Inorganica Chimica Acta 363 (2010) 3489–3497

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

C-*ansa*-zirconocene complexes with O/S donor ligands: Novel homoleptic six coordinate 4-mercaptophenolate complex of Zr(IV)

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ARTICLE INFO

Article history:
Received 11 March 2010
Received in revised form 23 June 2010
Accepted 1 July 2010
Available online 13 July 2010

Keywords:
Zirconium
Metallocene
Thiolate
Phenolate
Homoleptic

ABSTRACT

New C-*ansa*-zirconocene complexes containing methoxythiophenolate and mercaptophenolate ligands have been synthesized and characterized. The reaction of (HSC_6H_4-*n*-OMe) (*n* = 2, 3 or 4) with [Zr{(*t*-Bu)HC(η^5-C_5Me_4)(η^5-C_5H_4)}Me_2] (**1**) led to the formation of monosubstituted complexes [Zr{(*t*-Bu)HC(η^5-C_5Me_4)(η^5-C_5H_4)}Me(κ,S-SC_6H_4-*n*-OMe)] (*n* = 2 (**2**); *n* = 3 (**3**)) and the disubstituted complex [Zr{(*t*-Bu)HC(η^5-C_5Me_4)(η^5-C_5H_4)}(κ,S-SC_6H_4-4-OMe)$_2$] (**4**). The complexes [Zr{(R)HC(η^5-C_5Me_4)(η^5-C_5H_4)}(κ,O-OC_6H_4-4-SH)$_2$] (R = *t*-Bu (**6**); R = $CH_2CH{=}CH_2$ (**7**)) and [Zr(η^5-C_5H_4)$_2$(OC_6H_4-*n*-SH)$_2$] (*n* = 3 (**9**); *n* = 4 (**10**)) have been synthesized using the corresponding dimethyl zirconocene and mercaptophenol. However, the reaction of [Zr{(*t*-Bu)HC(η^5-C_5Me_4)(η^5-C_5H_4)}Cl_2] (**11**) with 4-mercaptophenol in the presence of NEt_3 led to the formation of the first example of a homoleptic six-coordinate mercaptophenolate complex of zirconium, namely [$HNEt_3$]$_2$[Zr(κ,O-OC_6H_4-4-SH)$_6$] (**12**). Complex **12** can be obtained in higher yield by the reaction of $ZrCl_4$ with six equivalents of 4-mercaptophenol and NEt_3. The reaction of **12** with [Zr(η^5-C_5H_4)$_2Cl_2$] gave the unexpected disubstituted complex [Zr(η^5-C_5H_4)$_2$(OC_6H_4-4-SH)$_2$] (**10**). The molecular structures of **4** and **12** have been determined by single-crystal X-ray diffraction studies.

1. Introduction

There is a great deal of interest in the role of alkoxide complexes [1] in several stoichiometric and catalytic processes [2] and also as molecular models for catalyst–substrate surface interactions [3]. On the other hand, thiolate complexes are of particular interest in the field of bioinorganic chemistry due to their relevance to the structure, bonding and function of biologically active reaction centres such as nitrogenase or metallothioneins [4]. More specifically, the alcoholate and thiolate complexes of group 4 have been studied extensively [5] – including systems with diol and dithiol ligands – by Stephan and co-workers [6].

The study of ligand systems with two different donor atoms are attracting increasing interest in the chemistry of metal complexes due to the possible coordination of the remaining donor atom to the metal centre [7] and the stabilization of heterometallic complexes. In this sense, several mono- and disusbtituted zirconocene and titanocene complexes that bear functionalised mercapto-alkoxide ligands have been reported. These ligands contain a hard donor and a soft donor atom at each end and are coordinated in a monodentate fashion [8]. A systematic study of the chemistry of mono- and bis(cyclopentadienyl) complexes of group 4 and 5 transition metals has been carried out by our research group in recent years [9].

We previously reported the preparation of the synthon (C_5Me_4)=CH({C_5H_4}K) for the facile synthesis of C-*ansa*-metallocene precursors with variable substitution at the bridging atom [10] and, more recently, we described the synthesis, characterization and reactivity of chiral *ansa*-metallocenes with an alkyl- or aryl-substituted *ansa* methylene bridge [10c]. We also reported the development of new *ansa*-metallocene complexes of group 4 that have vinyl or allyl substituents at the silicon *ansa* bridge or at the cyclopentadinyl rings [11]. Herein we report the reactivity studies of some of these chiral C-*ansa*-metallocenes of group 4 complexes with polyfunctional organic molecules contain a hard donor and a soft donor atom at each end. We have chose for our study chiral *ansa*-metallocenes containing a terc butyl group in the bridge in order to increase the lipophility of the new complexes an also to introduce a group easily followed in the NMR characterization.

We report the synthesis and characterization of several mono- and disubstituted C-*ansa* zirconocene thiolate complexes containing SC_6H_4OMe ligands, the reactivity of dichloro or dimethyl zirconocene complexes with HOC_6H_4-4-SH and the synthesis and reactivity of a new unexpected homoleptic

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doi:10.1016/j.ica.2010.07.003

hexa-mercaptophenolate zirconium complex. In this field few homoleptic six-coordinate mononuclear zirconium complexes with alkoxide ligands are known, with $[Zr\{OCH(CF_3)_2\}_6]^{2-}$ being the first such complex to be completely characterized [12]. Prior to the synthesis and characterization of the homoleptic zirconium complexes with six phenolate ligands, $[Zr(OC_6H_4\text{-}R)_6]^{2-}$ by Giolando and co-workers [13], had only been characterized heteroleptics six coordinate complexes with one, two or three phenolate groups [14].

2. Result and discussion

2.1. Synthesis and characterization

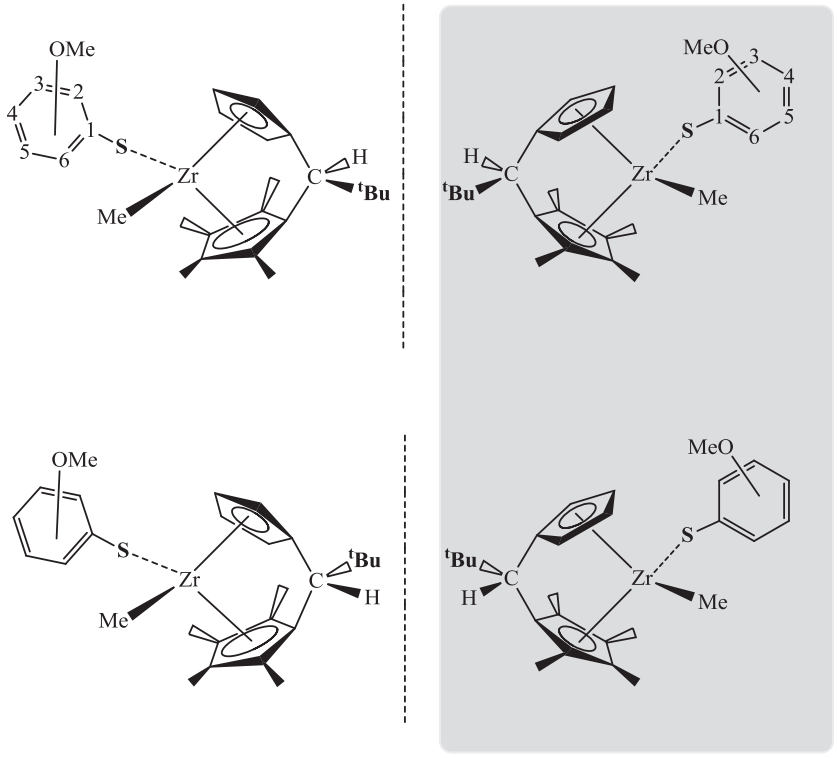
The most widely used methods for the synthesis of alkoxide or thiolate derivatives of early transition metals are (a) the reaction of appropriate metal halide precursors with alcohols or thiols in the presence of an amine such as NEt_3, which promotes the elimination of X^- by formation of the corresponding ammonium salts R_3NHX, and (b) the reaction of alkyl complexes with alcohol or thiol derivatives to yield the corresponding alkane derivative and the alkoxide or thiolate complex [15].

These methods were used to synthesize several asymmetric C-*ansa* biscyclopentadienyl complexes of group 4 with different alkyl or aryl substituents at the carbon *ansa* bridge. The disubstituted complexes have a chiral centre at the carbon bridge atom and this chirality makes the other two ligands diastereotopic, as evidenced by the NMR spectra, whereas the monosubstituted C-*ansa* complexes have an additional chiral centre at the zirconium atom and this generates a wide variety of geometries [10].

In view of these results we focused our attention on the preparation of new thiolate and alkoxide zirconocene and chiral C-*ansa* zirconocene complexes. Reaction of $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me_2]$ (**1**) [10b] with the methoxythiophenol derivatives HSC_6H_4-*n*-OMe, (*n* = 2, 3 or 4) in toluene in a 1:1 and 1:2 ratio at room temperature in all cases led to the evolution of methane. The reaction with HSC_6H_4-2-OMe and HSC_6H_4-3-OMe only gave the monothiolate complexes $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me(\kappa,S\text{-}SC_6H_4\text{-}2\text{-}OMe)]$ (**2**) and $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me(\kappa,S\text{-}SC_6H_4\text{-}3\text{-}OMe)]$ (**3**), respectively, even in the presence of a large excess of ligand. This finding could be due to the steric hindrance caused by the *ortho* or *meta* methoxy-substituent of the thiophenolate moiety [16]. The new complexes **2** and **3** have two chiral centres – one at the zirconium atom and the other already existing at the carbon bridge atom of the *ansa* ligand. This situation gives rise to new isomers, two of which **A** and **B** (50:50 ratio) were observed in the NMR studies (Scheme 1). On the other hand, when two equivalents of the reagent HSC_6H_4-4-OMe were used the dithiolate compound $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa,S\text{-}SC_6H_4\text{-}4\text{-}OMe)_2]$ (**4**) was isolated as a white solid. Nevertheless when the stoichiometry used was lower than 1:2, a mixture of **4** and the starting material **1** was obtained. Complexes **2**–**4** were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (see Section 4).

The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic and analytical data for **2** and **3** are consistent with the proposed structure and the presence of two isomers is clearly evident in the NMR spectra. For example, the ^1H NMR spectrum of **2** shows signals for the two isomers, a singlet at −0.05 ppm integrates as six protons for the methyl groups bonded to the zirconium atom, two singlets at 1.15 and 1.17 ppm corresponding to the *tert*-butyl ligand, eight singlets at 1.57–2.06 for the methyl groups of the tetramethylcyclopentadienyl ring, two singlets at 3.18 and 3.19 ppm for the methoxy groups, two singlets at 3.52 and 3.82 ppm for the proton *ansa*-C*H* bridge and eight signals between 4.98 and 6.41 ppm for the unsubstituted cyclopentadienyl ring.

In contrast to the above, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** do not show any resonances for the metal-bonded methyl groups and the spectra therefore correspond to a single product with a singlet observed for the *tert*-butyl group *of the ansa*-biscyclopentadienyl moiety at 1.09 ppm, four singlets at 1.79–1.92 ppm for the four



Scheme 1. Different observable isomers in NMR studies for the monothiometoxyphenolate complexes **2** and **3**.

methyl groups of the tetramethylcyclopentadienyl fragment, one singlet corresponding to the proton of the *ansa*-C*H* bridge at 3.59 ppm and four multiplets at 5.01–6.20 due to the unsubstituted cyclopentadienyl ring. The signals observed are consistent with the presence of only one chiral centre at the *ansa*-CH bridge and the enantiomers are not distinguishable by the NMR spectra. However, the chirality of the complex makes the two 4-methoxythiophenol ligands diastereotopic and four multiplets were observed at 7.23, 7.40, 7.63 and 7.73 ppm for the aromatic protons (one multiplet for the *ortho* protons and the other for the *meta* protons of each methoxythiophenolate ligand in each isomer) and one singlet at 3.24 ppm, integrating as six protons, corresponding to the two methoxy groups.

This situation was confirmed by X-ray diffraction studies. The X-ray crystal structure of **4** is depicted in Fig. 1. Selected bond lengths and angles for **4** are given in Table 1.

Compound **4** crystallizes in the $P\bar{1}$ space group as a racemic mixture. The structure of **4** has the typical bent metallocene conformation observed in zirconocene complexes with a pseudo-tetrahedral geometry around the zirconium atom. The *ansa* ligand chelates the zirconium atom and both C_5 rings are bound to the metal in a η^5 mode. The pseudo-tetrahedral environment of the zirconium atom is completed by the two S atoms of the methoxythiophenolate groups. The centroid of the cyclopentadienyl rings forms an angle with the zirconium atom of 117.53°, which is typical for carbon atom-bridged *ansa*-zirconocene complexes [10,17].

The most characteristic bond distances of this compound correspond to Zr(1)–S(1) (2.5167(9) Å) and Zr(1)–S(2) (2.511(1) Å). Both distances are within the normal range for similar zirconium diphenolate complexes. The Zr(1)–S(1)–C(1) and Zr(1)–S(2)–C(8) angles are 115.0(1)° and 111.0(1)°, respectively, while the S(1)–Zr(1)–S(2) angle has a value of 105.64(3)°. These parameters are within the range expected for similar dithiophenolate complexes [18].

Compound **4** has a torsion angle, defined by C1–S1–S2–C8, of 1.02° and such a low value has not been reported previously in the literature [19]. On the other hand, the two aromatic rings of the methoxythiophenolate groups are arranged with a dihedral angle of 63.04° between them and these lie as far as possible from the C_5Me_4 ring (see Fig. 1). The two Ph groups participate in intra- and intermolecular C–H/π interactions with the H16 and H17 protons of the unsubstituted cyclopentadienyl ring but not with the tetramethylcyclopentadienyl ring (see Fig. 2).

The H16–(centroid of C1–C6) distance is 2.652 Å and the H16 atom is 2.651 Å from the plane containing the (C1–C6) ring. The H17–(centroid of C8–C13) distance is 3.140 Å and the H17 atom is 2.734 Å out of plane of the (C8–C13) ring.

The intermolecular C–H/π interaction between the H16 proton of the Cp ring and the (C1–C6) Ph ring leads to the formation of chains (Fig. 3). These chains are joined by means of the C5–H5/π interaction with the Ph ring (C8–C13) and this in turn leads to the formation of a laminar structure (Fig. 4).

The reactivity of complexes **1** and [Zr{(CH_2=$CHCH_2$)HC(η^5-C_5Me_4)(η^5-C_5H_4)}Me_2] (**5**) with 4-mercaptophenol, HOC_6H_4-4-SH, was considered. In this case the reagent has a hard oxygen donor and a soft sulfur donor and it is able to behave as a monodentate ligand through coordination of the oxygen atom or the sulfur atom to the metal centre. In addition, the atom that remains free could give rise to homo- or heterobimetallic complexes. Reaction of a solution of **1** or **5** in toluene with 2 equivalents of HOC_6H_4-4-SH yielded the complex [Zr{(*R*)HC(η^5-C_5Me_4)(η^5-C_5H_4)}(κ-O-OC_6H_4-4-SH)$_2$] (R = *t*-Bu (**6**), CH_2=$CHCH_2$ (**7**)) and these were characterized by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopy. Complexes **6** and **7** have the same symmetry properties as complex **4**. The NMR spectra contain a similar number of signals to the spectrum of complex **4**, with evidence for two diastereotopic mercaptophenolate ligands and two singlets at 3.10 and 3.11 ppm corresponding to the inequivalent *SH* protons. The κ-oxygen-coordination mode of the mercaptophenolate ligands is proposed on the basis of the IR spectra, which show the characteristic stretching vibrations at ca. ν_{SH} = 2553 cm^{-1} and ν_{ZrO} = 459 cm^{-1}.

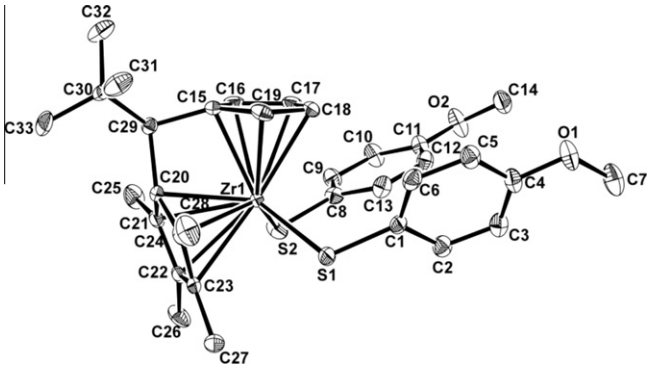


Fig. 1. ORTEP drawing of complex [Zr{(*t*-Bu)HC(η^5-C_5Me_4)(η^5-C_5H_4)}(κ S-SC_6H_4-4-$OMe)_2$] (**4**) with the atomic labelling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30% level of probability.

Table 1
Selected bond lengths (Å) and angles (°) for **4**.

Zr(1)–Ct(1)	2.1983	Ct(1)–Zr(1)–S(2)	111.94
Zr(1)–Ct(2)	2.2103	Ct(1)–Zr(1)–S(1)	113.61
Zr(1)–C(19)	2.460(3)	Ct(2)–Zr(1)–S(2)	103.84
Zr(1)–S(2)	2.511(1)	Ct(2)–Zr(1)–S(1)	102.83
Zr(1)–S(1)	2.5167(9)	Ct(1)–Zr(1)–Zt(2)	117.53
S(1)–C(1)	1.780(3)	S(2)–Zr(1)–S(1)	105.64(3)
S(2)–C(8)	1.776(3)	C(1)–S(1)–Zr(1)	115.0(1)
O(1)–C(4)	1.381(3)	C(8)–S(2)–Zr(1)	111.0(1)
O(1)–C(7)	1.430(4)	C(4)–O(1)–C(7)	117.0(3)
O(2)–C(11)	1.380(4)	C(11)–O(2)–C(14)	117.5(3)
O(2)–C(14)	1.412(4)	C(15)–C(29)–C(20)	99.4(4)
C(15)–C(29)	1.537(6)		
C(20)–C(29)	1.588(6)		

Ct(1) is the centroid of the cyclopentadienyl ring and Ct(2) is the centroid of the teramethylcyclpentadienyl ring.

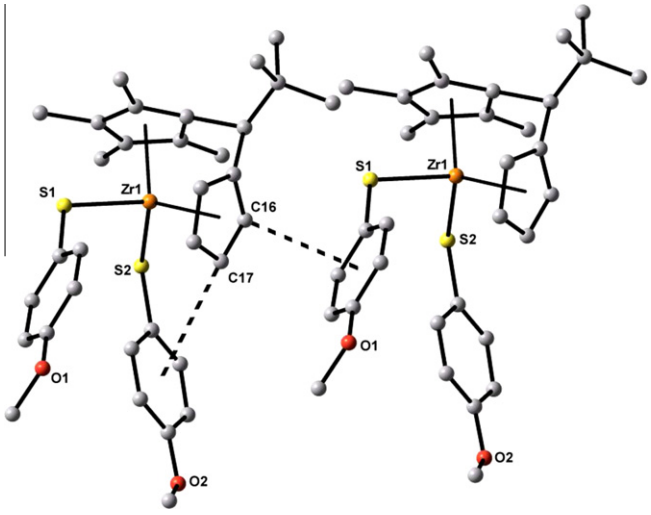


Fig. 2. Intra and intermolecular C–H/π interactions of the phenylenic groups with the C16(H16) and C17(H17) protons of the not substituted cyclopentadienyl ring.

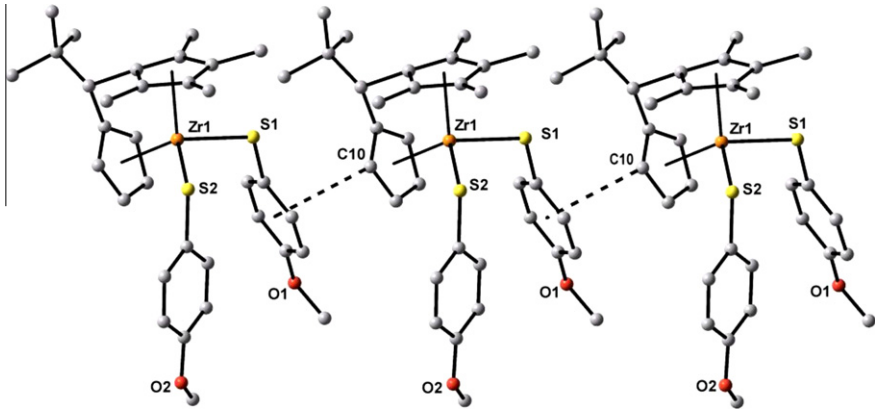


Fig. 3. Chains forming along *b* due to the intermolecular C16–H16/π interaction of Cp group and phenylenic ring. View down *a* axis.

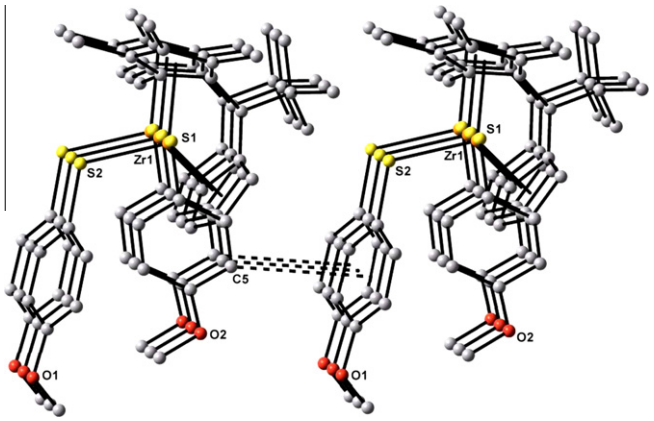


Fig. 4. Laminar structure forming due to the juntion of chains in **4**. View down *b* axis. The H5–(centroid of C8–C13) distance is a value of 3.172 Å and the H5 atom is a 3.057 Å of plane defined by (C8–C13) ring.

In the same way, we also explored the reactivity of [Zr(η^5-$C_5H_4)_2Me_2$] (**8**) towards mercaptophenol ligands. Reaction of **8** with *n*-mercaptophenol (*n* = 3, 4) in a 1:2 M ratio afforded the complexes [Zr(η^5-$C_5H_4)_2$(κ-O-OC_6H_4-3-SH)$_2$] (**9**) and [Zr(η^5-$C_5H_4)_2$(κ-O-OC_6H_4-4-SH)$_2$] (**10**). Both complexes were characterized by the usual spectroscopic techniques. As an example, the ^{1}H NMR spectrum of **10** in C_6D_6 presents a broad signal at 3.21 ppm, corresponding to the protons of two equivalent *SH* groups, one singlet at 5.84 ppm due to the protons of the two cyclopentadienyl rings and two doublets at 6.48 ppm and 7.17 ppm with a coupling constant $^3J_{H-H}$ = 8.5 Hz assigned to the *ortho* and *meta* protons of two phenylenic rings. These compounds were fully characterized by $^{13}C\{^1H\}$ NMR spectroscopy and the IR spectra provide supplementary information, with the characteristic stretching vibration *ν*(Zr–O) at ca. 512 cm^{-1} and *ν*(S–H) at ca. 2538 cm^{-1}.

2.2. Synthesis and crystal structure of complex **12**

We attempted to synthesize complex **6** by a metathesis reaction between [Zr{(*t*-Bu)(η^5-C_5H_4)(η^5-C_5Me_4)}Cl_2] (**11**) [10a] and 4-mercaptophenol in the presence of NEt_3 in a 1:2:2 ratio. However, only a small amount of the desired product **6** was obtained. In order to increase the yield of the reaction the stoichiometric amounts of 4-mercaptophenol and NEt_3 were increased (to a 1:6:6 ratio) and, after the appropriate work up, a new crystalline product **12** was obtained. The ^{1}H NMR spectrum of **12** contains a triplet at 0.57 ppm ($^3J_{H-H}$ = 7.1 Hz) and a quartet at 2.08 ppm with the same coupling constant. These signals correspond to the protons of the ethyl group of the $[HNEt_3]^+$ cation, the acid proton of which appears as a broad signal at 11.24 ppm. A very broad resonance is also observed at 4.50 ppm and this corresponds to the proton of the *SH* groups. The aromatic region contains two doublets at 6.85 and 7.24 ppm with $^3J_{H-H}$ = 8.4 Hz for the *ortho* and *meta* phenylenic ring protons, respectively. It is worth noting that resonances corresponding to the C-*ansa*-biscyclopentadienyl ligand are not observed. The $^{13}C\{^1H\}$ NMR spectrum contains only one signal for each of the groups evidenced in the ^{1}H NMR spectrum. The IR spectrum shows stretching vibrations at ν_{SH} = 2512 and ν_{ZrO} = 498, which are characteristic of the κ-oxygen-coordination mode of mercaptophenolate ligands. Monocrystals of **12** suitable for study by X-ray diffraction were obtained. The ORTEP diagram and atom numbering scheme are shown in Fig. 5 and a selection bond lengths and angles are given in Table 2.

The complex $[HNEt_3]_2[Zr(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_6]$ (**12**) crystallized in the orthorhombic space group *Pbca* with two C_6D_6 molecules. The asymmetric unit contains half a molecule of complex **12**, with the zirconium atom located on a crystallographic inversion centre,

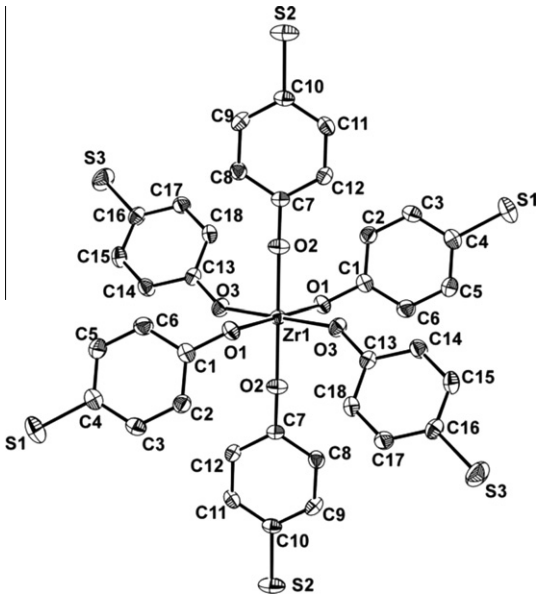


Fig. 5. ORTEP drawing of $[Zr(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_6]^{2-}$ dianionic complex with the atomic labelling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at the 30% level of probability.

Table 2
Selected bond lengths (å) and angles (°) for $12 \cdot 2C_6D_6$.

Zr(1)–O(1)	2.048(2)	O(1)–Zr(1)–O(2)	88.97(7)
Zr(1)–O(2)	2.006(2)	O(1)–Zr(1)–O(3)	91.06(7)
Zr(1)–O(3)	2.117(2)	O(1)–Zr(1)–O(1)[a]	180.0
O(1)–C(1)	1.332(3)	O(2)–Zr(1)–O(3)	90.50(7)
O(2)–C(7)	1.332(3)	O(2)–Zr(1)–O(1)[a]	91.03(7)
O(3)–C(13)	1.350(3)	O(2)–Zr(1)–O(3)[a]	89.50(7)
S(1)–C(4)	1.774(3)	O(2)–Zr(1)–O(2)[a]	180.0
S(2)–C(10)	1.777(3)	O(3)[a]–Zr(1)–O(3)	180.0
S(3)–C(16)	1.775(3)	O(1)–Zr(1)–O(3)[a]	88.94(7)
		C(1)–O(1)–Zr(1)	146.1(2)
		C(7)–O(2)–Zr(1)	178.7(2)
		C(13)–O(3)–Zr(1)	126.6(1)

[a] Symmetry transformations used to generate equivalent atoms: $-x, -y, -z+1$.

and one molecule of C_6D_6. Structural analysis of **12** by X-ray crystallography revealed the presence of a dianionic complex consisting of a zirconium centre coordinated by six oxygen atoms of six 4-mercaptophenolate ligands in an octahedral geometry, thus corroborating the assignment of the ^{1}H NMR and IR spectra.

It is interesting to note that the Zr–O bond lengths are not equal and the distances between the oxygen atoms and the Zr centre are as follows: Zr(1)–O(3), 2.117(2) Å; Zr(1)–O(1), 2.048(2) Å; Zr(1)–O(2), 2.006(2) Å. These values are in agreement with three different coordination modes of the oxygen atoms. This situation is related with the Zr–O–C(Ph) bond angles, for which three different values are observed: Zr(1)–O(3)–C(13) 126.6(1)°; Zr(1)–O(1)–C(1) 146.1(2)°; Zr(1)–O(2)–C(7) 178.7(2)°.

These structural data (angles and distances) are consistent with the different hybridization modes of the oxygen atoms around the zirconium centre. For example, atom O(3) has the longest Zr–O bond distance and lowest Zr–O–C(Ph) bond angle as it has sp^2 hybridization and therefore has a lower donor capacity to the zirconium atom. In this particular case the metal–oxygen interaction could be considered as double bond due to additional electronic transfer from the non-hybridized p orbital of the oxygen atom to the zirconium atom. In contrast, the O(2) oxygen atom has the lowest Zr–O bond distance and highest Zr–O–C(Ph) bond angle – this oxygen would have sp hybridization and will act as a better donor atom. In the latter case the metal–oxygen interaction can be considered as a triple bond and the oxygen atom interacts with the metal atom through its two lone pairs. Finally, the O(1) oxygen atom has intermediate bond angles and bond distances and correspondingly presents intermediate behaviour between the sp and sp^2 hybridization modes.

If we define the equatorial plane (EP) formed by the O1–O1A–O3–O3A atoms and Ph1 by the mean plane of the (C1–C6) atoms, Ph2 by the mean plane of (C7–C12) and Ph3 by the mean plane of (C13–C19), we can see the different orientations for the phenyl rings of the phenolate ligands. Thus, the dihedral angle formed between EP and Ph2 is very close to 90° (89.63°), while for Ph1 and Ph3 the values are only 53.71° and 71.29°, respectively. Closer inspection of the structure provides a plausible explanation for this observation: the Ph1 ring takes part in an intermolecular C–H/π interaction with the methylenic proton H23B of the $[HNEt_3]^+$ cation (the H23B–(centroid of C1–C6) distance is 3.130 Å and that for H23B is 2.727 Å out of the plane defined by C1–C6); the Ph3 ring is involved in an intermolecular S–H/π interaction [20] established with the S2(HB) atom (Fig. 6) (the HB–(centroid of C13–C18) distance is 2.833 Å and that for HB is 2.504 Å out of the plane defined by C13–C18). In contrast, Ph2 does not take part in any interactions.

In this structure, the $[HNEt_3]^+$ cation should be stabilized by the two hydrogen bonds observed (see Table 3 and Fig. 6). Each $[HNEt_3]^+$ cation shows two intermolecular hydrogen bonds with

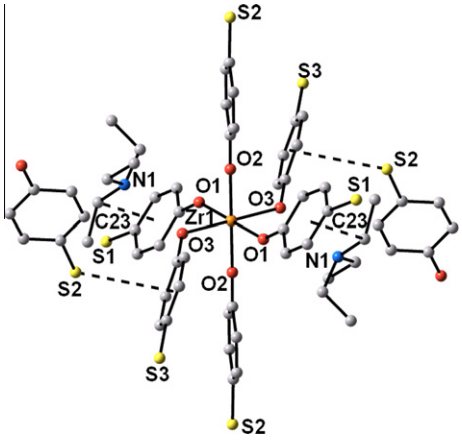


Fig. 6. View of the intermolecular S–H/π and C–H/π interactions in $[Zr(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_6]^{2-}$ dianionic complex of **12**. The hydrogen atoms are omitted for clarity.

the dianionic complex: the O(3) atom is involved in an intermolecular hydrogen bond with the H(1) atom of the $[HNEt_3]^+$ cation. Another weaker hydrogen bond is established between the oxygen

Table 3
Crystal data and structure refinement for **4** and **12**.

	4	**12**
Empirical formula	$C_{33}H_{40}O_2S_2Zr$	$[C_{36}H_{30}O_6S_6Zr][C_6H_{16}N]_2 \times 2C_6H_6$
Formula weight	623.99	1202.85
Temperature	180(2) K	180(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
Unit cell dimensions	a = 8.8369(10) Å b = 9.1048(10) Å c = 19.996(2) Å α = 86.144(2)° β = 82.088(2)° γ = 68.772(2)°	a = 18.3856(18) Å b = 17.6546(17) Å c = 18.7389(18) Å α = 90° β = 90° γ = 90°
Volume	6082.5(10) Å^3	6082.5(10) Å^3
Z	2	4
Density (calculated)	1.395 mg/m^3	1.313 mg/m^3
Absorption coefficient	0.539 mm^{-1}	0.436 mm^{-1}
F(0 0 0)	652	2528
Crystal size	0.38 × 0.21 × 0.08 mm^3	0.43 × 0.36 × 0.34 mm^3
Theta range for data collection	2.06–26.41°	1.93–26.46°
Index ranges	$-11 \leqslant h \leqslant 11$ $-11 \leqslant k \leqslant 11$ $-25 \leqslant l \leqslant 25$	$-22 \leqslant h \leqslant 23$ $-21 \leqslant k \leqslant 22$ $-22 \leqslant l \leqslant 23$
Reflections collected	10 150	39 973
Independent reflections	5967 [R_{int} = 0.0324]	6266 [R_{int} = 0.1578]
Completeness to theta = 26.46°	98.0%	99.8%
Max. and min. transmission	0.9581 and 0.8214	0.8659 and 0.8346
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5967/18/392	6266/0/343
Goodness-of-fit on F^2	1.029	0.837
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0425, wR_2 = 0.0929	R_1 = 0.0402, wR_2 = 0.0899
R indices (all data)	R_1 = 0.0534, wR_2 = 0.0980	R_1 = 0.0728, wR_2 = 0.0979
Largest diff. peak and hole	0.439 and −0.318 eÅ^{-3}	0.443 and −0.520 eÅ^{-3}

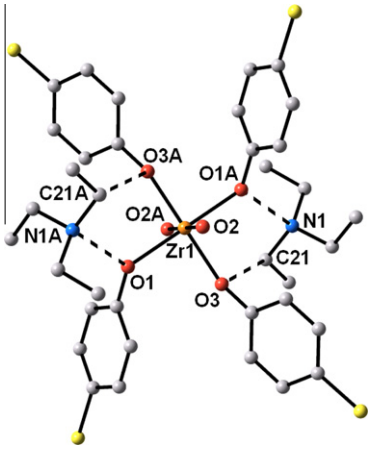
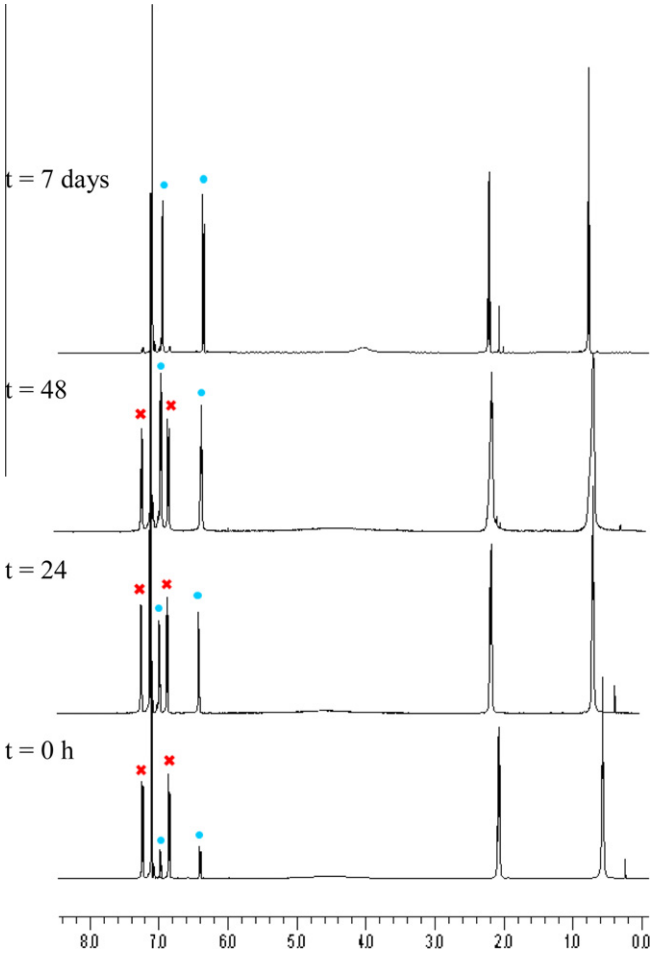


Fig. 7. View of the hydrogen bonds between $[HNEt_3]^+$ cation with $[Zr(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_6]^{2-}$ dianionic complex. The hydrogen atoms are omitted.



Scheme 2. ^1H NMR in C_6D_6 at $T = 25$ °C evolution of complex **12** overtime.

atoms O(1) and the methylenic proton H21B of one ethyl group of the triethylammonium cations. Similar interactions have been observed in analogous homoleptic octahedral complexes [12] (Fig. 7).

Compound **12** can also be obtained by the reaction between six equivalents of 4-mercaptophenol and NEt_3 with a $ZrCl_4$ suspension in toluene. This reaction affords a colourless solution. The appropriate work up procedure furnishes white crystals that give spectroscopic and X-ray diffraction data that are consistent with those of compound **12**.

2.3. Stability and reactivity of complex *12*

According to the ^1H NMR spectrum at 25 °C the six mercaptophenolate ligands of **12** are equivalent, which reveals a dynamic exchange between them. In the solid state, however, this equilibrium is blocked by the presence of hydrogen bonds as described above.

The homoleptic six-coordinate complex **12** decomposes slowly in the solid state under an inert atmosphere and more rapidly in solution. Similar results have been observed for other related complexes that contain a dialkylammonium cation [21]. This behaviour was followed by ^1H NMR spectroscopy of **7** in C_6D_6 over one week at 25 °C (Scheme 2). The initial ^1H NMR spectrum shows the signals for the octahedral complex **12** along with two much lower intensity signals in the aromatic region, which were identified as being due to $[HNEt_3][OC_6H_4SH]$ (**13**). Over time the intensity of the signals of **12** decreased while the additional aromatic signals increased in intensity. At the same time a white precipitate began to form. After seven days the ^1H NMR spectrum corresponded only to the salt $[HNEt_3][OC_6H_4\text{-}4\text{-}SH]$ (**13**).

It was established by NMR experiments that this process is highly dependent on the temperature and the nature of the solvent. Thus, the evolution of **12** is faster on increasing the temperature and on using non-aromatic solvents.

Attempts to prepare the tetracoordinate complex from zirconium tetrachloride with 4-mercaptophenol in a 1:4 stoichiometry and NEt_3 in excess were unsuccessful and the only product isolated was **12** – in 23% yield after crystallization from a toluene solution.

We previously mentioned that the uncoordinated SH groups in complex **12** should be able to act as bridges to give homo- or heteronuclear species. In this respect, we attempted the reaction of **12** with 2 equivalents of **8** in toluene at room temperature to generate a trinuclear zirconium compound. However, the product obtained was complex **10** and this was characterized by NMR and IR spectroscopy (Scheme 3). This behaviour could be due to the faster reaction of **8** with the ammonium salt **13** (always present in a solution of **12**) rather than the reaction with the zirconium complex **12**.

3. Conclusions

In conclusion, we have described the synthesis and characterization of several new chiral C-*ansa* and not *ansa* zirconocene complexes with functionalised methoxythiolate and mercaptophenolate ligands. These ligands are coordinated to the metal centre in a monodentate fashion by the sulfur donor atom in the case of the methoxythiolate ligands and by the oxygen atom in the mercaptophenolate ligands. The steric hinderance caused by the functionalised phenylenic ligands on position 2 or 3 gives rise to

$$[HNEt_3]_2[Zr(OC_6H_4\text{-}4\text{-}SH)_6] + Zr(\eta^5\text{-}C_5H_5)_2Cl_2 \longrightarrow [Zr(\eta^5\text{-}C_5H_5)_2(OC_6H_4\text{-}4\text{-}SH)_2] + [Zr(OC_6H_4\text{-}4\text{-}SH)_4] + 2NEt_3.HCl$$

Scheme 3. Synthesis of $[Zr(\eta^5\text{-}C_5H_5)_2(OC_6H_4\text{-}4\text{-}SH)_2]$ from $[HNEt_3]_2[Zr(OC_6H_4\text{-}4\text{-}SH)_6]$.

monosubstituted complexes but the presence of the substituent on position 4 produces the disubstituted complexes.

The new homoleptic six-coordinate zirconium complex **12** has been synthesized by the reaction of the C-*ansa*-dichlorozirconocene derivative **11** with the protic compound 4-mercaptophenol in the presence of NEt_3.

Finally, the reaction of complex **12** with $[Zr(\eta^5\text{-}C_5H_5)_2Me_2]$ gives the disubstituted complex $[Zr(\eta^5\text{-}C_5H_4)_2(\kappa\text{-}O\text{-}OC_6H_4\text{-}4\text{-}SH)_2]$ (**10**).

4. Experimental

4.1. General procedures

All reactions were performed using standard Schlenk tube techniques under dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Racemic mixtures of complexes $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me_2]$ (**1**), $[Zr\{(CH_2{=}CHCH_2)CH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me_2]$ (**5**) and $[Zr\{t\text{-}BuCH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}_2Cl_2]$ (**11**) were prepared as described earlier [4]. $ZrCl_4$, HSC_6H_4-4-OH, HSC_6H_4-2-OMe, HSC_6H_4-3-OMe and HSC_6H_4-4-OMe were purchased from Aldrich and used directly. NEt_3 purchased from Aldrich was distilled and stored over molecular sieves under an inert atmosphere before use. Literature methods were used to prepare $[Zr(\eta^5\text{-}C_5H_4)_2Me_2]$ (**8**) from commercial $[Zr(\eta^5\text{-}C_5H_4)_2Cl_2]$ [22] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

4.2. Synthesis of $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me(\kappa,S\text{-}SC_6H_4\text{-}2\text{-}OMe)]$ (**2**)

To a solution of $[Zr\{t\text{-}BuHC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}_2Me_2]$ (0.50 g, 1.33 mmol) in toluene (50 mL) was added HSC_6H_4-2-OMe (0.36 g, 2.66 mmol) at room temperature and stirred for 2 h. The evolution of methane was observed. The solution was evaporated to dryness under vacuum to yield complex **2** (0.54 g, 81%). ^1H NMR (500 MHz, C_6D_6, 25 °C) isomer A and isomer B: δ/ppm = −0.05 (s, 6H, Zr*Me*), 1.15, 1.17 (2s, each 9H, C(CH_3)$_3$), 1.57, 1.66, 1.68, 1.77, 1.82, 1.89, 2.04, 2.06 (8s, each 3H, C_5Me_4), 3.18, 3.19 (2s, each 3H, O*Me*), 3.52, 3.82 (2s, each 1H, C*H*), 4.92, 4.98, 5.46, 5.70, 5.73, 6.02, 6.16, 6.41 (8m, each 1H, C_5H_4), 6.52, 6.93, 7.80, 7.96 (4m, each 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C) isomer A and isomer B: δ/ppm = 29.9, 30.9 (Zr*Me*), 10.3, 10.7, 11.6, 11.9, 12.0, 13.2, 15.2, 15.6 (C_5Me_4), 32.1, 33.0 ($C(CH_3)_3$), 32.3, 33.1 ($C(CH_3)_3$), 50.1, 50.9 (*C*H), 55.1 (O*Me*), 98.3–126.4 (C_5Me_4 and C_5H_4), 127.5, 127.9, 128.1, 129.3, 136.1, 136.2, 158.2, 158.3 (C_6H_4). *Anal.* Calc. for $C_{27}H_{36}OSZr$ (499.86): C, 64.88; H, 7.26; S, 6.41. Found: C, 64.72; H, 7.01; S, 6.14%.

4.3. Synthesis of $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me(\kappa,S\text{-}SC_6H_4\text{-}3\text{-}OMe)]$ (**3**)

The preparation of **3** was carried out in an identical manner to that of **1**: from a solution of $[Zr\{t\text{-}BuCH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}_2Me_2]$ (0.50 g, 1.33 mmol) in toluene (50 mL) and HSC_6H_4-3-OMe (0.36 g, 2.66 mmol). Yield: 0.53 g, 80%. ^1H NMR (500 MHz, C_6D_6, 25 °C) isomer A and isomer B: δ/ppm = −0.04, −0.05 (2s, each 3H, Zr*Me*), 1.04, 1.05 (2s, each 9H, C(CH_3)$_3$), 1.60, 1.64, 1.74, 1.77, 1.88, 1.89, 2.04, 2.07 (8s, each 3H, C_5Me_4), 3.37, 3.39 (2s, each 3H, O*Me*), 3.44, 3.57 (2s, each 1H, C*H*), 4.77, 5.01, 5.13, 5.18, 5.70, 6.16, 6.18, 6.20 (8m, each 1H, C_5H_4), 7.32, 7.36, 7.48, 7.56 (4m, each 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ/ppm = 11.3, 11.4, 12.0, 12.1 13.6, 13.8, 16.5, 17.2 (C_5Me_4), 29.3, 29.5 (Zr*Me*), 30.0, 30.1 ($C(CH_3)_3$), 33.3, 33.4 ($C(CH_3)_3$), 51.3, 52.5 (*C*H), 54.9, 55.0 (O*Me*), 100.2–146.6 (C_5Me_4 and C_5H_4), 126.2, 126.3, 128.7, 128.8, 129.0, 129.1, 145.6, 145.8, 159.8, 160.0 (C_6H_4). *Anal.* Calc. for $C_{27}H_{36}OSZr$ (499.86): C, 64.88; H, 7.26; S, 6.41. Found: C, 64.51; H, 6.98; S, 6.26%.

4.4. Synthesis of $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa,S\text{-}SC_6H_4\text{-}4\text{-}OMe)_2]$ (**4**)

The preparation of **4** was carried out in an identical manner to that for **1**: from a solution of $[Zr\{t\text{-}BuCH(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}_2Me_2]$ (0.50 g, 1.33 mmol) in toluene (50 mL) and HSC_6H_4-4-OMe (0.36 g, 2.66 mmol). In this case crystals for an X-ray study were obtained by cooling to −30 °C a concentrated solution of 5 mL in toluene. Yield: 0.55 g, 83%. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ/ppm = 1.09 (s, 9H, C(CH_3)$_3$), 1.79, 1.82, 1.91, 1.92 (4s, each 3H, C_5Me_4), 3.24 (s, 6H, 2 × O*Me*), 3.59 (s, 1H, C*H*), 5.01, 5.17, 6.16, 6.20 (4m, each 1H, C_5H_4), 7.23, 7.40, 7.63, 7.73 (4m, each 2H, 2 × C_6H_4). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ/ppm = 11.3, 11.4, 13.6, 13.8 (C_5Me_4), 30.3 ($C(CH_3)_3$), 30.5 ($C(CH_3)_3$), 51.5 (*C*H), 54.8 (2 × O*Me*), 99.7–134.0 (C_5Me_4 and C_5H_4), 127.4, 127.9, 128.1, 128.3, 132.6, 133.2, 135.4, 135.5, 157.9, 158.0 (2 × C_6H_4). *Anal.* Calc. for $C_{33}H_{40}O_2S_2Zr$ (624.02): C, 63.52; H, 6.46; S, 10.28. Found: C, 63.19; H, 6.33; S, 10.07%.

4.5. Synthesis of $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_2]$ (**6**)

To a solution of $[Zr\{t\text{-}BuHC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}_2Me_2]$ (0.50 g, 1.33 mmol) in toluene (50 mL) was added HOC_6H_4-4-SH (0.33 g, 2.66 mmol) at room temperature and stirred for 6 h. The evolution of methane was observed. The resulting pale yellow solution was filtered and evaporated under vacuum. The yellow residue was washed with hexane (2 × 20 mL) to give the title complex (0.45 g, 56%). IR (KBr; ν(cm^{-1})): ν_{SH} = 2553, ν_{ZrO} = 459. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ/ppm = 1.21 (s, 9H, C(CH_3)$_3$), 1.67, 1.68, 1.70, 1.91 (4s, each 3H, C_5Me_4), 3.10, 3.11 (2s, each 1H, S*H*), 4.02 (s, 1H, C*H*), 5.13, 5.40, 5.80, 6.03 (4m, each 1H, C_5H_4), 6.53, 6.54, 7.17, 7.18 (4d, $^3J_{H-H}$ = 8.8 Hz, each 2H, 2 × C_6H_4). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ/ppm = 10.8, 29.5, 30.5, 30.6 (C_5Me_4), 33.6 ($C(CH_3)_3$), 39.3 ($C(CH_3)_3$), 52.5 (*C*H), 105.2, 109.8, 112.6, 118.8, 129.3 (C_5H_4), 112.5, 116.2, 120.7, 125.0, 132.8 (C_5Me_4), 112.7, 112.9, 119.4, 133.3 164.2, 164.4 (2 × C_6H_4). *Anal.* Calc. for $C_{31}H_{36}O_2S_2Zr$ (595.97): C, 62.47; H, 6.09; S, 10.76. Found: C, 63.09; H, 6.63; S, 11.28%.

4.6. Synthesis of $[Zr\{(CH_2{=}CHCH_2)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_2]$ (**7**)

The preparation of **7** was carried out in an identical manner to that of **6**; from **5** (0.50 g, 1.39 mmol) and HSC_6H_4-4-OMe (0.35 g, 2.78 mmol). Yield: 0.44 g, 54%. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ/ppm = 1.65, 1.67, 1.80 (3s, 6:3:3H, C_5Me_4), 2.84 (m, 2H, $CH_2CH{=}CH_2$), 3.09, 3.11 (2s, 2H, S*H*), 4.16 (t, $^3J_{H-H}$ = 8.5 Hz, 1H, C*H*), 5.05, 5.17 (m, 2H, $CH_2CH{=}CH_2$), 5.18, 5.34, 5.88, 5.97 (4m, 4H, C_5H_4), 5.88 (m, 1H, $CH_2CH{=}CH_2$), 6.54 (d, $^3J_{H-H}$ = 8.7 Hz, 4H, 2 × C_6H_4), 7.16, 7.17 (2d, $^3J_{H-H}$ = 8.4 Hz, 4H, 2 × C_6H_4) $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ/ppm 10.5, 10.7, 11.8, 13.7 (C_5Me_4), 39.7 (*C*H), 35.4 ($CH_2CH{=}CH_2$), 103.4, 106.1, 114.6, 116.7, 125.8 (C_5H_4), 109.2, 113.8, 116.2, 119.9, 126.7 (C_5Me_4), 116.6 ($CH_2CH{=}CH_2$), 118.0, 118.1, 119.4, 133.3, 136.0, 164.2, 164.3 (2 × C_6H_4). *Anal.* Calc. for $C_{30}H_{32}O_2S_2Zr$ (579.64): C, 62.13; H, 5.56; S, 11.06. Found: C, 60.79; H, 6.03; S, 9.75%.

4.7. Synthesis of [Zr(η5-C5H5)2(OC6H4-3-SH)2] (9)

Method a. To a solution of [Zr(η5-C5H5)2Me2] (**8**) (0.50 g, 1.98 mmol) in toluene (50 mL) was added HOC6H4-3-SH (0.50 g, 3.97 mmol) at room temperature. The evolution of methane was observed and the solution was stirred for 6 h. The resulting suspension was filtered and the solvent was dried in vacuo to yield a yellow solid (0.71 g, 75%). *Method b*. To a solution of [Zr(η5-C5H5)2Cl2] (0.50 g, 1.71 mmol) in toluene (50 mL) were added HOC6H4-4-SH (0.43 g, 3.42 mmol) and NEt3 (0.47 mL, 3.42 mmol) at room temperature. The resulting solution was stirred for 15 h. After filtration the solvent was evaporated to dryness and the residue washed with hexane (2 × 20 mL) to give complex **7** (0.47 g, 58%). IR (KBr; ν(cm^{-1})): ν_{SH} = 2581, ν_{ZrO} = 621. ^{1}H NMR (500 MHz, C6D6, 25 °C): δ/ppm = 3.22 (s, 2H, 2 × *SH*), 5.83 (s, 10H, 2 × C5*H*5), 6.43 (d, $^3J_{H-H}$ = 7.9 Hz, 2H, C6*H*4), 6.66 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, C6*H*4), 6.69 (s, 2H, C6*H*4), 6.93 (t, $^3J_{H-H}$ = 7.9 Hz, 2H, C6*H*4). ^{13}C{^{1}H} NMR (125 MHz, C6D6, 25 °C): δ/ppm = 113.4 (*C*5H5), 115.9, 119.3, 120.7, 130.2, 132.2, 166.2 (2 × *C*6H4). *Anal.* Calc. for C22H20O2S2Zr (471.75): C, 56.01; H, 4.27; S, 13.59. Found: C, 55.61; H, 4.38; S, 13.77%.

4.8. Synthesis of [Zr(η5-C5H5)2(OC6H4-4-SH)2] (10)

The preparation of **10** was carried out in an identical manner to that of **9**: *Method a*. From [Zr(η5-C5H5)2Me2] (**8**) (0.50 g, 1.98 mmol) and HOC6H4-4-SH (0.50 g, 3.97 mmol). Yield 0.73 g, 78%. *Method b*. From [Zr(η5-C5H5)2Cl2] (0.50 g, 1.71 mmol), HOC6H4-4-SH (0.43 g, 3.42 mmol) and NEt3 (0.47 mL, 3.42 mmol). Yield 0.56 g, 70%. IR (KBr; ν(cm^{-1})): ν_{SH} = 2538, ν_{ZrO} = 512. ^{1}H NMR (500 MHz, C6D6, 25 °C): δ/ppm = 3.21 (s, 2H, 2 × *SH*), 5.84 (s, 10H, 2 × C5*H*5), 6.48, 7.17 (2d, $^3J_{H-H}$ = 8.6 Hz, each 4H, 2 × C6*H*4). ^{13}C{^{1}H} NMR (125 MHz, C6D6, 25 °C): δ/ppm = 113.2 (C5H5), 117.6, 118.3, 119.1, 132.7, 133.1, 164.8 (2 × *C*6H4). *Anal.* Calc. for C22H20O2S2Zr (471.75): C, 56.01; H, 4.27; S, 13.59. Found: C, 56.21; H, 4.51; S, 13.26%.

4.9. Synthesis of [HNEt3]2[Zr(κ,O-OC6H4-4-SH)6] (12)

Method a. To a solution of [Zr{*t*-BuHC(η5-C5Me4)(η5-C5H4)}Cl2] (**11**) (0.50 g, 1.20 mmol) in THF (50 mL) were added NEt3 (0.33 mL, 2.40 mmol) and HOC6H4-4-SH (0.30 g, 2.40 mmol) at room temperature and stirred for 12 h to give a pale yellow oil and a colourless solution. The solution was filtered, concentrated and cooled to −30 °C to yield colourless crystals of the title complex (0.42 g, 33%). *Method b*. To a solution of ZrCl4 (0.50 g, 2.14 mmol) in toluene (50 mL) were added HOC6H4-4-SH (1.62 g, 12.87 mmol) and NEt3 (1.79 mL, 12.87 mmol) at room temperature and stirred for 15 h to give pale yellow oil and a colourless solution. The solution was filtered, concentrated and cooled to −30 °C to yield colourless crystals of the title complex (1.04 g, 46%). IR (KBr; ν(cm^{-1})): ν_{SH} = 2512, ν_{ZrO} = 498. ^{1}H NMR (500 MHz, C6D6, 25 °C): δ/ppm = 0.57 (t, $^3J_{H-H}$ = 7.1 Hz, 18H, 2 × [HN(CH2C*H*3)3]$^+$, 2.08 (q, $^3J_{H-H}$ = 7.1 Hz, 12H, 2 × [HN(C*H*2CH3)3]$^+$, 4.50 (s. broad, 6H, 6 × *SH*), 6.85, 7.24 (2d, $^3J_{H-H}$ = 8.4 Hz, each 12H, 6 × C6*H*4), 11.24 (s. broad, 2H, [*H*N(CH2CH3)3]$^+$). ^{13}C{^{1}H} NMR (125 MHz, C6D6, 25 °C): δ/ppm = 9.5 (2 × [HN(CH2CH3)3]$^+$), 45.8 (2 × [HN(CH2CH3)3]$^+$), 115.2, 121.5, 133.2, 163.7 (6 × *C*6H4). *Anal.* Calc. for C62H78N2O6S6Zr (1230.91): C, 60.50; H, 6.39; N, 2.28; S, 15.63. Found: C, 59.89; H, 7.07; N, 2.77; S, 17.16%.

4.10. X-ray structure determinations of [Zr{(t-Bu)HC(η5-C5Me4)(η5-C5H4)}(κ,S-SC6H4-4-OMe)2] (4) and [HNEt3]2[Zr(κ,O-OC6H4-4-SH)6] (12)

A summary of crystal data collection and refinement parameters for all compounds is given in Tables 1–4. The single crystals of **4** and **12** were mounted on a glass fibre and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å). Several sets of narrow data "frames" were collected using 0.3° wide ω scan frames covering the complete spheres of the reciprocal space with a crystal-to-detector distance of 6.0 cm. Data were integrated using SAINT [23] and an absorption correction was based on multiple scans with the program SADABS [24]. The software package SHELXTL version 6.12 [25] was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed using a "riding model" and were included in the refinement at calculated positions. For **3**, the *tert*-butyl group is disordered over two positions and this was modelled as a 50:50 mixture.

Table 4
Hydrogen bonds for compound **12** (Å, °).

D–H···A	*d*(H–A)	∠DHA	*d*(D···A)
N1–H1···O3	1.771(2)	175.8(1)	2.757(3)
C21–H21B···O(1A)[a]	2.477(2)	138.9(2)	3.287(3)

[a] The symmetry operation that generates the atoms is: −*x*, −*y*, −*z* + 1.

5. Supplementary material

CCDC 768525 and 768526 contain the supplementary crystallographic data for **3** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We gratefully acknowledge financial support from the Ministerio de Educación y Ciencia, Spain (Grant No. CTQ2009-09214), the Junta de Comunidades de Castilla-La Mancha (Grant No. PCI08-0032-0957) and the program Consolider-Ingenio 2010 ORFEO CSD2007-00006.

References

[1] D.C. Bradley, R.C. Mehrotra, A. Singh, I.P. Rothwell, Alkoxo and Aryloxo Derivatives of Metals, Academic Press, London, 2001.
[2] P. Sobota, Coord. Chem. Rev. 248 (2004) 1047.
[3] (a) J.M. Basset, B.C. Gates, J.P. Candy, A. Choplin, M. Leconte, F. Quignard, C. Santini, Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, Kluwer, Dordrecht, The Netherlands, 1988;
(b) C. Coperet, M. Chabanas, R.P. Saint-Arroman, J.M. Basset, Angew. Chem., Int. Ed. 42 (2003) 156.
[4] (a) J.R. Dilworth, J. Hu, Adv. Inorg. Chem. 40 (1993) 411, and references therein;
(b) D. Sellmann, R. Ruf, F. Knoch, M. Moll, Inorg. Chem. 34 (1995) 4745.
[5] (a) R.C. Fay, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 3, Pergamon Press, Oxford, 1987 (Chapter 32);
(b) M.H. Chisholm, I.P. Rothwell, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon Press, Oxford, 1987 (Chapter 15.3).
[6] (a) T.T. Nadasdi, D.W. Stephan, Inorg. Chem. 33 (1994) 1532;
(b) T.T. Nadasdi, D.W. Stephan, Inorg. Chem. 32 (1993) 5933;
(c) T.T. Nadasdi, Y. Huang, D.W. Stephan, Inorg. Chem. 32 (1993) 347;
(d) T.T. Nadasdi, D.W. Stephan, Organometallics 11 (1992) 116;
(e) D.W. Stephan, Organometallics 10 (1991) 2037;
(f) D.W. Stephan, J. Chem. Soc., Chem. Commun. (1991) 129;
(g) D.W. Stephan, Organometallics 9 (1990) 2718.
[7] (a) P. Jutzi, T. Redeker, B. Neumann, H.G. Stammler, Organometallics 15 (1996) 4153;
(b) P. Jutzi, T. Heidemann, B. Neumann, H.G. Stammler, J. Organomet. Chem. 472 (1994) 27.
[8] R. Fandos, C. Hernandez, A. Otero, A. Rodríguez, M.J. Ruiz, P. Terreros, J. Organomet. Chem. 606 (2000) 156.
[9] (a) R. Fandos, C. Hernandez, A. Otero, A. Rodríguez, M.J. Ruiz, P. Terreros, Eur. J. Inorg. Chem. (2003) 493;
(b) R. Fandos, M. Lanfranchi, M.A. Pellinghelli, A. Otero, M.J. Ruiz, P. Terreros,

Organometallics 15 (1996) 4725;
(c) A. Antiñolo, F. Carrillo-Hermosilla, A. Corrochano, R. Fandos, J. Fernández-Baeza, A.M. Rodríguez, M.J. Ruiz, A. Otero, Organometallics 18 (1999) 5219.
[10] (a) A. Antiñolo, R. Fernández-Galán, A. Otero, S. Prashar, I. Rivilla, A.M. Rodríguez, M.A. Maestro, Organometallics 23 (2004) 5108;
(b) A. Antiñolo, R. Fernández-Galán, A. Otero, S. Prashar, I. Rivilla, A.M. Rodríguez, J. Organomet. Chem. 691 (2006) 2924;
(c) A. Antiñolo, R. Fernández-Galán, N. Molina, A. Otero, I. Rivilla, A.M. Rodríguez, J. Organomet. Chem. 694 (2009) 1959.
[11] (a) A. Antiñolo, M. Fajardo, S. Gómez-Ruiz, I. López-Solera, A. Otero, S. Prashar, A.M. Rodríguez, J. Organomet. Chem. 683 (2003) 11;
(b) D. Polo-Cerón, S. Gómez-Ruiz, S. Prashar, M. Fajardo, A. Antiñolo, A. Otero, Eur. J. Inorg. Chem. (2007) 4445.
[12] J.A. Samuels, E.B. Lobkovsky, W.E. Streib, K. Folting, J.C. Huffman, J.W. Zwanziger, K.G. Caulton, J. Am. Chem. Soc. 115 (1993) 5093.
[13] T.C. Rosen, K. Kirschbaum, D.M. Giolando, J. Chem. Soc., Dalton Trans. (2003) 120.
[14] R.A. Kresinski, L. Isam, T.A. Hamor, C.J. Jones, J.A. McCleverty, J. Chem. Soc., Dalton Trans. (1991) 1835.
[15] (a) R. Fandos, J. Fernández-Gallardo, M.I. López-Solera, A. Otero, A. Rodríguez, M.J. Ruiz, P. Terreros, Organometallics 27 (2008) 4803;
(b) D.J. Cardin, M.F. Lappert, C.L. Raston, Chemistry of Organo-Zirconium and Hafnium Compounds, Ellis Horwood Limited, Halsted Press, New York, 1986.
[16] (a) M.F. Lappert, C.J. Pickett, P.I. Riley, P.I.W. Yarrow, J. Chem. Soc., Dalton Trans. (1981) 805;
(b) J.L. Atwood, G.K. Barker, J. Holton, W.E. Hunter, M.F. Lappert, R. Pearce, J. Am. Chem. Soc. 99 (1977) 6645;
(c) M.F. Lappert, P.I. Riley, P.I.W. Yarrow, J.L. Atwood, W.E. Hunter, M.J. Zaworotko, J. Chem. Soc., Dalton Trans. (1981) 814;
(d) A. Antiñolo, R. Fernández-Galán, B. Gallego, A. Otero, S. Prashar, A.M. Rodríguez, Eur. J. Inorg. Chem. (2003) 2626.
[17] (a) T. Koch, S. Blaurock, F.B. Somoza Junior, A. Voigt, R. Kirmse, E. Hey-Hawkins, Organometallics 19 (2000) 2556;
(b) I.E. Nifant'ev, P.V. Ivchenko, V.V. Bagrov, L.G. Kuz'mina, Organometallics 17 (1998) 4734;
(c) E.S. Cho, U.G. Joung, B.Y. Lee, H. Lee, Y.-W. Park, Ch.-H. Lee, D.M. Shin, Organometallics 23 (2004) 4693;
(d) J.C. Green, M.L.H. Green, G.C. Taylor, J. Saunders, J. Chem. Soc., Dalton Trans. (2000) 317;
(e) I.F. Urazowski, L.O. Atovmyan, S.G. Mkoyan, R. Broussier, P. Perron, B. Gautheron, F. Robert, J. Organomet. Chem. 536 (1997) 531;
(f) C.E. Zachmanoglou, A. Docrat, B.M. Bridgewater, G. Parkin, C.G. Brandow, J.E. Bercaw, C.N. Jardine, M. Lyall, J.C. Green, J.B. Keister, J. Am. Chem. Soc. 124 (2002) 9525;
(g) B.Y. Lee, Y.H. Kim, Y.C. Won, J.W. Han, W.H. Suh, I.S. Lee, Y.K. Chung, K.H. Song, Organometallics 21 (2002) 1500;
(h) A.D. Miller, J.L. McBee, T.D. Tilley, J. Am. Chem. Soc. 130 (2008) 4992.
[18] W.A. Howard, T.M. Trnka, G. Parkin, Inorg. Chem. 34 (1995) 5900.
[19] (a) C.R. Baar, C.J. Levy, E.Y-J. Min, L.M. Henling, M.W. Day, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 8216;
(b) N.W. Alcock, H.J. Clase, D.J. Duncalf, S.L. Hart, A. McCamley, P.J. McCormack, P.C. Taylor, J. Organomet. Chem. 605 (2000) 45;
(c) V.W.-W. Yam, G.-Z. Qi, K.-K. Cheung, J. Organomet. Chem. 548 (1997) 289.
[20] M.S. Rozenberg, T. Nishio, T. Steiner, New J. Chem. 23 (1999) 585.
[21] (a) W. Stüer, K. Kirschbaum, D.M. Giolando, Angew. Chem., Int. Ed. Engl. 33 (1994) 1981;
(b) C.J. Carmalt, C.W. Dinnage, I.P. Parkin, J.W. Steed, Inorg. Chem. 39 (2000) 2693;
(c) C.J. Carmalt, C.W. Dinnage, I.P. Parkin, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (2000) 3500.
[22] E. Samuel, M.D. Rausch, J. Am. Chem. Soc. 95 (1973) 6263.
[23] SAINT+ v7.12a, Area-Detector Integration Program, Bruker-Nonius AXS, Madison, Wisconsin, USA, 2004.
[24] G.M. Sheldrick, SADABS Version 2004/1, A Program for Empirical Absorption Correction, University of Göttingen, Göttingen, Germany, 2004.
[25] SHELXTL-NT Version 6.12, Structure Determination Package, Bruker-Nonius AXS, Madison, Wisconsin, USA, 2001.