ELSEVIER

Journal of Organometallic Chemistry 555 (1998) 127–134

Journal of Organo metallic Chemistry

Bis(triisopropylsiloxyindenyl) zirconocenes

Hendrik J.G. Luttikhedde [a,*], Reko Leino [a], Ari Lehtonen [b], Jan H. Näsman [a]

[a] *Department of Polymer Technology, Åbo Akademi University, FIN-20500 Åbo, Finland*
[b] *Department of Chemistry, University of Turku, FIN-20500 Turku, Finland*

Received 13 November 1997

Abstract

The synthesis and characterization of 1- and 2-triisopropylsiloxy substituted bis(indenyl) zirconocenes is reported. The molecular structures of *rac*-[ethylenebis(2-(triisopropylsiloxy)-1-indenyl)]zirconium dichloride (**6**) and *rac*-[ethylenebis(2-(triisopropylsiloxy)-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**8**) have been determined and reveal that complex (**6**) crystallizes in the indenyl-forward (Π) conformation while (**8**) adopts the indenyl-backward (Y) conformation. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Indenyl; Triisopropylsiloxy; *Ansa*-zirconocene

1. Introduction

Ansa-metallocenes are well established catalyst precursors for olefin polymerization [1] and have been exploited as stereoselective catalysts or reagents for a wide variety of other reactions [2]. The catalyst performance is determined by the ligand substitution patterns and has been optimized for isospecific propylene polymerization to dimethylsilylene bridged 2,2′-dimethyl-4,4′-diaryl-substituted [3] and 2,2′-dimethyl-benzo-fused bis(indenyl) *ansa*-zirconocenes [4]. Although the first hetero-atom functionalized group IV metallocene, 1,1′-bis(*N*,*N*-dimethylamino)titanocene dichloride, was reported as early as 1984 ([5]a) only recently a new interest in related complexes has emerged as to alter the properties of metallocenes [5–9].

This paper, describing the synthesis and characterization of triisopropylsiloxy-functionalized bis(indenyl) zirconocenes, is a continuation of our recent studies on hetero atom substituted metallocenes ([5]b, e [7]).

2. Results and discussion

Synthesis of the metallocenes is illustrated in Scheme 1. Reaction of triisopropylchlorosilane with 2- or 1-indanone in the presence of DBU yields 2-(triisopropylsiloxy)indene (**1**), respectively 3-(triisopropylsiloxy)indene (**2**) as pale yellow oils in fairly good yields. The subsequent introduction of the ethylene bridge proceeds via a standard procedure ([7]a). For bis(2-(triisopropylsiloxy)-1-indenyl)ethane (**3**) a diastereomerically pure crystalline solid was obtained, while bis(3-(triisopropylsiloxy)-1-indenyl)ethane (**4**) was obtained as an oil (1:1 diastereomeric mixture), which could not be crystallized.

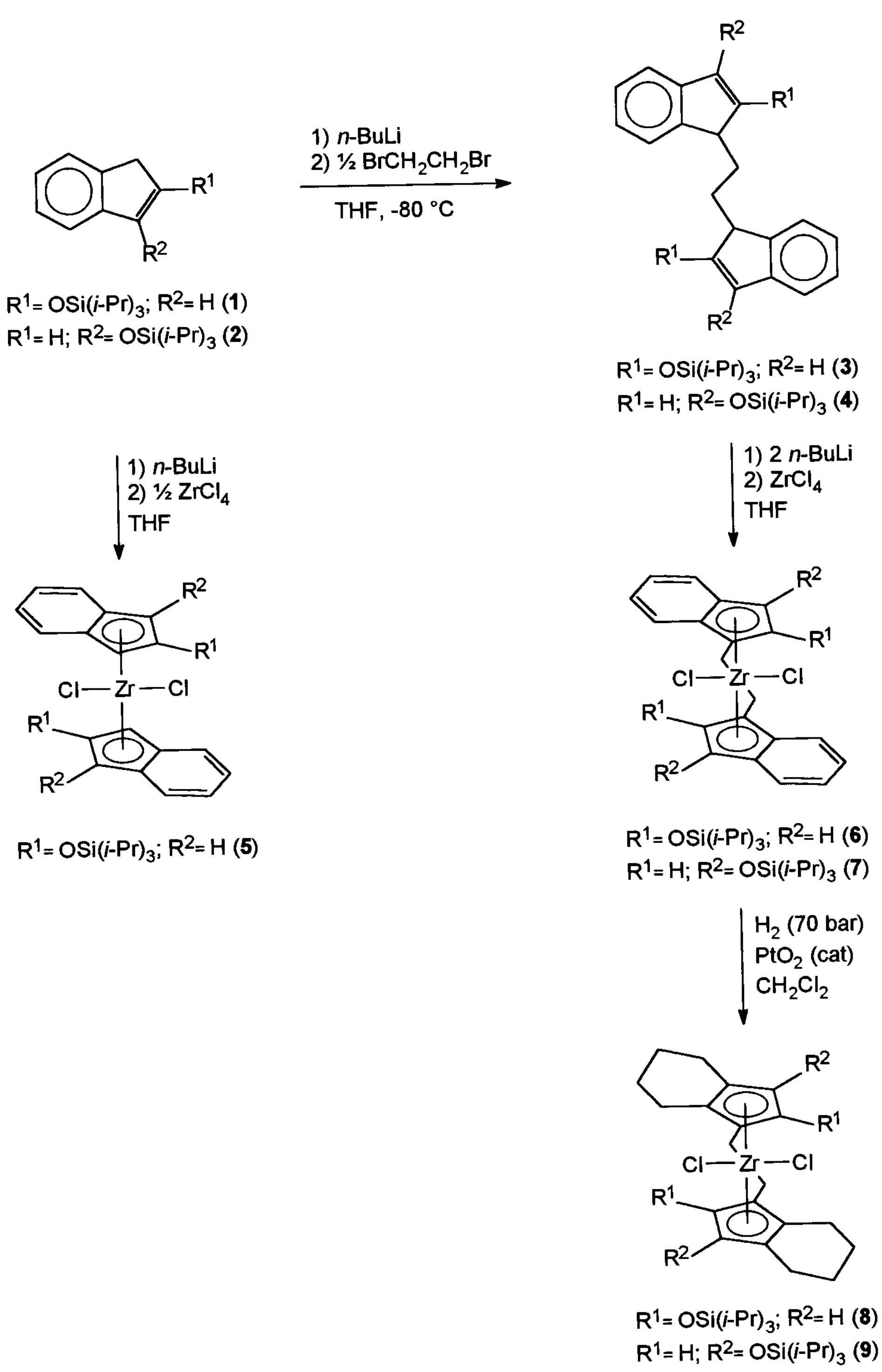
Treatment of $ZrCl_4$ with two equivalents of Li-**1** in THF yielded, after work-up and crystallization, bis[2-(triisopropylsiloxy)indenyl]zirconium dichloride (**5**) as yellow crystals in 42% yield. The ^{1}H and ^{13}C-NMR spectra of **5** at room temperature were consistent with molecular C_{2v} symmetry.

When the dianion of **3** was added to a solution of $ZrCl_4$ in THF only the racemic diastereomer was formed, as determined by ^{1}H-NMR (vide infra). For the less sterically congested 2-*tert*-butyldimethylsiloxy analogue a *rac*:*meso* ratio of ≈14:1 was obtained

---

* Corresponding author. Fax: +358 2 2154866; e-mail: hluttikh@abo.fi

PII S0022-328X(98)00376-3



Scheme 1.

([7]a). The increased steric bulk at the 2-position apparently inhibits *meso* formation. Pure bright yellow crystalline *rac*-[ethylenebis(2-(triisopropylsiloxy)-1-indenyl)]zirconium dichloride (**6**) was obtained, after work-up and crystallization from toluene, in 28% overall yield. Hydrogenation of **6** gave *rac*-[ethylenebis(2-(triisopropylsiloxy)-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**8**) as light green crystals. The ^{1}H-NMR spectra of **6** and **8** are consistent with C_2 symmetry. The chemical shifts of the β-H protons (6.03 (**6**) and 5.75 ppm (**8**)) are shielded considerably compared to those of *rac*-Et(Ind)$_2$ZrCl$_2$ (6.58 ppm) ([10]d) and

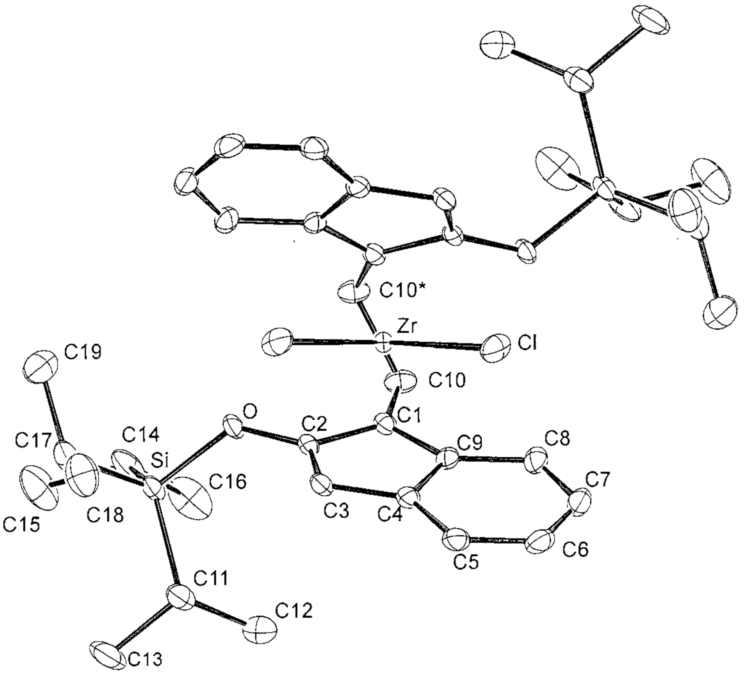


Fig. 1. Molecular structure of *S*,*S*-**6** (ORTEP view, ellipsoids at 20% probability level).

rac-Et(IndH$_4$)$_2$ZrCl$_2$ (6.32 ppm) ([10]a, b) and are comparable to those reported for the 2-*tert*-butyldimethylsiloxy- and 2-thexyldimethylsiloxy analogues ([7]a, c).

Ethylene-bridged metallocenes, depending on the ligand substitution pattern, metal substituent or even crystallization conditions, adopt a range of conformations in the solid state ([2]b[7,10,11]). The molecular structures of **6** (Fig. 1) and **8** (Fig. 2) have been determined and reveal that **6** crystallizes in the indenyl forward (Π) conformation. The previously reported 2-siloxy substituted ethylenebis(indenyl) and bis(tetrahydroindenyl) metallocenes adopt the indenyl backward (Y) conformation as observed here for **8** ([7]a–c). Comparison of intramolecular distances and angles (Tables 1 and 2) shows that the relevant geometric features of **6** and **8** are very similar and well within the range observed for other crystallographically determined structures of racemic ethylene-bridged bis(indenyl) and bis(tetrahydroindenyl) zirconocenes ([5]b[7,10]). The C–O bond lengths for **6** and **8** are typical for siloxy substituted group IV metallocenes ([7]a–e). The cyclopentadienyl-oxygen moieties are essentially planar, deviation from planarity being < 0.03 Å. Intramolecular repulsions determine, to a certain extent, the conformation of *ansa*-metallocenes in the solid state [11], but a combination of steric and electronic effects must account for the observations made here. It appears, that the preferred conformation in these complexes is indenyl backward, with the chlorine and oxygen atoms in closer contact. For example for *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydro-3-indenyl)]zirconium dichloride the chlorine-oxygen distance is 3.16 Å ([7]d) and for bis[2-(*tert*-butyldimethylsiloxy)-4,7-dimethylindenyl]zirconium dichloride a value of 3.14 Å was found ([7]e), which both are within the sum of their van der Waals radii (3.20 Å). Nitrogen-chlorine close contacts (sum of the van der Waals radii 3.30 Å), have been reported for the non-bridged metallocenes 1,1′-bis(*N*,*N*-dimethylamino)titanocene dichloride (Cl–N = 3.14 Å) ([5]a) and bis(2-*N*,*N*-dimethylaminoindenyl)zirconium dichloride (Cl–N = 3.20 Å) ([5]b). A comparison of intramolecular bond distances relevant to steric repulsions (Table 3) indicates that, by adopting the Π conformation, complex **8** could relieve steric hindrance between C(8)–C(30), C(28)–C(10) and at the same time increase the Cl–O distances. This would, however, introduce minor additional steric interference between the chlorine atoms and methylene groups of the hydrogenated six-membered rings. The conformations of **6** and **8** seem to be determined by a delicate balance of factors and further studies will be necessary to clarify this matter [12].

Reaction of the dilithium salt of **4** with ZrCl$_4$ in THF gave a 5:1 mixture of *rac*- (**7a**) and *meso*- (**7b**) [ethylenebis(1-triisopropylsiloxy)-3-indenyl]zirconium dichlorides, as determined by ^{1}H-NMR. Purification was accomplished by a simple washing step with Et$_2$O, to give the racemic diastereomer **7a** in 44% yield. Hydrogenation of **7a** gave *rac*-[ethylenebis(1-(triisopropylsiloxy)-4,5,6,7-tetrahydro-3-indenyl)]zirconium dichloride (**9**) as light green needles. Accordingly the chemical shifts of the α-H protons (5.63 (**7a**) and 5.01 ppm (**9**)) are now shielded compared to those of *rac*-Et(Ind)$_2$ZrCl$_2$ (6.20 ppm) ([10]d) and *rac*-

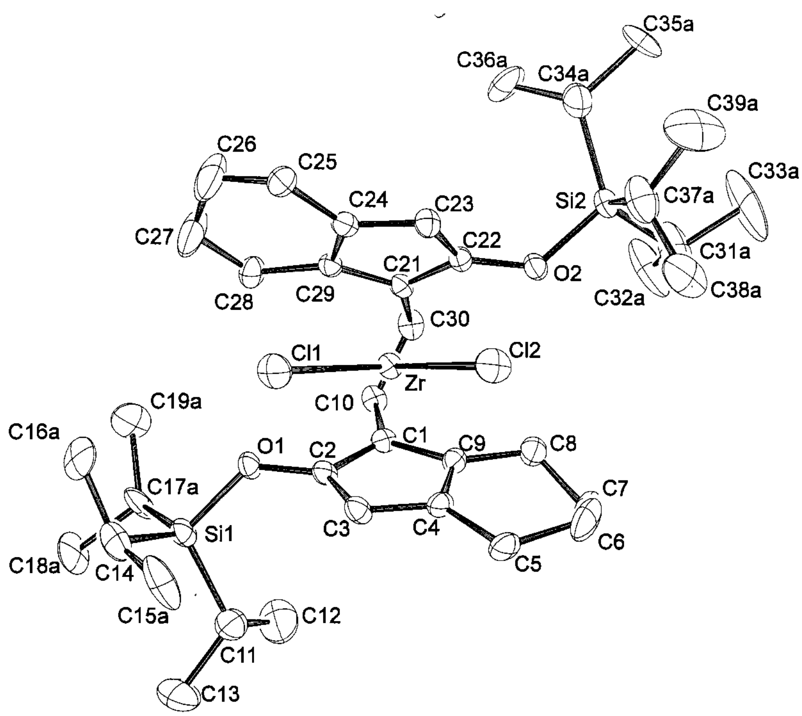


Fig. 2. Molecular structure of *S,S*-**8** (ORTEP view, ellipsoids at 20% probability level). Only one orientation of disordered isopropyl groups is shown.

$Et(IndH_4)_2ZrCl_2$ (5.61 ppm) ([10] a, b) and are equal to those observed for the 1-*tert*-butyldimethylsiloxy congeners ([7]d). The assignment of the stereochemistry was made by comparison of the ^{1}H- and ^{13}C-NMR spectra with those of 1-*tert*-butyldimethylsiloxy analogues whose stereochemistries were unambigiously determined by single-crystal X-ray diffraction ([7]d). The α-H resonances of *meso*-1-siloxy and β-H resonances of *meso*-2-siloxy substituted ethylene bridged metallocenes consistently appear at slightly lower field in the ^{1}H-NMR spectra compared to their racemic analogues and are a convenient tool for the determination of diastereomeric purity. Furthermore, the colors of **7a** and **7b** are remarkably different; the racemic complex is orange while the meso diastereomer is dark red, as observed for the 1-*tert*-butyldimethylsiloxy analogues ([7]d). Although **7a** and **9** could be crystallized from a variety of solvents at different temperatures, crystals suitable for a molecular structure determination were not obtained. The introduction of the bulky triisopropylsiloxy-groups at the more open 1-position of the indenyl ligands seems to be a major perturbation to the molecules' self-recognition.

Table 1
Selected intramolecular distances (Å) and angles (°) for **6**

Zr–Cl	2.414(2)	Cl–Zr–Cl	94.3(6)
C(2)–O	1.366(6)	C(2)–O–Si	129.2(2)
O–Si	1.686(3)	Cp–Cp[b]	57.69
Zr–Cen[a]	2.237	Cen–Zr–Cen	125.54

[a] Cen denotes the centroid of the five-membered portion of the indene rings.

[b] Angle between the cyclopentadienyl planes.

The polymerization behavior of the new catalyst percursors is currently under investigation.

3. Experimental

All operations were carried out in an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled under argon prior to use. The ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions using a JEOL JNM-LA400 NMR spectrometer and are referenced against the ^{1}H and ^{13}C solvent resonances. Direct inlet ionization mass spectra

Table 2
Selected intramolecular distances (Å) and angles (°) for **8**

Zr–Cl(1)	2.431(2)	Cl–Zr–Cl	94.3(6)
Zr–Cl(2)	2.432(2)	C(2)–O(1)–Si(1)	129.5(4)
C(2)–O(1)	1.365(7)	C(22)–O(2)–Si(2)	131.0(4)
C(22)–O(2)	1.357(7)	Cp–Cp[b]	57.79
O(1)–Si(1)	1.670(4)	O(2)–Si(2)	1.666(4)
Zr–Cen(1)[a]	2.228	Cen(1)–Zr–Cen(2)[a]	125.07
Zr–Cen(2)[a]	2.229		

[a] Cen(1) and Cen(2) denote the centroids of the five-membered portions of the indene rings, with lowest and highest crystallographic numbering, respectively.

[b] Angle between the cyclopentadienyl planes.

Table 3
Comparison of intramolecular distances (Å) for **6** and **8**

	6		**8**
Cl–O	4.06	Cl(1)–O(1)	3.53
		Cl(2)–O(2)	3.72
Cl–C(5)	3.29	Cl(2)–C(5)	3.30
		Cl(1)–C(25)	3.34
Cl–C(8)	3.58	Cl(2)–C(8)	4.16
		Cl(1)–C(28)	3.97
C(8)–C(10)*	4.51	C(8)–C(30)	3.42
		C(28)–C(10)	3.45

(EIMS) were obtained on a Varian-8000 mass spectrometer. Triisopropylchlorosilane, 1-indanone, 2-indanone, 1,2-dibromoethane, *n*-BuLi (Acros Chimica) and zirconium tetrachloride (Aldrich) were used without further purification.

*3.1. Synthesis of **1–9***

*3.1.1. 2-(Triisopropylsiloxy)indene (**1**)*

A solution of triisopropylchlorosilane (50.65 g, 262.7 mmol) and 2-indanone (33.70 g, 255.0 mmol) in benzene (400 ml) was treated dropwise with a solution of DBU (40.34 g, 265.0 mmol) in benzene (100 ml) at room temperature and stirred overnight. The suspension was washed with 5% HCl (3 × 200 ml) and the organic phase dried over anhydrous Na_2SO_4. Evaporation gave a brown oil which was fractionated under reduced pressure to give **1** (55.17 g, 191.2 mmol, 75%) as a pale yellow oil (bp 110–112°C/0.01 mbar). ^{1}H-NMR ($CDCl_3$, δ): 7.25–7.22 (m, 1H), 7.19–7.14 (m, 1H), 7.11–7.09 (m, 1H), 7.00 (m, 1H), 5.76 (m, 1H), 3.32 (m, 2H), 1.34–1.23 (m, 3H), 1.12 (d, $^3J = 7.1$ Hz, 18H). ^{13}C-NMR($CDCl_3$, δ): 162.92, 145.42, 136.60, 126.45, 123.05, 122.27, 118.84, 106.39, 39.58, 17.86, 12.46.

Table 4
Crystallographic data for **6** and **8**

	6	**8**
Empirical formula	$C_{38}H_{56}O_2Si_2Cl_2Zr$	$C_{38}H_{64}O_2Si_2Cl_2Zr$
Formula weight	763.16	771.22
Crystal dimensions (mm)	0.20 × 0.20 × 0.20	0.20 × 0.25 × 0.20
T (K)	291	293
Crystal system	Monoclinic	Monoclinic
Space group	C2/c (# 15)	$P2_1/n$ (# 14)
Unit cell dimension		
a (Å)	30.253(8)	8.822(5)
b (Å)	8.803(10)	22.614(9)
c (Å)	17.540(6)	20.861
β (°)	123.34(2)	98.11(5)
Z	4	4
V (Å^3)	3903(4)	4120(3)
D_c (g cm^{-3})	1.299	1.243
Scan type	$\omega-2\theta$	$\omega-2\theta$
Scan rate (° min^{-1})	8.0 (in ω)	4.0° (in ω)
Scan width	(1.47 + 0.30 tan θ)°	(1.15 + 0.30 tan θ)°
$2\theta_{max}$ (°)	50.0	50.0
Total reflections	3768	7775
Refinement method	Full-matrix least-squares on *F*	Full-matrix least-squares on F^2
Unique reflections	3688 [R(int) = 0.015]	7268 [R(int) = 0.0556]
Final *R* indices [$I > n\sigma(I)$] (%)	$R = 3.9$; $R_w = 3.6$ ($n = 3$)	$R = 6.2$; $R_w = 15.5$ ($n = 2$)
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$	0.53/−0.58	0.46/−0.42

Table 5
Atomic coordinates and equivalent isotropic displacement coefficients (Å^2) for **6**

Atom	*x*	*y*	*z*	B_{eq}
Zr	$\frac{1}{2}$	0.19462(6)	$\frac{1}{4}$	2.13(2)
Cl	0.46712(5)	0.0081(1)	0.30790(8)	4.97(5)
Si	0.65642(4)	0.4717(1)	0.28727(8)	3.13(5)
O	0.5958(1)	0.4325(3)	0.2647(2)	3.2(1)
C(1)	0.5461(1)	0.4299(4)	0.3380(3)	2.7(2)
C(2)	0.5821(1)	0.3653(4)	0.3192(3)	2.6(1)
C(3)	0.5998(1)	0.2235(4)	0.3623(3)	2.9(2)
C(4)	0.5794(1)	0.2043(5)	0.4184(2)	3.1(2)
C(5)	0.5874(2)	0.0891(6)	0.4815(3)	4.2(2)
C(6)	0.5618(2)	0.1057(6)	0.5258(3)	5.0(2)
C(7)	0.5276(2)	0.2290(6)	0.5091(3)	4.7(2)
C(8)	0.5184(2)	0.3398(5)	0.4480(3)	3.8(2)
C(9)	0.5453(1)	0.3312(5)	0.4014(2)	2.9(2)
C(10)	0.5180(2)	0.5806(5)	0.3070(3)	3.9(2)
C(11)	0.7083(2)	0.4237(5)	0.4081(3)	4.2(2)
C(12)	0.7014(2)	0.4954(7)	0.4816(3)	6.5(3)
C(13)	0.7642(2)	0.4570(7)	0.4299(4)	6.9(3)
C(14)	0.6521(2)	0.6757(6)	0.2557(4)	5.2(2)
C(15)	0.6935(2)	0.7265(7)	0.2351(4)	8.3(3)
C(16)	0.6513(2)	0.7855(6)	0.3230(5)	7.7(3)
C(17)	0.6659(2)	0.3508(6)	0.2085(3)	4.7(2)
C(18)	0.6707(2)	0.1813(7)	0.2314(4)	6.9(3)
C(19)	0.6237(2)	0.3783(8)	0.1067(4)	8.1(3)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

*3.1.2. 3-(Triisopropylsiloxy)indene (**2**)*

To a solution of triisopropylchlorosilane (32.22 g, 167.1 mmol) and 1-indanone (20.09 g, 152.0 mmol) in benzene (800 ml) was added dropwise DBU (20.02 g, 131.5 mmol). The reaction mixture was stirred overnight, diluted with Et_2O (400 ml), washed with water (2 × 500 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvents and distillation under reduced pressure gave **2** (30.80 g, 106.7 mmol, 70%) as a yellow oil (bp 114–117°C/0.3 mbar). ^{1}H-NMR ($CDCl_3$, δ): 7.44–7.42 (m, 1H), 7.39–7.37 (m, 1H), 7.32–7.27 (m, 1H), 7.23–7.19 (m, 1H), 5.40 (t, $^3J = 2.4$ Hz, 1H), 3.26 (m, $^3J = 2.4$ Hz, $^4J = 0.5$ Hz, 2H), 1.38–1.27 (m, 3H), 1.14 (d, $^3J = 7.2$ Hz, 18H). ^{13}C-NMR ($CDCl_3$, δ): 153.85, 142.67, 142.01, 125.96, 125.01, 123.68, 118.23, 105.18, 33.87, 17.98, 12.54.

3.1.3. *Bis(2-(triisopropylsiloxy)-1-indenyl)ethane (3)*

To a solution of **1** (28.85 g, 100.0 mmol) in THF (150 ml) was added dropwise *n*-butyllithium (40 ml of 2.5 M in hexanes, 100.0 mmol) at −15°C. The reaction mixture was stirred at ambient temperature for 2 h. To this green solution was added dropwise 1,2-dibromoethane (9.02 g, 48.0 mmol) in THF (30 ml) at −78°C, and the reaction mixture was stirred at room temperature for 12 h. The mixture was poured into water (80 ml) and the organic phase separated and dried over anhydrous Na_2SO_4. Evaporation of the solvents and crystallization from Et_2O at −15°C gave **3** (12.34 g, 20.5 mmol, 43%) as white crystals. Recrystallization from Et_2O gave diastereomerically pure **3** which was used for characterization. EIMS (calc/found): *m/e* 602.3972/602.3975. Mp: 88–89°C. ^{1}H-NMR ($CDCl_3$, δ): 7.19–7.05 (m, 6H), 6.96 (m, 2H), 5.67 (s, 2H), 3.20 (m, 2H), 1.97–1.91 (m, AA′, 2H), 1.63–1.57 (m, BB′, 2H), 1.31–1.21 (m, 6H), 1.10 (d, $^3J = 7.3$Hz, 18H), 1.08 (d, $^3J = 7.3$Hz, 18H). ^{13}C-NMR($CDCl_3$, δ): 165.14, 144.55, 140.58, 126.45, 122.60, 122.27, 118.63, 104.73, 49.27; 24.43, 18.00, 17.97, 12.44.

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å^2)for **8**

Atom	*x*	*y*	*z*	U_{eq}
Zr	−1681(1)	−1960(1)	−8750(1)	43(1)
Cl(1)	−2133(3)	−2997(1)	−8537(1)	81(1)
Cl(2)	−4234(2)	−1617(1)	−8623(1)	80(1)
Si(1)	796(2)	−3312(1)	−10167(1)	59(1)
Si(2)	−1367(2)	18(1)	−7725(1)	55(1)
O(1)	483(4)	−2778(2)	−9648(2)	52(1)
O(2)	−1044(5)	−546(2)	−8201(2)	53(1)
C(1)	−74(6)	−1712(3)	−9615(3)	45(2)
C(2)	−514(6)	2314(3)	−9731(3)	48(2)
C(3)	−2133(7)	−2345(3)	−9906(3)	57(2)
C(4)	−2697(7)	−1758(3)	−9942(3)	55(2)
C(5)	−4301(8)	−1547(4)	−10205(4)	76(2)
C(6)	−4410(10)	−864(5)	−10125(5)	108(3)
C(7)	−3069(11)	−533(4)	−10264(5)	108(3)
C(8)	−1624(9)	−704(3)	−9807(3)	67(2)
C(9)	−1438(7)	−1369(3)	−9756(3)	49(2)
C(10)	1496(7)	−1480(3)	−9415(3)	50(2)
C(11)	47(11)	−3065(4)	−10999(4)	91(3)
C(12)	790(15)	−2525(5)	−11196(5)	146(5)
C(13)	55(14)	−3538(5)	−11529(5)	148(5)
C(14)	−191(11)	−4026(4)	−9968(5)	98(3)
C(15A)	−1920(2)	−3942(17)	−10170(2)	199(18)
C(16A)	180(6)	−4364(15)	−9322(12)	132(15)
C(17A)	2959(18)	−3324(17)	−10104(14)	103(13)
C(18A)	3450(5)	−3852(14)	−10499(19)	135(17)
C(19A)	3850(3)	−3224(14)	−9430(11)	111(9)
C(21)	664(7)	−1379(3)	−8321(3)	44(1)
C(22)	−547(7)	−1104(3)	−8056(3)	44(2)
C(23)	−1117(7)	−1503(3)	−7630(3)	55(2)
C(24)	−212(7)	−2022(3)	−7596(3)	53(2)
C(25)	−199(10)	−2536(3)	−7137(4)	73(2)
C(26)	1246(15)	−2873(5)	−7118(6)	143(5)
C(27)	2007(14)	−2916(5)	−7635(6)	138(5)
C(28)	2126(7)	−2405(3)	−8090(4)	65(2)
C(29)	856(7)	−1954(3)	−8034(3)	46(1)
C(30)	1601(7)	−1114(3)	−8797(3)	55(2)
C(31A)	−370(2)	671(7)	−8077(8)	63(5)
C(32A)	−900(4)	733(13)	−8808(9)	111(10)
C(33A)	1390(2)	627(10)	−7970(14)	127(9)
C(34A)	−710(3)	−93(12)	−6848(8)	93(9)
C(35A)	−880(4)	448(15)	−6416(16)	138(13)
C(36A)	830(3)	−394(11)	−6739(13)	119(10)
C(37A)	−3504(16)	179(7)	−7882(14)	109(9)
C(38A)	−4030(2)	810(8)	−7847(15)	151(11)
C(39A)	−4320(3)	−277(10)	−7519(15)	115(10)

$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j \times 10^3$.

3.1.4. *Bis(3-(triisopropylsiloxy)-1-indenyl)ethane (4)*

To a solution of **2** (28.85 g, 100.0 mmol) in THF (200 ml) at −40°C was added dropwise *n*-BuLi (40.4 ml of a 2.5 M solution in hexanes, 101.0 mmol), and the reaction mixture was stirred 1 h at room temperature. The resulting solution was cooled to −80°C and treated dropwise with a solution of 1,2-dibromoethane (9.39 g, 50.0 mmol) in THF (100 ml). The reaction mixture was gradually warmed to room temperature, stirred overnight and washed with saturated ammonium chloride solution (300 ml). The organic phase was dried over anhydrous Na_2SO_4. Solvents were evaporated and the remaining red oil was dried in vacuo, yielding fairly pure **4** (29.92 g, 49.6 mmol, 99%) as a 1:1 mixture of two diastereomers. ^{1}H-NMR ($CDCl_3$, δ): 7.46–7.12 (m, 16H), 5.36 (d, $^3J = 2.3$ Hz, 2H), 5.35 (d, $^3J = 2.3$ Hz, 2H), 3.41–3.31 (m, 4H), 2.10–1.93 (m, AA′, 2H), 1.81–1.76 (m, AA′, 2H), 1.66–1.58 (m, BB′, 2H), 1.46–1.24 (m, BB′, 2H; m, 12H), 1.14 (d, $^3J = 6.9$ Hz, 18H), 1.13 (d, $^3J = 7.3$ Hz, 36H), 1.12 (d, $^3J = 7.3$ Hz, 18H). ^{13}C-NMR ($CDCl_3$, δ): 153.37, 153.30, 146.61, 146.53, 141.63, 141.61, 126.23 (2 × C), 125.25, 125.22, 122.57, 122.52, 118.26 (2 × C), 110.20, 109.87, 45.45, 45.39, 29.77, 29.37, 17.99 (2 × C), 12.53 (2 × C).

3.1.5. *Bis[2-(triisopropylsiloxy)indenyl]zirconium dichloride (5)*

To a solution of **1** (4.50 g, 15.6 mmol) in THF (50 ml) was added dropwise *n*-butyllithium (6.3 ml of 2.5 M in hexanes, 15.7 mmol) at −15°C. The reaction mixture was stirred at ambient temperature for 2 h and then added dropwise to a solution of $ZrCl_4$ (1.81 g, 7.8 mmol) in THF (50 ml) at room temperature and stirred for 3 h. The solvents were evaporated and the residue extracted with CH_2Cl_2 (80 ml) and filtered through Celite to remove lithium chloride. Evaporation left a orange solid which was crystallized from Et_2O at −15°C to yield **5** (2.38 g, 3.23 mmol, 42%) as a bright yellow microcrystalline powder. ^{1}H-NMR (CD_2Cl_2, δ): 7.54–7.49 (m, AA′, 4H), 7.21–7.17 (m, BB′, 4H), 5.51(s, 4H), 1.29–1.15 (m, 6H), 1.10 (d, $^3J = 7.0$ Hz, 36H). ^{13}C-NMR(CD_2Cl_2, δ): 158.66, 125.58, 125.23, 122.54, 94.89, 17.92, 12.83. In the mass spectrum of **5**, parent ions of the composition $C_{36}H_{54}Si_2O_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* 734–742. The base peak corresponds to $C_{18}H_{28}OSi^+$(2-(*i*-Pr$_3$)SiOInd$^+$) at *m*/*e* 288.

3.1.6. *rac-[Ethylenebis(2-(triisopropylsiloxy)-1-indenyl)] zirconium dichloride* (**6**)

To a solution of **3** (5.80 g, 9.6 mmol) in THF (80 ml) was added dropwise *n*-butyllithium (7.7 ml of 2.5 M in hexanes, 19.2 mmol) at −15°C. The reaction mixture was stirred at ambient temperature for 2 h and then added dropwise to a solution of $ZrCl_4$ (2.24 g, 9.6 mmol) in THF (50 ml) at room temperature and stirred for 3 h. The solvents were evaporated and the residue extracted with CH_2Cl_2 (140 ml) and filtered through Celite to remove lithium chloride. Evaporation left a yellow solid which was crystallized from toluene at −30°C to yield **6** (2.10 g, 2.7 mmol, 28%) as bright yellow crystals. ^{1}H-NMR ($CDCl_3$, δ): 7.63–7.59 (m, 2H), 7.35–7.27 (m, 4H), 7.04 (m, 2H), 6.03 (d, $^4J = 0.8$ Hz, 2H), 4.00–3.89 (m, AA′, 2H), 3.66–3.55 (m, BB′, 2H), 1.30–1.16 (m, 6H), 1.12 (d, $^3J = 7.4$ Hz, 18H), 1.02 (d, $^3J = 7.4$ Hz, 18H). ^{13}C-NMR($CDCl_3$, δ): 150.47, 125.81, 125.00, 124.67, 124.02, 122.64, 116.99, 107.44, 98.85, 26.12, 17.76, 17.73, 12.49. In the mass spectrum of **6**, parent ions of the composition $C_{38}H_{56}Si_2O_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* 760–768.

3.1.7. *rac-* (**7a**) *and meso-* (**7b**) *[Ethylenebis(1-triisopropylsiloxy)-3-indenyl)]zirconium dichloride*

To a solution of crude **4** (6.00 g, 9.9 mmol) in THF (70 ml) at −60°C was added dropwise *n*-BuLi (8.0 ml of a 2.5 M solution in hexanes, 20.0 mmol), and the reaction mixture was stirred for 6 h at room temperature. The resulting dark red solution was added dropwise to a solution of $ZrCl_4$ (2.32 g, 9.9 mmol) in THF (60 ml) at room temperature and stirred overnight. The solvents were evaporated and the residue extracted with CH_2Cl_2 (140 ml) and filtered through Celite to remove lithium chloride. Evaporation of the solvent left a bright orange solid which was shown to be a 5/1 mixture of **7a**/**7b** by ^{1}H-NMR. The solid was washed with Et_2O (2 × 150 ml) to yield fairly pure **7a** (3.35 g, 4.4 mmol, 44%). Crystallization of this powder from toluene gives analytically pure **7a** as orange crystals. The combined Et_2O extracts were evaporated and the residue was taken up in boiling hexane (150 m). Filtration through a short path of Celite, concentration and cooling to −15°C gave **7b** (0.48 g, 0.6 mmol, 6%), as a dark red crystalline solid. **7a**: ^{1}H-NMR (CD_2Cl_2, δ): 7.36–7.32 (m, 4H), 7.11–7.07 (m, 2H), 6.99–6.94 (m, 2H), 5.63 (s, 2H), 3.74–3.64 (m, AA′, 2H), 3.44–3.34 (m, BB′, 2H), 1.27–1.15 (m, 6H), 1.07 (d, $^3J = 7.4$ Hz, 18H), 1.00 (d, $^3J = 7.4$ Hz, 18H). ^{13}C-NMR (CD_2Cl_2, δ): 146.06, 126.52, 124.90, 122.54, 122.10, 121.93, 117.50, 110.94, 100.33, 28.51, 17.91, 12.94. **7b**:^{1}H-NMR ($CDCl_3$, δ):7.39–7.35 (m, 4H), 7.03–6.93 (m, 4H), 5.68 (s, 2H), 4.00–3.89 (m, AA′, 2H), 3.47–3.37 (m, BB′, 2H), 1.31–1.18 (m, 6H), 1.12 (d, $^3J = 7.3$ Hz, 18H), 1.04 (d, $^3J = 7.3$ Hz, 18H). ^{13}C-NMR ($CDCl_3$, δ): 144.33, 126.54, 124.45, 122.63, 121.66, 121.45, 118.21, 109.50, 102.29, 29.66, 17.88, 17.84, 12.61. In the mass spectra of **7a** and **7b**, which are almost superimposable, parent ions of the composition $C_{38}H_{56}Si_2O_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* 760–768.

3.1.8. *rac-[Ethylenebis(2-(triisopropylsiloxy)-4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride* (**8**)

A mixture of **6** (699 mg, 0.9 mmol) and PtO_2 (5 mg) in CH_2Cl_2 (50 ml) was hydrogenated at 70 bar in a stirred reactor for 16 h. The light green suspension was filtered through Celite and the solvent evaporated. The residue was dissolved in hexane (20 ml) and cooled to −15°C to provide **8** (460 mg, 0.6 mmol, 67%) as light green crystals. Concentration of the mother liquor and cooling yielded a second crop (52 mg, total yield 73%). ^{1}H-NMR ($CDCl_3$, δ):5.75 (s, 2H), 3.42–3.31 (m, AA′, 2H), 3.06–2.94 (m, 2H), 2.84–2.66 (m, 2H; m, BB′, 2H), 2.50–2.33 (m, 4H), 1.96–1.72 (m, 4H), 1.62–1.38 (m, 4H), 1.24–0.96 (m, 6H), 1.09 (d, $^3J = 7.0$ Hz, 18 H), 1.01 (d, $^3J = 7.2$ Hz, 18 H). ^{13}C-NMR ($CDCl_3$, δ): 143.32, 127.87, 117.41, 114.90, 107.10, 24.95, 24.05, 22.45, 22.08, 22.00, 17.72, 17.70, 12.46. In the mass spectrum of **8**, parent ions of the composition $C_{38}H_{64}Si_2O_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* 768–776.

3.1.9. *rac-[Ethylenebis(1-triisopropylsiloxy)-4,5,6,7-tetrahydro-3-indenyl)]zirconium dichloride* (**9**)

A mixture of **7a** (600 mg, 0.9 mmol) and PtO_2 (5 mg) in CH_2Cl_2 (50 ml) was hydrogenated at 70 bar in a stirred reactor for 16 h. The light green suspension was filtered through Celite and the solvent evaporated. The residue was dissolved in hexane (20 ml) and cooled to −15°C to give **9** (460 mg, 0.6 mmol, 67%) as light green needles. ^{1}H-NMR ($CDCl_3$, δ): 5.01 (s, 2H), 3.08–2.98 (m, AA′, 2H), 2.87–2.74 (m, BB′, 2H), 2.75–2.67 (m, 2H), 2.48–2.29 (m, 6H), 1.96–1.91 (m, 4H), 1.48–1.30 (m, 4H), 1.22–1.14 (m, 6H), 1.03 (d, $^3J = 7.2$ Hz, 18H), 1.07 (d, $^3J = 7.2$ Hz, 18H). ^{13}C-NMR ($CDCl_3$, δ):151.19, 121.28, 121.11, 115.76, 95.29, 27.19, 23.10, 21.82, 21.61, 20.56, 17.54, 17.51, 12.35. In the mass spectrum of **9**, parent ions of the composition $C_{38}H_{64}Si_2O_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* 768–776. The base peak corresponds to $C_{35}H_{57}Si_2O_2ZrCl_2^+$($M^+$-$C_3H_7$) at *m*/*e* 725–733.

3.2. Molecular structure determinations

Single crystals of **6** and **8** were obtained as described in the experimental part. The data sets were collected on a Rigaku AFC5S diffractometer using Mo–K_α radiation. The intensities were corrected for Lorentz and polarization effects. Experimental correction was carried out (Ψ-scan). The structures were solved by direct methods and refined by least-square techniques. Heavy atoms were refined with anisotropic and hydrogen atoms with isotropic displacement parameters except hydrogens of the isopropyl groups, which were included in calculated positions with fixed displacement parameters (1.2 × that of the host atom. For **8** two isopropyl groups of Si(1) and all three of Si(2) were disordered and were refined isotropically in two different positions, A and B. Refinements were performed using SHELXS97 [13]. Figures were plotted on ORTEP II [14]. The crystallographic data and atomic coordinates for **6** and **8** are collected in Tables 4–6. The atomic coordinates from **8**B and ORTEP top- and side-views from **6** and **8** can be obtained from the authors upon request.

Acknowledgements

Financial support from the Finnish Technology Development Center (TEKES) (HL, JN) and the Academy of Finland (RL) is gratefully acknowledged. The authors wish to thank P. Pennanen (NMR spectra), M. Reunanen (EIMS) and A. Penninkangas (synthesis of **2**) for their assistance.

References

[1] For recent reviews, see: (a) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1. (b) K.B. Sinclair, R.B. Wilson, Chem. Ind. 20 (1994) 257. (c) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (d) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255. (e) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143.

[2] (a) A.H. Hoveyda, J.P. Morken, Angew. Chem. Int. Engl. Ed. 35 (1996) 1262. (b) G.M. Diamond, R.F. Jordan, J.F. Petersen, J. Am. Chem. Soc. 118 (1996) 8024 and references therein.

[3] W. Spaleck, M. Antberg, B. Aulbach, B. Bachmann, V. Dolle, S. Haftka, F. Küber, J. Rohrmann, A. Winter, in: G. Fink, G. Mülhaupt, H.H. Brintzinger (Eds.), Ziegler Catalysts, Springer, Berlin, 1995, p. 83, and references therein.

[4] N. Schneider, M.E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper, H.H. Brintzinger, Organometallics 16 (1997) 3413, and references therein.

[5] Nitrogen substituted: (a) K.-P. Stahl, G. Boche, W. Massa, J. Organomet. Chem. 227 (1984) 113. (b) H.J.G. Luttikhedde, R.P. Leino, C.-E. Wilén, J.H. Näsman, M.J. Ahlgrén, T.A. Pakkanen, Organometallics 15 (1996) 3092. (c) H. Plenio, D. Burth, J. Organomet. Chem. 519 (1996) 269. (d) E. Barsties, S. Schaible, M.-H. Prosenc, U. Rief, W. Röll, O. Weyand, B. Dorer, H.H. Brintzinger, J. Organomet. Chem. 520 (1996) 63. (e) H.J.G. Luttikhedde, R. Leino, M.J. Ahlgrén, T.A. Pakkanen, J.H. Näsman, J. Organomet. Chem. in press.

[6] Boron substituted: (a) M.T. Reetz, H. Brümmer, M. Kessler, J. Kuhnigk, Chimia 49 (1995) 501. (b) K.A. Rufanov, V.V. Kotov, N.B. Kazennova, D.A. Lemenovskii, E.V. Avtomov, J. Lorberth, J. Organomet. Chem. 525 (1996) 287. (c) S.A. Larkin, J.T. Golden, P.J. Shapiro, G.P.A. Yap, D. Ming Jin Foo, A.L. Rheingold, Organometallics 15 (1996) 2393. (d) K. Rufanov, E. Avtomov, N. Kazennova, V. Kotov, A. Khvorost, D. Lemenovskii, J. Lorberth, J. Organomet. Chem. 536-537 (1997) 361. (e) D.S. Stelck, P.J. Shapiro, N. Basickes, A.L. Rheingold, Organometallics 16 (1997) 4546.

[7] Oxygen substituted: (a) R. Leino, H. Luttikhedde, C.-E. Wilén, R. Sillanpää, J.H. Näsman, Organometallics 15 (1996) 2450. (b) R. Leino, H.J.G. Luttikhedde, P. Lehmus, C.-E. Wilén, R. Sjöholm, A. Lehtonen, J.V. Seppälä, J.H. Näsman, Macromolecules 30 (1997) 3477. (c) R. Leino, H.J.G. Luttikhedde, P. Lehmus, C.-E. Wilén, R. Sjöholm, A. Lehtonen, J.V. Seppälä, J.H. Näsman, submitted to J. Organomet. Chem. (d) R. Leino, H.J.G. Luttikhedde, A. Lehtonen, P. Ekholm, J.H. Näsman, submitted to J. Organomet. Chem. (e) R. Leino, H.J.G. Luttikhedde, A. Lehtonen, R. Sillanpää, A. Penninkangas, J. Strandén, J. Mattinen, J.H. Näsman, submitted to J. Organomet. Chem.

[8] Sulfur substituted: R. Broussier, C. Bourdon, O. Blacque, A. Vallat, M.M. Kubicki, B. Gautheron, J. Organomet. Chem. 538 (1997) 83.

[9] Arsenic substituted: ref. 6d.

[10] (a) F.R.W.P. Wild, M. Wasiucionek, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 288 (1985) 63. (b) S. Collins, B. Kuntz, N. Taylor, D. Ward, J. Organomet. Chem. 342 (1988) 21. (c) J.A. Ewen, M.J. Elder, R.L. Jones, L. Haspeslagh, J.L. Atwood, S.G. Bott, K. Robinson, Makromol. Chem., Macromol. Symp. 48/49 (1991) 253. (d) F. Piemontesi, I. Camurati, L. Resconi, D. Balboni, M. Moret, R. Zeigler, N. Piccolrazzavi, Organometallics 14 (1995) 1256. (e) W. Kaminsky, O. Rabe, A.M. Schauwienold, G.U. Schupfner, J. Hanss, J. Kopf, J. Organomet. Chem. 497 (1995) 181. (f) L. Resconi, F. Piemontesi, I. Camurati, D. Balboni, A. Sironi, M. Moret, H. Rychlicki, R. Zeigler, Organometallics 15 (1996) 5046.

[11] S. Collins, Y. Hong, R. Ramachandran, N.J. Taylor, Organometallics 10 (1991) 2349, and references therein.

[12] Molecular mechanics calculations are in progress and will be reported elsewhere.

[13] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[14] C.K. Johnson, ORTEP II, Report ORNL-5138; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.