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Titanium and zirconium complexes bearing new tridentate [OSO] bisphenolato-based ligands: synthesis, characterization and catalytic properties for alkene polymerization†

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A number of new sulfur-bridged tridentate [OSO] bisphenolato-based ligand precursors S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2OH)_2$ [R = CMe_3 (H_2**L1**), CMe_2Ph (H_2**L2**), $CMePh_2$ (H_2**L3**), CPh_3 (H_2**L4**), and C(*p*-Tol)$_3$ (H_2**L5**)] were synthesized by reactions of $Na_2S{\cdot}9H_2O$ with 2 eq. of the corresponding 2-(bromomethyl)-4-(*tert*-butyl)-6-R-phenol. Their neutral titanium complexes [S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2$]$TiCl_2$ [R = CMe_3 (**1**), CMe_2Ph (**2**), $CMePh_2$ (**3**), CPh_3 (**4**), and C(*p*-Tol)$_3$ (**5**)] were synthesized in high yields by direct HCl-elimination reactions of $TiCl_4$ with the corresponding ligand precursors in toluene. Ionic titanium complexes [$NHEt_3$][S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2TiCl_3$] [R = CMe_3 (**6**), $CMePh_2$ (**7**)] and [NH_2Et_2][S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2TiCl_3$] [R = CMe_3 (**8**) and $CMePh_2$ (**9**)] were obtained in high yields from the reactions of $TiCl_4$ with the corresponding ligand precursors in the presence of 2 eq. of triethylamine or diethylamine. Neutral zirconium complexes [S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2$]$ZrCl_2$(THF) [R = CMe_2Ph (**10**·THF), and $CMePh_2$ (**11**·THF)] were synthesized by reactions of $ZrCl_4$ with 1 eq. of the dilithium salt of the corresponding ligand precursors Li_2L in THF. The new titanium and zirconium complexes were characterized by ^{1}H and ^{13}C NMR, IR and elemental analyses. The molecular structures of complexes **4**, **6** and **10**·THF were determined by single-crystal X-ray diffraction analysis. The X-ray crystallography analysis reveals that titanium complex **4** has a five-coordinating environment surrounding the central metal atom, while the titanium complex **6** and the THF-solvated zirconium complex **10**·THF possess a six-coordinating pseudo-octahedral environment around the central metal atom. Upon activation with MAO or Al^iBu_3/$Ph_3CB(C_6F_5)_4$, all these titanium and zirconium complexes exhibit moderate to high catalytic activities for ethylene polymerization and ethylene/1-hexene copolymerization with moderate to high comonomer incorporation, and the ionic titanium complexes **6**, **7**, **8** and **9** show lower catalytic activity than their corresponding neutral complexes under similar conditions.

Introduction

In the past few decades, exploring effective catalysts for olefin homo- and co-polymerization reactions has attracted considerable attention in both academic and industrial communities. In particular, group 4 transition metal complexes have been intensively studied for developing new olefin polymerization catalysts. So far, a large number of titanium, zirconium and hafnium olefin polymerization catalysts carrying different types of ligands have been reported.[1–8] Among these catalysts, group 4 transition metal complexes bearing a tridentate or tetradentate bridged bisphenolato chelating ligand with one or two bridging O or S atom(s) have attracted attention from several research groups due to their unique structural characteristics.[9–23] Kakugo and coworkers reported the first sulfur-bridged tridentate bisphenolato titanium complexes [OSO]$TiCl_2$ (**A** in Chart 1) which exhibit good catalytic activity for the polymerization of ethylene, propylene, styrene, and dienes, as well as in the copolymerization of ethylene with styrene upon activation with methylaluminoxane.[15,16] It was reported that the replacement of a methylene bridge by a sulfide atom in these catalyst precursors leads to a remarkable

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†Electronic supplementary information (ESI) available: NMR spectra for ligands and metal complexes, ^{13}C NMR spectra for typical poly(ethylene-*co*-1-hexene) samples, crystal data and structure refinements. CCDC 1945274–1945276. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt03225h

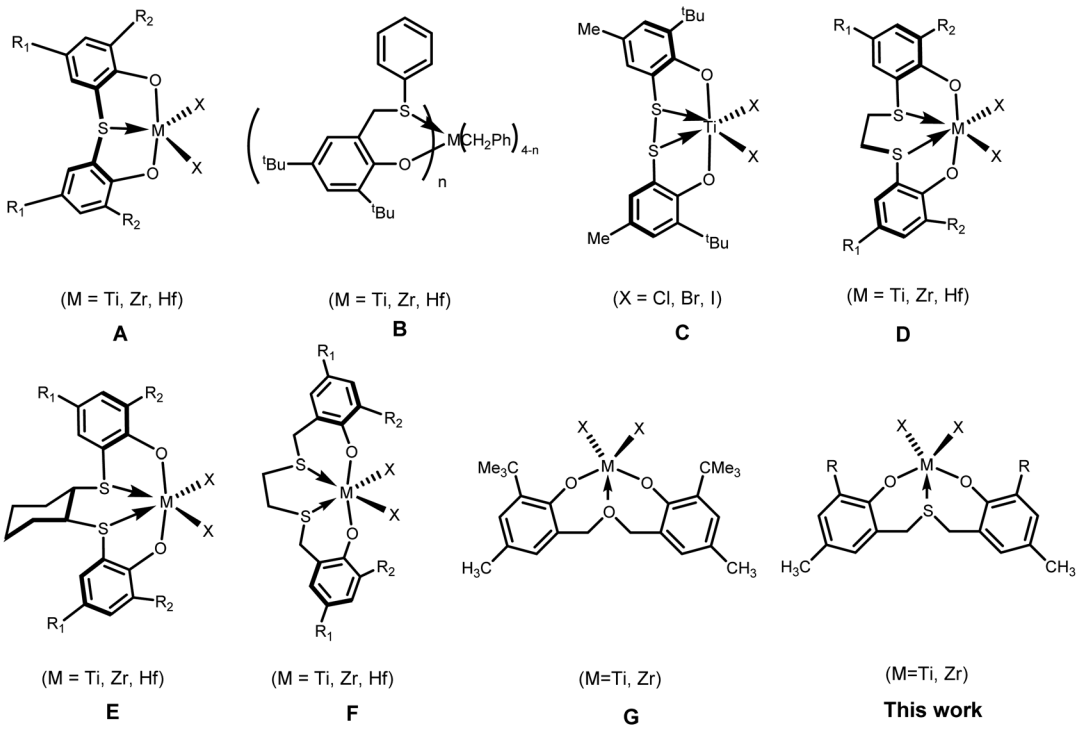


Chart 1 Known group 4 metal complexes bearing a chelating bisphenolato ligand with one or two bridging O or S atom(s).

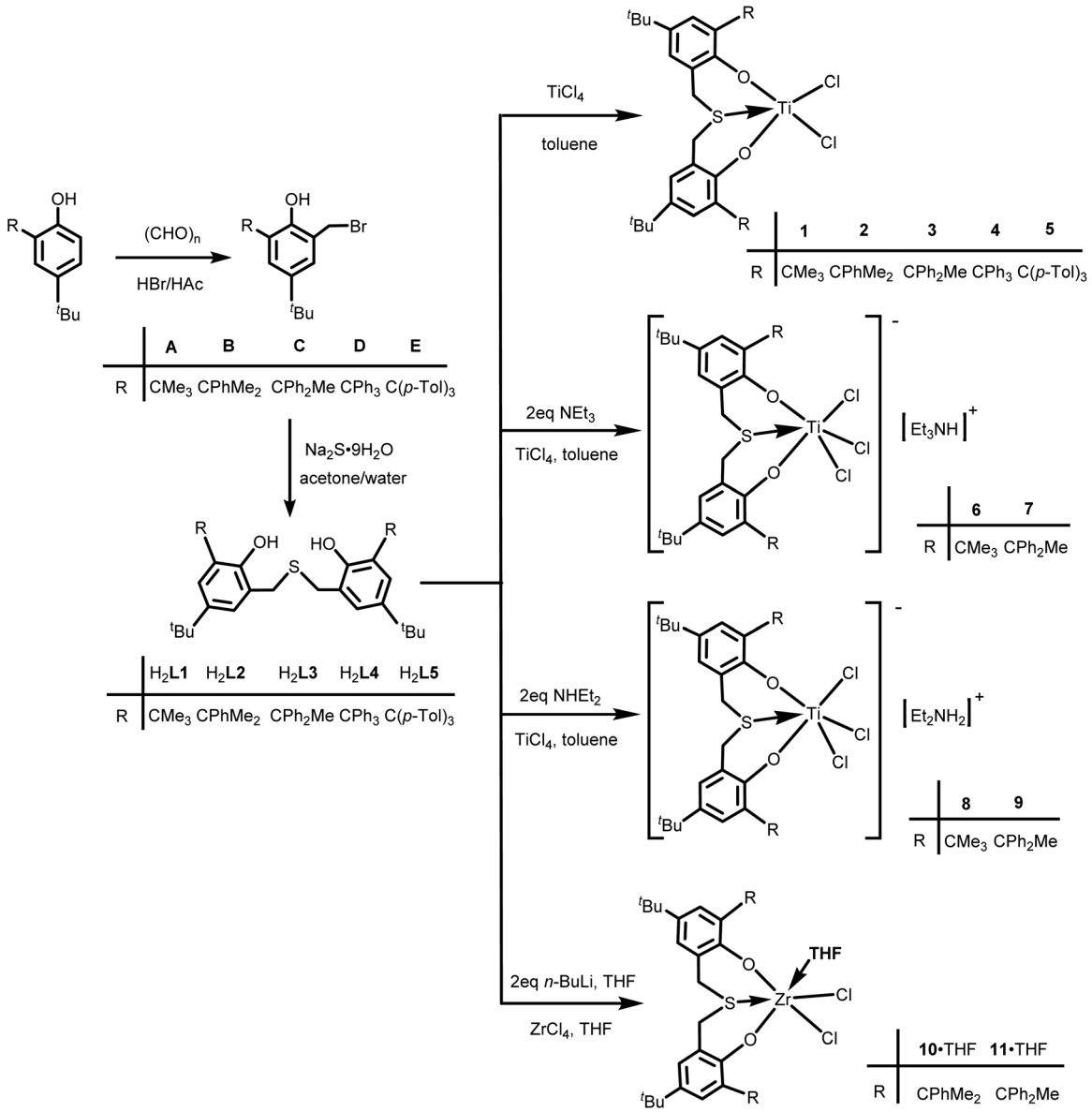
increase in their catalytic activity.[17] Computational studies have indicated that the sulfur donor plays an important role in improving the catalytic activity of these complexes due partially to possible π-donation from S to Ti.[18] Inspired by the group 4 transition metal complexes bearing two bidentate [OS] ligands (**B** in Chart 1),[19] group 4 transition metal complexes carrying a [OSSO] tetradentate bisphenolato ligand (**C**, **D**, **E**, and **F** in Chart 1) have been developed and found to display excellent catalytic activities in the polymerization of ethylene, propylene, styrene, long chain α-olefins and dienes, as well as in the copolymerization of ethylene with styrene.[20–23] It was reported that titanium complexes bearing a [OOO] tridentate CH_2OCH_2-bridged bisphenolato ligand (**G** in Chart 1) show only low or moderate catalytic activity for the polymerization of ethylene and styrene upon activation with methyaluminoxane (MAO).[14] We have recently developed a number of similar titanium complexes and zirconium bearing a CH_2SCH_2-bridged [OSO] tridentate bisphenolato ligand and found that these new complexes show moderate to high catalytic activities for ethylene polymerization and ethylene/1-hexene copolymerization with moderate to high comonomer incorporation. We herein report the synthesis, characterization and catalytic performances of these new titanium and zirconium complexes.

Results and discussion

Synthesis of ligands and complexes

The new CH_2SCH_2-bridged tridentate [OSO] bisphenolato-based ligand precursors S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2OH)_2$ [R = CMe_3 (H_2**L1**), CMe_2Ph (H_2**L2**), $CMePh_2$ (H_2**L3**), CPh_3 (H_2**L4**), and C(*p*-Tol)$_3$ (H_2**L5**)] were synthesized in high yields by reactions of $Na_2S{\cdot}9H_2O$ with 2 eq. of the corresponding 2-(bromomethyl)-4-(*tert*-butyl)-6-R-phenols which were prepared by treating the corresponding R-substituted phenols with $(CHO)_n$ and HBr/HOAc according to a literature procedure as shown in Scheme 1.[23b] These ligand precursors were characterized by IR, ^{1}H and ^{13}C NMR and elemental analyses.

The general synthetic routes of these titanium and zirconium complexes are shown in Scheme 1. The new titanium complexes **1**–**5** were synthesized in high yields (>90%) by direct HCl-elimination reactions of $TiCl_4$ with the corresponding ligand precursors in toluene. Complexes **1**, **2**, **4** and **5** are soluble in ether, THF, CH_2Cl_2, and toluene, while complex **3** is hardly soluble in common organic solvents. We have tried to synthesize complex **3** with lithium elimination reaction in toluene and the same product with poor solubility was obtained. We also tried to synthesize the titanium complexes by reactions of $TiCl_4$ with ligand precursors H_2**L1** and H_2**L3** in the presence of 2 eq. of Et_3N or Et_2NH. However, ionic titanium complexes [$NHEt_3$][S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2TiCl_3$] [R = CMe_3 (**6**), $CMePh_2$ (**7**)] and [NH_2Et_2][S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2TiCl_3$] [R = CMe_3 (**8**) and $CMePh_2$ (**9**)] were isolated in over 90% yields from these reactions. These titanium complexes were characterized by ^{1}H and ^{13}C NMR, IR and elemental analyses. In the ^{1}H NMR spectra of the titanium complexes **1**–**5**, the methylene protons of the $ArCH_2$ groups gave broad signals (**1**: 3.85 ppm, **2**: 3.58 ppm, **3**: 3.77 ppm, **4**: 2.5–4.0 ppm, **5**: 2.8–4.1 ppm). The methyl protons of the *p*-Tol group in complex **5** also show broad signals due probably to a dynamic



Scheme 1 Synthesis of ligand precursors H_2**L1**–H_2**L5** and complexes **1**–**11**.

procedure of its bulky ligand in solution. In complexes **6** and **7**, the presence of a $[NHEt_3]^+$ cation can be clearly seen from the resonances for the three Et groups and the broad resonance for the NH group (**6**: 8.96 ppm, **7**: 10.73 ppm) in their ^{1}H NMR spectra. Similarly, the presence of $[NH_2Et_2]^+$ cations in complexes **8** and **9** can also be observed from the resonances of the two Et groups and the broad resonance for the NH_2 group (**8**: 8.48 ppm, **9**: 8.98 ppm) in their ^{1}H NMR spectra. The molecular structures of titanium complexes **4** and **6** were determined by single-crystal X-ray diffraction analysis.

Attempts to synthesize similar zirconium complexes bearing these [OSO] bisphenolato-based ligands by reactions of $ZrCl_4$ with the corresponding ligand precursors H_2**L** in the absence or presence of Et_3N or Et_2NH were unsuccessful and no identifiable product was isolated from these reactions. Fortunately, mixtures of complexes **L**$ZrCl_2$ [**L** = **L2** (**10**), **L3** (**11**)] and THF-solvated complexes **L**$ZrCl_2$(THF) [**L** = **L2** (**10**·THF), **L3** (**11**·THF)] were obtained from the reactions of $ZrCl_4$ with 1 equiv. of freshly prepared Li_2**L2** or Li_2**L3** in THF at −78 °C. However, similar reactions of $ZrCl_4$ with 1 equiv. of Li_2**L1**, Li_2**L4** or Li_2**L5** in THF produced only some unidentifiable precipitates. Attempts to prepare the desirable zirconium complexes **L**$ZrCl_2$ by reactions of $ZrCl_4$ with the corresponding Li_2**L** in toluene were also unsuccessful and only unidentified polymeric products were obtained. Attempts to remove the coordinated THF from the mixtures of **10**/**10**·THF and **11**/**11**·THF by heating the mixtures under vacuum were not successful and unidentified polymeric products were formed after the coordinated THF was completely removed. Attempts were also made to isolate pure complexes **10** and **11** by recrystallization

of the mixtures of **10**/**10**·THF and **11**/**11**·THF in different solvents, and were unsuccessful too. The mixtures of **10**/**10**·THF and **11**/**11**·THF were characterized by ^{1}H and ^{13}C NMR spectroscopy and the molecular structure of complex **10**·THF was determined by single-crystal X-ray diffraction. In the ^{1}H NMR spectra of **10**/**10**·THF and **11**/**11**·THF, the methylene protons of the $ArCH_2$ groups in these complexes give characteristic resonances of doublet of doublets (**10**: 4.51, 3.80 ppm, J_{H-H} = 11.2 Hz; **10**·THF: 3.89, 3.36 ppm, J_{H-H} = 11.0 Hz; **11**: 4.59, 3.87 ppm, J_{H-H} = 11.2 Hz; **11**·THF: 3.97, 3.46 ppm, J_{H-H} = 11.2 Hz).

Crystal structures of complexes 4, 6 and 10·THF

The solid-state structures of complexes **4**, **6** and **10**·THF were determined by single-crystal X-ray diffraction. The ORTEP representations of their molecular structures are shown in Fig. 1–3, respectively. The crystallographic data including the collection and refinement parameters are summarized in Table S1 (see the ESI†). The X-ray diffraction analysis reveals that complex **4** has a mononuclear structure with the central titanium atom having a five-coordinating environment and being coordinated by the tridentate [OSO] ligand in a meridional fashion. The overall coordination geometry around the titanium atom can be described as a distorted trigonal bipyramid with the Cl1, Cl2, and S1 atoms defining the equatorial plane and the O1 and O2 atoms occupying the apical positions. The Ti–O bond distances (1.800(3) and 1.800(3) Å) between the titanium atom and the phenolic oxygen atoms in complex **4** are shorter than those in the previously reported similar titanium complexes (TBP)$TiCl_2$ (TBP = 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo)) (1.821(4) and 1.815(4) Å)[9] and [OOO]$Ti(OiPr)_2$ (1.852(2) and 1.863(2) Å).[14] The bond angles O1–Ti–O2 and C–S–C (113.27(15) and 105.0(2)°, respectively) for complex **4**

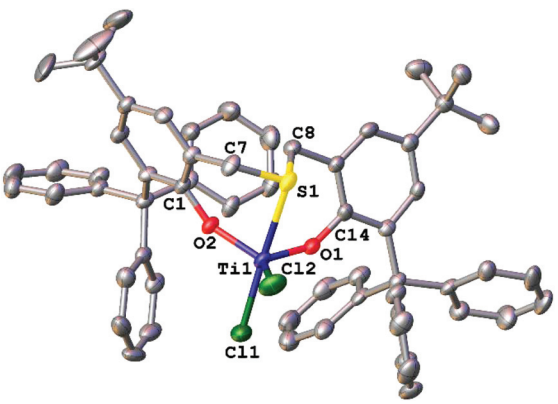


Fig. 1 Perspective view of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (°): Ti(1)–O(2) 1.800(3), Ti(1)–O(1) 1.800(3), Ti(1)–Cl(1) 2.2531(16), Ti(1)–Cl(2) 2.2937(16), Ti(1)–S(1) 2.5607(16), S(1)–C(8) 1.808(5), S(1)–C(7) 1.829(5), O(2)–Ti(1)–O(1) 113.27(15), O(2)–Ti(1)–Cl(1) 102.31(11), O(1)–Ti(1)–Cl(1) 102.29(11), O(2)–Ti(1)–Cl(2) 117.53(11), O(1)–Ti(1)–Cl(2) 122.14(11), Cl(1)–Ti(1)–Cl(2) 92.43(6), O(2)–Ti(1)–S(1) 81.82(11), O(1)–Ti(1)–S(1) 81.75(11), Cl(1)–Ti(1)–S(1) 172.27(6), Cl(2)–Ti(1)–S(1) 79.85(6), C(8)–S(1)–C(7) 105.0(2), C(8)–S(1)–Ti(1) 95.89(16), C(7)–S(1)–Ti(1) 97.68(17), C(1)–O(2)–Ti(1) 152.6(3).

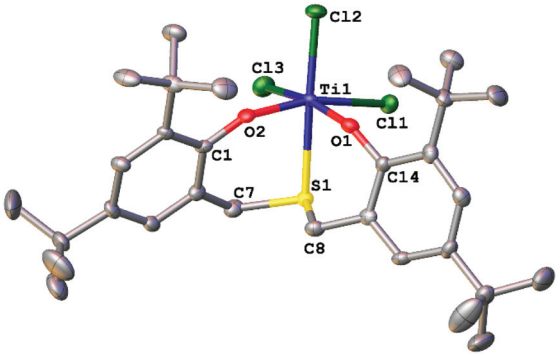


Fig. 2 Perspective view of the $[S(2\text{-}CH_2\text{-}4\text{-}^{t}Bu\text{-}6\text{-}CMe_3\text{-}C_6H_2O)_2TiCl_3]^-$ anion in **6** with thermal ellipsoids drawn at the 30% probability level. The $[NHEt_3]^+$ cation, uncoordinated solvent and hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (°): Ti(1)–O(2) 1.815(5), Ti(1)–O(1), 1.834(5), Ti(1)–Cl(1) 2.438(2), Ti(1)–Cl(2) 2.300(2), Ti(1)–Cl(3) 2.388(2), Ti(1)–S(1) 2.587(2), S(1)–C(8) 1.824(8), S(1)–C(7) 1.839(8), O(2)–Ti(1)–O(1) 95.3(2), O(2)–Ti(1)–Cl(1) 162.75(17), O(1)–Ti(1)–Cl(1) 86.92(17), O(2)–Ti(1)–Cl(2) 100.52(17), O(1)–Ti(1)–Cl(2) 97.81(17), O(2)–Ti(1)–Cl(3) 88.73(18), O(1)–Ti(1)–Cl(3) 165.54(18), Cl(1)–Ti(1)–Cl(2) 96.11(8), Cl(2)–Ti(1)–Cl(3) 95.10(8), Cl(1)–Ti(1)–Cl(3) 85.24(8), O(2)–Ti(1)–S(1) 82.20(16), O(1)–Ti(1)–S(1) 83.17(16), Cl(1)–Ti(1)–S(1) 81.08(7), Cl(2)–Ti(1)–S(1) 176.98(9), Cl(3)–Ti(1)–S(1) 83.62(7), C(8)–S(1)–C(7) 101.8(4), C(8)–S(1)–Ti(1) 98.8(3), C(7)–S(1)–Ti(1) 101.9(3), C(1)–O(2)–Ti(1) 152.8(5).

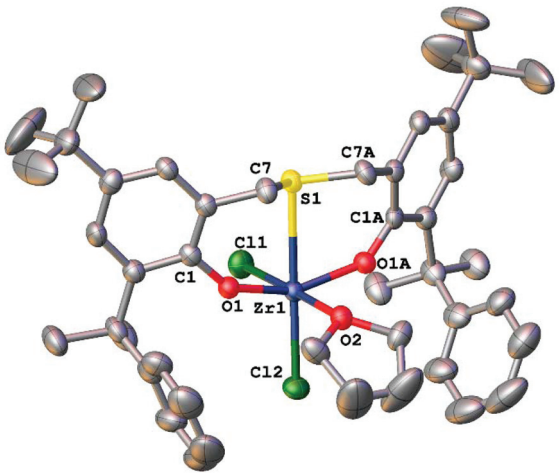


Fig. 3 Perspective view of **10**·THF with thermal ellipsoids drawn at the 30% probability level. The uncoordinated solvent and hydrogen atoms are omitted for clarity. The selected bond lengths (Å) and angles (°): Zr(1)–O(1) 1.982(4), Zr(1)–O(2) 2.225(5), Zr(1)–Cl(1) 2.438(2), Zr(1)–Cl(2) 2.433(2), Zr(1)–S(1) 2.758(2), S(1)–C(7) 1.820(5), O(1)–Zr(1)–O(1A) 153.4(2), O(1)–Zr(1)–Cl(1) 93.98(12), O(1)–Zr(1)–Cl(2) 102.44(11), Cl(2)–Zr(1)–Cl(1) 93.22(8), O(1)–Zr(1)–S(1) 77.50(11), O(2)–Zr(1)–S(1) 94.36(14), Cl(1)–Zr(1)–S(1) 87.53(7), Cl(2)–Zr(1)–S(1) 179.25(7), C(7)–S(1)–C(7A) 101.4(4), C(7)–S(1)–Zr(1) 97.8(2), C(1)–O(1)–Zr(1) 146.6(3).

are significantly narrower than those in [OOO]$Ti(OiPr)_2$ (161.2(1) and 118.3(3)°, respectively).[14] In contrast, the bond angle Cl–Ti–Cl (92.43(6)°) in complex **4** is wider than Cl–Ti–Cl (bridging) angles in (TBP)$TiCl_2$ (78.55(7)°)[9] and [{Te(4-Me-6-$^{t}BuC_6H_2O)_2$}$TiCl_2]_2$ (80.43(6)°).[9] The bond angles O–Ti–S (81.82(11) and 81.75(11)°) in complex **4** are also wider than

those in (TBP)$TiCl_2$ [9] (76.9(1) and 76.8(1)°). The Ti–S bond distance (2.5607(16) Å) from the central titanium atom to the coordinating sulphur atom for complex **4** is shorter than those in complexes $[(TBMP)Ti(OiPr)_2]_2$ (TBMP = 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxo)) (2.719(1) Å)[10b] and (TBP)$TiCl_2$ (2.664(2) Å),[9] but much longer than that of the Ti–O bond length (2.096(3) Å) from the titanium center to the coordinating ether oxygen atom in complex $[OOO]Ti(OiPr)_2$.[14] The Ti–Cl bond lengths (2.2531(16) and 2.2937(16) Å) are comparable to those observed in some titanium complexes with similar structures.[9,24a]

The unit cell of complex **6** consists of a $[S(2\text{-}CH_2\text{-}4\text{-}^tBu\text{-}6\text{-}CMe_3\text{-}C_6H_2O)_2TiCl_3]^-$ anion, $[NHEt_3]^+$ cation and CH_2Cl_2 solvent molecule in a ratio of 1 : 1 : 1, and only the structure of the $[S(2\text{-}CH_2\text{-}4\text{-}^tBu\text{-}6\text{-}CMe_3\text{-}C_6H_2O)_2TiCl_3]^-$ anion is shown in Fig. 2 with the $[NHEt_3]^+$ cation and the CH_2Cl_2 solvent molecule being omitted for clarity. The $[S(2\text{-}CH_2\text{-}4\text{-}^tBu\text{-}6\text{-}CMe_3\text{-}C_6H_2O)_2TiCl_3]^-$ anion has a mononuclear structure with the central titanium atom having a six-coordinating octahedral environment, in which the O1, O2, Cl1and Cl3 atoms define the equatorial plane and the S1 and Cl2 atoms occupy the apical positions. The Ti–O distances of 1.815(5) and 1.834(5) Å are slightly longer than those found in complex **4** (1.800(3) Å). The Ti–S bond distance (2.587(2) Å) from the central titanium atom to the coordinating sulphur atom is also slightly longer than the one seen in complex **4** (2.5607(16) Å). The Ti–Cl bond lengths (2.438(2), 2.300(2) and 2.388(2) Å) are close to those observed in a similar titanium complex $[OSO]TiCl_3^-$,[13c] but evidently longer than the ones seen in complex **4**.

The crystal structure analysis of complex **10**·THF reveals that the complex has a pseudo-octahedral Zr center, where the tridentate **L2** ligand meridionally coordinates to the metal center with two chlorine atoms in *cis*-positions and THF occupying an axial position. The Zr–O bond lengths (1.982(4) and 2.225(5) Å) between the zirconium atom and the phenolic oxygen atoms in **10**·THF are close to those observed in THF-solvated zirconium complexes with similar tridentate ligands previously reported.[24] The angle O–Zr–O (153.4(2)°) is slightly larger than that of 149.19(1)° in the [ONO] zirconium complex,[24a] but smaller than that of 158.96(1)° in the pyridine-bis(phenolate) zirconium complex.[24b] The Zr–S bond distance (2.758(2) Å) in **10**·THF is slightly shorter than those in [OSSO] zirconium complexes (2.7591(11)–2.8485(7) Å),[23] but much longer than that of Zr–O bond lengths (2.334(2) and 2.353(2) Å) from the zirconium center to the ether oxygen atom in the bis(ligand) zirconium complex $[OOO]_2Zr$.[14] The Zr–Cl bond lengths (2.438(2) and 2.433(2) Å) in **10**·THF are comparable to those observed in similar zirconium complexes.[24]

Polymerization reactions

Upon activation with MAO or $Al^iBu_3/Ph_3CB(C_6F_5)_4$, these complexes were used as catalysts for ethylene polymerization. The results are summarized in Table 1. Titanium complexes **1–9** as catalyst precursors were found to show moderate to high catalytic activities for ethylene polymerization upon activation with MAO or $Al^iBu_3/Ph_3CB(C_6F_5)_4$, and obviously higher catalytic activities were observed when these complexes were activated with MAO than when activated with $Al^iBu_3/Ph_3CB(C_6F_5)_4$. The

Table 1 Summary of polymerization of ethylene under various conditions[a]

Entry	Cat.	Cat. (μmol)	Cocat.	Time (h)	T (°C)	Al/M	Yield (g)	Activity[b]	M_w [c] (×10^4)	PDI[c]	T_m [d] (°C)
1	**1**	0.2	MAO	0.5	50	2000	0.62	6200	14.4	4.8	137.8
2	**2**	0.2	MAO	0.5	50	2000	0.84	8400	14.6	3.0	138.4
3	**3**	0.2	MAO	0.5	50	2000	0.16	1600	17.8	3.3	134.2
4	**4**	0.2	MAO	0.5	50	2000	0.34	3400	20.8	5.1	134.9
5	**5**	0.2	MAO	0.5	50	2000	0.080	800	26.2	2.8	132.8
6	**2**	0.2	MAO	0.5	70	2000	0.64	6400	11.8	4.3	136.7
7	**2**	0.2	MAO	0.5	30	2000	0.64	6400	20.1	4.0	136.6
8	**2**	0.2	MAO	0.5	50	3000	0.48	4800	10.7	3.3	137.6
9	**2**	0.2	MAO	0.5	50	1000	0.10	1000	19.5	3.5	136.7
10	**2**	0.2	MAO	2	50	2000	1.55	7100	18.2	3.7	137.7
11	**2**	0.2	MAO	1	50	2000	2.84	7750	17.9	3.3	138.3
12	**2**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	50	500	0.57	1140	12.2	3.8	137.9
13	**2**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	70	500	0.33	660	10.0	3.0	136.3
14	**2**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	30	500	0.89	1780	13.9	3.3	137.9
15	**2**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	10	500	0.22	440	14.5	5.4	137.0
16	**2**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	30	600	0.80	1600	13.2	4.6	138.7
17	**2**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	30	400	0.46	920	16.0	4.1	135.6
18	**6**	0.2	MAO	0.5	50	2000	0.28	2800	13.9	2.7	136.9
19	**7**	0.2	MAO	0.5	50	2000	0.42	4200	18.0	4.0	137.9
20	**8**	0.2	MAO	0.5	50	2000	0.23	2300	18.4	3.5	138.1
21	**9**	0.2	MAO	0.5	50	2000	0.38	3800	21.7	3.7	137.3
22	**10**	0.2	MAO	0.5	50	2000	0.18	1800	8.2	2.5	138.2
23	**10**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	30	500	0.19	380	5.3	2.8	137.6
24	**11**	0.2	MAO	0.5	50	2000	0.15	1500	8.8	2.3	137.8
25	**11**	1	$Al^iBu_3/[Ph_3CB(C_6F_5)_4]$	0.5	30	500	0.16	320	7.1	2.5	137.3

[a] Polymerization conditions: solvent 70 mL of toluene; ethylene pressure 5 bar; B/Ti molar ratio 1.2. [b] Units of kg PE (mol M)$^{-1}$ h^{-1}. [c] M_w and PDI determined from GPC measurements, where PDI is defined as M_w/M_n. [d] Determined by DSC at a heating rate of 10 °C min^{-1}.

influences of the catalyst structure, the Al/Ti ratio, and the reaction temperature on both the catalytic activity and the molecular weight of the resulting polyethylene were also examined. It was found that, under the same conditions, complex **2** shows obviously higher catalytic activity (8.4×10^6 g PE (mol Ti)$^{-1}$ h^{-1}) than other titanium complexes and most reported titanium complexes with bridged bisphenolato tridentate chelating ligands.[9,14,24a] The catalytic activities of these titanium catalyst systems were found to be dependent on the Al/Ti molar ratio and the maximal catalytic activity was observed with an Al/Ti molar ratio of 2000 when activated with MAO (Table 1, entries 2, 8 and 9) and an Al/Ti molar ratio of 500 when activated with $Al^iBu_3/Ph_3CB(C_6F_5)_4$ (Table 1, entries 14, 16 and 17). Ethylene polymerization experiments with these catalyst systems at different polymerization temperatures (30, 50 and 70 °C) were also carried out and the highest catalytic activity was observed at 30 °C and 50 °C for the $Al^iBu_3/Ph_3CB(C_6F_5)_4$ activated systems (Table 1, entries 12–15) and the MAO activated systems (Table 1, entries 2, 6 and 7), respectively. It seems that these catalyst systems show relatively long lifetime since the observed catalytic activity for complex **2** only decreases slightly as the polymerization time increased from 30 min to 120 min (Table 1, entries 2, 10 and 11). The steric hindrance of the R substituents on the *ortho*-position of the phenoxide groups of the [OSO] ligands was proved to strongly influence the catalytic performance of these complexes. As seen from the results listed in Table 1, the catalytic activity of these complexes increases first with the increase of the steric hindrance of the R substituent from the *tert*-butyl group (in complex **1**) to the cumyl group (in complex **2**), then decreases rapidly with the further increase of the steric hindrance of the R substituent from the cumyl group to the 1,1-diphenylethyl group (in complex **3**), triphenylmethyl group (in complex **4**) and tri(4-tolyl)methyl group (in complex **5**). It is possible that the R group in complexes **3**, **4** and **5** is so bulky that the coordination environment of the catalytically active centers in them becomes congested for the coordination and insertion of the ethylene molecule. Noticeably, complex **3** shows much lower catalytic activity than complex **2** under the same conditions due probably to its poor solubility in toluene (Table 1, entries 1–5). Except for complex **5**, the catalytic activities of these complexes are obviously higher (320–1680 kg PE (mol Ti)$^{-1}$ h^{-1} atm^{-1}) than those of similar titanium complexes [OSO]$TiCl_2$ (**A** in Chart 1) (220 kg PE (mol Ti)$^{-1}$ h^{-1} atm^{-1})[9] and [OOO]$TiCl_2$ (**G** in Chart 1) (34 kg PE (mol Ti)$^{-1}$ h^{-1} atm^{-1})[14] under similar conditions. It seems that both the bridged methylene group and the S atom in these new titanium complexes make positive impacts on their catalytic activity. The catalytic activities of ionic titanium complexes **6** and **8** were found to be slightly lower than that of complex **1** under similar conditions (Table 1, entries 3, 18 and 20), while the catalytic activities of ionic titanium complexes **7** and **9** were found to be higher than that of complex **3** under similar conditions (Table 1, entries 5, 19 and 21) since complex **3** shows low catalytic activity as mentioned above. Ethylene polymerization reactions using the zirconium complexes **10** and **11** as catalyst precursors under different conditions were also examined (see Table 1). Upon activation with MAO or $Al^iBu_3/Ph_3CB(C_6F_5)_4$, all the zirconium complexes exhibit moderate catalytic activity for the ethylene polymerization reaction. Under similar conditions, the zirconium complexes were found to show slightly lower catalytic activity than the corresponding titanium complexes. Theoretical calculation on similar complexes with [OXO] tridentate ligands reported previously suggests that the Ti-based catalysts are more active than their zirconium counterparts due to a slightly lower activation energy barrier.[18] The molecular weights of the obtained polymers were found to increase with the increase in the steric hindrance of the R group (Table 1, entries 1–5), which is understandable since a bulkier R group would make both processes, the β-hydrogen elimination and the chain transfer to the aluminum cocatalyst, more difficult. The molecular weights of polyethylenes produced by the zirconium complexes are slightly lower than those of the polymers produced by the titanium complexes. ^{13}C NMR analysis on the polyethylene samples demonstrates that they are linear polymers with no detectable branches. The DSC analysis on the polymers shows that their T_m values fall in between 132.8 and 138.7 °C. The GPC analysis reveals that the polyethylenes produced by these catalysts possess moderate molecular weights (M_w = 5.3–26.2 × 10^4 g mol^{-1}) and the molecular weight distribution is basically unimodal.

The copolymerization reactions of ethylene with 1-hexene were also investigated using these titanium and zirconium complexes as precatalysts activated with the MAO or $Al^iBu_3/Ph_3CB(C_6F_5)_4$ cocatalyst, and the experimental results are summarized in Table 2. It was found that the MAO-activated catalyst systems show very low catalytic activity and produce polyethylenes with no 1-hexene incorporation. However, the $Al^iBu_3/Ph_3CB(C_6F_5)_4$-activated catalyst systems were found to show relatively high catalytic activity and comonomer incorporation ability. The catalytic activity of the **1–11**/$Al^iBu_3/Ph_3CB(C_6F_5)_4$ catalyst systems for the ethylene/1-hexene copolymerization under similar conditions varies almost in the same order as seen above for the ethylene homopolymerization. Among them, the **2**/$Al^iBu_3/Ph_3CB(C_6F_5)_4$ catalyst system shows the highest catalytic activity. The obtained poly(ethylene-*co*-1-hexene)s were analyzed by ^{13}C NMR and GPC. The ^{13}C NMR spectra for typical copolymer samples are given in the ESI.† On the basis of the ^{13}C NMR analysis,[25] the values of the comonomer content in the poly(ethylene-*co*-1-hexene)s were calculated and the data are given in Table 2. It can be seen from the comonomer content data that the comonomer incorporation ability of these catalyst systems is evidently dependent on the structure of the catalyst. Complexes **2**, **3**, **7** and **9** were found to produce poly(ethylene-*co*-1-hexene)s with high comonomer contents of up to ~24% (Table 2, entries 4, 5, 6, 10 and 12), which is comparable to the copolymers produced by CGC catalysts and similar titanium catalysts with [ONX] tridentate ligands.[26] In comparison, complexes **4** and **5** bearing ligands with relatively large steric hindrance and complexes **1**, **6**, and **8** carrying ligands with relatively small steric hindrance all

Table 2 Summary of copolymerization of ethylene/1-hexene under various conditions[a]

Entry	Cat.	1-Hexene (mL)	Yield (g)	Activity[b]	1-Hexene content[c] (mol%)	M_w [d] ($\times 10^4$)	PDI[d]	T_m [f] (°C)
1	**1**	6	0.66	7920	8.2	6.9	3.2	109.3
2	**2**	2	0.82	9840	5.3	10.2	2.7	110.2
3	**2**	4	0.77	9240	7.0	9.4	3.5	108.8
4	**2**	6	0.75	9000	20.1	8.8	3.2	84.8
5	**2**	8	0.16	1920	23.8	8.1	3.7	67.0
6	**3**	6	0.19	2280	21.0	7.6	2.9	74.0
7	**4**	6	0.54	6480	4.0	13.2	3.1	112.7
8	**5**	6	0.10	1200	4.0	15.7	2.6	111.6
9	**6**	6	0.26	3120	8.9	8.5	2.8	98.3
10	**7**	6	0.43	5160	20.1	7.9	3.8	83.9
11	**8**	6	0.16	1920	11.6	9.3	2.9	90.4
12	**9**	6	0.30	3600	22.3	8.8	2.7	69.6
13	**10**	6	0.14	1680	2.3	4.8	3.3	123.9
14	**11**	6	0.11	1320	1.5	5.6	3.2	124.7
15	**2**[e]	6	0.22	2640	Trace	13.6	2.9	137.9
16	**7**[e]	6	0.13	1560	Trace	16.9	3.5	136.1

[a] Polymerization conditions: toluene + 1-hexene, total 70 mL; catalyst, 1×10^{-6} mol; Al/Ti molar ratio, 500; B/Ti molar ratio, 1.2; time, 5 min; temperature, 90 °C; ethylene pressure, 5 bar. [b] In units of kg of polymer (mol of M)$^{-1}$ h^{-1}. [c] Calculated on the basis of ^{13}C NMR spectra. [d] M_w and PDI determined from GPC measurements, where PDI is defined as M_w/M_n. [e] MAO was used as a cocatalyst. [f] Determined by DSC at a heating rate of 10 °C min^{-1}.

produce copolymers with relatively low comonomer contents (Table 2, entries 1, 7, 8, 9 and 11). It has been known that the comonomer incorporation ability of a catalyst system can be remarkably affected by the structure of the catalyst and the steric bulk of its ligand.[4a,26a] The zirconium complexes **10** and **11** were found to show low catalytic activity and low comonomer incorporation ability (Table 2, entries 13 and 14) for the ethylene/1-hexene copolymerization reaction. The GPC analysis reveals that the poly(ethylene-*co*-1-hexene)s produced by these catalyst systems possess moderate molecular weights (M_w = 4.8–15.7 $\times 10^4$ g mol^{-1}) and the molecular weight distribution is basically unimodal and narrow, similar to metallocene polyolefins. The DSC analysis of the copolymers shows their T_m values around 67.0–124.7 °C, which are largely in agreement with their comonomer contents.

Conclusions

A number of new sulfur-bridged tridentate [OSO] bisphenolato-based ligand precursors S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2OH)_2$ have been synthesized by reactions of $Na_2S{\cdot}9H_2O$ with 2 eq. of the corresponding 2-(bromomethyl)-4-(*tert*-butyl)-6-R-phenol. Their neutral titanium complexes [S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2$]$TiCl_2$ [R = CMe_3 (**1**), CMe_2Ph (**2**), $CMePh_2$ (**3**), CPh_3 (**4**), C(*p*-Tol)$_3$ (**5**)] and zirconium complexes [S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2$] $ZrCl_2$(THF) [R = CMe_2Ph (**10**·THF), $CMePh_2$ (**11**·THF)] were synthesized in high yields by direct HCl-elimination reactions of $TiCl_4$ with the corresponding ligand precursors in toluene or by reactions of $ZrCl_4$ with the dilithium salt of the corresponding ligand precursors in THF. A number of ionic titanium complexes [$NHEt_3$][S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2TiCl_3$] [R = CMe_3 (**6**), $CMePh_2$ (**7**)] and [NH_2Et_2][S(2-CH_2-4-^{t}Bu-6-R-$C_6H_2O)_2TiCl_3$] [R = CMe_3 (**8**), $CMePh_2$ (**9**)] have also been synthesized in high yields from the reactions of $TiCl_4$ with the corresponding ligand precursors in the presence of triethylamine or diethylamine. The molecular structures of complexes **4**, **6** and **10**·THF have been determined by single-crystal X-ray diffraction analysis. Upon activation with MAO or Al^iBu_3/$Ph_3CB(C_6F_5)_4$, these complexes exhibit moderate to high activities for ethylene polymerization and ethylene/1-hexene copolymerization reactions, producing polyethylenes and poly(ethylene-*co*-1-hexene)s with moderate molecular weights and moderate to high comonomer incorporation (up to ~24% of comonomer contents). In comparison with the neutral complexes, the ionic titanium complexes **6**, **7**, **8** and **9** show low catalytic activity under similar conditions. The catalytic performance of these complexes, as well as the molecular weights of the obtained polymers and the comonomer contents in the copolymers can be tuned over a wide range by the structural modification of the catalyst precursors and variation of the reaction parameters, such as the Al/M molar ratio, the comonomer concentration and the polymerization temperature. The poly(ethylene-*co*-1-hexene)s produced by these catalyst systems possess moderate molecular weights, unimodal molecular weight distribution and high comonomer contents, which are just the required features for polyolefin elastomers.

Experimental section

General methods and materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene was dried over sodium/benzophenone and distilled under nitrogen prior to use. CH_2Cl_2 and *n*-hexane were dried by distilling over calcium hydride before use. Polymerization grade ethylene was further purified by passage through columns of 4 Å molecular sieves and MnO. MAO, hexene, $ZrCl_4$, and $TiCl_4$ were purchased from Aldrich. Al^iBu_3

and all other chemicals were commercially available and were used as received unless stated otherwise. $Ph_3CB(C_6F_5)_4$ [27] and $(p\text{-Tol})_3CCl$ [28] were prepared following literature procedures. The elemental analysis was performed on a Vario EL cube analyzer. Infrared spectra were recorded using KBr disks with a Nicolet Avatar 360. NMR spectra were recorded on a Varian 400 MHz instrument at room temperature in $CDCl_3$ solution. The molecular weights and polydispersity indices of the polymer samples were determined at 150 °C by PL-GPC 220 type high-temperature gel permeation chromatography. 1,2,4-Trichlorobenzene was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The melting points of the polyethylenes were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 at a heating/cooling rate of 10 °C min^{-1} from 35 to 160 °C and the data from the second heating scan were used.

Synthesis of 4-(*tert*-butyl)-2-(tri-*p*-tolylmethyl)phenol. This compound was prepared following a literature procedure.[29] Sodium metal (1.00 g, 0.0435 mol) was added to *p-tert*-butylphenol (46.5 g, 0.310 mol) in a 250 mL single-necked round-bottom flask at 100 °C with vigorous stirring. Tri(*p*-tolyl) methyl chloride (10.0 g, 0.0312 mol) was then added and the reaction mixture was heated at 135–145 °C for 3 h with vigorous stirring. After cooling down to room temperature, the reaction mixture was treated with 7% NaOH aq. solution (100 mL) and the product was extracted with diethyl ether (2 × 80 mL). The organic layers were combined and washed with 7% NaOH aq. solution (5 × 80 mL), brine (30 mL), and water (100 mL). The organic layer was separated. The solution was dried ($MgSO_4$), filtered and concentrated. Column chromatography using a 50 : 1 mixture of petroleum ether and ethyl acetate yielded a white powder in 60.6% yield (8.22 g, 0.0189 mol). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.21 (dd, J = 2.0 Hz, J = 2.0 Hz, 1H, Ar*H*), 7.10–7.07 (m, 13H, Ar*H*), 6.75 (d, J = 8.4 Hz, 1H, Ar*H*), 4.40 (s, 1 H, O*H*), 2.32 (s, 9H, ArCH_3), 1.15 (s, 9H, C(CH_3)$_3$).

Synthesis of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (A). This compound was prepared following a literature procedure.[23b] 2,4-Di-*tert*-butylphenol (22.7 g, 0.110 mol) was dissolved in 60 mL of acetic acid in a 250 mL single-necked round-bottom flask. Paraformaldehyde (3.60 g, 0.120 mol) was added and the suspension was stirred at room temperature for 2 h. Then 42 mL of 33 wt% HBr (0.220 mol) in acetic acid was added within 15 min and the reaction mixture was stirred at room temperature for further 30 min. Removal of acetic acid and other volatile contents under vacuum yielded an orange-color viscous oil which changed to a solid material upon keeping at −30 °C for 3 h. The solid material was filtered and dried to give the product (29.0 g, 0.0969 mol, 88.1%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.26 (d, J = 2.8 Hz, 1H, Ar*H*), 7.02 (d, J = 2.8 Hz, 1H, Ar*H*), 5.20 (s, 1H, O*H*), 4.50 (s, 2H, CH_2), 1.36 (s, 9H, C(CH_3)$_3$), 1.22 (s, 9H, C(CH_3)$_3$).

Synthesis of 2-(bromomethyl)-4-(*tert*-butyl)-6-(2-phenylpropan-2-yl)phenol (B). This compound was prepared in a manner analogous to that described for the synthesis of **A** with 4-(*tert*-butyl)-6-(2-phenylpropan-2-yl)phenol (29.5 g, 0.110 mol), paraformaldehyde (3.60 g, 0.12 mol) and 33 wt% HBr (42 mL, 0.220 mol) in acetic acid as the starting materials. The product was isolated as a pale white powder (33.4 g, 0.0924 mol, 84.0%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.48 (d, J = 3.2, 1H, Ar*H*), 7.34–7.24 (m, 6H, Ar*H*), 4.54 (s, 1H, O*H*), 4.47 (s, 2H, ArCH_2), 1.69 (s, 6H, ArC(CH_3)$_2$), 1.35 (s, 9H, C(CH_3)$_3$).

Synthesis of 2-(bromomethyl)-4-(*tert*-butyl)-6-(1,1-diphenylethyl)phenol (C). This compound was prepared in a manner analogous to that described for the synthesis of **A** with 4-(*tert*-butyl)-6-(1,1-diphenylethyl)phenol (36.4 g, 0.110 mol), paraformaldehyde (3.60 g, 0.120 mol) and 33 wt% HBr (42 mL, 0.220 mol) in acetic acid as the starting materials. The product was isolated as a pale white powder (40.3 g, 0.0951 mol, 86.4%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δH (ppm): 7.34–7.22 (m, 11H, Ar*H*), 6.87 (d, J = 3.2, 1H, Ar*H*), 4.70 (s, 1H, O*H*), 4.54 (s, 2H, ArCH_2), 2.21 (s, 3H, ArCCH_3), 1.17 (s, 9H, C(CH_3)$_3$).

Synthesis of 2-(bromomethyl)-4-(*tert*-butyl)-6-(triphenylmethyl)phenol (D). This compound was prepared following a literature procedure.[30] 4-(*tert*-Butyl)-6-(triphenylmethyl)phenol (43.2 g, 0.110 mol), paraformaldehyde (3.60 g, 0.120 mol) and 33 wt% HBr (42 mL, 0.220 mol) in acetic acid were placed in a 250 mL single-necked round-bottom flask. The reaction mixture was stirred at 70 °C for 1 hour, during which time a white precipitate appeared. The reaction mixture was cooled to room temperature and the solid material was collected by filtration, washed with water and dried under vacuum to give the product (43.8 g, 0.0902 mol, 82.0%) as a pale white powder. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δH (ppm): 7.33–7.05 (m, 17H, Ar*H*), 4.68 (s, 1H, O*H*), 4.50 (s, 2H, ArCH_2), 1.14 (s, 9H, C(CH_3)$_3$).

Synthesis of 2-(bromomethyl)-4-(*tert*-butyl)-6-(tri-*p*-tolylmethyl)phenol (E). This compound was prepared in a manner analogous to that described for the synthesis of **D** with 4-(*tert*-butyl)-6-(tri-*p*-tolylmethyl)phenol (47.8 g, 0.110 mol), paraformaldehyde (3.54 g, 0.120 mol) and 33 wt% HBr (42 mL, 0.220 mol) in acetic acid as the starting materials. The product was isolated as a pale white powder (49.3 g, 0.0934 mol, 85.0%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.09–7.03 (m, 14H, Ar*H*), 4.77 (s, 1H, O*H*), 4.51 (s, 2H, ArCH_2), 2.33 (s, 9H, ArCH_3), 1.15(s, 9H, C(CH_3)$_3$).

Synthesis of ligands H_2L1–H_2L5

S(2-CH$_2$-4-^{t}Bu-6-CMe$_3$-C$_6$H$_2$OH)$_2$ (H_2L1). To a solution of $Na_2S{\cdot}9H_2O$ (2.40 g, 10.0 mmol in 3 mL of H_2O and 7 mL of acetone) was added a solution of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (5.98 g, 20.0 mmol in 10 mL acetone) dropwise at room temperature. The reaction mixture was stirred at room temperature for 3 h. Work-up was conducted by adding 40 mL of dichloromethane and 5 mL of 5% HCl aqueous solution. The organic layer was separated, dried over anhydrous $MgSO_4$ and evaporated to give a pale yellow solid. The solid was recrystallized from methanol to give white crystals as the desired product H_2L1 (4.10 g, 8.72 mmol, 87.2%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.29 (d, J = 2.4 Hz, 2H, Ar*H*), 6.97 (d, J = 2.4 Hz, 2H, Ar*H*), 6.00 (s, 2H, O*H*), 3.76 (s, 4H, CH_2S), 1.44 (s, 18H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (100 MHz,

$CDCl_3$, 298 K) δ C (ppm): 151.69, 142.65, 137.23, 125.39, 124.15, 121.85 (Ar*C*), 35.13 ($C(CH_3)_3$), 34.41 ($C(CH_3)_3$), 33.44 (CH_2S), 31.78 ($C(CH_3)_3$), 30.03 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 3637w, 2956s, 2906m, 2870m, 1681w, 1599w, 1479s, 1414m, 1392w, 1364s, 1246m, 1221s, 1200s, 1159w, 1120w, 918w, 878m, 822w, 795w, 766m, 723w, 688w, 648w. Anal. Calcd for $C_{30}H_{46}O_2S$ (470.76): C, 76.54; H, 9.85; found: C, 76.47; H, 9.82.

S(2-CH_2-4-^{t}Bu-6-CMe_2Ph-$C_6H_2OH)_2$ (H_2L2). The ligand H_2**L2** was prepared in a manner analogous to that described for the synthesis of H_2**L1** with 2-(bromomethyl)-4-(*tert*-butyl)-6-(2-phenylpropan-2-yl)phenol (7.23 g, 20.0 mmol) and $Na_2S{\cdot}9H_2O$ (2.40 g, 10.0 mmol) as the starting materials. The product was isolated as a pale white powder (4.90 g, 8.24 mmol, 82.4%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.38 (d, J = 2.1 Hz, 2H, Ar*H*), 7.29–7.17 (m, 10H, Ar*H*), 7.05 (d, J = 1.9 Hz, 2H, Ar*H*), 5.03 (s, 2H, O*H*), 3.56 (s, 4H, CH_2S), 1.67 (s, 12H, $C(CH_3)_2$), 1.32 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 150.34, 149.43, 142.50, 135.57, 128.84, 126.46, 125.97, 125.94, 124.45, 123.00 (Ar*C*), 42.23 ($C(CH_3)_2$), 34.43 ($C(CH_3)_3$), 32.41 (CH_2S), 31.82, 29.86 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 3510s, 3055w, 2964s, 2903m, 2868m, 1770w, 1599m, 1479s, 1443s, 1362s, 1323w, 1298m, 1281m, 1240m, 1215s, 1144m, 1107w, 1072m, 1030m, 879m, 818m, 764s, 702s, 646m, 611m, 534m. Anal. Calcd for $C_{40}H_{50}O_2S$ (594.90): C, 80.76; H, 8.47; found: C, 80.68; H, 8.39.

S(2-CH_2-4-^{t}Bu-6-$CMePh_2$-$C_6H_2OH)_2$ (H_2L3). The ligand H_2**L3** was prepared in a manner analogous to that described for the synthesis of H_2**L1** with 2-(bromomethyl)-4-(*tert*-butyl)-6-(1,1-diphenylethyl)phenol (8.47 g, 20.0 mmol) and $Na_2S{\cdot}9H_2O$ (2.40 g, 10.0 mmol) as the starting materials. The product was isolated as a pale white powder (6.00 g, 8.34 mmol, 83.4%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.29–7.17 (m, 20H, Ar*H*), 7.06 (d, J = 1.8 Hz, 2H, Ar*H*), 6.69 (d, J = 1.8 Hz, 2H, Ar*H*), 5.31 (s, 2H, O*H*), 3.67 (s, 4H, CH_2S), 2.22 (s, 6H, $C(CH_3)$), 1.12 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 150.64, 147.40, 142.42, 135.25, 128.46, 128.39, 126.81, 126.53, 126.17, 124.35 (Ar*C*), 51.81 ($C(CH_3)$), 34.26 ($C(CH_3)_3$), 32.74 (CH_2S), 31.56 ($C(CH_3)$), 28.57 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 3495s, 3086w, 3061w, 3024w, 3006w, 2957s, 2926m, 2864w, 1738w, 1597m, 1580w, 1493m, 1466s, 1443s, 1362m, 1321m, 1298m, 1277w, 1252m, 1198s, 1174m, 1155m, 1115m, 1099m, 1072m, 1024s, 918m, 883m, 798m, 764m, 742m, 704s, 644m, 627m. Anal. Calcd for $C_{50}H_{54}O_2S$ (719.04): C, 83.52; H, 7.57; found: C, 83.46; H, 7.51.

S(2-CH_2-4-^{t}Bu-6-CPh_3-$C_6H_2OH)_2$ (H_2L4). The ligand H_2**L4** was prepared in a manner analogous to that described for the synthesis of H_2**L1** with 2-(bromomethyl)-4-(*tert*-butyl)-6-tritylphenol (9.71 g, 20.0 mmol) and $Na_2S{\cdot}9H_2O$ (2.40 g, 10.0 mmol) as the starting materials. The product was isolated as a pale white powder (6.90 g, 8.18 mmol, 81.8%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.22–7.15 (m, 30H, Ar*H*), 7.12 (d, J = 2.2 Hz, 2H, Ar*H*), 6.99 (d, J = 2.2 Hz, 2H, Ar*H*), 4.90 (s, 2H, O*H*), 3.55 (s, 4H, CH_2S), 1.10 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 150.56, 144.87, 142.29, 133.44, 131.14, 127.73, 127.58, 126.53, 126.48, 125.29 (Ar*C*), 63.31(*C*), 34.31 ($C(CH_3)_3$), 31.94 (CH_2S), 31.54 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 3516s, 3082w, 3057w, 3030w, 2960s, 2930m, 2904m, 2866w, 1597m, 1477s, 1444s, 1414w, 1362m, 1323m, 1294m, 1254w, 1207s, 1115m, 1086w, 1034m, 1001w, 926w, 881m, 843w, 822m, 806m, 771m, 754s, 702s, 658m, 640m, 598w, 569w. Anal. Calcd for $C_{60}H_{58}O_2S$ (843.18): C, 85.47; H, 6.93; found: C, 85.45; H, 6.96.

S(2-CH_2-4-^{t}Bu-6-C(*p*-Tol)$_3$-$C_6H_2OH)_2$ (H_2L5). The ligand H_2**L5** was prepared in a manner analogous to that described for the synthesis of H_2**L1** with 2-(bromomethyl)-4-(*tert*-butyl)-6-(tri-*p*-tolylmethyl)phenol (10.6 g, 20.0 mmol) and $Na_2S{\cdot}9H_2O$ (2.40 g, 10.0 mmol) as the starting materials. The product was isolated as a pale white powder (8.00 g, 8.63 mmol, 86.3%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.13 (d, J = 2.3 Hz, 2H, Ar*H*), 7.05–6.99 (m, 26H, Ar*H*), 4.86 (s, 2H, O*H*), 3.55 (s, 4H, CH_2S), 2.28 (s, 18H, $ArCH_3$), 1.11 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 150.50, 142.11, 135.84, 133.54, 130.91, 128.67, 128.43, 127.40, 126.24, 125.42 (Ar*C*), 62.28 (*C*), 34.31 ($C(CH_3)_3$), 31.73 (CH_2S), 31.57 ($C(CH_3)_3$), 21.05 ($ArCH_3$). FT-IR (KBr disk, cm^{-1}): 3514s, 3020m, 2953s, 2922m, 2866m, 1906w, 1659w, 1605w, 1508s, 1475s, 1364m, 1325w, 1277m, 1259w, 1190s, 1113w, 1022m, 881m, 810s, 771s, 725w, 690w, 640w, 596m, 567m. Anal. Calcd for $C_{66}H_{70}O_2S$ (927.34): C, 85.48; H, 7.61; found: C, 85.42; H, 7.66.

[S(2-CH_2-4-^{t}Bu-6-CMe_3-$C_6H_2O)_2$]$TiCl_2$ (1). $TiCl_4$ (0.161 g, 0.850 mmol) was dissolved in 10 mL of toluene at room temperature. To the resulting red solution was added dropwise a solution of H_2**L1** (0.400 g, 0.850 mmol) in 10 mL of toluene at room temperature with stirring, during which period the color of the reaction mixture changed to red brown. The reaction mixture was stirred for further 3 h at room temperature and the solvent was then removed under reduced pressure. The residue was washed with *n*-hexane and dried *in vacuo* to give 0.475 g (0.808 mmol, 95.1%) of pure **1** as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.25 (d, J = 2.4 Hz, 2H, Ar*H*), 7.03 (d, J = 2.0 Hz, 2H, Ar*H*), 3.85 (br s, 4H, CH_2S), 1.47 (s, 18H, $C(CH_3)_3$), 1.26 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 163.38, 145.71, 137.15, 125.57, 123.99, 123.40 (Ar*C*), 35.79 ($C(CH_3)_3$), 35.36 ($C(CH_3)_3$), 34.75 (CH_2S), 31.58 ($C(CH_3)_3$), 30.18 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 2960s, 2906m, 2870m, 1597w, 1465m, 1441s, 1364m, 1246s, 1203w, 1169m, 1124m, 914m, 891m, 881s, 858s, 760m, 735w, 584m. Anal. Calcd for $C_{30}H_{44}Cl_2O_2STi$ (587.51): C, 61.33; H, 7.55; found: C, 61.22; H, 7.63.

[S(2-CH_2-4-^{t}Bu-6-CMe_2Ph-$C_6H_2O)_2$]$TiCl_2$ (2). Complex **2** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L2** (0.506 g, 0.850 mmol) and $TiCl_4$ (0.161 g, 0.850 mmol) as the starting materials. Pure **2** (0.560 g, 0.787 mmol, 92.6%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.42 (d, J = 2.0 Hz, 2H, Ar*H*), 7.08–7.05 (m, 8H, Ar*H*), 7.01 (d, J = 2.0 Hz, 2H, Ar*H*), 6.89(s, 2H, Ar*H*), 3.58 (br s, 4H, CH_2S), 1.72 (s, 12H, $C(CH_3)_2$), 1.32 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 162.99, 149.09, 145.98, 136.51, 128.08, 125.82, 125.71, 125.49, 124.46, 122.06 (Ar*C*),

42.51 ($C(CH_3)_2$), 34.79 ($C(CH_3)_3$), 34.53 (CH_2S), 31.62 ($C(CH_3)_2$), 30.18 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 2960s, 2868m, 1595w, 1444s, 1363m, 1250s, 1209s, 895m, 850m, 762m, 698m, 592m, 573m. Anal. Calcd for $C_{40}H_{48}Cl_2O_2STi$ (711.65): C, 67.51; H, 6.80; found: C, 67.42; H, 6.73.

[S(2-CH$_2$-4-^{t}Bu-6-CMePh$_2$-C$_6$H$_2$O)$_2$]TiCl$_2$ (3). Complex **3** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L3** (0.611 g, 0.850 mmol) and $TiCl_4$ (0.161 g, 0.850 mmol) as the starting materials. Pure **3** (0.670 g, 0.802 mmol, 94.3%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.24–7.05 (m, 22H, Ar*H*), 6.55 (d, J = 2.0 Hz, 2H, Ar*H*), 3.77 (br s, 4H, CH_2S), 2.35 (s, 6H, $C(CH_3)$), 1.08 (s, 18H, $C(CH_3)_3$). Due to the poor solubility of complex **3** in $CDCl_3$, the ^{13}C NMR spectrum could not be obtained. FT-IR (KBr disk, cm^{-1}): 3057w, 3026w, 2962s, 2866w, 1597w, 1493m, 1444s, 1361w, 1250s, 1203s, 879s, 860m, 756m, 730m, 696s, 607w, 571w. Anal. Calcd for $C_{50}H_{52}Cl_2O_2STi$ (835.78): C, 71.85; H, 6.27; found: C, 71.77; H, 6.23.

[S(2-CH$_2$-4-^{t}Bu-6-CPh$_3$-C$_6$H$_2$O)$_2$]TiCl$_2$ (4). Complex **4** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L4** (0.717 g, 0.850 mmol) and $TiCl_4$ (0.161 g, 0.850 mmol) as the starting materials. Pure **4** (0.740 g, 0.771 mmol, 90.7%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.43–6.90 (m, 34H, Ar*H*), 4.04–2.52 (br s, 4H, CH_2S), 1.18 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 162.28, 145.99, 144.86, 134.05, 131.13, 130.53, 128.74, 127.82, 125.54, 122.65 (Ar*C*), 64.15 (*C*), 34.65 ($C(CH_3)_3$), 31.53 (CH_2S), 31.38 ($C(CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 3055w, 3028w, 2960s, 2866w, 1595w, 1491m, 1446s, 1414w, 1361w, 1236s, 1184s, 878s, 856s, 770m, 741m, 702s, 567w. Anal. Calcd for $C_{60}H_{56}Cl_2O_2STi$ (959.92): C, 75.07; H, 5.88; found: C, 75.12; H, 5.91.

[S(2-CH$_2$-4-^{t}Bu-6-C(*p*-Tol)$_3$-C$_6$H$_2$O)$_2$]TiCl$_2$ (5). Complex **5** was synthesized in the same way as described above for the synthesis of complex **1** with the ligand H_2**L5** (0.788 g, 0.850 mmol) and $TiCl_4$ (0.161 g, 0.850 mmol) as the starting materials. Pure **5** (0.820 g, 0.785 mmol, 92.4%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.47 (s, 2H, Ar*H*), 7.25–6.88 (m, 26H, Ar*H*), 4.14–2.79 (br s, 4H, CH_2S), 2.39–1.63 (br s, 18H, $ArCH_3$), 1.17 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 162.29, 145.60, 141.83, 134.64, 130.87, 129.05, 128.42, 125.78, 125.34, 122.46 (Ar*C*), 63.02 (*C*), 38.01 ($C(CH_3)_3$), 34.56 (CH_2S), 31.34 ($C(CH_3)_3$), 20.91 ($ArCH_3$). FT-IR (KBr disk, cm^{-1}): 3020w, 2960s, 2920m, 2866w, 1595w, 1508s, 1448s, 1414w, 1364w, 1238s, 1184s, 1126w, 1022w, 912m, 877s, 856s, 806s, 783s, 742m, 580s, 561m. Anal. Calcd for $C_{66}H_{68}Cl_2O_2STi$ (1044.08): C, 75.92; H, 6.56; found: C, 75.83; H, 6.62.

[NHEt$_3$][S(2-CH$_2$-4-^{t}Bu-6-CMe$_3$-C$_6$H$_2$O)$_2$TiCl$_3$] (6). $TiCl_4$ (0.161 g, 0.850 mmol) was dissolved in 10 mL of toluene at room temperature. To the resulting red solution was added dropwise a solution of H_2**L1** (0.400 g, 0.850 mmol) and triethylamine (0.236 mL, 1.70 mmol) in 10 mL of toluene at room temperature with stirring, during which period the color of the reaction mixture changed to red brown. The reaction mixture was stirred for further 3 h at room temperature. The resulting dark red suspension was filtered. All the volatiles of the filtrate were removed *in vacuo*. The residue was washed with *n*-hexane and dried *in vacuo* to give pure **6** as a red brown solid (0.570 g, 0.786 mol, 92.5%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 8.96 (br s, 1H, $NH(CH_2CH_3)_3$), 7.24 (s, 2H, Ar*H*), 7.00 (s, 2H, Ar*H*), 4.15 (d, J = 12 Hz, 2H, CH_2S), 3.56 (d, J = 12 Hz, 2H, CH_2S), 3.25 (m, 6H, $NH(CH_2CH_3)_3$), 1.52 (s, 18H, $C(CH_3)_3$), 1.37 (t, J = 6.8 Hz, 9H, $NH(CH_2CH_3)_3$), 1.25 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 162.10, 143.02, 136.93, 125.19, 124.01, 123.68 (Ar*C*), 46.78 ($NH(CH_2CH_3)_3$), 36.36 ($C(CH_3)_3$), 35.36 ($C(CH_3)_3$), 34.48 (CH_2S), 31.67 ($C(CH_3)_3$), 30.51 ($C(CH_3)_3$), 8.82 ($NH(CH_2CH_3)_3$). FT-IR (KBr disk, cm^{-1}): 3510w, 2957s, 2906m, 2868m, 1605w, 1468s, 1441s, 1414m, 1392w, 1362m, 1304w, 1246s, 1200m, 1167m, 1126m, 908m, 891m, 874m, 847m, 810w, 773m, 756s, 702m, 650w, 638w, 586m, 569s, 472s. Anal. Calcd for $C_{36}H_{60}Cl_3NO_2STi$ (725.16): C, 59.63; H, 8.34; N, 1.93; found: C, 58.49; H, 8.21; N, 1.84.

[NHEt$_3$][S(2-CH$_2$-4-^{t}Bu-6-CMePh$_2$-C$_6$H$_2$O)$_2$TiCl$_3$] (7). Complex **7** was synthesized in the same way as described above for the synthesis of complex **6** with the ligand H_2**L3** (0.611 g, 0.850 mmol), $TiCl_4$ (0.161 g, 0.850 mmol) and triethylamine (0.236 mL, 1.70 mmol) as the starting materials. Pure **7** (0.780 g, 0.801 mol, 94.2%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 10.73 (br s, 1H, $NH(CH_2CH_3)_3$), 7.23–7.03 (m, 22H, Ar*H*), 6.51 (d, J = 1.8 Hz, 2H, Ar*H*), 3.80 (br s, 4H, CH_2S), 3.13 (m, 6H, $NH(CH_2CH_3)_3$), 2.36 (s, 6H, $C(CH_3)$), 1.38 (t, J = 7.2 Hz, 9H, $NH(CH_2CH_3)_3$), 1.06 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 161.84, 149.15, 143.26, 135.76, 129.38, 128.74, 127.71, 125.71, 125.61, 123.42 (Ar*C*), 52.59 ($C(CH_3)$), 46.66 ($NHCH_2CH_3$), 36.02 ($C(CH_3)_3$), 34.26 (CH_2S), 31.30 ($C(CH_3)$), 28.60 ($C(CH_3)_3$), 8.82 ($NHCH_2CH_3$). FT-IR (KBr disk, cm^{-1}): 3506bm, 3055w, 3020w, 2958s, 2866m, 1597m, 1443s, 1410m, 1362m, 1250s, 1203s, 1128w, 1074w, 1026m, 897m, 876m, 854m, 804w, 758m, 727m, 698s, 644w, 608w, 559m, 474m. Anal. Calcd for $C_{56}H_{68}Cl_3NO_2STi$ (973.44): C, 69.10; H, 7.04; N, 1.44; found: C, 68.89; H, 7.22; N, 1.34.

[NH$_2$Et$_2$][S(2-CH$_2$-4-^{t}Bu-6-CMe$_3$-C$_6$H$_2$O)$_2$TiCl$_3$] (8). Complex **8** was synthesized in the same way as described above for the synthesis of complex **6** with the ligand H_2**L1** (0.400 g, 0.850 mmol), $TiCl_4$ (0.161 g, 0.850 mmol) and diethylamine (0.175 mL, 1.70 mmol) as the starting materials. Pure **8** (0.530 g, 0.760 mol, 89.4%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 8.48 (br s, 2H, $NH_2(CH_2CH_3)_2$), 7.24 (d, J = 2.4 Hz, 2H, Ar*H*), 7.00 (d, J = 2.4 Hz, 2H, Ar*H*), 4.11 (bs, 2H, CH_2S), 3.57 (bs, 2H, CH_2S), 3.09 (m, 4H, $NH_2(CH_2CH_3)_2$), 1.50 (s, 18H, $C(CH_3)_3$), 1.42 (t, J = 7.2 Hz, 6H, $NH_2(CH_2CH_3)_2$), 1.25 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 162.12, 143.42, 136.94, 125.20, 123.93, 123.80 (Ar*C*), 42.51 ($NH_2(CH_2CH_3)_2$), 36.30 ($C(CH_3)_3$), 35.34 ($C(CH_3)_3$), 34.49 (CH_2S), 31.63 ($C(CH_3)_3$), 30.47 ($C(CH_3)_3$), 11.23 ($NH_2(CH_2CH_3)_2$). FT-IR (KBr disk, cm^{-1}): 3499w, 2960s, 2912m, 2866m, 2824m, 2775m, 2482w, 2386w,

1597w, 1454s, 1441s, 1412m, 1392m, 1362m, 1304w, 1250s, 1230s, 1203m, 1165m, 1126m, 1063w, 1051w, 914m, 879m, 852s, 810w, 758m, 729w, 571s, 476s. Anal. Calcd for $C_{34}H_{56}Cl_3NO_2STi$ (697.10): C, 58.58; H, 8.10; N, 2.01; found: C, 58.72; H, 8.19; N, 2.09.

[NH_2Et_2][S(2-CH_2-4-^{t}Bu-6-$CMePh_2$-C_6H_2O)$_2TiCl_3$] (9). Complex **9** was synthesized in the same way as described above for the synthesis of complex **6** with the ligand H_2**L3** (0.611 g, 0.85 mmol), $TiCl_4$ (0.161 g, 0.85 mmol) and diethylamine (0.175 mL, 1.70 mmol) as the starting materials. Pure **9** (0.766 g, 0.810 mol, 95.3%) was obtained as a red brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 8.98 (br s, 2H, N*H*$_2$(CH$_2$CH$_3$)$_2$), 7.24–7.04 (m, 22H, Ar*H*), 6.51 (d, J = 1.8 Hz, 2H, Ar*H*), 3.79 (br s, 4H, C*H*$_2$S), 3.04 (m, 4H, NH$_2$(*CH*$_2$CH$_3$)$_2$), 2.36 (s, 6H, C(C*H*$_3$)), 1.43 (t, J = 7.2 Hz, 6H, NH$_2$(CH$_2$C*H*$_3$)$_2$), 1.06 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ C (ppm): 161.60, 149.24, 143.20, 135.72, 129.60, 128.69, 127.72, 125.80, 125.65, 123.63 (Ar*C*), 52.35 (*C*(CH$_3$)), 42.26 (NH$_2$(*C*H$_2$CH$_3$)$_2$), 36.12 (*C*(CH$_3$)$_3$), 34.23 (*C*H$_2$S), 31.27 (C(*C*H$_3$)), 28.62 (C(*C*H$_3$)$_3$), 11.19 (NH$_2$(CH$_2$*C*H$_3$)$_2$). FT-IR (KBr disk, cm^{-1}): 3495w, 3055m, 3022m, 2960s, 2866m, 2471w, 2386w, 1597m, 1393m, 1444s, 1410m, 1392m, 1362m, 1248s, 1203s, 1128w, 1074w, 1028m, 897m, 877s, 854s, 802w, 760s, 727m, 700s, 644w, 606w, 561s, 476m. Anal. Calcd for $C_{54}H_{64}Cl_3NO_2STi$ (945.39): C, 68.61; H, 6.82; N, 1.48; found: C, 68.52; H, 7.02; N, 1.39.

[S(2-CH_2-4-^{t}Bu-6-CMe_2Ph-C_6H_2O)$_2$]$ZrCl_2$(THF) (10·THF). To a solution of free ligand H_2**L2** (0.506 g, 0.850 mmol) in 20 mL of THF was added dropwise a solution of *n*-BuLi (0.680 mL, 1.70 mmol) in *n*-hexane at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The resulting solution was then added dropwise to a solution of $ZrCl_4$ (0.198 g, 0.850 mmol) in THF (20 mL) at room temperature and the reaction mixture was stirred overnight. After the solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 and filtered. The filtrate was concentrated and mixed with hexane. Cooling to room temperature afforded the mixture of complexes **10** and **10**·THF as colorless crystals (0.320 g) in a ratio of **10**/**10**·THF = 1 : 2 according to ^{1}H NMR. Therefore, we did not obtain the exact ^{13}C NMR spectra and CHN analysis results. Complex **10**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.51 (s, 4H, Ar*H*), 7.20 (d, J = 7.2 Hz, 6H, Ar*H*), 7.07 (s, 2H, Ar*H*), 7.00 (s, 2H, Ar*H*), 4.51 (d, J = 11.2 Hz, 2H, C*H*$_2$S), 3.80 (d, J = 11.2 Hz, 2H, C*H*$_2$S), 1.98 (s, 6H, C(C*H*$_3$)$_2$), 1.48 (s, 6H, C(C*H*$_3$)$_2$), 1.34 (s, 18H, C(C*H*$_3$)$_3$). Complex **10**·THF: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.55 (s, 2H, Ar*H*), 7.16 (m, 6H, Ar*H*), 7.06 (s, 2H, Ar*H*), 7.05–6.93 (m, 4H, Ar*H*), 3.89 (d, J = 11.0 Hz, 2H, C*H*$_2$S), 3.36 (d, J = 11.0 Hz, 2H, C*H*$_2$S), 2.78 (m, 4H, THF), 2.07 (s, 6H, C(C*H*$_3$)$_2$), 1.59 (s, 6H, C(C*H*$_3$)$_2$), 1.41 (m, 4H, THF), 1.34 (s, 18H, C(C*H*$_3$)$_3$).

[S(2-CH_2-4-^{t}Bu-6-$CMePh_2$-C_6H_2O)$_2$]$ZrCl_2$(THF) (11·THF). Complex **11** was synthesized in the same way as described above for the synthesis of complex **10** with the ligand H_2**L3** (0.611 g, 0.850 mmol), *n*-BuLi (0.680 mL, 1.70 mmol) in *n*-hexane and $ZrCl_4$ (0.198 g, 0.850 mmol) as the starting materials. The mixture of complexes **11** and **11**·THF was afforded as colorless crystals (0.360 g) in a ratio of **11**/**11**·THF = 1 : 4 according to ^{1}H NMR. Therefore, we did not obtain the exact ^{13}C NMR spectra and CHN analysis results. Complex **11**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.32–6.88 (m, 22H, Ar*H*), 6.67 (s, 1H, Ar*H*), 6.62 (s, 1H, Ar*H*),4.59 (d, J = 11.2 Hz, 2H, C*H*$_2$S), 3.87 (d, J = 11.2 Hz, 2H, C*H*$_2$S), 2.53 (s, 6H, C(C*H*$_3$)$_2$), 1.06 (s, 18H, C(C*H*$_3$)$_3$). Complex **11**·THF: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ H (ppm): 7.24–7.04 (m, 22H, Ar*H*), 6.75 (s, 2H, Ar*H*), 3.97 (d, J = 11.2 Hz, 2H, C*H*$_2$S), 3.46 (d, J = 11.2 Hz, 2H, C*H*$_2$S), 3.01 (m, 4H, THF), 2.65 (s, 6H, C(C*H*$_3$)), 1.50 (m, 4H, THF), 1.10 (s, 18H, C(C*H*$_3$)$_3$).^{13}C NMR (100 MHz, $CDCl_3$, only resonances for the major product **11**·THF are reported) δ 157.87, 149.73, 148.59, 141.81, 129.65, 129.01, 128.84, 128.57, 127.80, 127.71, 125.94, 125.47, 125.44, 121.59 (Ar*C*), 74.04 (THF), 52.42 (*C*(CH$_3$)), 39.07 (*C*(CH$_3$)$_3$), 34.22 (*C*H$_2$S), 31.43 (C(*C*H$_3$)), 28.89(C(*C*H$_3$)$_3$), 25.00 (THF).

X-ray crystallographic studies

Single crystals of complexes **4**, **6** and **10**·THF suitable for X-ray crystal structural analysis were obtained from the CH_2Cl_2/*n*-hexane (v/v = 1–2 : 10) mixed solvent system. The data were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods[31] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.[32] The structures of **6** and **10**·THF contain disordered solvent molecules. Attempts to obtain a suitable disorder model failed. Accordingly the SQUEEZE of the PLATON program was applied to obtained a new set of $F^2(hkl)$ values without the contribution of solvent molecules, leading to the presence of significant voids in these structures.[33]

Polymerization reaction

The ethylene polymerization experiments were carried out as follows: a dry 250 mL steel autoclave with a magnetic stirrer was charged with 60 mL of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 atm). The polymerization reaction was started by injection of a mixture of MAO and a catalyst in toluene or by addition of a mixture of a catalyst and Al^{i}Bu$_3$ in toluene and a solution of $Ph_3CB(C_6F_5)_4$ in toluene at the same time. The vessel was pressurized to 5 atm with ethylene immediately, and the pressure was maintained by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature for 30 min. The polymerization was then quenched by injecting acidified ethanol containing HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum. For the ethylene/1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

Conflicts of interest

The authors declare no competing financial interest.

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