral conformation with the five-membered rings almost eclipsed. A pseudo 2-fold axis bisects the Cl−M−Cl angle for both structures.

As observed for other pairs of ($\eta^5$-RCp)$_2$M$Cl_2$ compounds with M = Ti or Zr,[6] the Zr−Cl distance is on average 0.08 Å longer than the Ti−Cl bond. These distances are slightly smaller than in the analogous

**Scheme 2**



**Scheme 3**



bis-lateral (anti) lateral/central (gauche-like) bis-central (syn)

**Table 3. Rotational Activation Energies ($\Delta G^{\ddagger}_{\mathrm{rot}}$ kcal mol$^{-1}$)**

| compound | $T_c$ (K) | $\Delta_\nu$ (Hz) | $\Delta G^{\ddagger}_{\mathrm{rot}}$ (kcal mol$^{-1}$) | signal used |
|---|---|---|---|---|
| (isodiCpMe)$_2$TiCl$_2$, **4** | 262 | 105 | 12.1 ± 0.4 | CpH |
| (isodiCpMe)$_2$ZrCl$_2$, **5** | 231 | 165 | 10.4 ± 0.4 | CpH |
| (isodiCpSiMe$_3$)$_2$TiCl$_2$, **6** | 198 | 247 | 8.7 ± 0.4 | bridgehead |
| (isodiCpSiMe$_3$)$_2$ZrCl$_2$, **7** | | | | |
| (isodiCpPPh$_2$)$_2$TiCl$_2$, **8** | 243 | 55 | 11.5 ± 0.4 | bridgehead |
| (isodiCpPPh$_2$)$_2$ZrCl$_2$, **9** | 200 | 33 | 9.6 ± 0.4 | CpH |
| isodiCp$_2$TiCl$_2$ | | | 9.8 ± 0.4[a] | |
| isodiCp$_2$ZrCl$_2$ | | | <7[a] | |

[a] From ref 3.

isodicyclopentadienyl compounds. The Zr−ring centroid distance is on average 0.13 Å longer than the Ti−ring centroid distance, and these distances are slightly larger than in the analogous isodicyclopentadienyl complexes.

The angles about the metal atoms are in the expected ranges with the ring centroid−Zr−ring centroid (129.02°) and Cl−Zr−Cl (92.94°) angles slightly smaller and larger than the respective angles in the titanium structure (131.85° and 91.84°).

The metal−ring carbon distances are larger than in the (isodicyclopentadienyl)$_2$MCl$_2$ (M = Ti or Zr) structures and indicate that the metal−ring interaction is asymmetric. These bond lengths are in the ranges of 2.391−2.449 and 2.375−2.452 Å for the titanium compound and 2.514−2.551 and 2.501−2.559 Å for the zirconium compound.

One of the longer metal−ring carbon distances involves the carbon atom bonded to the phosphido group. In fact, for three out of the four rings in these two structures, that is the longest metal−ring carbon distance observed. Like the other two carbon atom substituents on the Cp ring, the P atom lies significantly out of the least-squares plane through the Cp ring and in the direction away from the metal atom for both structures.

As observed in previous structures involving the isodiCp ligand,[6] there is a slight bending of this ligand about the bond common to the Cp ring and the norbornane fragment. This bending can be described by the dihedral angle between the least-squares planes through atoms C1−C2−C3−C4−C5 and atoms C6−C5−C1−C9 (as an example). For the Ti and Zr structures, these dihedral angles are 13.5(4)/14.1(4)° and 12.6(3)/13.0(3)°, respectively. The bending is in the endo direction.

Complexes **4**−**9** were activated with methylalumoxane[9] to give homogeneous Ziegler-type propene polymerization catalysts. The titanium complexes/MAO catalysts produced atactic polypropylene in toluene solution (2 bar propene pressure, 0 °C, activity $a \approx 7$ g of polymer (g of Ti)$^{-1}$ h$^{-1}$ bar$^{-1}$ for **4**, **6**, and **8**; −20 °C, $a \approx 40$ g of polymer (g of Ti)$^{-1}$ h$^{-1}$ bar$^{-1}$ for **4**, and $a \approx 11$ g of polymer in the same units for **6** and **8**).

The corresponding zirconium/MAO catalysts are more active and stereoselective. In the temperature range of −50 to +10 °C, the **7**/MAO catalyst exhibits a maximum activity at −20 °C (activity (g of polymer (g of Zr)$^{-1}$ h$^{-1}$ bar$^{-1}$): $a \approx 286$(−50 °C), 517(−40 °C), 633(−20 °C), 280(0 °C), 86(+10 °C)). The molecular weight $M_\eta$ decreases from ca. 234 600 to ca. 18 500 within this temperature range. For the **5**/MAO catalyst, the activity is maximum at 0 °C ($a \approx 381$ g of polymer (g of Zr)$^{-1}$ h$^{-1}$ bar$^{-1}$) in the temperature range of −40 to +10 °C, but atactic polypropylene is produced. The last catalyst (**9**/MAO) is minimally active (maximum activity at −20 °C: 4 g of polymer (g of Zr)$^{-1}$ h$^{-1}$ bar$^{-1}$).

The stereochemistry of the polypropylenes obtained at the catalysts derived from **5** and **7**, respectively, is exclusively determined by chain end control;[10,11] thus, the catalysts behave as if they were achiral. At low temperature (−50 °C), a slightly isotactic polymer is obtained for the **7**/MAO catalyst in toluene ($\sigma = 0.75$, determined by $^{13}$C NMR pentad analysis). Increasing the polymerization temperature results in rapid loss of stereocontrol to give atactic material.

## Conclusion

Several compounds from the family of substituted *exo,exo*-bis(isodicyclopentadienyl) transition metal complexes have been prepared, and the X-ray structures of two representative examples have been established. The rotational barrier of the pentahapto ligands has increased by comparison to the unsubstituted analogues,

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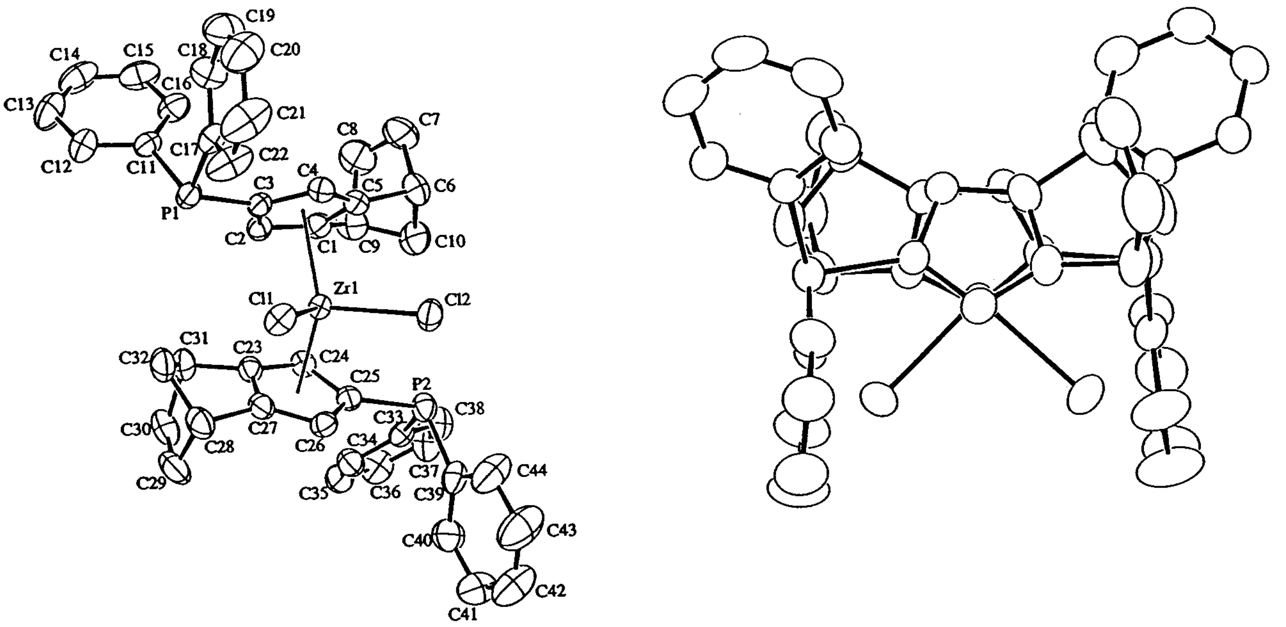

**Figure 1.** Two ORTEP drawings for **9** with atoms drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The view on the right is a projection onto the $ZrCl_2$ plane.

**Table 4. Selected Bond Lengths (Å) for 8 and 9**[a]

| atom−atom | **8** (M = Ti) | **9** (M = Zr) | atom−atom | **8** (M = Ti) | **9** (M = Zr) |
|---|---|---|---|---|---|
| M−Cl(1) | 2.342(1) | 2.4285(8) | M−Cl(2) | 2.355(1) | 2.4375(8) |
| M−C(1) | 2.418(4) | 2.514(3) | M(1)−C(23) | 2.430(4) | 2.508(3) |
| M−C(2) | 2.438(5) | 2.517(3) | M(1)−C(24) | 2.444(4) | 2.501(3) |
| M−C(3) | 2.449(4) | 2.551(3) | M(1)−C(25) | 2.452(4) | 2.554(3) |
| M−C(4) | 2.397(4) | 2.548(3) | M(1)−C(26) | 2.375(4) | 2.559(3) |
| M−C(5) | 2.391(4) | 2.529(3) | M(1)−C(27) | 2.380(4) | 2.544(3) |
| C(1)−C(2) | 1.402(6) | 1.414(4) | C(23)−C(24) | 1.407(6) | 1.414(4) |
| C(1)−C(5) | 1.396(6) | 1.403(4) | C(23)−C(27) | 1.395(6) | 1.406(4) |
| C(1)−C(9) | 1.515(6) | 1.517(4) | C(23)−C(31) | 1.509(6) | 1.513(4) |
| C(2)−C(3) | 1.414(6) | 1.422(4) | C(24)−C(25) | 1.428(6) | 1.428(4) |
| C(3)−C(4) | 1.428(6) | 1.428(4) | C(25)−C(26) | 1.415(6) | 1.417(4) |
| C(4)−C(5) | 1.415(6) | 1.406(4) | C(26)−C(27) | 1.418(6) | 1.418(4) |
| C(5)−C(6) | 1.518(6) | 1.519(4) | C(27)−C(28) | 1.515(6) | 1.504(4) |
| C(6)−C(7) | 1.559(7) | 1.554(5) | C(28)−C(29) | 1.554(7) | 1.560(5) |
| C(6)−C(10) | 1.539(7) | 1.548(5) | C(28)−C(32) | 1.540(7) | 1.539(5) |
| C(7)−C(8) | 1.553(8) | 1.549(6) | C(29)−C(30) | 1.550(8) | 1.547(5) |
| C(8)−C(9) | 1.552(7) | 1.556(5) | C(30)−C(31) | 1.557(7) | 1.556(5) |
| C(9)−C(10) | 1.531(7) | 1.537(5) | C(31)−C(32) | 1.536(7) | 1.537(5) |
| M−RC(1) | 2.100(2) | 2.228(2) | M−RC(2) | 2.097(3) | 2.228(2) |

[a] RC(1) is the ring centroid for the ring defined by the atoms C1, C2, C3, C4, and C5. RC(2) is the ring centroid for the ring defined by the atoms C23, C24, C25, C26, and C27. Estimated standard deviations in the least significant figure are given in parentheses.

but this effect causes the catalytic activity of the complexes in propene polymerization to decrease. This eventuality may be due to the high steric congestion at the metal center, which renders more difficult the approach to the reaction center.

## Experimental Section

All manipulations were conducted under an argon atmosphere. The solvents were dried and distilled prior to use. Elemental analyses were performed by the Service de Microanalyses du L.S.E.O. (Université de Bourgogne). $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded with Bruker AC200 and Varian Unity Plus 600 NMR spectrometers. The activation barriers were determined at the coalescence temperature of a suitable pair of signals[12] for each compound.

Propene polymerization reactions were carried in a Büchi glass autoclave at 2 bar of propene pressure in toluene, following the procedure previously described in detail.[10] The molecular weights of the polymers were determined with an Ubbelohde viscosimeter (Schott AVS 440) in Decalin solution at 137 °C. The $^{13}$C NMR spectra of the polymers were recorded in 1,2,4-trichlorobenzene/[$d_6$]benzene (4:1) solution at 350 K. The methyl pentad signals were integrated by a curve-fitting procedure as previously described and then subjected to a statistical treatment to determine the partition between enantiomorphic site control ($\omega$) and end chain stereocontrol ($1-\omega$), the isotacticity ($\sigma$), and the syndiotacticity ($1-\sigma$) of the obtained polymer sample under chain end control.

Mass spectra were determined with a KRATOS concept IS instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne; electronic ionization 70 eV) and a KRATOS MS.30 (Campus Chemical Instrumentation Center of The Ohio State University).

***exo,exo*-Bis(3-methylisodicyclopentadienyl)titanium Dichloride (4).** A solution of **3-Me** (0.94 g, 6.45 mmol) in dry diethyl ether (20 mL) was prepared according to a previous paper[5a] under argon and cooled at −78 °C. To the cold solution was added 1.2 equiv of *n*-butyllithium (1.6 M in hexane) via a syringe, and the mixture was warmed to room temperature overnight. A white solid appeared. The reaction mixture was cooled at −78 °C, filtered, and washed with diethyl ether (3 × 5 mL). The white solid was dried and dissolved in dry tetrahydrofuran (10 mL). A suspension of $TiCl_3 \cdot 3THF$ (1.18 g, 3.20 mmol) in dry THF (30 mL) was prepared on which the solution of the lithium salt was transferred via cannula at room temperature to give a green coloration. After 4 h of stirring, carbon tetrachloride (3 mL) was added, affording a reddish reaction mixture, which was diluted 1.5 h after addition with methylene chloride/water 1:1 (10 mL). The aqueous layer was extracted three times with methylene chloride. The combined organic layers were washed with water, dried over magnesium sulfate, and evaporated. The red solid was recrystallized from methylene chloride: yield 0.30 g (23%); mp > 264 °C; MS, *m*/*z* (relative intensity), 408-(68), 373 (12), 263 (28), 145 (100), 130 (18); $^1$H NMR ($CD_2Cl_2$, 599.9 MHz, $T = 263$ K) $\delta = 5.79$ (br s, 4H, peripheral), 3.27 (br s, 4H, bridgehead), 2.11 (s, 6H, Me), 1.79 (br s, 4H, exo-

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(12) (a) Günther, H. *La Spectroscopie de RMN*; Masson: Paris, France, 1993; pp 330−333. (b) Green, M. L. H.; Wong, L.-L. *Organometallics* **1992**, *11*, 2660.

**Table 5. Selected Bond Angles (deg) for 8 and 9**

| angle | **8** (M = Ti) | **9** (M = Zr) | angle | **8** (M = Ti) | **9** (M = Zr) |
|---|---|---|---|---|---|
| C(2)−C(1)−C(5) | 108.8(4) | 108.3(3) | C(24)−C(23)−C(27) | 109.1(4) | 108.3(3) |
| C(2)−C(1)−C(9) | 142.3(4) | 142.8(3) | C(24)−C(23)−C(31) | 141.7(4) | 142.7(3) |
| C(5)−C(1)−C(9) | 107.1(4) | 106.6(3) | C(27)−C(23)−C(31) | 107.6(4) | 106.5(3) |
| C(1)−C(2)−C(3) | 108.1(4) | 107.5(3) | C(23)−C(24)−C(25) | 107.4(4) | 107.7(3) |
| C(2)−C(3)−C(4) | 107.3(4) | 107.9(3) | C(24)−C(25)−C(26) | 107.4(4) | 107.8(3) |
| C(3)−C(4)−C(5) | 107.5(4) | 107.3(3) | C(25)−C(26)−C(27) | 108.0(4) | 107.7(3) |
| C(1)−C(5)−C(4) | 108.2(4) | 109.0(3) | C(23)−C(27)−C(26) | 107.9(4) | 108.5(3) |
| C(1)−C(5)−C(6) | 106.8(4) | 107.1(3) | C(23)−C(27)−C(28) | 106.8(4) | 107.2(3) |
| C(4)−C(5)−C(6) | 142.3(4) | 142.3(3) | C(26)−C(27)−C(28) | 142.2(4) | 142.6(3) |
| C(5)−C(6)−C(7) | 103.9(4) | 103.7(3) | C(27)−C(28)−C(29) | 104.1(4) | 104.1(3) |
| C(5)−C(6)−C(10) | 99.9(4) | 100.3(3) | C(27)−C(28)−C(32) | 99.9(4) | 100.8(3) |
| C(7)−C(6)−C(10) | 100.2(4) | 100.0(3) | C(29)−C(28)−C(32) | 99.8(4) | 99.2(3) |
| C(6)−C(7)−C(8) | 103.6(4) | 103.9(3) | C(28)−C(29)−C(30) | 103.7(4) | 103.9(3) |
| C(7)−C(8)−C(9) | 103.5(4) | 103.4(3) | C(29)−C(30)−C(31) | 103.8(4) | 103.4(3) |
| C(1)−C(9)−C(8) | 103.3(4) | 105.0(3) | C(23)−C(31)−C(30) | 103.3(4) | 104.4(3) |
| C(1)−C(9)−C(10) | 100.8(4) | 100.1(3) | C(23)−C(31)−C(32) | 100.7(4) | 100.1(3) |
| C(8)−C(9)−C(10) | 100.2(4) | 100.5(3) | C(30)−C(31)−C(32) | 99.1(4) | 100.3(3) |
| C(6)−C(10)−C(9) | 96.0(4) | 95.5(3) | C(28)−C(32)−C(31) | 96.3(4) | 95.8(3) |
| Cl(1)−M−Cl(2) | 91.84(5) | 92.94(3) | RC(1)−M−RC(2) | 131.85(9) | 129.02(5) |

ethano bridge), 1.24 (dt, $^2J_{HH} = 9.2$ Hz, $^3J_{HH} = 1.5$ Hz, 2H, syn-methano bridge), 1.04 (br s, 4H, endo-ethano bridge), 0.74 (dt, $^2J_{HH} = 9.2$ Hz, $^3J_{HH} = 1.4$ Hz, 2H, anti-methano bridge) ppm; $^1$H NMR ($CD_2Cl_2$, 599.9 MHz, $T = 243$ K) $\delta = 5.87$, 5.69 (each br s, each 2H, peripheral), 3.34, 3.15 (each br s, each 2H, bridgehead), 2.11 (s, 6H, Me), 1.76 (br s, 4H, exo-ethano bridge), 1.23 (dt, $^2J_{HH} = 9.1$ Hz, $^3J_{HH} = 1.5$ Hz, 2H, syn-methano bridge), 1.05, 0.99 (each br s, each 2H, endo-ethano bridge), 0.70 (br d, $^2J_{HH} = 9.1$ Hz, 2H, anti-methano bridge) ppm. Coalescence of cyclopentadienyl-H is reached at 262 K, $\Delta\nu(243\ K) = 105$ Hz, $\Delta G^{\ddagger}(262\ K) = 12.1 \pm 0.4$ kcal mol$^{-1}$. Anal. Calcd for $C_{22}H_{26}TiCl_2 + 0.25CH_2Cl_2$: C, 62.08; H, 6.25. Found: C, 61.92; H, 6.25.

***exo,exo*-Bis(3-methylisodicyclopentadienyl)zirconium Dichloride (5).** Methylisodicyclopentadienyllithium prepared as for the titanium complex from 1.45 g (9.91 mmol) of **3-Me** and dissolved in 15 mL of dimethoxyethane (DME) was slowly added to a suspension of $ZrCl_4$ (1.15 g, 4.93 mmol) in 20 mL of DME cooled at −20 °C. The mixture was allowed to warm gradually to room temperature and was refluxed for 48 h. The solvent was evaporated, and the solid reaction mixture was extracted with toluene (3 × 10 mL) and washed with pentane (3 × 10 mL). Evaporation of the solvent gave a brown solid. Recrystallization from methylene chloride afforded 0.84 g (19%) of yellow crystals: mp >264 °C; MS, *m*/*z* (relative intensity), 450 (55), 414 (60), 386 (100), 305 (30), 269 (35), 241 (51), 145 (19); $^1$H NMR ($CD_2Cl_2$, 200 MHz, $T = 233$ K) $\delta =$ 5.85 (s, 4H, peripheral), 3.38 (s, 4H, bridgehead), 2.42 (s, 6H, Me), 1.79 (d, exo-ethano bridge, 4H, $^2J_{HH} = 7.3$ Hz), 1.26 (d, syn-methano bridge, 2H, $^2J_{HH} = 10.2$ Hz), 1.10 (d, endo-ethano bridge, 4H, $^2J_{HH} = 7.3$ Hz), 0.75 (d, anti-methano bridge, 2H, $^2J_{HH} = 9.3$ Hz) ppm; $^1$H NMR ($CD_2Cl_2$, 200 MHz, $T = 213$ K) $\delta = 6.28$, 5.46 (each s, each 2H, peripheral), 3.44, 3.32 (each s, each 2H, bridgehead), 2.41 (s, 6H, Me), 1.80 (br s, 4H, exo-ethano bridge), 1.26 (d, $^2J_{HH} = 10.8$ Hz, 2H, syn-methano bridge), 1.09 (d, $^2J_{HH} = 7.3$ Hz, 4H, endo-ethano bridge), 0.71 (d, $^2J_{HH} = 9.7$ Hz, 2H, anti-methano bridge) ppm. Coalescence of cyclopentadienyl-H is reached at 231 K, $\Delta\nu(213\ K) = 165$ Hz, $\Delta G^{\ddagger}(231\ K) = 10.4 \pm 0.4$ kcal mol$^{-1}$. Anal. Calcd for $C_{22}H_{26}ZrCl_2 + 0.25CH_2Cl_2$: C, 56.40; H, 5.64. Found: C, 56.36; H, 5.80.

***exo,exo*-Bis(3-trimethylsilylisodicyclopentadienyl)titanium Dichloride (6).** A solution of **3-SiMe$_3$** in dry diethyl ether (20 mL) was prepared as previously described.[5b] A solution of the lithium salt trimethylsilylisodicyclopentadienyllithium (obtained from 1.26 g (6.17 mmol) of **3-SiMe$_3$**) in dry THF (10 mL) was slowly added at room temperature to a suspension of $TiCl_3{\cdot}3THF$ (1.23 g, 3.33 mmol) in dry THF (30 mL) to give a dark green mixture. After overnight stirring, carbon tetrachloride (3 mL) was added and the reaction mixture became brown. After 1.5 h of stirring, the solvent was evaporated and the solid residue was extracted with toluene (3 × 10 mL) and washed with pentane (3 × 10 mL). Evaporation of the solvents afforded a solid which was crystallized from methylene chloride to give 0.40 g (25%) of a brown powder: mp 263 °C; MS, *m*/*z* (relative intensity), 524 (14), 509 (7), 321 (100), 306 (38), 203 (34), 175 (18), 160 (28), 145 (56); $^1$H NMR ($CD_2Cl_2$, 599.9 MHz, $T = 233$ K) $\delta = 6.01$ (s, 4H, peripheral), 3.25 (br s, 4H, bridgehead), 1.79 (d, $^2J_{HH} = 7.4$ Hz, 4H, exo-ethano bridge), 1.30 (dt, $^2J_{HH} = 9.2$ Hz, $^3J_{HH} = 1.3$ Hz, 2H, syn-methano bridge), 1.11 (d, $^2J_{HH} = 9.2$ Hz, 2H, anti-methano bridge), 0.98 (dd, $^2J_{HH} = 7.4$ Hz, $^3J_{HH} = 2.2$ Hz, 4H, endo-ethano bridge), 0.11 (s, 18H, SiMe$_3$) ppm; $^1$H NMR ($CD_2Cl_2$, 599.9 MHz, $T = 183$ K) $\delta = 6.14$, 5.83 (each s, each 2H, peripheral), 3.42, 3.01 (each br s, each 2H, bridgehead), 1.80, 1.70 (each br s, each 2H, exo-ethano bridge), 1.26 (d, $^2J_{HH} = 8.3$ Hz, 2H, syn-methano bridge), 0.96 (br s, 4H, endo-ethano bridge), 0.92 (br s, 2H, anti-methano bridge), 0.05 (br s, 18H, SiMe$_3$) ppm. Coalescence of bridgehead-H is reached at 198 K, $\Delta\nu(183\ K) = 247$ Hz, $\Delta G^{\ddagger}(198\ K) = 8.7 \pm 0.4$ kcal mol$^{-1}$. Anal. Calcd for $C_{26}H_{38}Si_2TiCl_2 + 0.25CH_2Cl_2$: C, 57.66; H, 7.10. Found: C, 57.57; H, 6.95.

***exo,exo*-Bis(3-trimethylsilylisodicyclopentadienyl)zirconium Dichloride (7).** Trimethylsilylisodicyclopentadienyllithium was prepared as for titanium complex from 1.26 g (6.17 mmol) of **3-SiMe$_3$** in 40 mL of DME. The solution was cooled at −40 °C and treated gradually with zirconium tetrachloride (0.87 g, 3.73 mmol). The mixture was allowed to warm to room temperature and stirred for 36 h. After this time, the solvent was evaporated and the residue was extracted with toluene (3 × 10 mL). Evaporation of the solvent gave an orange solid. Recrystallization from methylene chloride afforded 0.55 g (31%) of yellow crystals: decomposition at 150 °C; MS, *m*/*z* (relative intensity), 566 (23), 551 (79), 363 (61), 348 (27), 315 (13), 145 (48). No coalescence is reached at 183 K. Anal. Calcd for $C_{26}H_{38}Si_2ZrCl_2 + 0.25CH_2Cl_2$: C, 53.43; H, 6.57. Found: C, 53.29; H, 6.59.

***exo,exo*-Bis(3-diphenylphosphinoisodicyclopentadienyl)titanium Dichloride (8).** A solution of the lithium salt diphenylphosphinoisodicyclopentadienyllithium (prepared as for methylisodicyclopentadienyllithium from 0.94 g (2.99 mmol) of **3-PPh$_2$**) in dry THF (10 mL) was transferred via a cannula at room temperature to a suspension of $TiCl_3{\cdot}3THF$ (0.56 g, 1.51 mmol) in dry THF (20 mL) giving a green mixture. After overnight stirring, carbon tetrachloride (3 mL) was added, changing the reaction mixture to dark red. After 1.5 h of stirring, the solvent was evaporated and the residue was extracted with toluene (3 × 10 mL) and then washed with pentane (3 × 10 mL). Evaporation of the solvents gave a pink powder. Recrystallization from methylene chloride afforded

0.40 g (36%) of pink crystals: mp 264 °C; MS, $m/z$ ($M^+$) calcd 748.1462, obsd 748.1461, $m/z$ (relative intensity), 713 (76), 433 (17), 398 (32), 315 (100), 185 (43), 108 (46); $^{31}P$ NMR (81 MHz, $CDCl_3$) $-10.8$ ppm; $^1H$ NMR ($CD_2Cl_2$, 599.9 MHz, $T = 263$ K) $\delta = 7.6-7.0$ (m, 20H, Ph), 5.95 (s, 4H, peripheral), 3.32 (s, 4H, bridgehead), 1.90 (d, $^2J_{HH} = 7.8$ Hz, 4H, exo-ethano bridge), 1.45 (br s, 2H, syn-methano bridge), 1.30 (d, $^2J_{HH} = 9.5$ Hz, 2H, anti-methano bridge), 1.19 (dd, $^2J_{HH} = 7.8$ Hz, $^3J_{HH} = 2.2$ Hz, 4H, endo-ethano bridge) ppm; $^1H$ NMR ($CD_2Cl_2$, 599.9 MHz, $T = 213$ K) $\delta = 7.49$ (4H), 7.29 (12H), 7.04 (4H) (each m, Ph), 5.94, 5.92 (each s, each 2H, peripheral), 3.36, 3.27 (each s, each 2H, bridgehead), 1.90 (m, 4H, anti + syn-methano bridge), 1.33 (m, 4H, exo-ethano bridge), 1.20 (m, 4H, endo-ethano bridge) ppm. Coalescence of bridgehead-H is reached at 243 K, $\Delta\nu(213\ \mathrm{K}) = 55$ Hz, $\Delta G^\ddagger(243\ \mathrm{K}) = 11.5 \pm 0.4$ kcal mol$^{-1}$. Anal. Calcd for $C_{44}H_{40}P_2TiCl_2 + 0.5CH_2Cl_2$: C, 67.49; H, 5.22. Found: C, 67.45; H, 5.33.

***exo,exo*-Bis(3-diphenylphosphinoisodicyclopentadienyl)zirconium Dichloride (9).** Diphenylphosphinoisodicyclopentadienyllithium was prepared as for titanium complex from 1.89 g (5.97 mmol) of **3-PPh$_2$** in 40 mL of DME. The solution was cooled at $-40$ °C and treated gradually with zirconium tetrachloride (0.72 g, 3.09 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 39 h. After that, the solvent was evaporated and the residue was extracted with methylene chloride (3 × 10 mL). The solution so obtained was concentrated to give yellow crystals: yield 0.80 mg (34%), mp 233 °C; MS, $m/z$ (relative intensity), 475 (94), 315 (8), 287 (30), 133 (12), 185 (23), 108 (37), 102 (11); $^{31}P$ NMR (81 MHz, $CDCl_3$) $-14.1$ ppm; $^1H$ NMR ($CD_2Cl_2$, 200 MHz, $T = 202$ K) $\delta = 7.27$ (br s, 20H, Ph), 5.78 (br s, 4H, peripheral), 3.32 (br s, 4H, bridgehead), 1.88 (br s, 4H, exo-ethano bridge), 1.41 (br s, 4H, anti + syn-methano bridge), 1.17 (br s, 4H, endo-ethano bridge) ppm; $^1H$ NMR ($CD_2Cl_2$, 200 MHz, $T = 183$ K) $\delta = 6.98$ (4H), 7.23 (6H), 7.30 (6H), 7.43 (4H) (each br s, Ph), 5.70, 5.87 (each s, each 2H, peripheral), 3.30, 3.36 (each s, each 2H, bridgehead), 1.87 (br s, 4H, exo-ethano bridge), 1.42 (br s, 4H, anti + syn-methano bridge), 1.18 (d, $^2J_{HH} = 7.8$ Hz, 4H, endo-ethano bridge) ppm. Coalescence of cyclopentadienyl-H is reached at 200 K, $\Delta\nu(183\ \mathrm{K}) = 33$ Hz, $\Delta G^\ddagger(200\ \mathrm{K}) = (9.6 \pm 0.4)$ kcal·mol$^{-1}$. Anal. Calcd for $C_{44}H_{40}P_2ZrCl_2 + 0.85\ CH_2Cl_2$: C, 62.27; H, 4.86. Found: C, 62.20; H, 4.94.

**X-ray Crystallographic Analysis of 8.** Data sets for **8** and **9** were measured on a Rigaku AFC5S diffractometer equipped with graphite-monochromated Mo Kα radiation. The data collection crystal was a dark red rod. Unit cell constants were obtained by a least-squares fit of the setting angles for 25 reflections in the $2\theta$ range 21−30° ($\lambda(K\alpha_1) = 0.709\ 30$ Å). During data collection six standard reflections were measured after every 150 reflections and indicated that the crystal was stable. Data reduction was done with the teXsan package.[13] A total of 9832 reflections were measured by the $\omega-2\theta$ scan method.

The structure was solved in $P\bar{1}$ (No. 2) by the direct methods procedure of SHELXS-86.[14] Full-matrix least-squares refinements based on $F$ were performed in teXsan.[13] An empirical Ψ-scan absorption correction was applied to the data.[15] One solvent molecule of dichloromethane is present in the asymmetric unit. The hydrogen atoms were fixed at calculated positions with C−H = 0.98 Å. The final refinement cycle was based on the 5655 intensities with $I > 1\sigma(I)$ and 469 variables and resulted in final agreement factors of $R = 0.066$ and $R_w = 0.058$. The final difference electron density map contains maximum and minimum peaks of 0.75 and −0.66 e/Å$^3$. The maximum peak is in the vicinity of the solvent molecule. For both structures neutral atom scattering factors were used[16] and include terms for anomalous dispersion.[17]

**Table 6. Crystallographic Details for 8 and 9**

| | **8** | **9** |
|---|---|---|
| formula | $C_{44}H_{40}Cl_2P_2Ti\cdot CH_2Cl_2$ | $C_{44}H_{40}Cl_2P_2Zr\cdot CH_2Cl_2$ |
| fw | 834.49 | 877.81 |
| space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) |
| $a$, Å | 11.126(2) | 11.230(2) |
| $b$, Å | 11.321(2) | 11.337(2) |
| $c$, Å | 18.628(2) | 18.751(1) |
| α, deg | 84.73(1) | 84.41(1) |
| $\beta$, deg | 76.33(1) | 76.008(8) |
| $\gamma$, deg | 62.58(1) | 63.00(1) |
| $V$, Å$^3$ | 2023.4(5) | 2063.8(5) |
| $Z$ | 2 | 2 |
| temp, °C | 23 | 23 |
| cryst size, mm | 0.15 × 0.15 × 0.42 | 0.19 × 0.31 × 0.35 |
| density, g/cm$^{-3}$ (calcd) | 1.37 | 1.41 |
| $\mu$, cm$^{-1}$ | 5.84 | 6.34 |
| trans factors | 0.92−1.0 | 0.95−1.0 |
| $2\theta$ limits | $4° \le 2\theta \le 55°$ | $4° \le 2\theta \le 55°$ |
| data collected | $+h, \pm k, \pm l$ | $+h, \pm k, \pm l$ |
| no. of unique data | 9349 ($R_{int} = 0.036$) | 9551 ($R_{int} = 0.019$) |
| no. of unique data, with $I > 1\sigma(I)$ | 5655 | 7138 |
| no. of variables | 469 | 474 |
| $R(F)$; $R_w(F)$[a] | 0.066; 0.058 | 0.042; 0.042 |
| goodness of fit | 1.83 | 1.65 |

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 1/\sigma^2(F_o)$.

**X-ray Crystallographic Analysis of 9.** The data collection crystal was a yellow chunk. Unit cell constants were obtained by a least-squares fit of the setting angles for 25 reflections in the $2\theta$ range 21−30° ($\lambda(K\alpha_1) = 0.709\ 30$ Å). Of the six standard reflections measured during the course of data collection, four decreased slightly in intensity while the other two increased slightly. Data reduction was done with the teXsan package,[13] and no correction was made for the changes observed in the standard reflections. A total of 10 041 reflections were measured by the $\omega-2\theta$ scan method.

The Zr atom was located by the Patterson method in $P\bar{1}$ (No. 2) using SHELXS-86.[14] Phasing on the Zr atom in DIRDIF[18] revealed the remaining non-hydrogen atoms. Full-matrix least-squares refinements based on $F$ were performed in teXsan.[13] An empirical Ψ-scan absorption correction was applied to the data.[15] There is a disordered solvent molecule of dichloromethane present in the asymmetric unit. The disorder was modeled in terms of two positions for the carbon atom (C(45) and C(46)) and two positions for one of the chlorine atoms (Cl(4) and Cl(5)). The other chlorine atom, Cl(3), appears to be ordered. While Cl(4) is considered to be bonded to C(45) or C(46) in that it makes a reasonable angle with Cl(3) and either carbon atom, Cl(5) is only bonded to C(46). The occupancy factors for C(45) and C(46) were restricted to add to 1.0, as were those for Cl(4) and Cl(5). Atoms Cl(5), C(45), and C(46) were refined isotropically, while Cl(3) and Cl(4) were refined anisotropically. All of the hydrogen atoms were fixed at calculated positions with C−H = 0.98 Å. Only one set of disordered hydrogen atoms was added to dichloromethane. These were the hydrogens bonded to C(45), and their occupancy factors were restricted accordingly. The final refinement cycle was based on the 7138 intensities with $I > 1\sigma(I)$

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(13) *teXsan*, Crystal Structure Analysis Package, version 1.7−2; Molecular Structure Corporation: The Woodlands, TX, 1995.

(14) *SHELXS86*: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(15) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351−359.

(16) Scattering factors for the non-hydrogen atoms are from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. Scattering factors for the hydrogen atom: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175−3187.

(17) Creagh, D. C.; McAuley, W. J. *International Tables for Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C, Table 4.2.6.8.

(18) *DIRDIF*: Parthasarathi, V.; Beurskens, P. T., Slot, H. J. B. *Acta Crystallogr.* **1983**, *A39*, 860−864.

**Table 7. Details of the Polymerization Reactions**

| catalyst | mmol of catalyst | MAO/Zr (Ti) ratio | pressure (bar) | reaction temperature (°C) | duration of the polymerization reaction (min) | g of polymer recovered | activity: g of polymer (g of Zr or Ti)$^{-1}$ h$^{-1}$ bar$^{-1}$ | $M_\eta$ |
|---|---|---|---|---|---|---|---|---|
| **4** | 0.046 | 794 | 2 | 0 | 225 | 0.121 | 7 | |
| | 0.081 | 451 | 1 | −20 | 198 | 0.512 | 40 | |
| **5** | 0.022 | 872 | 2 | +10 | 180 | 2.293 | 211 | 164 000 |
| | 0.024 | 799 | 2 | 0 | 220 | 5.626 | 381 | 219 000 |
| | 0.022 | 872 | 1 | −20 | 180 | 0.274 | 50 | |
| | 0.022 | 872 | 1 | −40 | 157 | 0.239 | 50 | |
| | 0.029 | 661 | 1 | −50 | 312 | 0.249 | 19 | |
| **6** | 0.038 | 962 | 2 | 0 | 225 | 0.100 | 7 | |
| | 0.059 | 619 | 1 | −20 | 192 | 0.104 | 11 | |
| **7** | 0.017 | 1128 | 2 | +10 | 180 | 2.693 | 280 | 18 500 |
| | 0.021 | 913 | 2 | 0 | 230 | 1.265 | 86 | 21 000 |
| | 0.016 | 1199 | 2 | −20 | 180 | 5.486 | 633 | 47 000 |
| | 0.019 | 1010 | 1 | −40 | 180 | 2.734 | 517 | 169 000 |
| | 0.023 | 834 | 1 | −50 | 300 | 2.979 | 286 | 233 000 |
| **8** | 0.027 | 1354 | 2 | 0 | 210 | 0.067 | 7 | |
| | 0.043 | 850 | 1 | −20 | 318 | 0.122 | 11 | |
| **9** | 0.011 | 1744 | 2 | +10 | 210 | 0.052 | 7 | |
| | 0.019 | 1010 | 2 | 0 | 155 | 0.036 | 4 | |
| | 0.013 | 1476 | 1 | −20 | 236 | 0.065 | 14 | |

and 474 variables and resulted in final agreement factors of $R = 0.042$ and $R_w = 0.042$. The final difference electron density map contains maximum and minimum peaks of 0.66 and −0.58 e/Å$^3$. The top six peaks in this map are in the immediate vicinity of the disordered dichloromethane molecule. Additional crystallographic details are given in Table 6.

**Propene Polymerization Reactions (General Procedure). Reactions at 2 bar Propene Pressure.** In the autocave, 20 mL of methylalumoxane (10 wt % in toluene) was added to 300 mL of dry toluene under argon. The solution was brought to the desired temperature, and propene was added to the solution until 2 bar pressure. When the temperature was stable, a solution of the catalyst (10−30 mg) in toluene (5 mL) was added. After about 3 h of stirring, the polymerization was stopped by slowly introducing a mixture of aqueous hydrogene chloride/methanol, 1:1. Stirring was maintained for 30 min to destroy the excess of reagents. After several extractions with toluene, the organic layer was washed with water and the solvent evaporated. The residue was finally dried under vacuum for 1 day.

**Propene Polymerization under 1 bar at a Temperature below −20 °C.** The experimental procedure was the same for these polymerizations as it was described above, excepted that 40−50 mL of propene was condensed into the autoclave. Details of the polymerization reactions are given in Table 7.

**Supporting Information Available:** Tables of bond lengths and angles, least-squares planes, positional parameters, anisotropic displacement parameters, and calculated positional parameters for the hydrogen atoms for **8** and **9**, along with one ORTEP drawing for **8** (27 pages). Ordering information is given on any current masthead page.

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