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Synthesis, structure and α -olefin polymerization activity of group 4 metal complexes with [OSSO]-type bis(phenolate) ligands

Marcin Konkol^a, Masaaki Nabika^a, Tetsuya Kohno^b, Takahiro Hino^a, Tatsuya Miyatake^{a,*}

^a Petrochemicals Research Laboratory, Sumitomo Chemical Co., Ltd., 2-1 Kitasode, Sodegaura, Chiba 299-0295, Japan ^b Genomic Science Laboratories, Dainippon Sumitomo Pharma Co., Ltd., 3-1-98 Kasugadenaka, Konohana-ku, Osaka 554-0022, Japan

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ABSTRACT

The tetradentate [OSSO]-type bis(phenol) ligands, $[{2,2'-(HOC_6H_2-4,6-R_2)_2CH_2SCH_2CH_2SCH_2}]$ (R = ^tBu, **2**; Br, **3**) react with MBz₄ (M = Zr, Hf) to yield the corresponding dibenzyl complexes, $[M{2,2'-(OC_6H_2-4,6 R_2_2CH_2SCH_2CH_2SCH_2Bz_2$ (R = Br, M = Zr, **4**^{Br}; Hf, **5**^{Br}; R = ^tBu, M = Hf, **5**) in a good to very good yield. Zirconium diamido complexes, $[Zr{2,2'-(OC_6H_2-4,6-R_2)_2CH_2SCH_2SCH_2SCH_2}(NMe_2)_2]$ (R = ^tBu, **6**; Br, **6**^{Br}) were prepared in a reaction of the corresponding disodium salt of 2 or 3 generated in situ with ZrCl₂(NMe₂)₂(THF)₂. Heating of **6** with TMSCl at 35 °C afforded zirconium dichloro complex, [Zr{2,2'- $(OC_6H_2-4,6^{-t}Bu_2)_2CH_2SCH_2CH_2SCH_2]$ (7), whereas the titanium analog 8 was prepared in a direct reaction with TiCl₄. While for complexes 4^{Br} , 5, 5^{Br} , 6, 6^{Br} and 7 single C₂-symmetric isomers were observed in solution at room temperature, as revealed by the NMR spectroscopic data, titanium complex **8** formed as a mixture of $cis-\alpha$ (**8a**) and $cis-\beta$ (**8b**) isomers in a ratio of approx. 20:80% (measured in CD₂Cl₂). The VT NMR studies revealed a reversible conversion of **8a** into **8b** above 60 °C. The X-ray crystal structure determination of complexes 4^{Br} , 5^{Br} and 7 confirmed their C_2 -symmetrical configuration in the solid state with *cis*-arranged benzyl/chloro groups and the *trans*-coordination of two bulky phenolato moieties. The zirconium dibenzyl complexes exhibit good catalytic activities in homopolymerization of 1-hexene (atactic poly(1-hexene), PDI = 1.5-1.7) and vinylcyclohexane (isotactic poly(vinylcyclohexane), PDI = 1.2-1.8) upon activation with a co-catalyst. In both polymerizations no increase of activity was observed for the complex 4^{Br} with electron-withdrawing substituents on phenolate rings. Moreover, polymerization of liquid propylene catalyzed by the titanium dichloro isomeric mixture 8 afforded at 5 °C ultrahigh molecular weight atactic/isotactic polypropylene mixtures.

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1. Introduction

The design and development of new non-metallocene multidentate ligand frameworks for transition metal-based α -olefin polymerization catalysts is of particular interest from the viewpoint of better understanding of the structure-property relationships and thus achieving better control over molecular weight and stereochemistry of polymers [1,2]. In recent few years non-metallocene group 4 complexes of the type [MX₂(ODo)₂] and [MX₂(ODoDoO)] (Do = heteroatom donor, ODo⁻ = monoanionic, ODoDoO²⁻ = chelating, dianionic ligand) based on hard, electronegative, π -donor aryl alkoxide ligands [3] with a sulfur [4,5], nitrogen [6,7], phosphorus [8] or oxygen [9] donor function have been receiving particular attention, since these ligands allow

* Corresponding author. *E-mail address:* miyataket1@sc.sumitomo-chem.co.jp (T. Miyatake). considerable stereoelectronic variations of the resulting precatalysts. It has been demonstrated that the nature of the link between the phenolate moieties in tetradentate bis(phenolate) ligands may have an influence on the ligand wrapping around a metal center and may thus affect reactivity and stereospecificity [7h]. The group 4 metal complexes with [OSSO]-type bis(phenolate) ligands possessing 1,4-dithiabutanediyl-bridge developed by Okuda et al. have been shown to lead to interesting chemical activities such as the controlled isospecific polymerization of styrene [5b,e,i-k,n] and nonstereospecific oligomerization of 1hexene [5f]. Kol et al. featured a methylene spacer between the S donor and the arene ring, achieving higher activity in polymerization of 1-hexene than the corresponding Salan-type analog but with no stereocontrol (atactic polymer) [5g]. In contrast, high isoselectivity in 1-hexene polymerization has been recently observed by Ishii et al. for the zirconium dibenzyl complex with the related bis(phenolate) ligand bearing trans-1,2-cyclooctanediyl backbone [5a]. Moreover, Kol et al. have demonstrated for the

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Scheme 1. Synthetic route for the ligands 2 and 3.

Salan-type/diamine bis(phenolate) complexes that incorporation of the electron-withdrawing halo substituents on phenolate rings increases the catalyst activity in highly isospecific polymerization of vinylcyclohexane [7e] and in living isospecific polymerization of 1-hexene [7j].

As a part of our investigations on group 4 metal complexes supported by bis(phenolate) ligands with S-containing linkers [4e,f], we were interested in influence of the methylene spacer incorporated between the phenoxy group and the sulfur atom (six-membered chelate ring) as well as the electron-withdrawing substituents on the phenolate ring of the [OSSO]-type ligand on polymerization activity and stereoselectivity of group 4 metal complexes. We report here the coordination of [OSSO]-type 1,4-dithiabutanediyl-bridged bis (phenolate) ligands, possessing a Salan-type methylene spacer, at tetravalent titanium, zirconium and hafnium centers and the activity of complexes as catalyst precursors in 1-hexene, vinylcyclohexane and propylene homopolymerization.

2. Results and discussion

2.1. Synthesis and structure of complexes

The tetradentate bis(phenol), 2,2'-[ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-di-*tert*-butylphenol) (**2**) was prepared according to a procedure reported by Kol et al. [5g]. The Br-substituted bis(phenol), 2,2'-[ethane-1,2-diylbis(sulfanediylmethylene)] bis(4,6dibromophenol) (**3**) was synthesized in an analogous manner. Reacting 2 equiv. of 2,4-dibromo-6-(bromomethyl)phenol with 1,2ethanedithiol in the presence of triethylamine gave the ligand precursor **3** in 64% yield (Scheme 1).

A reaction of the ligand precursors **2** and **3** with zirconium/ hafnium tetrabenzyl complexes at room temperature led cleanly to the corresponding bis(phenolate) dibenzylzirconium $(4/4^{Br})$ and hafnium $(5/5^{Br})$ complexes (Scheme 2).

The zirconium dibenzyl complex **4** has been previously reported by Kol et al. [5g]. The complexes were prepared as yellow ($\mathbf{4}^{Br}$) or off-white/beige ($\mathbf{5}/\mathbf{5}^{Br}$) solids in a good ($\mathbf{5}$, 57%) to very good yield ($\mathbf{4}^{Br}/\mathbf{5}^{Br}$, 89/89%). The ¹H NMR spectroscopic data of all zirconium ($\mathbf{4}/\mathbf{4}^{Br}$) and hafnium ($\mathbf{5}/\mathbf{5}^{Br}$) dibenzyl complexes indicate a molecular C_2 -symmetry at ambient temperature, which is evident from the symmetry-related chemically equivalent phenolate rings, the AB spin pattern for the CH₂SCH₂CH₂SCH₂ bridge and the AB doublets for the CH₂ groups of both *cis*-benzyl ligands.

The complexes 4^{Br} and 5^{Br} were further characterized by means of X-ray crystallography and the crystals were found to be isostructural. The ORTEP diagrams of 4^{Br} and 5^{Br} with selected bond lengths and angles are shown in Figs. 1 and 2. The crystallographic data for 4^{Br} and 5^{Br} are shown in Table 1.

The results confirm the C_2 -symmetrical configuration of the complexes in the solid state with *cis*-arranged benzyl (**4**^{Br},



Scheme 2. Synthetic route for the complexes 4/4^{Br}, 5/5^{Br} and 6/6^{Br}.



Fig. 1. ORTEP diagram of the molecular structure of $[Zr\{2,2'-(OC_6H_2-4,6-Br_2)_2CH_2SCH_2CH_2SCH_2]$ (**4**^{Br}). Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Zr1-S1 2.7934(7), Zr1-S2 2.7932(6), Zr1-O1 2.028(2), Zr1-O2 2.007(2), Zr1-C7 2.307(3), Zr1-C14 2.314(3), Zr1-C6 2.516(2), S1-Zr1-S2 73.60(2), 01-Zr1-02 156.35 (7), C7-Zr1-C14 126.55(11), Zr1-C7-C6 80.6(2), Zr1-C14-C13 120.0(2), S1-Zr1-C14 157.36(7), S2-Zr1-C7 149.37(8).

C7-Zr1-C14 126.55(11)°; 5^{Br}, C21-Hf1-C14 125.6(2)°) and thioether groups (4^{Br}, S1–Zr1–S2 73.60(2)°; 5^{Br}, S1–Hf1–S2 73.82 $(4)^{\circ}$). The *trans*-coordination of two bulky phenolato moieties (4^{Br} , 01–Zr1–O2 156.35(7)°; **5^{Br}**, 01–Hf1–O2 157.30(17)°) is enforced by the gauche (synclinal) conformation of the sulfur atoms of the SCH₂CH₂S bridge with the corresponding dihedral angles of -40.8 $(3)^{\circ}$ (**4**^{Br}) and $-39.1(6)^{\circ}$ (**5**^{Br}). In both structures, one of the benzyl groups binds in a η^1 -mode with an M–C–C angle of ca. 120.1°, whereas the second benzyl group shows a η^2 -binding mode via the *ipso* carbon atom (**4**^{Br}, Zr1–C7–C6 80.6(2)°; **5**^{Br}, Hf1–C14–C13 81.3 (4)°) with the corresponding $M-C_{ipso}$ bond distances of 2.516(2) and 2.514(5) Å, respectively. A similar η^2 -coordination mode of a benzyl group in group 4 metal complexes was observed by Ishii [5a], Okuda [5b] and Carpentier [6c]. In both structures 4^{Br} and 5^{Br} coplanarity of the zirconacyclopropane ring, the methylene carbon atom of the second benzyl group and the two sulfur atoms results in pentagonal bipyramidal geometry around a heptacoordinate metal center. This higher coordination number of the metal center may be attributed to its electron deficiency as was postulated by Kol et al. for the related zirconium dibenzyl complexes of [ONNO']type Salan ligands [7b]. Moreover, in $\mathbf{4^{Br}}$ and $\mathbf{5^{Br}}$ a phenyl ring of the η^2 -benzyl group is pointed toward the η^1 -benzyl group. Compared to the other reported hafnium dibenzyl complex of 1,4dithiabutanediyl-bridged [OSSO]-type ligand, [Hf{2,2'-(OC₆H₂-4,6-^tBu₂)₂SCH₂CH₂S}Bz₂] [5n], where two benzyl groups are directed outwards from each other, this results in an increase of the C–Hf–C bond angle in $\mathbf{5}^{\mathbf{Br}}$ (125.6(2)° vs. 94.3(1)°) and in shorter Hf–S bond distances (2.7714(12) and 2.7696(14) Å in **5**^{Br} vs. 2.9222 (9) and 2.8260(8) Å). In the case of $\mathbf{4}^{\mathbf{Br}}$, although the C–Zr–C bond angle is increased compared to the zirconium dibenzyl complex of 1,4-dithia-trans-1,2-cyclooctanediyl-bridged complex, [Zr {2,2'-(OC₆H₂-4,6-^tBu₂)₂CH₂S(Cyoct)SCH₂}Bz₂] [5a] (126.55(11)° vs.



Fig. 2. ORTEP diagram of the molecular structure of $[Hf[2,2'-(OC_6H_2-4,6-Br_2)_2CH_2SCH_2SCH_2]Bz_2]$ (**5**^{Br}). Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Hf1–S1 2.7714(12), Hf1–S2 2.7696(14), Hf1–C11 1.994(3), Hf1–O2 2.006(3), Hf1–C14 2.287(7), Hf1–C21 2.293(6), Hf1–C13 2.514(5), S1–Hf1–S2 73.82(4), 01–Hf1–O2 157.30(17), C14–Hf1–C21 125.6(2), Hf1–C14–C13 81.3(4), Hf1–C21–C20 120.2(3), S1–Hf1–C14 150.30(17), S2–Hf1–C21 157.63(14).

114.05(19)°), the Zr–S bond distances are similar (2.7934(7) and 2.7932(6) Å in **4**^{Br} vs. 2.8107(8) and 2.7682(8) Å). They are, however, shorter than the Zr–S bond lengths for the [Zr{2,2'-(OC₆H₂-4,6-^tBu₂)₂CH₂SCH₂CH₂SCH₂}(O^tBu)₂] complex (2.8279(7) and 2.8485(7) Å) [5g].

Table 1

Summary of crystallographic data for **4**^{Br}, **5**^{Br} and **7**.

5 5	0 1		
Complex	$\mathbf{4^{Br} \cdot CH_2Cl_2}$	$\mathbf{5^{Br} \cdot CH_2Cl_2}$	$7 \cdot CH_2Cl_2$
Empirical	C31H28Br4	C ₃₁ H ₂₈ Br ₄	C ₃₃ H ₅₀
formula	Cl ₂ O ₂ S ₂ Zr	Cl ₂ O ₂ S ₂ Hf	Cl ₄ O ₂ S ₂ Zr
Mr	978.42	1065.69	775.91
Crystal size/mm	$0.20\times0.10\times0.10$	$0.10\times0.10\times0.05$	$0.20 \times 0.10 \times 0.10$
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	8.9386(4)	8.9328(4)	13.2966(3)
b/Å	22.6139(9)	22.625(1)	17.3620(4)
c/Å	17.1700(7)	17.1494(7)	18.3052(4)
V/Å ³	3408.6(2)	3404.1(3)	3761.0(2)
Space group	P2 ₁ /c (#14)	P2 ₁ /c (#14)	P-1 (#2)
Ζ	4	4	4
$D_{calc}/g \text{ cm}^{-3}$	1.906	2.079	1.370
F(000)	1904.00	2032.00	1810.00
μ (CuK α)/cm ⁻¹	110.445	139.828	62.466
T/K	93 ± 1	93 ± 1	93 ± 1
2θ _{max} /deg	143.4	143.7	136.4
No. of reflections	53690	39238	51106
No. of obs.	6428	6062	13128
No. of variables	491	491	1106
Refls./Parameter ratio	13.09	12.35	11.87
Residuals: R1 $(I > 2\sigma(I))$	0.0260	0.0334	0.0517
Residuals: R (all data)	0.0309	0.0432	0.0598
Residuals: wR2 (all data)	0.0733	0.0442	0.0874
GOF	1.014	1.017	1.003
Max/min peak/e ⁻ Å ⁻³	1.64/-0.77	1.56/-1.16	4.26/-1.93



Scheme 3. Synthetic route for the complexes 7 and 8a/8b.

Two bis(phenolate) zirconium diamido complexes 6 and 6^{Br} could be accessed in a moderate (**6**^{Br}, 59%) to good (**6**, 73%) yield by reacting the corresponding disodium salt of 2 or 3 generated in situ with $ZrCl_2(NMe_2)_2(THF)_2$ (Scheme 2). The ¹H NMR spectrum of **6** shows at room temperature a configurationally stable C_2 symmetric structure with two aromatic doublets, four pseudo-AB doublets for the protons of the CH₂SCH₂CH₂SCH₂ bridge and a singlet resonance at δ 3.39 ppm for the NMe₂ group. On the other hand, the ¹H NMR spectrum of the analogous complex **6**^{Br} with Brsubstituted phenolate rings displays a pattern of broad signals at room temperature, suggesting a fluxional structure. Heating of 6 with TMSCl at 35 °C afforded zirconium dichloro complex 7 as a white solid in 68% yield (Scheme 3). In contrast, the analogous reaction of 6^{Br} with TMSCl was not clean and the corresponding dichloro complex was not isolated. Presumably, a Cl/Br exchange occurred. Similarly to zirconium dibenzyl and diamido complexes, the complex **7** has a C_2 -symmetric structure in solution as revealed by the NMR spectroscopic data.

The structure of **7** was unambiguously determined by X-ray crystallography. The ORTEP diagram of **7** with selected bond lengths and angles is shown in Fig. 3. The crystallographic data for **7** are shown in Table 1. The asymmetric unit contains two homochiral molecules and two molecules of dichloromethane. The structure of only one of the two homochiral molecules will be discussed. The central zirconium atom adopts a distorted octahedral geometry with chloro ligands in mutual *cis* position and *trans*-coordination of phenolato moieties (O1–Zr1–O2 159.33(12)°, Zr1–O1 1.977(3), Zr1–O2 1.977(3) Å). The smaller steric bulkiness of the chloro ligands compared to benzyl ligands is reflected in a decrease in the respective bond angle from 126.55(11) (C7–Zr1–C14) to 108.18(4)° (Cl1–Zr1–Cl2). The decrease of this angle causes a widening of the S–Zr–S angle from 73.60(2) in **4**^{Br} to 74.70(3) in **7** and subsequent shortening of the Zr–S bonds by about 0.03 Å.

In contrast with zirconium, reaction of **2** with TiCl₄ at room temperature afforded the titanium dichloro complex as a mixture of *cis*- α (*C*₂-symmetry, *trans*(O,O)-*cis*(S,S)) isomer **8a** and *cis*- β (*C*₁-symmetry,



Fig. 3. ORTEP diagram of the molecular structure of $[Zr\{2,2'-(OC_6H_2-4,6-'Bu_2)_2CH_2SCH_2CH_2SCH_2]$ (**7**). One of two molecules in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Zr1–S3 2.7613(9), Zr1–S4 2.7591(11), Zr1–O1 1.977(3), Zr1–O2 1.977(3), Zr1–Cl1 2.4133(11), Zr1–Cl2 2.4034(9), S3–Zr1–S4 74.70(3), O1–Zr1–O2 159.33(12), Cl1–Zr1–Cl2 108.18(4), S4–Zr1–Cl1 163.29(3), S3–Zr1–Cl2 162.42(3).

Table 2

Polymerization of 1-hexene catalyzed by zirconium complexes $4/4^{Br}$ and hafnium complex 5 with co-catalysts. $^{\rm a}$

Entry	Catalyst	Co-catalyst ^b	Activity ^c	M_w^d	M_w/M_n^d
1	4	$B(C_6F_5)_3$	227.3	74600	1.7
2	4	MAO	165.2	46600	1.5
3	4 ^{Br}	$B(C_6F_5)_3$	5.2	102000	1.3
4	5	$B(C_6F_5)_3$	1.5	830	1.1
5	5	MAO	73.6	2040	1.1

 a Conditions: 20 mL glass reactor, 1-hexene (10 mL), catalyst 12.0 $\mu mol,$ polymerization time 2 h, room temperature.

^b B(C₆F₅)₃ 16.0 μmol; TMAO 1.2 mmol.

^c In kg mol(cat)⁻¹.

^d Determined by GPC with polystyrene standards.

cis(O,O)-cis(S,S)) isomer **8b** in a ratio of approx. 20:80% (measured in CD_2Cl_2) (Scheme 3). The VT NMR studies revealed a reversible conversion of **8a** into **8b** at 60 °C. This finding stands in contrast with a conversion of cis- β to cis- α isomer observed for the titanium dichloro complex with the [ONNO]-type 1,4-diazabutanediyl-bridged bis (phenolate) ligand [7a].

2.2. Polymerization studies

The results of 1-hexene polymerization with zirconium dibenzyl complexes $4/4^{Br}$ and hafnium dibenzyl complex **5** are summarized in Table 2.

The polymerization runs have been performed in neat monomer under the ambient conditions. At room temperature **4**^{Br} was found to be insoluble in 1-hexene, forming a slurry. However, after addition of tris(pentafluorophenyl)borane a clear solution could be obtained after a few minutes. On the contrary to the expectations, an introduction of the electron-withdrawing substituents on phenolate rings did not cause an increase in catalytic activity, as it was the case for the related diamine bis(phenolate) complexes reported by Kol et al. [7j]. Although the activity of **4**^{Br} with Br substituents was lower than that of **4** (227.3 vs 5.2 kg mol(cat)⁻¹), it afforded poly(1-hexene) with a higher molecular weight ($M_w = 102000$, **4**^{Br}; 74600, **4**, Table 2, entry 1 and 3) and a narrower molecular weight distribution ($M_w/M_n = 1.3$ vs 1.7). The

Table 3

Polymerization of vinylcyclohexane catalyzed by zirconium complexes $4/4^{Br}$ and hafnium complex 5 with co-catalysts.^a

Entry	Catalyst	Co-catalyst ^b	Activity ^c	M_w^d	$M_{\rm w}/M_{\rm n}^{\rm d}$
6	4	$B(C_6F_5)_3$	5.3	167000	1.8
7	4	MAO	60.7	20000	1.2
8	4 ^{Br}	$B(C_6F_5)_3$	1.5	n.d.	_
9	5	$B(C_6F_5)_3$	1.5	830	1.1
10	5	MAO	11.8	530	1.1

 a Conditions: 20 mL glass reactor, toluene (5 mL), vinylcyclohexane (5 mL), catalyst 12.0 μ mol, polymerization time 2 h, room temperature.

^b $B(C_6F_5)_3$ 16.0 µmol; PMAO 1.2 mmol. ^c In kg mol(cat)⁻¹.

^d Determined by GPC with polystyrene standards.

microstructure of the polymer was investigated by ¹³C NMR spectroscopy. The presence of six main peaks corresponding to six different carbon atoms of the polymer chain as well as the broadness and pattern of the methylene peaks indicate an atactic poly(1hexene) (Fig. 4).

The formation of atactic polymer is in agreement with the observations that, in the case of zirconium bis(phenolate) complexes, bulky phenolate substituents are necessary for stereospecific olefin polymerization [7j,p]. Moreover, in the case of TMAO co-catalyst the polymer obtained shows lower molecular weight than using tris(pentafluorophenyl)borane, indicating a chain transfer reaction to alkylaluminum compound (entry 2).

The results of vinylcyclohexane (VCH) polymerization with zirconium dibenzyl complexes $4/4^{Br}$ and hafnium dibenzyl complex **5** are summarized in Table 3.

Polymerization runs have been carried out in a toluene solution. The activity of the complex **4** was found to be higher upon activation with PMAO than with $B(C_6F_5)_3$ (5.3 vs 60.7 kg mol(cat)⁻¹, Table 3, entry 4 and 5). Polymerization with $B(C_6F_5)_3$, however, afforded poly(vinylcyclohexane) with a higher molecular weight ($M_w = 167000$) and with a broader molecular weight distribution ($M_w/M_n = 1.8$). Similarly to homopolymerization of 1-hexene, no increase of activity was observed for Br-substituted complex **4^{Br}**. Moreover, the activity even decreased from 5.3 to 1.5 kg mol(cat)⁻¹ (Table 3, entry 6). In contrast, ultrahigh activities up to 3600 g mmol



Fig. 4. ¹³C NMR spectrum of poly(1-hexene) obtained with 4^{Br}/B(C₆F₅)₃.



 $(cat)^{-1}$ h⁻¹ in isospecific vinylcyclohexane polymerization were observed for the halo-substituted [ONNO]-type dibenzylzirconium complexes with diaminoethane and diaminocyclohexane bridge [7e]. The ¹³C NMR analysis of poly(vinylcyclohexane) from entry 4 revealed an isotactic structure ([mm] = 0.77) (Fig. 5). This result indicates that it is easier to control VCH insertion and direction of poly(vinylcyclohexane) chain around a Zr center for this bulkier monomer compared to 1-hexene polymerization. The same high isotacticity in vinylcyclohexane polymerization was observed for the abovementioned [ONNO]-type dibenzylzirconium complexes, regardless of the nature of the phenolate substituents [7e].

On the other hand, 1-hexene or vinylcyclohexene polymerization using hafnium complex **5** gave only oligomers (Table 2, entries 4 and 5; Table 3, entries 9 and 10). The formation of a lower molecular weight polymer with an [OSSO]-type hafnium complex was also observed by Okuda et al. in styrene polymerization [5n]. However, it is quite unusual that the oligomers were formed with hafnium catalyst systems. The results of propylene polymerization with zirconium dichloro complex **7** and titanium dichloro isomeric mixture **8a/8b** are summarized in Table 4.

Polymerization runs have been carried out at varied temperatures (5, 40 and 60 °C). The catalytic activity was found to increase with an increasing temperature, with a molecular weight of polypropylene being the highest at 5 °C (**7**: $M_w = 3200$; **8a/8b**: $M_w = 2430000$, Table 4, entries 11–16). In the cases of polymerization runs at 5 and 40 °C using **8a/8b** the differential scanning calorimetry (DSC) thermograms of polypropylene samples show additional peaks with melting temperatures above 160 °C, indicating a presence of an isotactic polymer (Fig. 6). However, at 60 °C atactic polypropylene is formed and only a peak below 100 °C was observed. This can be rationalized by a reversible conversion of **8a** into **8b** above 60 °C revealed by VT NMR studies in toluene- d_8 . At

Table 4									
Polymerization	of	propylene	catalyzed	by	zirconium	complex	7	and	titanium
complex 8 with	TIE	BA/[Ph ₃ C][B	$(C_6F_5)_4].^{a}$						

Entry	Catalyst	Temp. (°C)	Activity ^b	<i>M</i> w ^c	M_w/M_n^c	$T_{\rm m}(^{\circ}{\rm C})$
11	7	5	350	3220	1.7	n.d.
12	7	40	1250	2770	1.7	n.d.
13	7	60	1120	2400	1.7	n.d.
14	8	5	22	2430000	22.2	164.7/115.6
15	8	40	45	974000	33.9	162.7/104.1
16	8	60	63	488000	22.2	94.2

 a Conditions: 3.0 L autoclave, toluene (1000 mL), propylene (100 g), catalyst 10.0 $\mu mol,~TIBA=1.5$ mmol, $[Ph_3C][B(C_6F_5)_4]$ 20.0 $\mu mol,~polymerization$ time 90 min.

^b In kg mol(cat)⁻¹

^c Determined by GPC with polystyrene standards.



Fig. 6. Melting temperatures of polypropylene produced using $8a/8b/\text{TIBA}/[\text{Ph}_3\text{C}]|B|(C_6F_5)_4].$



Fig. 7. GPC traces of polypropylene produced using 8a/8b/TIBA/[Ph₃C][B(C₆F₅)₄].

lower temperatures a mixture of C_2 - and C_1 -symmetrical isomers exists in solution, leading to isotactic/atactic polypropylene, respectively. Above 60 °C no *cis-* α structure is maintained and atactic polypropylene is formed. Moreover, the gel permeation chromatography (GPC) data of polypropylene samples revealed broad molecular weight distribution. The data for polypropylene show a trimodal distribution (Fig. 7). The intensity of the highest peak was found to decrease with increasing the polymerization temperature, while the intensity of other two peaks increased with increasing temperature. The results of DSC, NMR and GPC measurements show that the polymer melting at higher-temperature has a higher molecular weight than the one melting at lower temperature. Therefore, the GPC curve changed with polymerization temperature that reflects the conformational change of complex **8**.

The zirconium complex **7** exhibits higher activity than the titanium complex **8** and it affords polymers with a lower molecular weight and a narrower molecular weight distribution. The relationship observed is similar to that reported for 1-hexene polymerization using [ONNO]-type complex [7].

3. Conclusions

In conclusion, a series of group 4 metal complexes with the tetradentate bis(phenolate) [OSSO]-type ligand possessing electron-withdrawing substituents on the phenolate rings have been prepared. Configurationally stable C2-symmetrical complexes were obtained for zirconium and hafnium, as revealed by NMR spectroscopy and X-ray crystal structure diffraction analysis. For smaller titanium a mixture of $cis-\alpha$ (trans(0,0)-cis(S,S)) and $cis-\beta$ (cis(0,0)cis(S,S)) isomers is formed. The C₂-symmetrical isomer converts reversibly to the C₁-symmetrical one at temperatures above 60 °C. Upon activation with poly(methylaluminoxane) and tris(pentafluorophenyl)borane the zirconium dibenzyl complexes are active in polymerization of 1-hexene and vinylcyclohexane, affording atactic poly(1-hexene) and isotactic poly(vinylcyclohexane), respectively. However, in both cases an introduction of the electron-withdrawing substituents on phenolate rings did not result in an increase in catalytic activity. This finding indicates that the polymerization activity of zirconium dibenzyl complexes supported by the [OSSO]-type 1,4-dithiabutanediyl-bridged bis (phenolate) ligand with a Salan-type methylene spacer is presumably derived primarily from the bulkiness of phenolate substituents (activity decreases on reduction of bulkiness from ^rBu to Br). This trend stands in contrast with the results from Kol et al. for the diamine bis(phenolate) complexes, showing that incorporation of the electron-withdrawing halo substituents on phenolate rings increases the catalyst activity in isospecific polymerization of vinylcyclohexene [7e] and 1-hexene [7j]. The polymerization of liquid propylene catalyzed by the titanium dichloro isomeric mixture afforded at 5 °C ultrahigh molecular weight atactic/ isotactic polypropylene mixtures. As a result of reversible conversion of the C_2 -symmetrical to the C_1 -symmetrical isomer above 60 °C, at 60 °C only atactic polypropylene was obtained.

4. Experimental

All manipulations of air- and moisture-sensitive compounds were performed under an inert atmosphere of nitrogen using a VAC glovebox or standard Schlenk-line techniques. Toluene, pentane, hexane, THF, diethyl ether and dichloromethane were dried by passage through activated alumina towers and collected under nitrogen using the Glass Contour Solvent Purification System. ZrCl₂(NMe₂)₂(THF)₂ was prepared according to the published procedure [10]. Titanium tetrachloride, zirconium tetrabenzyl, hafnium tetrabenzyl and all other chemicals were commercially available and were used as received unless stated otherwise. Vinylcyclohexane and 1-hexene were stored over activated alumina and molecular sieves 13X and were deoxygenated by bubbling a stream of dry nitrogen gas before use. Triisobutylaluminum (TIBA) (1 M solution in toluene) and 2 types of poly(methylaluminoxane), namely, PMAO (2.6 M solution in toluene) and TMAO (3.4 M solution in hexane) were purchased from Tosoh Finechem. Co., Ltd. (PMAO-S and TMAO-341). Triphenylcarbenium tetrakis(pentafluorophenyl) borate (denoted as F20) was purchased from Asahi Glass Co., Ltd. and used as a 0.0050 M toluene solution. Tris(pentafluorophenyl)borane (denoted as F15) was purchased from Tokyo Chemical Industry Co., Ltd. and used as a 0.016 M toluene solution.

NMR spectra were recorded on a JEOL AL400 (¹H, 399.6 MHz; ¹³C, 100.4 MHz) spectrometer at 25 °C unless stated otherwise. Mass spectra were recorded using a Hewlett–Packard HP-5970B instrument. High-resolution mass spectra were recorded using a JEOL JMS-T100GC spectrometer and elemental analyses were performed by Sumika Chemical Analysis Service Ltd. using an ELEMENTAR element analyzer. Molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) were determined by high temperature GPC and calibrated using polystyrene standards. GPC analysis was performed with an HLC-8121GPC/HT liquid chromatograph at 152 °C in *o*-dichlorobenzene using a TSK-GEL GMHHR-H(20)HT column. Differential scanning calorimetry (DSC) melting curves were recorded at a rate of 5 °C/min using a Perkin Elmer Diamond DSC instrument. The melting point (T_m) of copolymers was measured from the second heating.

4.1. 2-Bromomethyl-4,6-di-tert-butylphenol (1)

This compound was prepared by modification of a literature procedure [11]. To a clear solution of 2,4-di-*tert*-butylphenol (8.70 g, 42.17 mmol) in glacial acetic acid (25 mL) paraformaldehyde (1.40 g, 46.62 mmol, 1.11 equiv.) was added at rt. The resulting slurry was stirred for 2 h at rt. A 5.1 M HBr solution in acetic acid (25 mL, 127.35 mmol, 3.02 equiv.) was then dropwise added resulting in the formation of a yellow clear solution. After 30 min of stirring acetic acid was removed in vacuum yielding orange viscous oil. The oil was stored at -30 °C and after 3 h an orange solid material formed. This material was washed with a small amount of diethyl ether and dried thoroughly in a stream of nitrogen for several hours to yield 10.6 g (84%) of a light orange powder.

¹H NMR (399.6 MHz, CDCl₃): δ = 1.22 (s, 9H, ^tBu), 1.36 (s, 9H, ^tBu), 4.50 (s, 2H, CH₂), 5.20 (s, 1H, OH), 7.02 (d, *J* = 2.4 Hz, 1H, Ar), 7.26 (d, *J* = 2.4 Hz, 1H, Ar).

4.2. 2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-di-tert-butylphenol) ([OSSO] H_2) (**2**)

This compound was prepared according to a literature procedure [5g].

¹H NMR (399.6 MHz, C₆D₆): δ = 1.28 (s, 18H, ^tBu), 1.61 (s, 18H, ^tBu), 2.13 (s, 4H, CH₂), 3.33 (s, 4H, CH₂), 6.74 (s, 2H, OH), 6.81 (d, *J* = 2.4 Hz, 2H, Ar), 7.46 (d, *J* = 2.4 Hz, 2H, Ar). ¹³C{¹H} NMR (100.4 MHz, C₆D₆): δ = 30.0 (CMe₃), 30.4 (CH₂), 31.8 (CMe₃), 34.1 (CH₂), 34.3 (CMe₃), 35.3 (CMe₃), 121.8 (C_{Ar}), 124.0 (CH_{Ar}), 125.5 (CH_{Ar}), 137.6 (C_{Ar}), 142.4 (C_{Ar}), 152.7 (C_{Ar}).

4.3. 2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-dibromophenol) ($[OSSO]^{Br}H_2$) (**3**)

To a solution of 2,4-dibromo-6-(bromomethyl)phenol (5.00 g, 14.50 mmol) in THF (30 mL) 1,2-ethanedithiol (0.71 g, 7.54 mmol, 0.52 equiv.) was added dropwise at rt. After complete dissolution triethylamine (1.467 g, 14.50 mmol, 1.00 equiv.) was added dropwise. A white precipitate formed and the flask warmed up. White slurry was stirred at rt in the dark for 24 h. The white precipitate was removed by filtration and the filtrate was concentrated in vacuum yielding yellow oil. Diethyl ether was added and a yellow solution was separated from a yellow smeary material by decantation. Diethyl ether was concentrated in vacuum affording yellow viscous oil. After addition of dehydrated methanol the resulting solution was stored overnight at -25 °C. An off-white precipitate, which had formed, was filtered off and washed with a small amount of methanol. Pentane was added and the resulting white slurry was stirred for ca. 1 h (within this time a bit sticky precipitate became fine). The precipitate was then filtered off, washed with pentane and dried to yield 2.92 g (64%) of **3**.

¹H NMR (399.6 MHz, CD₂Cl₂): δ = 2.69 (s, 4H, CH₂S), 3.77 (s, 4H, CCH₂), 6.16 (s, 2H, OH), 7.33 (d, *J* = 2.4 Hz, 2H, Ar), 7.56 (d, *J* = 2.4 Hz, 2H, Ar).

¹³C{¹H} NMR (100.4 MHz, CD₂Cl₂): δ = 31.7 (CH₂), 32.0 (CH₂), 112.0 (C_{Ar}-Br), 112.9 (C_{Ar}-Br), 128.2 (C_{Ar}), 133.1 (CH), 133.8 (CH), 150.7 (C_{Ar}-O).

Anal. Calc. for $C_{16}H_{14}Br_4O_2S_2$ (MW = 622.03): C, 30.89; H, 2.27. Found: C, 31.40; H, 2.40.

4.4. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-ditert-butylphenolato)} dibenzylzirconium ([OSSO]ZrBz₂) (**4**)

This compound was prepared according to a literature procedure [5g]. The ligand precursor **2** (0.20 g, 0.38 mmol) was dissolved in toluene (5 mL) and added dropwise to a solution of $ZrBz_4$ (0.173 g, 0.38 mmol) in toluene (3 mL). The reaction mixture was stirred at rt for 4 h. Toluene was removed in vacuum and pentane (ca. 4 mL) was added. Removal of pentane afforded 0.25 g (82%) of **4** as a yellow solid.

¹H NMR (399.6 MHz, C₆D₆): δ = 1.24 (s, 18H, ^tBu), 1.75 (s + m, 20H, ^tBu+CH₂), 1.85 (d, *J* = 9.2 Hz, 2H, CH₂, AB system), 2.10 (d, *J* = 8.8 Hz, 2H, CH₂, AB system), 2.60 (d, *J* = 9.2 Hz, 2H, CH₂, AB system), 2.85 (d, *J* = 14.4 Hz, 2H, CH₂, AB system), 3.03 (d, *J* = 14.8 Hz, 2H, CH₂, AB system), 6.50 (d, *J* = 2.4 Hz, 2H, Ar), 6.96 (t, *J* = 7.2 Hz, 2H, Ar), 7.12 (t, *J* = 7.6 Hz, 4H, Ar), 7.23 (d, *J* = 7.6 Hz, 4H, Ar), 7.45 (d, *J* = 2.4 Hz, 2H, Ar).

4.5. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6dibromophenolato)} dibenzylzirconium ([OSSO]^{Br}ZrBz₂) (**4**^{Br})

This complex was prepared in an analogous way as **4** with 89% yield.

¹H NMR (399.6 MHz, CD₂Cl₂): δ = 1.45 (d, *J* = 8.0 Hz, 2H, CH₂, AB system), 1.60 (d, *J* = 10.0 Hz, 2H, CH₂, AB system), 2.29 (d, *J* = 8.4 Hz,

2H, CH₂, AB system), 2.82–2.86 (d, 4H, $2 \times$ CH₂, AB system, overlapping), 3.26 (d, J = 14.8 Hz, 2H, CH₂, AB system), 6.89 (d, J = 6.8 Hz, 4H, Ar), 6.98 (d, J = 2.4 Hz, 2H, Ar), 7.08 (t, J = 7.2 Hz, 2H, Ar), 7.18 (t, J = 7.2 Hz, 4H, Ar), 7.60 (d, J = 2.4 Hz, 2H, Ar).

 $^{13}C\{^{1}H\}$ NMR (100.4 MHz, C_6D_6): $\delta=35.6$ (CH₂), 36.1 (CH₂), 58.5 (CH₂Ph), 110.6 (C_{Ar}-Br), 115.6 (C_{Ar}-Br), 124.0 (Ar), 126.9 (Ar), 128.8 (Ar), 130.6 (Ar), 130.9 (Ar), 135.3 (Ar), 144.6 (Ar), 157.4 (C_{Ar}-O).

Anal. Calc. for $C_{30}H_{26}Br_4O_2S_2Zr$ (MW = 893.50): C, 40.33; H, 2.93. Found: C, 40.40; H, 2.90. Yellow block crystals were grown from a dichloromethane/hexane solution at -35 °C.

4.6. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-ditert-butylphenolato)} dibenzylhafnium ([OSSO]HfBz₂) (**5**)

The ligand precursor **2** (0.50 g, 0.94 mmol) in pentane (8 mL) was added dropwise at rt to a solution of $HfBz_4$ (0.510 g, 0.94 mmol) in toluene (10 mL). The reaction mixture was stirred at rt for 3 h. The solvents were removed in vacuum and pentane (10 mL) was added. Removal of pentane afforded 0.48 g (57%) of **5** as an off-white solid.

¹H NMR (399.6 MHz, C₆D₆): δ = 1.24 (s, 18H, ^fBu), 1.70 (d, *J* = 8.8 Hz, 2H, CH₂, AB system), 1.81 (s, 18H, ^fBu), 1.86 (d, *J* = 9.2 Hz, 2H, CH₂, AB system, overlapping), 2.47 (d, *J* = 11.6 Hz, 2H, CH₂, AB system), 2.90 (d, *J* = 11.2 Hz, 14.8 Hz, 4H, 2×CH₂, AB system, overlapping), 3.07 (d, *J* = 14.0 Hz, 2H, CH₂, AB system), 6.53 (d, *J* = 2.4 Hz, 2H, Ar), 6.80 (t, *J* = 7.2 Hz, 2H, Ar), 7.11 (t, *J* = 7.8 Hz, 4H, Ar), 7.32 (d, *J* = 7.2 Hz, 4H, Ar), 7.54 (d, *J* = 2.4 Hz, 2H, Ar).

¹³C{¹H} NMR (100.4 MHz, C₆D₆): δ = 30.8 (CMe₃), 31.7 (CMe₃), 34.2, 34.3, 35.4, 35.6 (CMe₃/CH₂), 75.3 (CH₂Ph), 122.0 (Ar), 122.5 (Ar), 124.6 (Ar), 125.2 (Ar), 127.9 (Ar), 128.1 (Ar), 138.6 (Ar), 141.4 (Ar), 147.8 (Ar), 158.0 (C_{Ar}-O).

EI-MS m/z: 799.3 ([M – Bz]).

4.7. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6dibromophenolato)} dibenzylhafnium ([OSSO]^{Br}HfBz₂) (**5^{Br}**)

The ligand precursor **3** (0.30 g, 0.48 mmol) was dissolved in toluene (3 mL) and added dropwise at rt to a solution of HfBz₄ (0.26 g, 0.48 mmol) in toluene (7 mL). The reaction mixture was stirred at rt for 3 h. Toluene was removed in vacuum and pentane (5 mL) was added. Filtration of a beige precipitate, washing with pentane and drying in vacuum afforded 0.42 g (89%) of **5**^{Br}.

¹H NMR (399.6 MHz, CD₂Cl₂): δ = 1.49 (d, *J* = 10.0 Hz, 2H, CH₂, AB system), 1.56 (d, *J* = 9.6 Hz, 2H, CH₂, AB system), 2.27 (d, *J* = 10.0 Hz, 2H, CH₂, AB system), 2.77–2.84 (d, 4H, 2×CH₂, AB system, overlapping), 3.25 (d, *J* = 14.8 Hz, 2H, CH₂, AB system), 6.97–7.02 (m, 8H, Ar), 7.15 (t, *J* = 7.6 Hz, 4H, Ar), 7.65 (d, *J* = 2.0 Hz, 2H, Ar).

¹³C{¹H} NMR (100.4 MHz, CD₂Cl₂): δ = 35.8 (CH₂), 37.5 (CH₂), 64.6 (CH₂Ph), 111.2 (C_{Ar}-Br), 115.6 (C_{Ar}-Br), 123.7 (Ar), 127.0 (Ar), 129.0 (Ar), 129.7 (Ar), 131.3 (Ar), 135.5 (Ar), 144.6 (Ar), 157.2 (C_{Ar}-O). EI-MS m/z: 889.7 ([M – Bz]).

Yellow block crystals were grown from a dichloromethane solution at -35 °C.

4.8. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-ditert-butylphenolato)} bis(dimethyl) amidozirconium ([OSSO]Zr (NMe₂)₂) (**6**)

The ligand precursor **2** (0.50 g, 0.94 mmol) in THF (ca. 10 mL) was added dropwise at rt to a suspension of NaH (0.046 g, 1.93 mmol, 2.05 equiv.) in THF (10 mL). After 30 min a clear solution formed that was stirred at rt for 2 h. A solution of $ZrCl_2(NMe_2)_2(THF)_2$ (0.371 g, 0.94 mmol) in THF (5 mL) was subsequently syringed in at rt. The resulting milky solution was

stirred overnight at rt and then filtered using a syringe filter with a PTFE membrane. THF was removed in vacuum and pentane (4 mL) was added. The resulting white precipitate was filtered, washed with hexane/pentane and dried in vacuum to yield 0.486 g (73%) of **6** as a white powder.

¹H NMR (399.6 MHz, C_6D_6): $\delta = 1.32$ (s, 18H, ^tBu), 1.68 (d, J = 9.6 Hz, 2H, SCH₂, AB system), 1.74 (s, 18H, ^tBu), 2.08 (d, J = 9.2 Hz, 2H, SCH₂, AB system), 3.15 (d, J = 13.6 Hz, 2H, CCH₂, AB system), 3.39 (s, 12H, NMe₂), 3.76 (d, J = 13.6 Hz, 2H, CH₂C, AB system), 6.67 (d, J = 2.4 Hz, 2H, Ar), 7.51 (d, J = 2.8 Hz, 2H, Ar).

¹³C{¹H} NMR (100.4 MHz, C₆D₆): δ = 30.2 (CMe₃), 31.9 (CMe₃), 33.4, 34.2, 35.6, 36.2 (CMe₃/CH₂), 45.3 (NMe₂), 123.1 (C_{Ar}), 124.2 (CH_{Ar}), 125.2 (CH_{Ar}), 138.2 (C_{Ar}), 140.1 (C_{Ar}), 159.4 (C_{Ar}–O).

4.9. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6dibromophenolato)}bis(dimethyl) amidozirconium ([OSSO]^{Br}Zr (NMe₂)₂) (**6**^{Br})

The ligand precursor **3** (0.50 g, 0.80 mmol) in THF (ca. 10 mL) was added dropwise at rt to a suspension of NaH (0.039 g, 1.64 mmol, 2.05 equiv.) in THF (10 mL). A pale yellow cloudy solution formed that was stirred at rt for 3 h. Within this time the colour turned to pale brown. A solution of $ZrCl_2(NMe_2)_2(THF)_2$ (0.316 g, 0.80 mmol) in THF (5 mL) was subsequently syringed in at rt. The resulting pale yellow slurry was stirred overnight at rt and then filtered using a syringe filter with a PTFE membrane. THF was removed in vacuum and pentane (4 mL) was added. Removal of pentane afforded a bit sticky solid material. It was dissolved in dichloromethane and the product was precipitated with pentane. Filtration, washing with pentane and drying in vacuum gave 0.380 g (59%) of **6**^{Br} as an off-white powder.

¹H NMR (399.6 MHz, CD₂Cl₂): δ = 1.73 (br, 2H, CH₂), 2.54 (br, 2H, CH₂), 3.23 (s, 12H, NMe₂), 3.71 (br, 4H, CH₂, overlapping), 7.10 (d, *J* = 2.8 Hz, 2H, Ar), 7.63 (d, *J* = 2.8 Hz, 2H, Ar).

¹³C{¹H} NMR (100.40 MHz, CD₂Cl₂): δ = 34.1 (CH₂), 35.9 (CH₂), 45.0 (NMe₂), 109.9 (C_{Ar}-Br), 115.3 (C_{Ar}-Br), 126.8 (C_{Ar}), 132.0 (CH_{Ar}), 135.8 (CH_{Ar}), 158.5 (C_{Ar}-O).

4.10. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-ditert-butylphenolato)} dichlorozirconium ([OSSO]ZrCl₂) (7)

To a solution of complex **6** (0.50 g, 0.71 mmol) in toluene (10 mL) TMSCI (0.77 g, 7.06 mmol, 10.00 equiv.) was dropwise added at 0 °C. The solution was warmed up to 35 °C and stirred for 3 h. The volatiles were removed in vacuum and pentane was added. The resulting white precipitate was filtered off, washed with pentane and dried in vacuum to yield 0.330 g (68%) of **7** as a white powder.

¹H NMR (399.6 MHz, C₆D₆): δ = 1.27 (s, 18H, ^tBu), 1.80 (s, 18H, ^tBu), 3.11 (d, *J* = 13.6 Hz, 2H, CH₂C, AB system), 4.12 (d, *J* = 13.6 Hz, 2H, CH₂C, AB system), 6.56 (d, *J* = 2.4 Hz, 2H, Ar), 7.55 (d, *J* = 2.4 Hz, 2H, Ar), both SCH₂ resonances obscured by ^tBu ones.

¹³C{¹H} NMR (100.4 MHz, C₆D₆): δ = 30.5 (CMe₃), 31.0 (SCH₂), 31.7 (CMe₃), 34.4 (CMe₃), 35.6 (CH₂), 36.8 (CMe₃), 120.6 (C_{Ar}), 125.2 (CH_{Ar}), 125.9 (CH_{Ar}), 138.9 (C_{Ar}), 142.7 (C_{Ar}), 157.4 (C_{Ar}–O).

Anal. Calc. for $C_{32}H_{48}Cl_2O_2S_2Zr$ (MW = 690.98): C, 55.62; H, 7.00. Found: C, 55.20; H, 7.10. Colorless block crystals were grown from a dichloromethane/pentane solution at -35 °C.

4.11. {2,2'-[Ethane-1,2-diylbis(sulfanediylmethylene)]bis(4,6-ditert-butylphenolato)} dichlorotitanium ([OSSO]TiCl₂) (**8**)

To a solution of the ligand precursor 2 (0.20 g, 0.38 mmol) in toluene (5 mL) TiCl₄ (0.071 g, 0.38 mmol) was added dropwise at rt with vigorous stirring. The solution turned immediately red. The reaction mixture was stirred for ca. 1 h and then filtered. Toluene

was concentrated in vacuum until dryness and pentane was added. A red precipitate formed that was filtered off, washed with pentane and dried in vacuum to afford 0.195 g (80%) of **8**. The NMR analysis in C_6D_6 revealed two isomers, C_1 - and C_2 -symmetric, in a ratio 59%:41%, respectively. In CD_2Cl_2 this ratio was 80%:20%.

4.11.1. C₁-Symmetric isomer

¹H NMR (399.6 MHz, CD₂Cl₂): δ = 1.22 (s, 9H, ^tBu), 1.28 (s, 18H, ^tBu), 1.57 (s, 9H, ^tBu), 2.51–2.59 (m, 1H, CH₂, overlapping), 3.17–3.25 (m, 1H, CH₂), 3.41–3.45 (td, *J* = 11.6 Hz, 2.8 Hz, 1H, CH₂), 3.66–3.70 (td, *J* = 13.2 Hz, 2.8 Hz, 1H, CH₂), 3.91 (d, *J* = 14.4 Hz, 1H, CH₂), 4.07 (d, *J* = 12.4 Hz, 1H, CH₂), 4.46 (d, *J* = 14.4 Hz, 1H, CH₂, overlapping), 4.63 (d, *J* = 12.4 Hz, 1H, CH₂), 7.01 (d, *J* = 2.0 Hz, 1H, Ar, overlapping), 7.02 (d, *J* = 2.4 Hz, 1H, Ar, overlapping), 7.27 (d, *J* = 2.4 Hz, 1H, Ar), 7.32 (d, *J* = 2.4 Hz, 1H, Ar).

¹³C{¹H} NMR (100.4 MHz, CD₂Cl₂): δ = 30.2 (*CMe*₃), 30.4 (*CMe*₃), 31.5 (2×*CMe*₃), 32.2, 34.8, 35.6, 35.8 (CH₂/*C*Me₃), 37.7 (CH₂), 38.4 (CH₂), 40.4 (CH₂), 122.6 (Ar), 124.5 (Ar), 124.8 (Ar), 125.5 (Ar), 125.6 (Ar), 127.1 (Ar), 136.8 (Ar), 138.2 (Ar), 145.2 (Ar), 145.3 (Ar), 161.1 (C_{Ar}-O), 161.4 (C_{Ar}-O), one aliphatic resonance obscured.

4.11.2. C₂-Symmetric isomer

¹H NMR (399.6 MHz, CD₂Cl₂): δ = 1.29 (s, 18H, ^tBu, overlapping), 1.60 (s, 18H, ^tBu, overlapping), 2.51–2.59 (m, 2H, CH₂, overlapping), 2.86 (d, *J* = 8.8 Hz, 2H, CH₂, AB system), 3.83 (d, *J* = 14.8 Hz, 2H, CH₂, AB system), 4.44 (d, *J* = 14.0 Hz, 2H, CH₂, AB system, overlapping), 6.93 (d, *J* = 1.8 Hz, 2H, Ar), 7.38 (d, *J* = 1.8 Hz, 2H, Ar).

¹³C{¹H} NMR (100.4 MHz, CD₂Cl₂): δ = 30.4 (*CMe*₃), 31.6 (*CMe*₃), 31.4, 34.2, 35.7 (CH₂/*C*Me₃), 38.3 (CH₂), 122.8 (Ar), 125.0 (Ar), 126.3 (Ar), 138.4 (Ar), 144.7 (Ar), 160.2 (C_{Ar}-O).

Anal. Calc. for $C_{32}H_{48}Cl_2O_2S_2Ti$ (MW = 647.63): C, 59.35; H, 7.47. Found: C, 58.80; H, 7.30.

4.12. Typical neat 1-hexene polymerization experiment

In a glovebox, a solution of F15 (16.0 μ mol) in 1-hexene (1.0 mL) was combined with a solution of a bis(phenolate) complex (12.0 μ mol) and 1-hexene (9.0 mL). The reaction mixture was stirred at room temperature for 2 h. It was then quenched by adding methanol (1.0 mL). After several minutes the volatiles were removed in a high vacuum at 80 °C for 4 h, affording poly(1-hexene) as colorless sticky oil. Samples of poly(1-hexene) were analyzed by means of GPC and ¹³C NMR measurements.

4.13. Typical vinylcyclohexane polymerization experiment

In a glovebox, a solution of F15 (16.0 μ mol) in toluene (1.0 mL) was combined with a solution of a bis(phenolate) complex (12.0 μ mol) and vinylcyclohexane (5.0 mL) in toluene (4.0 mL). The reaction mixture was stirred at room temperature for 2 h. The polymerization reaction was quenched by adding methanol (1.0 mL). After several minutes the volatiles were removed in a high vacuum at 80 °C for 4 h, affording poly(vinylcyclohexane) as colorless sticky oil. Samples of poly(vinylcyclohexane) were analyzed by means of GPC and ¹³C NMR measurements.

4.14. Typical propylene polymerization experiment

An autoclave with an inner volume of 3.0 L was dried under vacuum. After charging with toluene (1.0 mL) and liquid propylene (100 g), the autoclave was corrected at given temperature (5, 40, 60 °C). After the system had stabilized, TIBA (1.5 mmol) was added to the reaction mixture. Subsequently, a bis(phenolate) complex (10.0 μ mol) and F20 (20.0 μ mol) were added. Polymerization was carried out for 90 min, while the temperature was maintained. The

polymerization mixture was quenched with methanol (5.0 mL). After a few minutes the gas was vented and the mixture was then poured into methanol (1.0 L) with hydrochloric acid (1 M, 10 mL). The polymer was isolated by filtration, washed with fresh methanol and dried in a high vacuum at 80 °C for 4 h.

4.15. X-ray crystallography

Crystals of **4**^{Br}, **5**^{Br} and **7** suitable for X-ray analysis were grown from a dichloromethane/hexane (**4**^{Br}), dichloromethane (**5**^{Br}) or dichloromethane/pentane (**7**) solution at -35 °C. X-ray diffraction measurements were performed on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-K α radiation using ω scans. The structures were solved by direct methods [12] and expanded using Fourier techniques [13]. The refinement against all F_0^2 data using anisotropic displacement parameters for nonhydrogen atoms and the calculations were performed using the CrystalStructure [14,15] crystallographic software package. Hydrogen atoms were refined isotropically or using the riding model.

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Appendix A. Supplementary material

CCDC 793742–793744 contain the supplementary crystallographic data for compounds **4**^{Br}, **5**^{Br} and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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