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Synthesis and characterization of Group 4 metallocene complexes with two disiloxanediyl bridges

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Abstract

Group 4 metallocene complexes with two disiloxanediyl bridges [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$]$ZrCl_2$ (**3**) and [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$]$HfCl_2$ (**4**) have been prepared by the reaction of MCl_4 (M = Zr, Hf) with distannylated bis(cyclopentadienes), while the zirconium complex, **3**, was subjected to a single-crystal X-ray diffraction study. The reaction of $TiCl_4$ with two equivalents of doubly disiloxane bridged distannylated bis(cyclopentadienes) gives rise to the formation of the doubly bridged dinuclear titanocene [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$][$TiCl_3$]$_2$ (**5**). Methylation and benzylation of the complex **3** results in [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$]$ZrMe_2$ (**6**) and [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$]-$Zr(CH_2C_6H_5)_2$ (**7**), respectively, without complications. Furthermore, the dibridged zirconium compound **3** polymerizes ethylene very efficiently in the presence of methylaluminoxane with an activity of 5 ton of PE/[Zr] mol h atm.

Keywords: Zirconium; Hafnium; Metallocene complexes; Doubly bridged metallocene; Disiloxane-bridged metallocene

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1. Introduction

Since the discovery by Kaminsky of the Cp_2ZrCl_2/methylaluminoxane system as an olefin polymerization catalyst, numerous metallocene complexes have been synthesized, and ansa-metallocenes having a conformational stability have particularly been adopted to produce stereospecific polymers [1]. In order to offer a more strained geometry compared with ansa-metallocenes, several types of doubly bridged metallocenes have been developed [2]. In 1994 Brintzinger and co-workers prepared a series of zirconocenes with two silanediyl and ethanediyl bridges and elucidated their structures. In addition they found out that these doubly bridged complexes tended to decompose when applied with the cocatalyst in olefin polymerization, probably due to the unusually large angle between Cp rings [3]. Recently, the groups of Bercaw and Weiss, however, demonstrated that doubly bridged metallocenes could be potentially useful for the development of a new polymerization catalyst [4]. More recently synthesis of the divalent samarium complex with two disiloxane bridges has been reported by Yasuda and co-workers [5]. We have been interested in the reactivity characteristics of polysiloxane-bridged ansa-metallocenes as well as dinuclear metallocenes [6] and here describe the synthesis and characterization of Group 4 metallocene complexes containing two adjacent disiloxanediyl bridges.

2. Results and discussion

The synthesis of doubly bridged metallocenes [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$]$ZrCl_2$ (**3**) and [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_3)_2$]$HfCl_2$ (**4**) can be conveniently achieved by the reaction of MCl_4 (M = Zr, Hf) with distannylated bis(cyclopentadienes), which is generated in situ from the reaction between dilithium salt of the ligand [μ,μ-$(Me_2SiOSiMe_2)_2(C_5H_4)_2$] (**2**) and two equivalents of trimethyltin chloride as shown in Scheme 1 [7]. Double bridged ligand **2** has been prepared in modest yield (60%) by treating $Na_2[C_5H_4{-}Si(CH_3)_2]_2O$ (**1**) with 1,3-dichlorotetramethyldisiloxane. Compound **2** is obtained

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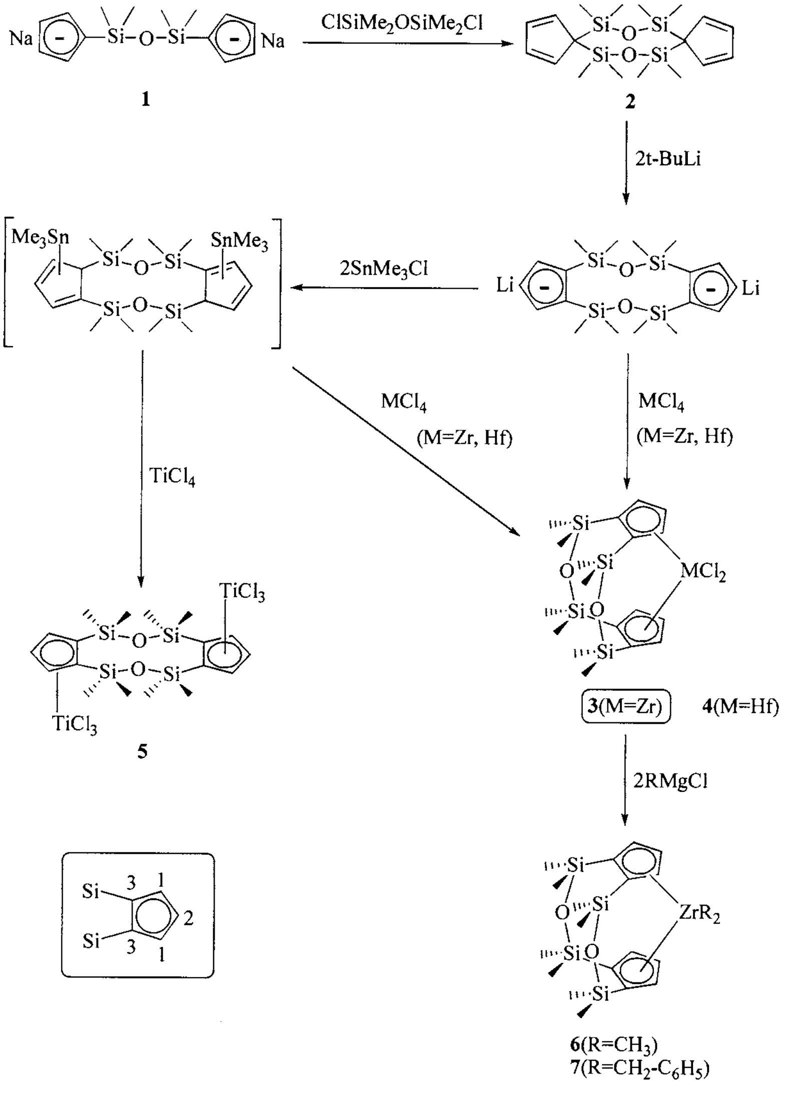
by sublimation as a white microcrystalline solid. Compound **2** in $CDCl_3$ exhibits signals diagnostic of the absence of a bridgehead proton, which indicates both bridges are attached to an identical carbon. In addition, the appearance of two sets of multiplets from Cp ring protons with the same integral at 6.75 and 6.63 ppm and one sharp signal at 0.08 ppm from Si–Me are consistent with its formulation [5,8]. Complexes **3** and **4** were characterized by ^1H- and ^{13}C-NMR, mass spectroscopy, and an X-ray crystal structure determination that confirmed the doubly bridged structure. The ^1H spectra of **3** and **4** in $CDCl_3$ exhibit a pseudo-doublet for the equivalent H_1 (δ 6.99 for **3**, $J_{HH} = 2.7$ Hz; δ 6.89 for **4**, $J_{HH} = 3$ Hz) and a pseudotriplet for H_2 protons (δ 6.86 for **3**, $J_{HH} = 2.7$ Hz; δ 6.74 for **4**, $J_{HH} = 3$ Hz) due to an AB_2 system indicating the existence of an adjacent double bridge as well as two singlets in the Si–Me region (δ 0.43 and 0.34 for **3**; δ 0.44 and 0.35 for **4**). The value of J can be used as a convenient parameter for distinguishing between an adjacent double bridge and a separated one. It is known that the magnitude of the coupling constant of Cp ring protons for the complex involving an adjacent bridge is 2.5–2.7 Hz, which is considerably higher than 1.5 Hz for the complex involving a separated double bridge, since protons that are not bonded to adjacent carbons will have a lower coupling constant [9]. This formulation is confirmed by X-ray crystallography (vide infra).

In contrast to the above reactions, the product formed from $TiCl_4$ treatment with distannylated ligand displays only one type of Si–Me protons at 0.5 ppm along with two AB_2 type resonances of Cp ring protons at 7.26 and 7.17 ppm. On the basis of the NMR data along with the earlier report, we assigned this complex as the *trans* isomer of the dinuclear titanocene complex $[\mu,\mu\text{-}(Me_2SiOSiMe_2)_2(C_5H_3)_2]ZrMe_2$ (**6**) since all eight methyl groups are equivalent for the *trans* isomer [10], which is actually well matched with the mass analysis



Scheme 1.

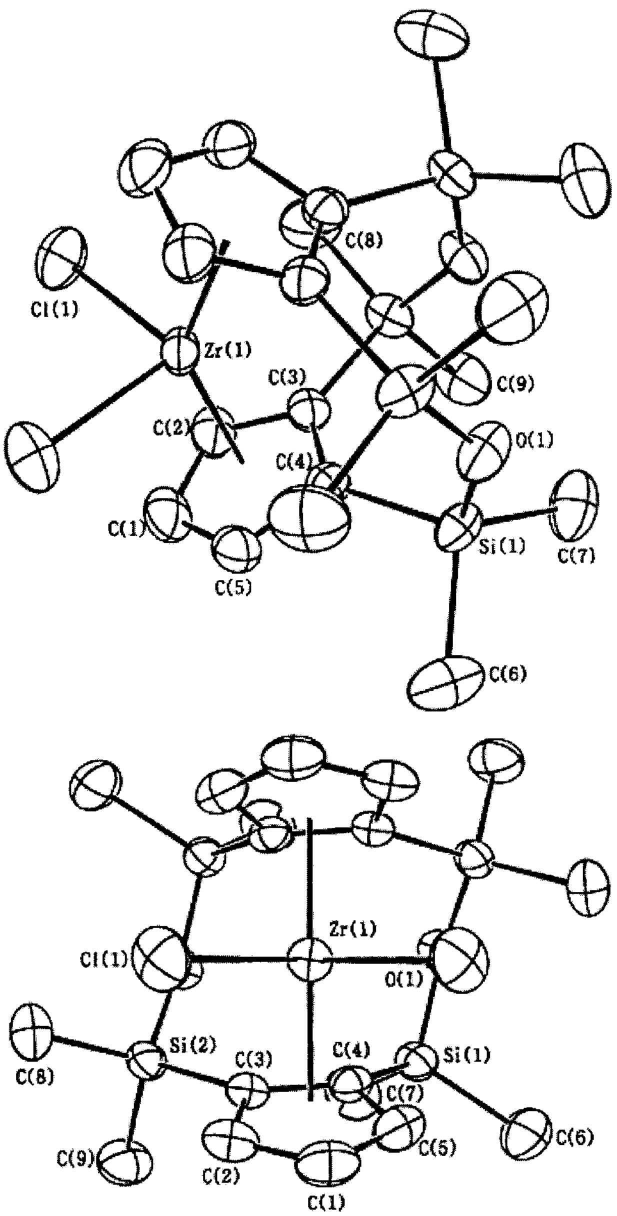


Fig. 1. Molecular structure of complex **3**.

data. An additional feature associated with NMR is that the ^{13}C resonance of the bridgehead carbon C_3 atom is sensitive to the mode of coordination. Generally it is known that the C_3 resonance is observed downfield from the C_1 and C_2 resonances for most dinuclear metallocene retaining the bridging mode of coordination, whereas the opposite behavior is observed for the mononuclear metallocene retaining the chelating mode of coordination [10]. The ^{13}C-NMR spectra of the complexes **3**, **4** and **6** demonstrate this feature very well. For the doubly bridged mononuclear metallocenes **3** and **4**, the chemical shifts of C_1 appear downfield (δ 138.6 for **3** and δ 137.6 for **4**) from those due to the C_2 and C_3 (δ 120–125). In contrast, the ^{13}C resonance of the *ipso*-carbon atom C_3 (δ 144.7) is downfield from those corresponding to C_1 (δ 135.4) and C_2 (δ 129) for the doubly bridged dinuclear titanocene **6**.

Complex **3** has been subjected to an X-ray crystallographic analysis, and an ORTEP diagram of its solid state molecular structure is shown in Fig. 1. The molecular structure of **3** exhibits C_2 symmetry and Cp rings are nearly eclipsed as in all double bridged metallocenes. The two Cp rings are adjacently bonded by two Si–O–Si chains. The oxygen atoms are out of the reflection plane defined by the zirconium and chlorine atoms. The most important feature in this structure is the angle between the mean plane of the two Cp rings of 44.1°, smaller than that of the corresponding complex with a single disiloxane bridge (51.1°) [11], which is the opposite trend to the known cases [3]. It is found that the dihedral angles of the complexes holding two silanediyl and ethanediyl bridges are larger than those of the single bridged ansa-metallocenes, offering extended room for the metallocene wedge. On the other hand, the dibridged complex **3** retains a slightly longer distance between Zr metal and Cp rings (2.225 Å) than the single disiloxane bridged complex (2.202 and 2.208 Å). This suggests that the introduction of two long bridging ligands such as (Si–O–Si) did not result in the additional expansion of the dihedral angle between the two Cp rings but resulted in an slight increase in the distance between the metal and the Cp ring (Tables 1–3).

Table 1
Summary of crystallographic data and intensity collection for **3**

Empirical formula	$C_{18}H_{30}O_2Si_4Cl_2Zr$
Formula weight	552.9
Crystal system	Monoclinic
Space group	*C*2/*c* (no. 15)
Z	4
Cell parameters	
a (Å)	8.612(1)
b (Å)	18.717(4)
c (Å)	15.323(2)
β (°)	91.08(1)
V (Å^3)	2469.7(7)
D_{calc} (g cm^{-3})	1.486
μ (cm^{-1} with Mo–K$_\alpha$)	8.3
Transmission factor (%)	77.56–99.92
Scan type	ω–2θ
$2\theta_{max}$ (°)	52.64
No. of reflections measured	2761
No. of reflections absorbed (unique) ($I > 3\sigma(I)$)	1999
No. of variables	123
Discrepancy indices	
R [a]	0.044
R_w [b]	0.068
Goodness-of-fit indicator [c]	2.23
Maximum shift in final cycles	Less than 0.01

[a] $R = \Sigma|F_o - |F_c|/\Sigma F_o|$.

[b] $R_w = [(\Sigma w(F_o - |F_c|)^2/\Sigma w(F_o^2))^{1/2}$, where $w = [\sigma(F^2)]^{-1}$.

[c] Estimated S.D. of an observation of unit weight: $[\Sigma w(F_o - |F_c|)^2/(N_o - N_v)]^{1/2}$.

Table 2
Positional parameters and their estimated S.D.s for **3** [a]

Atom	x	y	Z	$B(A2)$
Zr(1)	1.000	0.23189(3)	0.250	2.32(1)
Cl(1)	0.9251(2)	0.14505(7)	0.13874(9)	4.07(3)
Si(1)	1.2205(2)	0.41422(7)	0.31399(9)	2.66(3)
Si(2)	1.0558(2)	0.37562(8)	0.07559(8)	2.67(3)
O(1)	1.0661(4)	0.4261(2)	0.3721(2)	3.28(7)
C(1)	1.2817(6)	0.2167(3)	0.2084(4)	3.7(1)
C(2)	1.2047(6)	0.2467(3)	0.1355(4)	3.2(1)
C(3)	1.1540(5)	0.3160(3)	0.1584(3)	2.38(8)
C(4)	1.2043(5)	0.3295(3)	0.2479(3)	2.42(8)
C(5)	1.2828(6)	0.2668(3)	0.2750(4)	3.2(1)
C(6)	1.3933(7)	0.4032(4)	0.3879(4)	4.9(1)
C(7)	1.2433(7)	0.4957(3)	0.2466(4)	4.5(1)
C(8)	0.9489(7)	0.3184(4)	−0.0053(4)	4.5(1)
C(9)	1.1991(7)	0.4331(3)	0.0181(4)	4.3(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\times[a2\times B(1,1)+b2\times B(2,2)+c2\times B(3,3)+ab(\cos\gamma)\times B(1,2)+ac(\cos\beta)\times B(1,3)+bc(\cos\alpha)\times B(2,3)]$.

Table 3
Bond distances (Å) and bond angles (°) for **3** [a]

Bond distances			
Zr(1)–Cl(1)	2.434(1)	Si(2)–C(3)	1.879(5)
Zr(1)–C(1)	2.536(5)	Si(2)–C(8)	1.867(6)
Zr(1)–C(2)	2.526(5)	Si(2)–C(9)	1.869(6)
Zr(1)–C(3)	2.506(4)	C(1)–C(2)	1.406(8)
Zr(1)–C(4)	2.537(5)	C(1)–C(5)	1.386(8)
Zr(1)–C(5)	2.544(5)	C(2)–C(3)	1.416(7)
Si(1)–C(4)	1.885(5)	C(3)–C(4)	1.451(6)
Si(1)–C(6)	1.864(6)	C(4)–C(5)	1.414(7)
Si(1)–C(7)	1.855(6)	Zr(1)–$\mathrm{Cp_{cent}}$	2.2253
Bond angles			
Cl(1)–Zr(1)–Cl(1)′	96.20	C(3)–Si(1)–VO(1)′	57.25
$\mathrm{Cp_{cent}}$–Zr(1)–$\mathrm{Cp'_{cent}}$	137.33	C(4)–Si(1)–O(1)	56.13
$\mathrm{Cp_{cent}}$–$\mathrm{Cp'_{cent}}$	44.06	C(6)–Si(1)–C(7)	109.72
		C(3)–C(4)–C(5)	105.42

[a] Numbers in parentheses are estimated S.D.s in the least significant digits.

Table 4
Activity comparison of the various metallocenes in ethylene polymerization [a]

Catalyst	Activity	M_w ($\times 10^{-3}$)	M_w/M_n
Cp_2ZrCl_2	2250	61	2.6
Ind_2ZrCl_2	2452	66	2.6
$Et(Ind)_2ZrCl_2$	3073	68	2.6
Catalyst **3**	5245	12	2.3
Catalyst **4**	292	8	2.5

[a] Activity: kg PE/[M] h atm, [Al]/[M] = 10 000; polymerization temperature: 70°C; polymerization time: 2 h.

Alkylation of the complex **3** proceeds without complications. Compound **3** reacts with two equivalents of methyl Grignard to afford the crystalline, stable, dimethyl derivative **6** [12]. The dibenzyl derivative **7** is obtained under similar conditions. The proton and carbon NMR spectra of **6** display $\mathrm{Zr{-}C}H_3$ and $\mathrm{Zr{-}}C\mathrm{H_3}$ resonances at −0.40 and 30.9 ppm, respectively. The dibridged zirconium compound polymerizes ethylene very efficiently in the presence of methylaluminoxane (MAO) with an activity of 5 ton of PE/[Zr] mol h atm. It turned out that this number is almost identical to the activity of the monodisiloxane bridged zirconocene (5.5 ton of PE/[Zr] mol h atm). Under the same conditions, the polymerization activity of the hafnium complex is only 0.5 ton of PE/[Zr] mol h atm. Since reactivity in polymerization is sensitive to a variety of variables such as monomer purity and pressure, polymerization temperature, types of MAO employed, etc., we establish our standard using three typical metallocenes, Cp_2ZrCl_2, Ind_2ZrCl_2 and $Et(Ind)_2ZrCl_2$, obtaining an activity of 2, 2.5, and 3 ton of PE/[Zr] mol h atm, respectively, as shown in Table 4. This observation indicates that the characteristics of the dibridged complex with two disiloxane bridges are different from those of the reported dibridged complexes [3,4]. According to Brintzinger's experiments, the zirconocenes with two silanediyl and ethanediyl bridges tended to decompose during the olefin polymerizations. He reasoned this was a consequence of the lack of stable bonding between two Cp and zirconium due to the extraordinarily extended bonding angle between them (69.6° for two silanediyl bridging compounds and 62° for two ethanediyl bridging compounds). However, the complex **3** with two disiloxane bridges exhibits a much smaller dihedral angle of 44.1° between two Cp than those of the above-mentioned complexes. The difference in the dihedral angles might play a major role in distinguishing the catalytic properties of the doubly bridged metallocenes. Efforts to study the relationship between their detailed structural characteristics and the catalytic activity with the various products are in progress.

3. Experimental

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through a column of molecular sieve (4 Å) and Drierite (8 mesh). Tetrahydrofuran, diethyl ether, toluene, hexane, and pentane were distilled from sodium–benzophenone ketyl prior to use. Methylene chloride was distilled from phosphorus pentoxide prior to use. White filtering aid (Celite) was stored in a 130°C oven. 1,3-Dichlorotetramethyldisiloxane purchased from Adrich was used after distilling from calcium hydride. CpLi and CpNa (2.5 M solution in THF) were used as purchased from Aldrich. Modified methylaluminoxane (MMAO, type 4, 6.4 wt.% Al, Akzo, USA) was used without further purification. Proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in $CDCl_3$ at approximately 22°C on a Bruker DPX-300 FT-NMR spectrometer. Mass spectra were performed on a Autospec-Ultima E. IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer between 4000 and 200 cm^{-1}.

3.1. Synthesis of [μ,μ-($Me_2SiOSiMe_2$)$_2$(C_5H_4)$_2$] (**2**)

1,3-Dichlorotetramethyldisiloxane (5 g, 24.6 mmol) was added dropwise to a stirring solution of disodium tetramethyldisiloxanedicyclopentadienide (7.5 g, 24.6 mmol) in THF at room temperature (r.t.) and stirred overnight at r.t. As the reaction progressed, the precipitate Et(Ind)$ZrCl_2$ and NaCl ions were observed. After removing the precipitates by filtration, the solvent was removed in vacuo to give a yellow solution containing white solids. Sublimation of the resulting yellow oil at 80°C (0.01 mmHg) provides 5.5 g of pure **2** as a white microcrystalline solid (55%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.08 (s, 24H, Si–Me_2), 6.63 (m, 4H, C_5H_4), 6.74 (m, 4H, C_5H_4). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 0.05 (Si–Me_2), 63.35 (allylic carbon, C_5H_4), 131.39, 134.12 (vinyllic carbon, C_5H_4). High-resolution mass spectrum: [P^+] $C_{18}H_{32}O_2Si_4$, m/z 392.2 (M^+, 93%), 377.2 (M^+–CH_3, 47%). Anal. Calc. for $C_{18}H_{32}O_2Si_4$: C, 55.04; H, 8.21. Found: C, 54.91; H, 7.86%.

3.2. Synthesis of [μ,μ-($Me_2SiOSiMe_2$)$_2$(C_5H_3)$_2$]$ZrCl_2$ (**3**)

t-BuLi (1.7 M, 31.9 ml, 54.5 mmol) was added dropwise to a solution of the compound **2** (8.5 g, 21.7 mmol) in diethyl ether (100 ml) at r.t. The reaction immediately began to progress, and the formation of the white solid products, dilithium salts of the ligand **2**, was clearly observed within 5 min. The reaction mixture was allowed to stand overnight and then Me_3SnCl (10.8 g, 54.5 mmol) was introduced to the reaction mixture at -40°C. The solution was warmed to r.t. and stirred for 5 h. As the reaction progressed, the appearance of the white LiCl at the cost of the disappearance of the generated dilithium salts was easily conceivable. After filtration of LiCl the solvent was evaporated under vacuum, and then toluene with $ZrCl_4$ (5.1 g, 21.7 mmol) was added at r.t. The reaction mixture was heated to 80°C and stirred overnight. The solvent was removed in vacuo to leave light purple powder. Recrystallization from toluene yields pure **3** as a transparent solid (8.4 g, 70% based on the compound **2**, 40% total yield based on the CpNa). We got very clean spectroscopic data and provide proton and carbon NMR spectra of the purified product for reference, although our attempts to obtain a satisfactory analysis failed. M.p.: 180°C, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.35 (s, 12H, Si–Me_2), 0.43 (s, 12H, Si–Me_2), 6.86 (t, $J = 2.7$ Hz, 2H, C_5H_3), 6.99 (d, $J = 2.7$ Hz, 4H, C_5H_3). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 2.01, 2.42 (Si–Me_2), 123.41, 123.75, 138.63 (C_5H_3). High-resolution mass spectrum: [P^+] $C_{18}H_{30}O_2Si_4Cl_2Zr$, m/z 549.97 (M^+, 94%), 534.94 (M^+–CH_3, 81%).

3.3. Synthesis of [μ,μ-($Me_2SiOSiMe_2$)$_2$(C_5H_3)$_2$]$HfCl_2$ (**4**)

This reaction proceeded in an analogous fashion to the above reaction with the following exceptions: $HfCl_4$ (7.09 g, 21.7 mmol) was used in place of $ZrCl_4$ (5.1 g, 21.7 mmol). The product was recrystallized from hexane instead toluene to obtain colorless crystalline solids in 55% yield (30% based on the starting CpNa). As in the above case, attempts to obtain satisfactory analysis failed, probably due to the environmental contact during analysis. M.p.: 195°C, ^{1}H-NMR (300MHz, $CDCl_3$): δ 0.35 (s, 12H, Si–Me_2), 0.44 (s, 12H, Si–Me_2), 6.74 (t, $J = 3$ Hz, 2H, C_5H_3), 6.89 (d, $J = 3$ Hz, 4H, C_5H_3). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 1.96, 2.44 (Si–Me_2), 121.48, 122.13, 137.60 (C_5H_3). High-resolution mass spectrum: [P^+] $C_{18}H_{30}O_2Si_4Cl_2Hf$, m/z 640.02 (M^+, 39%), 624.99 (M^+–CH_3, 33%).

3.4. Synthesis of [μ,μ-($Me_2SiOSiMe_2$)$_2$(C_5H_3)$_2$][$TiCl_3$]$_2$ (**5**)

This reaction proceeded in an analogous fashion to the above reaction with the following exceptions: $TiCl_4$ (4.1 g, 21.7 mmol) was used in place of $ZrCl_4$ (5.1 g, 21.7 mmol). The product was recrystallized from hexane instead toluene to obtain yellow crystalline solids in 70% yield (40% total yield based on the CpNa). M.p.: 200°C, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.49 (s, 24H, Si–Me_2), 7.17 (t, $J = 3$ Hz, 2H, C_5H_3), 7.24 (d, $J = 3$ Hz, 4H, C_5H_3). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 1.95, 2.09 (Si–Me_2), 129.05, 134.62, 144.69 (C_5H_3). High-resolution mass spectrum: [P^+] $C_{18}H_{30}O_2Si_4Cl_6Ti$, m/z 627.0 (M^+–2Cl, 34%).

3.5. Synthesis of [μ,μ-($Me_2SiOSiMe_2$)$_2$(C_5H_3)$_2$]$ZrMe_2$ (**6**)

MeMgCl (3 M, 2.5 ml, 7.6 mmol) was added dropwise at -78°C to 50 ml of THF solution containing 2 g (3.6 mmol) of **3**. The reaction mixture was warmed to r.t. and stirred overnight. After evaporation of solvent, methylene chloride was added followed by filtration to remove $MgCl_2$. The solvent was removed under vacuum to leave white power. Recrystallization from hexane yields pure **6** (70% based on the compound **3**, 30% total yield based on the CpNa). M.p.: 190°C, ^{1}H-NMR (300 MHz, $CDCl_3$): δ -0.40 (s, 6H, Zr–Me_2), 0.21 (s, 12H, Si–Me_2), 0.34 (s, 12H, Si–Me_2), 6.79 (d, $J = 2.7$ Hz, 4H, C_5H_3), 6.82 (t, $J = 2.7$ Hz, 2H, C_5H_3). ^{13}C-NMR (75.46

MHz, $CDCl_3$): δ 1.95, 2.09 (Si–Me_2), 129.05, 134.62, 144.69 (C_5H_3).

3.6. Synthesis of [μ,μ-($Me_2SiOSiMe_2$)$_2$-(C_5H_3)$_2$]Zr($CH_2C_6H_5$)$_2$ (7)

$C_6H_5CH_2MgCl$ (1 M, 7.6 ml, 7.6 mmol) was added dropwise at -78°C to 50 ml of THF solution containing 2 g (3.6 mmol) of **3**. The reaction mixture was warmed to r.t. and stirred overnight. After evaporation of solvent, ether was added followed by filtration (50% yield based on the compound **3**, 20% yield based on the CpNa). M.p.: 220°C, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 12H, Si–Me_2), 0.33 (s, 12H, Si–Me_2), 0.18 (s, 4H, CH_2–C_6H_5), 6.28 (t, 2H, C_5H_3), 6.49 (d, 4H, C_5H_3), 6.85 (m, 6H, CH_2–C_6H_5), 7.18 (m, 4H, CH_2–C_6H_5) ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 2.48, 2.94 (Si–Me_2), 64.14 (CH_2–C_6H_5), 121.51, 121.58, 125.93 (C_5H_3), 128.48, 132.54, 153.73 (CH_2–C_6H_5).

3.7. Polymerization of ethylene

All operations were carried out under a nitrogen atmosphere. In a 400 ml glass reactor were introduced sequentially the proper amount of toluene (100 ml) and MMAO ([Al]/[M] $=$ 10 000) solution and then the system was saturated with ethylene. With continuous flow of ethylene, the polymerization was initiated by injecting the solution of metallocenes (compound **3**: [Zr] $= 6.19 \times 10^{-7}$ mol l^{-1}; compound **4**: [Hf] $= 7.82 \times 10^{-7}$ mol l^{-1}). After 2 h polymerization, polyethylene (3.25 g, 0.23 g) was precipitated in acidified methanol.

3.8. X-ray crystallographic analysis of **5**

A crystal used for the measurements was grown from toluene solution. X-ray diffraction data were collected on an Enraf–Nonius CAD 4 diffractometer with Mo–K_α radiation ($\lambda = 0.70930$ Å). The scan mode was the ω–2θ method, and the scan rate was 16.0° min^{-1}. Reflections were collected in the range $2\theta < 120°$. The structures were solved by direct methods (MULTAN) [13] and refined anisotropically by full-matrix least-squares methods by using a MolEN program [14]. Anisotropic thermal parameters were employed for non-hydrogen atoms, and isotropic, for hydrogens. The weighting scheme was $w^{-1} = \sigma F^2$. The final discrepancy indices $R = \Sigma||F_o - |F_c|/\Sigma F_o|$ and $R_w = [(\Sigma w(F_o - |F_c|)^2/\Sigma w(F_o^2))^{1/2}$ are 0.044 and 0.068, goodness-of-fit $=$ 2.23.

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References

[1] For recent reviews, see: (a) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 144. (b) M. Bochman, J. Chem. Soc. Dalton Trans. (1996) 255. (c) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1996) 1143. (d) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1. (e) R.F. Jordan, Adv. Organomet. Chem., 32 (1991) 325.

[2] (a) R.L. Halterman, A. Tretyakov, D. Combs, J. Chang, M.A. Khan, Organometallics 16 (1997) 3333. (b) A.M. Barriola, A.M. Cano, T. Cuenca, F.J. Fernandez, P. Gomez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 542 (1997) 247. (c) A. Cano, T. Cuenca, P. Gomez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 526 (1996) 227. (d) T. Cuenca, M. Galakhov, E. Royo, P. Royo, J. Organomet. Chem. 515 (1996) 33. (e) H. Lang, S. Blau, A. Muth, K. Weiss, U. Neugebauer, J. Organomet. Chem. 490 (1995) C32. (f) R.B. Grossman, J. Tsai, W.M. Davis, A. Gutierrez, S.L. Buchwald, Organometallics 13 (1994) 3892.

[3] (a) B. Dorer, M.H. Prosenc, U. Rief, H.-H. Brintzinger, Organometallics 13 (1994) 3868. (b) W. Mengele, J. Diebold, C. Troll, W. Röll, H.-H. Brintzinger, Organometallics 12 (1993) 1931.

[4] (a) T.A. Herzog, D.L. Zublis, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11 988. (b) K. Weiss, U. Neugebauer, S. Blau, H.J. Lang, Organomet. Chem. 520 (1996) 171.

[5] E. Ihara, M. Nodono, K. Katsura, Y. Adachi, H. Yasuda, M. Yamagashira, H. Hashimoto, N. Kanahisa, Y. Kai, Organometallics 17 (1996) 3945.

[6] (a) S.K. Noh, S. Kim, J. Kim, D.-H. Lee, K.-B. Yoon, H.-B. Lee, S.W. Lee, W.S. Huh, J. Polym. Sci. Part A Polym. Chem. 35 (1997) 3717. (b) S.K. Noh, S. Kim, D.-H. Lee, K.-B. Yoon, H.-B. Lee, Bull. Kor. Chem. Soc. 18 (1997) 618. (c) S.K. Noh, G.G. Byun, C.S. Lee, D.-H. Lee, K.-B. Yoon, K.S. Kang, J. Organomet. Chem. 518 (1996) 1. (d) D.-H. Lee, K.-B. Yoon, E.H. Lee, S.K. Noh, C.S. Lee, W.S. Huh, Macromol. Rapid Commun. 17 (1996) 325. (e) D.-H. Lee, K.-B. Yoon, E.H. Lee, S.K. Noh, G.G. Byun, C.S. Lee, Macromol. Rapid Commun. 16 (1995) 265.

[7] (a) I.E. Nifant'ev, P.V. Ivchenko, Organometallics 16 (1997) 713. (b) L. Resconi, F. Piemontesi, I. Camurati, O. Sudmeijer, I.E. Nifant'ev, P.V. Ivchenko, L.G. Kuz'mina, J. Am. Chem. Soc. 120 (1998) 2308.

[8] (a) P. Jutzi, R. Krallmann, G. Wolf, B. Neuman, H.-G. Stammler, Chem. Ber. 124 (1991) 2391. (b) J. Hiermeier,, F.H.G. KölerMüller, Organometallics 10 (1991) 1787.

[9] J.L. Huhmann, J.Y. Corey, N.P. Rath, Organometallics 15 (1996) 4063.

[10] (a) J.Y. Corey, J.L. Huhmann, N.P. Rath, Inorg. Chem. 34 (1995) 3203. (b) A. Cano, T. Cuenca, P. Gomez-Sal, B. Royo, P. Royo, Organometallics 13 (1994) 1688.

[11] (a) S. Ciruelos, T. Cuenca, P. Gomez-Sal, A. Manzanero, P. Royo, Organometallics 14 (1995) 177. (b) M.D. Curtis, J.J. D'Errico, P.S. Epstein, L.G. Bell, Organometallics 2 (1983) 1808.

[12] T. Cuenca, A. Padilla, A. Parra, M. Parra-Make, M.A. Pellinghelli, A. Tiripicchio, Organometallics 14 (1995) 848.

[13] P. Nain, S.J. Fiske, S.E. Hull, L. Lessinger, G. Gernain, J.P. Declerg, N.M. Woolfson, MULTAN 80, University of York, 1980.

[14] Uninteractive Structure Solution Procedure, Enraf–Nonius, Delft, The Netherlands, 1990.