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Titanium and zirconium complexes that contain a tridentate bis(phenolato) ligand of the [OOO]-type

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Dedicated in honor of Professor Richard R. Schrock

Abstract

The oxygen-linked bis(phenol) 2-oxapropanediyl-1,3-bis(2-*tert*-butyl-4-methylphenol), $[OOO]H_2$, was prepared in good yield by the condensation of 2-*tert*-butyl-6-hydroxymethyl-4-methylphenol at 155 °C. This bis(phenol) reacted cleanly with titanium tetrachloride to give the orange titanium dichloro complex $[OOO]TiCl_2$ in virtually quantitative yield. The solubility in pentane indicates a monomeric structure for $[OOO]TiCl_2$ in solution. The reaction of titanium tetra(isopropoxide) gave the di(isopropoxy) complex $[OOO]Ti(OiPr)_2$ which also adopts a monomeric structure of C_{2v} -symmetry in solution. The reaction of the dichloro complex $[OOO]TiCl_2$ with benzyl Grignard reagent in diethyl ether gave the highly light- and air-sensitive, orange dibenzyl complex $[OOO]Ti(CH_2Ph)_2$ in good yield. Single crystal X-ray crystallography revealed a penta-coordinate titanium center coordinated to two monohapto benzyl ligands and the tridentate [OOO] ligand in a meridional fashion. The reaction of zirconium tetrabenzyl with $[OOO]H_2$ gave the bis(ligand) complex $[OOO]_2Zr$, regardless of the stoichiometry employed. Crystallographic analysis shows an octahedral coordination geometry with *cis*-configuration of the two ligands. The compound can be transformed into the dichloro complex $[OOO]ZrCl_2$ by disproportionation with zirconium tetrachloride. Polymerization tests using $[OOO]TiCl_2$ under methylaluminoxane activation revealed moderate polymerization activity towards ethylene and styrene. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Zirconium; Phenolato ligands; Alkyl complexes; Polymerization catalysts

1. Introduction

Oxygen-linked bis(anilido) ligands of the [NON]-type such as $\{(tBu-d_6-N-o-C_6H_4)_2O\}^{2-}$ have been shown by Schrock et al. to be a class of ancillary ligands that stabilize cationic Group 4 metal alkyl moieties [1–5]. The tetra-coordinate alkyl cation [$\{(tBu-d_6-N-o-C_6H_4)_2O\}$ ZrMe]⁺ with a twisted *fac* coordination of this diamido/donor ligand acts as an efficient living α olefin polymerization initiator [2,5]. When such tridentate ligands adopt the *mer* coordination mode, the degree of the living polymerization character is dimin-

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ished. Following the unique polymerization activity of the titanium complexes containing the sulfur-bridged bis(phenolato) ligand 2,2'-thiobis(6-tert-butyl-4-methylphenolato), $\{2,2'-S(OC_6H_2-6-tBu-4-Me)_2\}^{2-}$ (tbmp) [6,7], we have been interested in developing Group 4 metal complexes that contain the homologous [OOO]type ligand $\{2,2'-O(OC_6H_2-6-tBu-4-Me)_2\}^{2-}$. Theoretical calculations [8] predicted that the barrier for ethylene insertion is reduced, when the sulfur donor is exchanged for oxygen in the putative intermediate $\{[OXO]TiMe(H_2C=CH_2)\}^+$ (X = O, S). However, the difficulty in synthesizing 2,2'-dihydroxydiphenylether derivatives prompted us to explore the coordination behavior of the somewhat more flexible ligand with a CH₂OCH₂ link between the bulky phenolato functions. Group 4 metal complexes with triatomic links

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CH₂NRCH₂ between two phenolato units have recently been demonstrated by Kol and coworkers to be living 1hexene polymerization catalysts, provided the amino substituent R features an appropriate pendant donor group [9–15]. We report here the first examples of titanium and zirconium complexes that contain a [OOO]-type bis(phenolato) ligand with a central ether function.

2. Experimental

2.1. General considerations

All manipulations were carried out under argon atmosphere in a glovebox or by using the standard Schlenk techniques in oven-dried glassware. The solvents Et₂O, C₆H₅CH₃, tetrahydrofuran, n-hexane and n-pentane were dried by refluxing over sodium/benzophenone and CH₂Cl₂ over CaH₂ under an inert gas and distilled freshly before use. Titanium tetrachloride and Ti(OiPr)₄ were purchased from Acros and used without further purification. Zr(CH₂Ph)₄ [16] and 6-tert-butyl-2hydroxymethyl-4-methylphenol [17] were synthesized according to the literature. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX 400 spectrometer (¹H: 400 MHz; ¹³C: 100 MHz) at 298 K. C₆D₆, THF-D₈, C₆D₅Br, and CDCl₃ were purchased from Deutero and purified by conventional methods before use. The chemical shifts were referenced internally according to the residual solvent resonances and reported relative to Me₄Si. Mass spectra were obtained on a Finnigan 8230 spectrometer. Elemental analysis was performed by the Microanalytical Laboratory of this department.

2.2. $[OOO]H_2(1)$

Neat 6-*tert*-butyl-2-hydroxymethyl-4-methylphenol (24.7 g, 127 mmol) was heated slowly to 155 °C for 5 h. The crude product was dissolved in pentane and cooled to -70 °C for several days. During this time a colorless solid precipitated which was filtered and dried in vacuo, yield 16.0 g (43.2 mmol, 68%). ¹H NMR (CDCl₃): δ 1.41 (s, 18H, C(CH₃)₃), 2.25 (s, 6H, 4-CH₃), 4.68 (s, 4H, CH₂O), 6.69 (s, 2H, 3-CH), 6.90 (s, 2H, OH), 7.08 (s, 2H, 5-CH). ¹³C NMR (CDCl₃): δ 20.7 (4-CH₃), 29.6 (C(CH₃)₃), 34.6 (C(CH₃)₃), 71.0 (CH₂O), 121.4 (C-2), 127.6 (C-5), 128.2 (C-3), 128.5 (C-4), 137.5 (C-6), 152.8 (C-1). EI MS (70 eV): *m*/*z* 370 (31%, [*M*]⁺), 194 (82%, [HOC₆H₂(C₄H₉)CH₃]⁺), 177 (100%, 1/2[*M*⁺ -OH]⁺). *Anal*. Calc. for C₂₄H₃₄O₃: C, 77.79; H, 9.25; Found: C, 77.73; H, 9.27%.

2.3. $[OOO]TiCl_2(2)$

Titanium tetrachloride (355 mg, 1.87 mmol) was stirred in 10 ml of Et₂O at 0 °C for 30 min. To the resulting yellow suspension was added dropwise a solution of 1 (693 mg, 1.87 mmol) in 10 ml of Et_2O . The color of the mixture changed to brown-red. The reaction mixture was stirred for 3 h at room temperature (r.t.) and the solvent was removed under reduced pressure. The residue was washed with C₅H₁₂ and dried in vacuo to give 893 mg (1.83 mmol, 98%) of pure 2 as an orange solid. ¹H NMR (CDCl₃): δ 1.45 (s, 18H, C(CH₃)₃), 2.30 (s, 6H, 4-CH₃), 4.91 (s, 4H, CH₂O), 6.85 (d, ${}^{4}J_{HH} = 1.6$ Hz, 2H, 3-CH), 7.10 (d, ${}^{4}J_{HH} = 1.6$ Hz, 2H, 5-CH). ${}^{13}C$ NMR (CDCl₃): δ 21.1 (4-CH₃), 29.6 (C(CH₃)₃), 34.7 (C(CH₃)₃), 74.6 (CH₂O), 123.3 (C-2), 126.6 (C-3), 128.2 (C-5), 132.9 (C-4), 136.1 (C-6), 161.3 (C-1). EI MS (70 eV): m/z 441 (19%, $[M^+ - CH_3]$), 414 $(17\%, [M^+ - C_4H_9 - CH_3]), 363 (18\%, [M^+ - C_4H_9 - CH_3])$ $2CH_3-CI$), 340 (21%, $[M^+-2C_4H_9-2CH_3]$). Anal. Calc. for C₂₄H₃₂Cl₂O₃Ti: C, 59.14; H, 6.62. Found: C, 59.21; H, 6.61%.

2.4. $[OOO]Ti(OiPr)_2$ (3)

A solution of 1 (91.0 mg, 245 µmol) in 5 ml of Et₂O was added to a stirred solution of titanium tetra(isopropoxide) (70.0 mg, 246 µmol) in 5 ml of Et₂O at 0 °C. During this time the color changed from colorless to yellow. The reaction mixture was stirred for 4 h, and the solvent was removed by freeze-drying. The residue was dissolved in C_6H_{14} and cooled at -70 °C. After several days yellow precipitate of 3 was isolated, yield: 114 mg (213 μ mol, 87%). ¹H NMR (C₆D₆): δ 1.31 (d, 12H, OCH(CH₃)₂), 1.64 (s, 18H, C(CH₃)₃), 2.22 (s, 6H, 4-CH₃), 4.48 (s, 4H, CH₂O), 4.95 (s, 2H, OCH(CH₃)₂), 6.57 (d, ${}^{4}J_{HH} = 1.8$ Hz, 2H, 3-CH), 7.18 (d, ${}^{4}J_{HH} = 1.8$ Hz, 2H, 5-CH). ¹³C NMR (C₆D₆): δ 21.1 (4-CH₃), 26.3 $(OCH(CH_3)_2), 30.1(C(CH_3)_3), 35.1 (C(CH_3)_3), 73.5$ (CH₂O), 80.0 (OCH(CH₃)₂), 124.6 (C-2), 127.2 (C-3), 128.1 (C-5), 128.6 (C-4), 136.5 (C-6), 160.1 (C-1). EI MS (70 eV): m/z 534 (24%, $[M]^+$), 475 (6%, $[M^+ OC_{3}H_{7}$]), 358 (100%, $[M^{+}-C_{4}H_{9}-OC_{3}H_{7}-2CH_{3}]$). Anal. Calc. for C₃₀H₄₆O₅Ti: C, 67.40; H, 8.67. Found: C, 67.17; H, 8.55%.

2.5. $[OOO]Ti(CH_2Ph)_2$ (4)

To a solution of **2** (320 mg, 657 μ mol) in 40 ml of Et₂O, cooled to 0 °C, was added dropwise a 1.21 M solution of Mg(CH₂Ph)Cl in Et₂O (0.93 ml, 1.12 mmol). The reaction mixture was stirred for 12 h at r.t. The solvent was removed under reduced pressure and the orange residue was extracted three times with 40 ml of C₆H₁₄. After filtration, hexane was removed to afford 336 mg (561 μ mol, 85%) of **4** as orange crystals. ¹H

NMR (C₆D₆): δ 1.95 (s, 18H, C(CH₃)₃), 2.20 (s, 6H, 4-CH₃), 3.33 (s, 4H, CH₂O), 3.63 (s, 4H, TiCH₂Ph), 6.27 (d, ⁴J_{HH} = 1.6 Hz, 2H, 3-CH), 6.58 (t, ³J_{HH} = 7.6 Hz, 2H, para CH₂C₆H₅), 6.78 (t, ³J_{HH} = 7.6 Hz, 4H, meta CH₂C₆H₅), 7.18 (d, 4H, ortho CH₂C₆H₅), 7.30 (d, ⁴J_{HH} = 1.6 Hz, 2H, 5-CH). ¹³C NMR (C₆D₆): δ 21.0 (4-CH₃), 31.4 (C(CH₃)₃), 35.4 (C(CH₃)₃), 78.4 (CH₂O), 86.0 (TiCH₂Ph), 123.5 (para CH₂C₆H₅), 125.4 (C-2), 126.0 (C-3), 128.4 (meta CH₂C₆H₅), 128.8 (C-5), 128.6 (C-4), 129.7 (ortho CH₂C₆H₅), 136.0 (C-6), 141.3 (ipso CH₂C₆H₅), 158.8 (C-1). Anal. Calc. for C₃₈H₄₆O₃Ti: C, 76.23; H, 7.74. Found: C, 75.98; H, 7.33%.

2.6. X-ray crystal structure analysis of 4

Single crystals suitable for X-ray crystal structure analysis were obtained by cooling a concentrated hexane solution to -30 °C. The structure was solved by direct methods (SHELXS-86) [18] and refined (SHELXL-97) [19] against all F^2 data, resulting in $R_1 = 0.1364$ and $wR_2 =$ 0.1287 for all reflections and $R_1 = 0.0555$ as well as $wR_2 = 0.1041$ for all observed reflections with $I > 2\sigma(I)$; Goodness-of-fit = 1.005. The crystal data of compound 4 are listed in Table 1.

Table 1

Crystal data and structure refinement parameters for complexes ${\bf 4}$ and ${\bf 5}$

Complex	4	5
Empirical formula	C ₃₈ H ₄₆ O ₃ Ti	$C_{48}H_{64}O_6Zr$. 0.5(C ₅ H ₁₂)
Formula weight	598.7	864.33
T (K)	296	193
Crystal system	monoclinic	triclinic
Diffractometer	Enraf–Nonius (CAD4)	Bruker AXS
Space group	$P2_1/c$	ΡĪ
Unit cell dimensions		
a (Å)	15.3961(9)	13.687(1)
b (Å)	13.980(1)	13.846(1)
c (Å)	16.861(1)	14.131(1)
α (°)		82.052(1)
β (°)	108.542(6)	85.799(1)
γ (°)		63.448(1)
V (Å ³)	3440.7(4)	2372.3(3)
Ζ	4	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.156	1.210
μ (Mo K α) (mm ⁻¹)	0.282	0.277
F(000)	1280	922
Crystal dimensions	$0.40 \times 0.80 \times 0.88$	$0.23\times0.31\times0.55$
(mm)		
θ Range (°)	3-24	3-28
$R_1, wR_2 [I > 2\sigma(I)]$	0.0555, 0.1041	0.0434, 0.0962
R_1 , wR_2 (all data)	0.1364, 0.1287	0.0681, 0.1083
Goodness-of-fit on F^2	1.005	1.043

2.7. Reaction of 4 with $B(C_6F_5)_3$

C₆D₅Br (0.5 ml) was added to an equimolar mixture of **4** (10 mg, 16.7 μmol) and B(C₆F₅)₃ (8.5 mg, 16.7 μmol) in an NMR tube at -30 °C. The color turned dark red immediately. ¹H NMR (C₆D₅Br, -25 °C): δ 1.33 (s, 18H, C(CH₃)₃), 2.21 (s, 6H, 4-CH₃), 3.37 (s, 2H, TiCH₂Ph), 3.82 (s, 2H, CH₂B(C₆F₅)₃), 4.30 (br, 4H, CH₂O), 6.61 (s, 2H, 3-CH), 6.84–7.40 (signals overlap. with solvent signals, 5-CH and CH₂C₆H₅). ¹⁹F NMR (C₆D₅Br, -25 °C): δ -129.8 (ortho-F), -162.6 (para-F), -165.5 (meta-F).

2.8. $[000]_2 Zr(5)$

To a solution of Zr(CH₂Ph)₄ (49.0 mg, 107 µmol) in 5 ml of Et₂O was added an ethereal solution of **1** (80.0 mg, 215 µmol) at 0 °C. The reaction mixture was stirred for 2 h at r.t. All volatiles were removed under reduced pressure to quantitatively give the zirconium complex **5** as a colorless solid. ¹H NMR (C₆D₆): δ 1.59 (s, 36H, C(CH₃)₃), 2.20 (s, 12H, 4-CH₃), 4.46 (s, 8H, CH₂O), 6.51 (d, ⁴J_{HH} = 1.8 Hz, 4H, 3-CH), 7.22 (d, ⁴J_{HH} = 1.8 Hz, 4H, 5-CH). ¹³C NMR (C₆D₆): δ 20.9 (4-CH₃), 30.4 (C(CH₃)₃), 35.1 (C(CH₃)₃), 75.1 (CH₂O), 123.5 (C-2), 127.5 (C-3), 127.8 (C-4), 128.8 (C-5), 137.7 (C-6), 157.8 (C-1). EI MS (70 eV): *m*/*z* 826 (65%, [*M*⁺]), 620 (100%, *M*⁺ -[OC₆H₂(C₄H₉)(CH₃)CH₂]-2CH₃). *Anal.* Calc. for C₄₈H₆₄O₆Zr: C, 69.61; H, 7.79. Found: C, 70.18; H, 8.38%.

2.9. X-ray crystal structure analysis of 5

Single crystals suitable for X-ray crystal structure analysis were obtained by cooling a concentrated C_5H_{12} solution to -30 °C. The structure was solved by direct methods (SHELXS-86) [18] and refined (SHELXL-97) [19] against all F^2 data, resulting in $R_1 = 0.0681$ and $wR_2 =$ 0.1083 for all reflections and $R_1 = 0.0434$ as well as $wR_2 = 0.0962$ for all observed reflections with $I > 2\sigma(I)$; Goodness-of-fit = 1.043. The crystal data of compound 5 are listed in Table 1.

2.10. $[OOO]ZrCl_2(THF)$ (6)

To a solution of $\text{ZrCl}_4(\text{THF})_2$ (18 mg, 53.3 µmol) in 5.0 ml of Et_2O was added a solution of **5** (45 mg, 54.3 µmol) in 5 ml of Et_2O at -70 °C. The mixture was warmed to r.t. and stirred further for 14 h to form a colorless solid precipitate. The solvent was removed in vacuo and the residue was treated with C_5H_{12} . Filtration and drying afforded the product as colorless crystals in 81% (51 mg) yield. ¹H NMR (THF-d_8): δ 1.45 (s, 18H, C(CH_3)_3), 2.23 (s, 6H, 4-CH_3), 5.04 (s, 4H, CH_2O), 6.82 (d, ⁴J_{HH} = 1.6 Hz, 2H, 3-CH), 7.09 (d, ⁴J_{HH} = 1.6 Hz, 2H, 2-CH), 3.06

(C(CH₃)₃), 35.4 (C(CH₃)₃), 79.2 (CH₂O), 125.2 (C-2), 127.5 (C-3), 129.0 (C-4), 129.3 (C-5), 137.2 (C-6), 157.4 (C-1). EI MS (70 eV): m/z = 544 (2%, $[M^+ - C_4H_9]$), 528 (2%, $[M^+ - THF]$), 493 (5%, $[M^+ - THF - CI]$), 163 (100%, $[HOC_6H_2(C_4H_9)CH_3]^+$). Anal. Calc. for C₂₈H₄₀Cl₂O₄Zr: C, 55.79; H, 6.69. Found: C, 55.24; H, 6.65%.

3. Results and discussion

The oxygen-linked bis(phenol) 2-oxapropanediyl-1,3bis(2-*tert*-butyl-4-methylphenol), [OOO]H₂ (1), was prepared in 68% yield by the condensation of neat 2-*tert*butyl-6-hydroxymethyl-4-methylphenol at 155 °C. A variety of other conditions to form the ether linkage starting from the readily available 2-*tert*-butyl-6-hydroxymethyl-4-methylphenol failed [20].

This bis(phenol) **1** cleanly reacted with equimolar amount of titanium tetrachloride to give the dichloro titanium complex [OOO]TiCl₂ (**2**) as pentane-soluble, orange microcrystals in virtually quantitative yield. It is sensitive to moisture, decomposing within minutes in air. The ¹H and ¹³C NMR spectra at room temperature indicate a molecule with C_{2v} -symmetry, since the CH₂O protons appear as a sharp singlet at δ 4.91 (δ 4.68 in **1**). This signal only broadens below -80 °C, suggesting a monomeric structure for [OOO]TiCl₂ in solution. In contrast, the [OXO]TiCl₂ derivatives containing a 2,2'thio- or 2,2'-tellurobis(6-*tert*-butyl-4-methylphenolato) ligand are dimeric both in the crystal and solution [21].

Reaction of bis(phenol) **1** with titanium tetra(isopropoxide) gave the yellow di(isopropoxy) complex [OOO]Ti(O*i*Pr)₂ (**3**). It is extremely soluble in aliphatic hydrocarbons and very difficult to recover from solutions. According to the ¹H and ¹³C NMR spectra, **3** adopts a monomeric structure with C_{2v} -symmetry in solution. In the absence of molecular weight measurements, we cannot definitely prove the monomeric unit with a penta-coordinate titanium center. However, it is notable that the di(isopropoxy) complex [(tbmp)-Ti(O*i*Pr)₂]₂ is dimeric and insoluble [22,23].

Reaction of the dichloro complex $[OOO]TiCl_2$ (2) with 2 equiv. of benzyl Grignard reagent Mg(CH₂Ph)Cl in diethyl ether afforded the highly light- and airsensitive, orange dibenzyl complex $[OOO]Ti(CH_2Ph)_2$ (4) in good yield (Scheme 1) [24]. The single crystal Xray crystallography of 4 revealed a molecule with a penta-coordinate titanium center coordinated to the tridentate [OOO] ligand in a meridional fashion. Fig. 1 shows an ORTEP diagram of 4 and Table 2 lists some pertinent bond parameters. The overall coordination geometry can be described as a distorted trigonal bipyramid with C25, C32, O3 defining the equatorial plane and O1 and O2 occupying the apical positions. The bond distances between the titanium atom and the





Fig. 1. ORTEP drawing of the molecular structure of $[OOO]Ti(CH_2Ph)_2$ (4). Ellipsoids are shown with 50% probability. Hydrogen atoms are omitted for clarity. Key atoms are labeled.

Table 2 Selected bond lengths (Å) and bond angles (°) for $[OOO]Ti(CH_2Ph)_2$

(4)	
Bond lengths	
Ti-O1	1.852(2)
Ti-O2	1.863(2)
Ti-O3	2.096(3)
Ti-C32	2.086(5)
Ti-C25	2.109(4)
O3-C12	1.454(5)
O3-C13	1.440(5)
Bond angles	
O1-Ti-O2	161.2(1)
C32-Ti-C25	108.8(2)
O1-Ti-O3	79.5(1)
O2-Ti-O3	82.75(1)
C1-O1-Ti	142.8(2)
Ti-O2-C15	141.1(2)
C12-O3-C13	118.3(3)
C26-C25-Ti	103.6(3)
C33-C32-Ti	102.8(3)

phenolic oxygen atoms are 1.852(2) and 1.863(2) Å and are longer than those in related bis(phenolato) dialkyl titanium complexes ($\{2,2'-(OC_6H_2-6-tBu-4-OMe)_2\}$ Ti-(CH₂Ph)₂: 1.821(8), 1.799(7) Å [24]; {2,2'-CH₂- $CH_2(OC_6H_2-6-tBu-4-Me)_2$ Ti(CH_2SiMe_3)₂: 1.784(3), 1.786(3) Å [25]; $\{2,2'-CH_2(OC_6H_2-6-tBu-4-Me)_2\}$ Ti-Me₂: 1.799(3) Å [26]), but comparable to those found in $\{2,2'-N(CH_2CH_2OMe)(OC_6H_2-4,6-tBu_2)_2\}Ti(CH_2Ph)_2$ (1.865(2) Å) [11]. The angle O1–Ti–O2 is 161.2(1)° and significantly deviates from linearity. The bond length from the titanium center to the central ether oxygen atom is 2.096(3) Å. This value is significantly smaller then the other bond distances between ether oxygen atom coordinated to tetravalent titanium center in related complexes, e.g. 2.402(4) Å in { $(tBu-d_6-N-o C_6H_4)_2O$ TiMe₂ [2,4]. The ether oxygen atom is close to sp²-hybridization, as can be seen from the angle C12-O3-C13 of 118.3(3)°. These geometrical features point at a fairly strong interaction between the ether oxygen and the titanium center.

The two benzyl ligands reside in the equatorial plane formed by the four atoms Ti, O3, C25 and C32. The sum of the angles at titanium C25–Ti–C32, C25–Ti–O3 and C32–Ti–O3 is 360°. They show titanium carbon distances of 2.086(5) and 2.109(4) Å, comparable to values found in other dibenzyl titanium complexes such as $\{2,2'-(OC_6H_2-6-tBu-4-OMe)_2\}$ Ti(CH₂Ph)₂ (2.08(1) Å) [24]. The angles at the α -carbon atoms of the benzyl groups are 103.6(3) and 102.8(3)°, indicating the absence of any agostic interaction.

The reaction of zirconium tetrabenzyl with $[OOO]H_2$ gave a bis(ligand) complex $[OOO]_2Zr$ (5) that formed regardless of the stoichiometry employed. Other zirconium precursors such as $ZrCl_4(THF)_2$, $Zr(NMe_2)_4$, and $Zr(NMe_2)_2Cl_2(THF)_2$ behaved similarly. The bis(ligand) complex, however, could be straightforwardly transformed into the dichloro complex $[OOO]ZrCl_2(THF)$ (6) by disproportionation with zirconium tetrachloride. The ready decomposition of **6** in solution precluded the systematic study of alkylation reactions (Scheme 2).





Fig. 2. ORTEP drawing of the molecular structure of $[OOO]_2 Zr$. 0.5(C₅H₁₂) (5). Ellipsoids are shown with 50% probability. Hydrogen atoms and the lattice solvent n-pentane are omitted for clarity. Key atoms are labeled.

The bis(ligand) complex **5** could be structurally characterized by single crystal X-ray analysis. Fig. 2 shows an ORTEP diagram of **5** and Table 3 summarizes some pertinent bond parameters. The two *fac* ligands coordinate the zirconium center octahedrally, as can be seen from the three angles at the zirconium center O1–Zr-O5 (176.19(6)°), O2–Zr-O6 (169.89(6)°), and O3–Zr-O4 (150.14(6)°). The two ligands are arranged in a *cis* fashion (O2–Zr-O5 96.09(5)°). Remarkably, the structurally characterized bis(ligand) titanium complexes of the type [ONO]₂Ti invariably contain *trans* configurated ligands (with *fac* conformation) [10]. The zirconium-to-phenolato oxygen distances of 1.965(2) to

Table 3										
Selected	bond	lengths (Å)	and	bond	angles	(°)	for	[000]	$_2$ Zr	(5)

	• • •	, .	
Bond lengths			
Zr-O1	1.977(2)	Zr-O2	2.334(2)
Zr-O3	2.013(2)	Zr-O4	2.003(2)
Zr-O5	2.353(2)	Zr-O6	1.965(2)
Bond angles			
O1-Zr-O3	100.68(6)	O3-Zr-O5	80.65(6)
O5-Zr-O4	77.94(6)	O4-Zr-O1	99.51(6)
O2-Zr-O3	76.58(6)	O3-Zr-O6	93.57(6)
O6-Zr-O4	102.80(6)	O4-Zr-O2	85.23(6)
O1-Zr-O2	80.81(6)	O2-Zr-O5	96.09(5)
O5-Zr-O6	79.83(5)	O6-Zr-O1	103.58(6)
O1-Zr-O5	176.19(6)	O2-Zr-O6	169.89(6)
O3–Zr–O4	150.14(6)		

Scheme 2.



2.013(2) Å are in the expected range [12], as are the two zirconium-to-ether oxygen distances of 2.334(2) and 2.353(1) Å ([$\{(tBu-d_6-N-o-C_6H_4)_2O\}ZrCl_2$]: 2.336(3) Å; [$\{(tBu-d_6-N-o-C_6H_4)_2O\}ZrMe_2$]: 2.418(3) Å [2]).

When two tridentate ligands are coordinated in an octahedral metal complex, three configurational isomers are conceivable [27]: the *trans*- and *cis*-isomer with *fac* conformation and an isomer with *mer* conformation of the ligand. The temperature independence of the ¹H NMR spectra of **5** in toluene indicates the occurrence of symmetrization processes, since only one set of ligand signals is recorded. The C_2 -symmetric configuration should render the two 'halves' of the [OOO] ligand inequivalent. We assume that a low-barrier fluxional process is operating in solution that allows the enantiomerization of the C_2 -symmetric solid state structure (Scheme 3).

Preliminary polymerization tests for [OOO]TiCl₂ (2) under methylaluminoxane activation (Al:Ti = 10,000:1, 1 h, 140 ml of toluene, T = 40 °C, $p_{\text{ethylene}} = 2$ bar) revealed moderate ethylene polymerization activity of 67 kg $(\text{mol}_{\text{Ti}} \text{ h})^{-1}$. The polyethylene showed $M_{\text{n}} = 66,000$ $(M_{\rm w}/M_{\rm n} = 6.5)$ and $T_{\rm m} = 132$ °C. Styrene was polymerized under similar conditions (Al:Ti = 1000:1; 1 h, 140 ml of toluene, T = 40 °C) with an activity of 138 kg $[mol_{Ti}]^{-1}$ h. The syndiotactic polystyrene isolated showed $M_{\rm n} = 16,200 \ (M_{\rm w}/M_{\rm n} = 6.6)$ and $T_{\rm m} = 259$ °C. NMR experiments directed at observing the benzyl cation remained inconclusive, as the product of the dibenzyl complex 4 and $B(C_6F_5)_3$ partially decomposed in bromobenzene even at -30 °C. The observation that the titanium complexes containing the [OOO] ligand are not so well behaved may be ascribed to the strong titanium-ether oxygen bond. Such an interaction probably increases the electron density at the metal center by π -donation. As a consequence, the bis(phenolato) ligation may not be able to stabilize the alkyl cation through the preferred twisted *fac* coordination of the [OOO] ligand.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. 190241–42 for compounds 4 and 5. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336-033 or e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc. cam.ac.uk).

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