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Journal of Organometallic Chemistry 606 (2000) 156–162

Journal of Organo metallic Chemistry

Synthesis and characterisation of Group 4 metallocene alkoxide complexes. X-ray crystal structure of $Cp^*_2ZrCl(OCH_2CH_2SPh)$

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Received 17 March 2000; accepted 19 May 2000

Abstract

Halo-alkoxide zirconocene complexes $(\eta^5\text{-}C_5Me_5)_2ZrCl(OCH_2CH_2SPh)$ (**1**) and $(\eta^5\text{-}C_5Me_5)_2ZrCl(OC_6H_4SH)$ (**2**) have been prepared by reaction of the corresponding zirconocene dichloride with $HOCH_2CH_2SPh$ or HOC_6H_4SH, respectively, in the presence of NEt_3. The molecular structure of **1** has been determined by X-ray diffraction studies. Alkyl- and aryl-containing species $(\eta^5\text{-}C_5Me_5)_2ZrMe(OCH_2CH_2SPh)$ (**3**) and $(\eta^5\text{-}C_5Me_5)_2ZrPh(OCH_2CH_2SPh)$ (**4**) were synthesised by reaction of the corresponding dialkyl or diaryl species with $HOCH_2CH_2SPh$, or by reaction of complex **1** with LiMe or LiPh, respectively. Finally, the dialkoxide complexes $L_2M(OCH_2CH_2SR)_2$ [$L = \eta^5\text{-}C_5H_5$, M = Ti, R = Ph (**5**); $L = \eta^5\text{-}C_5Me_5$, M = Ti, R = Ph (**6**); $L = \eta^5\text{-}C_5Me_5$, M = Ti, R = Me (**7**)] were prepared by reaction of the appropriate dichloride and alcohol in the presence of NEt_3, and $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2SMe)_2$ (**8**) was synthesised by reacting $(\eta^5\text{-}C_5H_5)_2ZrMe_2$ with two equivalents of $HOCH_2CH_2SMe$.

Keywords: Titanocene; Zirconocene; Alkoxide

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1. Introduction

Early-metal oxides such as titania and zirconia are often employed as support materials for heterogeneous catalysts [1,2]. The support may act simply as a dispersant for the late-metal centres or may play an active role in the catalytic cycle. The latter situation gives rise to the phenomenon known as strong metal support interactions (SMSI).

The similarity of metal alkoxide species to metal oxides and the propriety of such species as models for metal–oxide surfaces has promoted extensive research into this field [3].

Furthermore, ligand systems with two different donor atoms are attracting increased interest in the chemistry of metal complexes. Under appropriate conditions, the remaining donor atom can coordinate reversibly to the metal centre and temporarily block a vacant coordination site [4,5]. As a result, it seems possible to stabilise highly reactive intermediates in catalytic reactions and to increase their lifetimes. Another important feature of the additional donor function is the possibility of fixing catalytically active complexes on surfaces that have been functionalised previously. Finally, this class of ligand could be appropriate to stabilise heterometallic complexes. In this respect, $HOCH_2CH_2SR$ are interesting ligands that contain both a hard oxygen donor and a soft sulfur donor and can therefore act easily as bridging ligands for an early and a late transition metal to yield a heterometallic complex. In this paper we report the synthesis and structural characterisation of several families of zirconocene and titanocene complexes containing this type of ligand.

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PII: S0022-328X(00)00336-3

2. Experimental

2.1. General procedures

All reactions were carried out under nitrogen using standard vacuum line techniques. Toluene was distilled from sodium, pentane was distilled from sodium–potassium alloy and diethyl ether and THF were distilled from sodium–benzophenone. All solvents were deoxygenated prior to use.

The following reagents were prepared by literature procedures: Cp$^*_2$ZrCl$_2$ [6], Cp$^*_2$ZrMe$_2$ [7], Cp$^*_2$ZrPh$_2$ [7]. The commercially available compounds MeLi in diethyl ether, Cp$_2$ZrCl$_2$, Cp$_2$TiCl$_2$, ^{n}BuLi, PhLi, HOCH$_2$CH$_2$SPh, HOCH$_2$CH$_2$SMe, NEt$_3$, and 4-HO–C$_6$H$_4$SH were used as received from Aldrich.

IR spectra were recorded on a Perkin–Elmer PE 883IR spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were obtained on either Gemini 200 or Unity 300 MHz Varian Fourier transform spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million (ppm) relative to SiMe$_4$. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer.

2.2. Synthesis of Cp$^*_2$ZrCl(OCH$_2$CH$_2$SPh) (**1**)

To a solution of Cp$^*_2$ZrCl$_2$ (1.000 g, 2.31 mmol) in 15 ml of toluene were added NEt$_3$ (0.320 ml, 2.31 mmol) and HOCH$_2$CH$_2$SPh (0.31 ml, 2.31 mmol). After stirring for 3 h at 60°C, the suspension was filtered and the solution was evaporated to dryness under vacuum to yield complex **1**. IR (Nujol–PET, cm^{-1}): 1110 (vs), 546 (m), 335 (m). ^{1}H-NMR (C$_6$D$_6$): δ 1.78 (s, 30H, Cp*), 3.06 (m, 2H, CH$_2$S), 4.30 (m, 2H, CH$_2$O), 6.88–7.38 (m, 5H, Ph). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 11.6 (s, Cp*), 35.7 (s, CH$_2$S), 70.3 (s, CH$_2$O), 121.3 (s, Cp*), 125.8, 129.1, 129.3 (s, CH), 137.3 (s, C$_{ipso}$). Anal. Calc. for C$_{28}$H$_{39}$OSClZr: C, 61.05; H, 7.08. Found: C, 61.33; H, 7.05%.

2.3. Synthesis of Cp$^*_2$ZrCl(OC$_6$H$_4$-4-SH) (**2**)

To a suspension of Cp$^*_2$ZrCl$_2$ (0.275 g, 0.63 mmol) in 8 ml of THF were added, at room temperature, NEt$_3$ (0.088 ml, 0.63 mmol) and 4-hydroxythiophenol (0.080 g, 0.63 mmol). The mixture was stirred for 6 h at room temperature, filtered and the solvent removed under vacuum to yield an oily residue. This residue was purified by washing with pentane to give 0.296 g (90%) of a white solid, which was characterised as complex **2**. IR (Nujol–PET, cm^{-1}): 1566 (vs), 1151 (m), 1070 (w), 867 (s), 836 (s), 534 (w). ^{1}H-NMR (C$_6$D$_6$): δ 1.77 (s, 30H, Cp*), 6.63 (m, 2H, OC$_6$H$_4$SH), 7.43 (m, 2H, OC$_6$H$_4$SH). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 11.7 (s, Cp*), 122.6 (s, Cp*), 119.1, 134.6 (s, OC$_6$H$_4$SH), 125.9 (s, C–O), 164.6 (s, C–S). Anal. Calc. for C$_{26}$H$_{35}$OSZrCl: C, 59.74; H, 6.70. Found: C, 60.16; H, 6.68%.

2.4. Synthesis of Cp$^*_2$ZrMe(OCH$_2$CH$_2$SPh) (**3**)

2.4.1. Method (a)

To a solution of Cp$^*_2$ZrMe$_2$ (0.078 g, 0.20 mmol) in 6 ml of pentane was added HOCH$_2$CH$_2$SPh (0.027 ml, 0.20 mmol). The mixture was stirred at room temperature for 1 h. The solvent was partially evaporated under vacuum and the solution was cooled to -30°C to yield a white crystalline solid that was filtered off and characterised as **3** (0.032 g, 30%).

2.4.2. Method (b)

To a solution of Cp$^*_2$ZrCl(OCH$_2$CH$_2$SPh) (0.358 g, 0.65 mmol) in 10 ml of toluene was added MeLi (0.487 ml, 0.78 mmol) and the mixture was stirred at 70°C for 4 h. The solvent was removed under vacuum and the residue was extracted with pentane to yield 0.148 g (44%) of complex **3**. IR (Nujol–PET, cm^{-1}): 1119 (vs), 1019 (w), 689 (m), 567 (w). ^{1}H-NMR (C$_6$D$_6$): δ -0.16 (s, 3H, CH$_3$), 1.73 (s, 30H, Cp*), 2.88 (m, 2H, CH$_2$S), 4.16 (m, 2H, CH$_2$O), 6.87–7.34 (m, 5H, Ph). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 11.3 (s, Cp*), 27.9 (s, CH$_3$), 36.4 (s, CH$_2$S), 68.5 (s, CH$_2$O), 117.4 (s, Cp*), 125.8, 129.1, 129.2 (s, CH), 137.5 (s, C$_{ipso}$). Anal. Calc. for C$_{29}$H$_{42}$OSZr: C, 65.68; H, 7.92. Found: C, 65.31; H, 8.07%.

2.5. Synthesis of Cp$^*_2$ZrPh(OCH$_2$CH$_2$SPh) (**4**)

2.5.1. Method (a)

To a solution of Cp$^*_2$ZrCl(OCH$_2$CH$_2$SPh) (0.367 g, 0.66 mmol) in 12 ml of toluene was added PhLi (0.445 ml, 0.80 mmol) and the mixture was stirred at 75°C for 4 h. The solvent was removed under vacuum and the residue was extracted with pentane to yield an oily yellow compound, which was characterised as complex **4** (0.325 g, 83%).

2.5.2. Method (b)

To a solution of Cp$^*_2$ZrPh$_2$ (0.091 g, 0.17 mmol) in 6 ml of toluene was added HOCH$_2$CH$_2$SPh (0.047 ml, 0.35 mmol). The mixture was stirred at 90°C for 7 h and the solvent was removed under vacuum to yield an oily compound, which was characterised as **4**. IR (Nujol–PET, cm^{-1}): 1585 (m), 1273 (m), 1114 (vs), 1057 (m), 1051 (m), 764 (m), 554 (s), 497 (s), 490 (s), 474 (m). ^{1}H-NMR (C$_6$D$_6$): δ 1.62 (s, 30H, Cp*), 3.15 (m, 2H, CH$_2$S), 4.35 (m, 2H, CH$_2$O), 7.01–7.47 (m, 10H, Ph). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ 13.3 (s, Cp*), 38.4 (s, CH$_2$S), 70.8 (s, CH$_2$O), 120.7 (s, Cp*), 126.1, 127.8, 128.9, 130.9, 131.2, 139.8 (s, CH), 140.4, 192.3 (s, C$_{ipso}$).

2.6. Synthesis of $Cp_2Ti(OCH_2CH_2SPh)_2$ (5)

To a solution of Cp_2TiCl_2 (0.500g, 2.01 mmol) in 15 ml of toluene were added NEt_3 (0.56 ml, 4.03 mmol) and $HOCH_2CH_2SPh$ (0.54 ml, 4.03 mmol). The mixture was stirred for 16 h at room temperature. The ammonium salt was then separated by filtration. The solvent was removed under vacuum and the residue washed twice with pentane (2 × 8 ml) to yield 0.584 g (60%) of complex **5**. IR (Nujol–PET, cm^{-1}): 1098 (s), 1010 (w), 823 (m), 810 (s), 585 (w). ^{1}H-NMR (C_6D_6): δ 2.85 (t, 4H, $^{3}J_{H-H} = 7.3$ Hz, CH_2S), 4.38 (t, 4H, $^{3}J_{H-H} = 7.3$ Hz, CH_2O), 5.84 (s, 10H, Cp), 6.88–7.32 (m, 10H, Ph). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 36.2 (s, CH_2S), 80.1 (s, CH_2O), 116.6 (s, Cp), 125.8, 129.1, 129.2 (s, CH), 137.7 (s, C_{ipso}). Anal. Calc. for $C_{26}H_{28}O_2S_2Ti$: C, 64.45; H, 5.82. Found: C, 63.97; H, 5.77%.

2.7. Synthesis of $Cp^*_2Ti(OCH_2CH_2SPh)_2$ (6)

To a solution of $Cp^*_2TiCl_2$ (0.211 g, 0.54 mmol) in 10 ml of toluene were added NEt_3 (0.152 ml, 1.09 mmol) and $HOCH_2CH_2SPh$ (0.147 ml, 1.09 mmol). The resulting solution was stirred at 60°C for 4 h. After filtration the solvent was evaporated to dryness and the residue washed with pentane to give complex **6** (0.168 g, 50%). IR (Nujol–PET, cm^{-1}): 1146 (m), 1063 (m), 572 (m), 405 (m). ^{1}H-NMR (C_6D_6): δ 1.76 (s, 30H, Cp*), 3.04 (m, 4H, CH_2S), 4.41 (m, 4H, CH_2O), 7.01–7.38 (m, 10H, Ph). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 12.4 (s, Cp*), 36.9 (s, CH_2S), 77.7 (s, CH_2O), 126.3 (s, Cp*), 129.1, 129.2, 129.9 (s, CH), 136.2 (s, C_{ipso}). Anal. Calc. for $C_{36}H_{48}O_2S_2Ti$: C, 69.21; H, 7.74. Found: C, 68.84; H, 7.69%.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{28}H_{39}ClOSZr$
Formula weight	550.32
Temperature (K)	293(2)
Wavelength (Å)	0.7107
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.541(9)
b (Å)	17.339(2)
c (Å)	18.619(5)
β (°)	102.21(5)
V (Å^3)	2695(3)
Z	4
D_{calc} (g cm^{-3})	1.356
Absorption coefficient (cm^{-1})	6.0
F(000)	1152
θ Range for data collection (°)	2.24–26.99
Index ranges	$0 \leq h \leq 10$, $0 \leq k \leq 22$, $-23 \leq l \leq 23$
Reflections collected	5871
Data/restraints/parameters	5871/0/290
Goodness-of-fit on F^2	1.208
Final R indices $[I > 2\sigma(I)]$ [a]	$R_1 = 0.0707$, $wR_2 = 0.2433$
Largest difference peak and hole (e Å^{-3})	1.524 and −2.119

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

2.8. Synthesis of $Cp^*_2Ti(OCH_2CH_2SMe)_2$ (7)

To a solution of $Cp^*_2TiCl_2$ (0.307 g, 0.78 mmol) in 15 ml of toluene were added NEt_3 (0.219 ml, 1.50 mmol) and $HOCH_2CH_2SMe$ (0.265 ml, 3.00 mmol). The solution was heated at 70°C for 4 h. After filtration, the solvent was evaporated to dryness and the residue washed with Et_2O at −30°C to give 0.238 g of a deep-purple crystalline solid, which was characterised as complex **7** (0.238 g, 61%). IR (Nujol–PET, cm^{-1}): 1072 (vs), 1039 (m), 1018 (s), 776 (m), 573 (s), 410 (m). ^{1}H-NMR (C_6D_6): δ 1.77 (s, 30H, Cp*), 1.79 (s, 6H, SCH_3), 2.61 (m, 4H, CH_2S), 4.36 (m, 4H, CH_2O). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 12.4 (s, Cp*), 13.0 (s, S–CH_3), 38.3 (s, CH_2S), 78.3 (s, CH_2O), 124.9 (s, Cp*). Anal. Calc. for $C_{26}H_{44}O_2S_2Ti$: C, 62.30; H, 8.78. Found: C, 61.84; H, 8.79%.

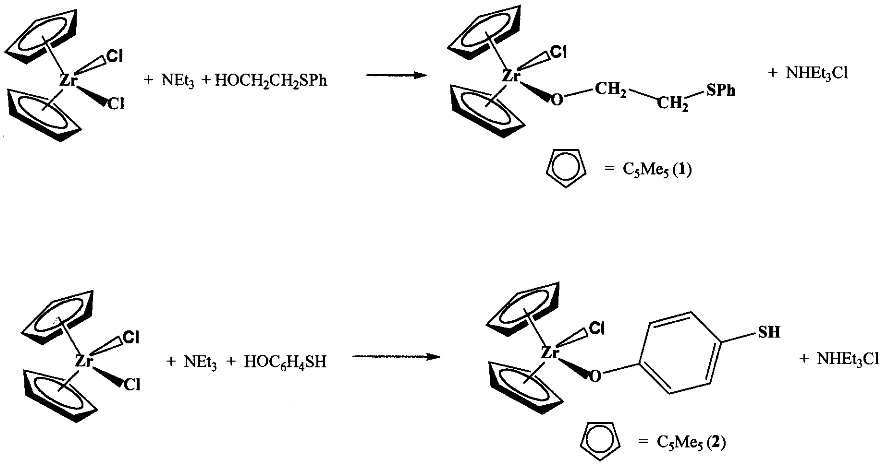
2.9. Synthesis of $Cp_2Zr(OCH_2CH_2SMe)_2$ (8)

A solution of Cp_2ZrMe_2 (0.250 g, 1.02 mmol) in 10 ml of pentane was stirred with $HOCH_2CH_2SMe$ (0.134 ml, 1.54 mmol) at room temperature for 72 h. A white solid was obtained, which was separated by filtration and identified as **8** (0.090 g, 22%). IR (Nujol–PET, cm^{-1}): 1014 (m), 819 (m), 796 (s), 521 (m). ^{1}H-NMR (C_6D_6): δ 1.85 (s, 6H, SCH_3), 2.52 (t, 4H, $^{3}J_{H-H} = 6.9$ Hz, CH_2S), 4.08 (t, 4H, $^{3}J_{H-H} = 6.9$ Hz, CH_2O), 6.02 (s, 10H, Cp). $^{13}C\{^{1}H\}$-NMR (C_6D_6): δ 15.9 (s, S–CH_3), 38.8 (s, CH_2S), 72.1 (s, CH_2O), 112.1 (s, Cp). Anal. Calc. for $C_{16}H_{24}O_2S_2Zr$: C, 47.56; H, 5.94. Found: C, 46.57; H, 5.59%.

2.10. X-ray structural determination of complex 1

Crystal, data collection, and refinement parameters are collected in Table 1. Suitable crystals were selected and mounted on a fine glass fibre with epoxy cement. The unit cell parameters were each determined from the angular setting of least-squares fit of 25 strong high-angle reflections. The asymmetric unit contained one independent molecule. Reflections were collected at 25°C on a NONIUS-MACH3 diffractometer equipped with a graphite monochromated radiation source ($\lambda = 0.71073$ Å). The sample showed no significant intensity decay over the duration of data collection.

Data were corrected in the usual fashion for Lorentz and polarisation effects and empirical absorption was applied [8]. The space group was determined from the systematic absences in the diffraction data. The struc-



Scheme 1.

tures were solved by direct methods [9] and refinements on F^2 were carried out by full-matrix least-squares analysis [10]. Anisotropic temperature parameters were considered for all non-hydrogen atoms, while hydrogen atoms were included in calculated positions but not refined. Final disagreement indices are $R_1 = 0.0707$, $wR_2 = 0.2433$, largest difference peak and hole 1.524 and -2.119 e Å^{-3}.

3. Results and discussion

Reaction of $Cp^*_2ZrCl_2$ ($Cp^* = \eta^5$-C_5Me_5) with one equivalent of 2-phenyl-mercaptoethanol in the presence of NEt_3 yields the monomeric complex **1** (Scheme 1). The same reaction in the presence of an excess of ligand and NEt_3 yielded the same product. It seems that substitution of the second chloride ion is not possible using this procedure. The inertness of the second chloride toward substitution has already been observed in similar reactions [11]. In the same way, $Cp^*_2ZrCl_2$ reacts, at room temperature, with 4-hydroxythiophenol in the presence of NEt_3 to yield $Cp^*_2ZrCl(OC_6H_4SH)$ (**2**) (Scheme 1).

Complexes **1** and **2** have been characterised by ^{1}H- and ^{13}C-NMR spectroscopy (see Section 2). In both cases, the NMR spectra indicate that the alkoxide ligand is acting in a monodentate fashion. As an example, the ^{1}H-NMR spectrum of **1** shows multiplet signals at 3.06 and 4.30 ppm, which are assigned to the methylene protons bonded to the sulfur and the oxygen atoms, respectively. The Cp* ligand gives rise to a singlet at 1.78 ppm, indicating that both rings are equivalent, and the phenyl group shows two multiplet signals at 6.88 and 7.38 ppm. The ^{13}C-NMR spectrum of **1** exhibits signals for methylene carbon atoms at 35.7 and 70.3 ppm and these are the carbons bonded to the sulfur and oxygen atoms, respectively. In addition, the C_{ipso} of the phenyl group resonates at 137.0 ppm. In the IR spectrum it is worth noting that the expected band corresponding to ν(Zr–O) appears at 546 cm^{-1}.

In order to confirm the proposed structural disposition, the molecular structure of complex **1** was solved by X-ray diffraction analysis. An ORTEP view of the molecule with the atom labelling scheme is shown in Fig. 1. Selected bond lengths and angles are given in Table 2.

The crystal structure consists of discrete molecules with no unusually short intermolecular distances. The complex exhibits the typical bent metallocene structure. The cyclopentadienyl rings are tilted by 44.2(2)° with respect to one another and are bonded to the zirconium atom in an almost symmetric η^5-fashion. The Zr(1)–CE(1) and Zr(1)–CE(2) (CE = ring centroid) distances of 2.2703(6) and 2.2596(7) Å compare well with those of other Cp_2Zr(IV) complexes [12].

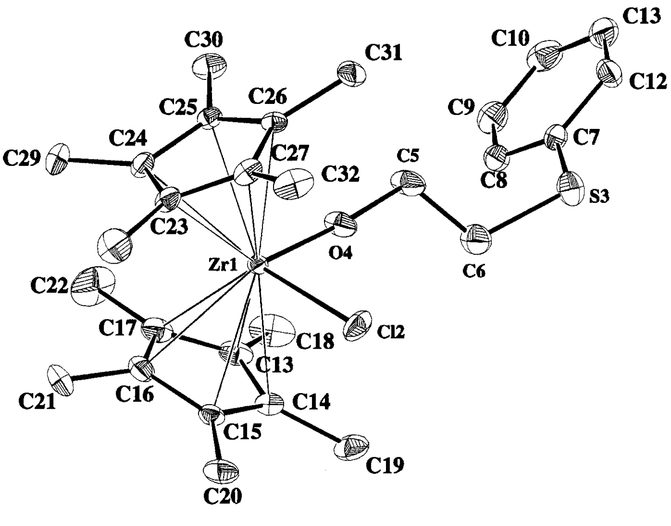


Fig. 1. Perspective ORTEP drawing of the molecular structure complex **1**.

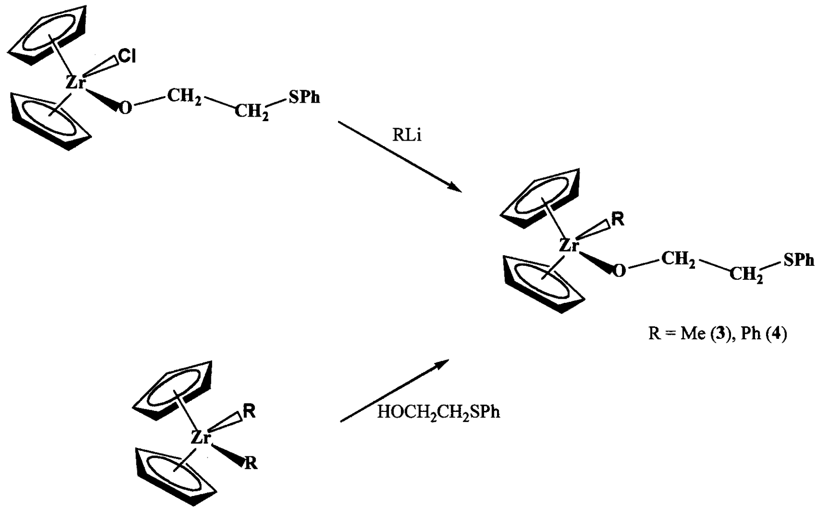
Table 2
Selected bonds distances (Å) and angles (°) for **1**

Bond angles	
Zr(1)–CE(1)	2.2703(6)
Zr(1)–CE(2)	2.2596(7)
Zr(1)–O(4)	1.930(5)
Zr(1)–Cl(2)	2.468(3)
S(3)–C(7)	1.756(8)
S(3)–C(6)	1.801(8)
O(4)–C(5)	1.395(8)
C(5)–C(6)	1.484(11)
Bond distances	
O(4)–Zr(1)–Cl(2)	94.3(2)
C(7)–S(3)–C(6)	106.6(4)
C(5)–O(4)–Zr(1)	162.9(6)
O(4)–C(5)–C(6)	111.6(6)
C(5)–C(6)–S(3)	113.7(6)

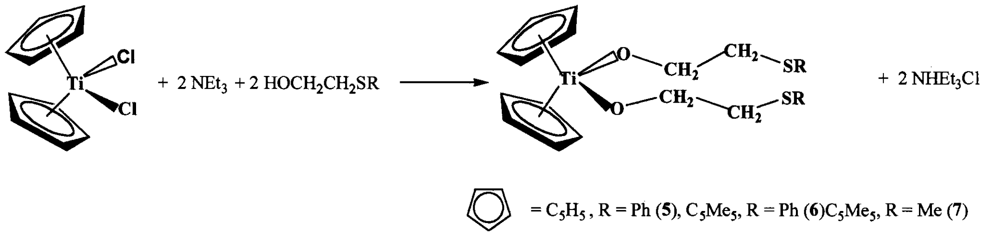
The Zr atom is bonded exclusively to the alkoxide ligand through the O(4) atom with a bond distance of 1.930(5) Å. This value falls into the range expected (1.92–2.00 Å) for zirconium alkoxide complexes [2,13] and is close to the Zr–O bond length found in the analogous mono-chloro complex $Cp_2ZrCl(OCH_2CH_2SPh)$ [1.921(2) Å] [14], although the Zr(1)–O(4)–C(5) angle is rather large [162.9(6)°]. These data indicate that an appreciable π-contribution from electronic donation of the oxygen atom to the Zr–O bond must be considered. Finally, the phenyl ring of the mercaptane moiety is twisted with respect to the coordination plane, defined by the plane Zr(1)–O(4)–Cl(2), with a dihedral angle of 41.9(2)°. No interaction between the sulfur and the zirconium atoms is observed, which is in agreement with proposed structural disposition.

The synthesis of alkyl(aryl)-alkoxide-containing zirconocene complexes was also considered. Complexes $Cp^*_2Zr(CH_3)(OCH_2CH_2SPh)$ (**3**) and $Cp^*_2ZrPh(OCH_2CH_2SPh)$ (**4**) were prepared either by a protonolysis reaction of the corresponding dialkyl derivatives $Cp^*_2Zr(R)_2$ (R = Me, Ph) with the alcohol $HOCH_2CH_2SPh$, or through a metathesis reaction of **1** with the appropriate lithium salt (MeLi or PhLi, respectively) (Scheme 2). In the first procedure complexes **3** and **4** were isolated even when a large excess of the alcohol was used. Nevertheless, complex **4** was always found to contain small amounts of $HOCH_2CH_2SPh$ as an impurity, even when a 1:1 ratio of reactants was used. Both complexes were characterised spectroscopically. The ^{1}H-NMR spectra of **3** and **4** exhibit a singlet at ca. 1.70 ppm for the methyl protons of the Cp* ring as well as two triplet signals at ca. 3.00 and 4.20 ppm, which are assigned to the methylene protons bonded to the sulfur and the oxygen atoms, respectively, of the alkoxide ligand. In addition, the methyl group for complex **3** resonates at −0.16 ppm, while the resonances for the phenyl groups in complex **4** appear between 6.87 and 7.34 ppm as a series of multiplet signals. The ^{13}C-NMR spectra show methylene carbon resonances at ca. 37.0 and 70.0 ppm for the carbons bonded to the sulfur and oxygen atoms, respectively. The resonance for the methyl group bonded to the zirconium atom in **3** appears at 27.9 ppm. Finally, the expected band in the IR spectra for ν(Zr–O) appears at ca. 500 cm^{-1} (see Section 2). These spectroscopic data are in agreement with a structural disposition analogous to that found in complex **1**, in which the alkoxide behaves as a monodentate ligand.

The reactions of Cp_2TiCl_2 and $Cp^*_2TiCl_2$ with 2-phenylmercaptoethanol were also considered. These complexes react with $HOCH_2CH_2SPh$ in the presence of NEt_3 to yield the corresponding dialkoxide derivatives $Cp_2Ti(OCH_2CH_2SPh)_2$ (**5**) and $Cp^*_2Ti(OCH_2CH_2SPh)_2$ (**6**), respectively (Scheme 3). However, while reaction of Cp_2TiCl_2 takes place at



Scheme 2.



Scheme 3.

room temperature, $Cp^*_2TiCl_2$ requires a temperature of 60°C to react.

Both complexes were characterised by the usual spectroscopic techniques. ^{1}H- and ^{13}C-NMR spectra indicate that there is no interaction between the sulfur atom and the titanium centre.

It is worth noting that in the case of zirconium it is not possible, under these experimental conditions, to substitute the second chlorine atom, but in the case of titanium, the substitution takes place readily.

In the same way, we also explored the reactivity of $Cp^*_2TiCl_2$ and Cp_2ZrMe_2 towards 2-methylmercaptoethanol. Reaction of $Cp^*_2TiCl_2$ with two equivalents of the mercaptoethanol, in the presence of NEt_3, yielded the complex $Cp^*_2Ti(OCH_2CH_2SMe)_2$ (**7**).

Reaction of Cp_2ZrMe_2 with 2-methylmercaptoethanol in a 1:2 molar ratio afforded the complex $Cp_2Zr(OCH_2CH_2SMe)_2$ (**8**).

All complexes were characterised spectroscopically. The ^{1}H-NMR spectra of complexes **5** and **8** exhibit two triplet signals at ca. 2.80 and 4.20 ppm, which correspond to the methylene groups of the dialkoxide ligand that are bonded to the sulfur and oxygen atoms, respectively. In addition, the spectra show a singlet at ca. 1.70 ppm for the methyl groups of the Cp* ring (in **6** and **7**) and at ca. 5.90 ppm for the Cp protons (in **5** and **8**).

Finally, reactions in order to prepare early–late heterometallic complexes were considered. In fact, we have studied the reactions of complexes **5**, **6** and **7** with rhodium and ruthenium species, namely $RhH(PPh_3)_4$ and Cp*RuCl(COD), (COD = cyclooctadiene), but unfortunately all experiments afford to an untractable mixtures of species.

In conclusion, we have described the synthesis and characterisation of several titanocene and zirconocene complexes that bear a functionalised alkoxide ligand. The X-ray crystal structure of one of them, as well as the spectroscopic data, indicate that the ligand is coordinated in a monodentate fashion.

4. Supplementary material

Crystallographic data of complex **1** have been deposited with the Cambridge Data Centre, CCDC, no. 140607. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 LE2, UK (fax: +44-1223-336033, or e-mail: depositccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Dirección General de Enseñanza Superior e Investigación Científica (grant no. PB95-0023-C01-C02) for financial support and the Junta de Comunidades de Castilla-La Mancha for a fellowship (C. Hernández).

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