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

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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 $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me_2]$ (**1**) led to the formation of monosubstituted complexes $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me(\kappa,S\text{-}SC_6H_4\text{-}n\text{-}OMe)]$ (*n* = 2 (**2**); *n* = 3 (**3**)) and the disubstituted complex $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa,S\text{-}SC_6H_4\text{-}4\text{-}OMe)_2]$ (**4**). The complexes $[Zr\{(R)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_2]$ (R = *t*-Bu (**6**); R = $CH_2CH{=}CH_2$ (**7**)) and $[Zr(\eta^5\text{-}C_5H_4)_2(OC_6H_4\text{-}n\text{-}SH)_2]$ (*n* = 3 (**9**); *n* = 4 (**10**)) have been synthesized using the corresponding dimethyl zirconocene and mercaptophenol. However, the reaction of $[Zr\{(t\text{-}Bu)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (**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 $[HNEt_3]_2[Zr(\kappa,O\text{-}OC_6H_4\text{-}4\text{-}SH)_6]$ (**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 $[Zr(\eta^5\text{-}C_5H_4)_2Cl_2]$ gave the unexpected disubstituted complex $[Zr(\eta^5\text{-}C_5H_4)_2(OC_6H_4\text{-}4\text{-}SH)_2]$ (**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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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

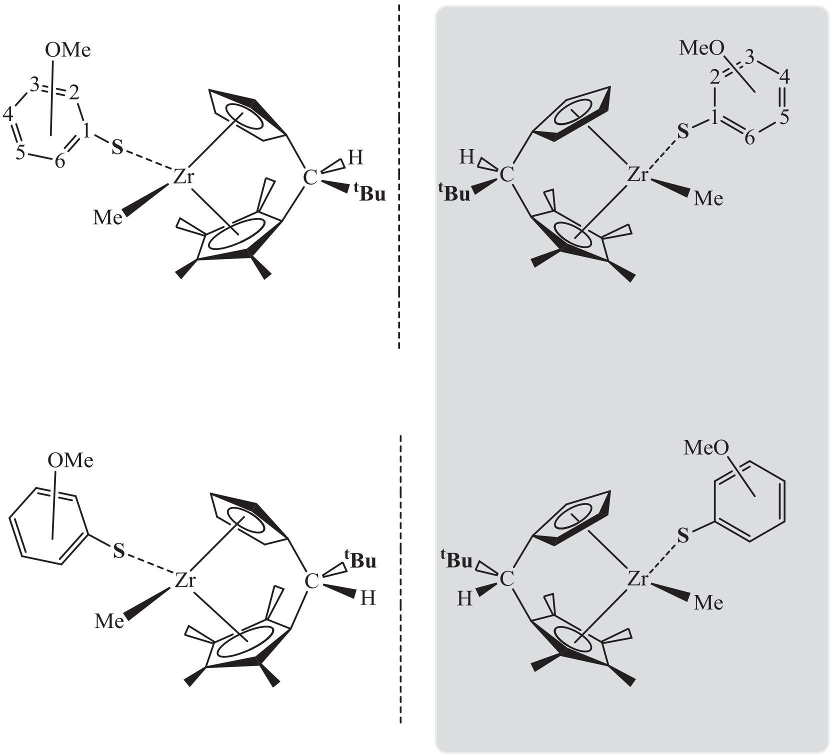
The most widely used methods for the synthesis of alkoxide or thiolate derivatives of early transition metals are (a) the reaction of appropriate metal halide precursors with alcohols or thiols in the presence of an amine such as NEt_3, which promotes the elimination of X^- by formation of the corresponding 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 $HSC_6H_4\text{-}n\text{-}OMe$, ($n = 2$, 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 $HSC_6H_4\text{-}2\text{-}OMe$ and $HSC_6H_4\text{-}3\text{-}OMe$ 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 $HSC_6H_4\text{-}4\text{-}OMe$ 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**.