



The preparation and characterisation of a series of group IV metallocene dithiolato complexes containing a naphthalene backbone

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Dedicated to Prof. M.B. Hursthouse on the occasion of his 65th birthday, in recognition of the enormous contribution he has made to chemical crystallography.

Abstract

Reduction of the sulfur–sulfur bond of naphtho[1,8-*cd*]-1,2-dithiole with 2 equivalents of Li(BEt)₃H to give the dilithium salt followed by the addition of an equivalent of bis(pentamethyl)metallocene dichloride [(Cp)^{*}₂MCl₂, M = Ti, Zr, Hf, Cp^{*} = C₅Me₅] gives the sulfur bonded complexes (Cp)^{*}₂TiS₂C₁₀H₆ (**1**), (Cp)^{*}₂ZrS₂C₁₀H₆ (**2**) and (Cp)^{*}₂HfS₂C₁₀H₆ (**3**) containing six-membered MS₂C₃ rings. The products were obtained in moderate yield as crystals and have been fully characterised and had their X-ray crystal structures determined.

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1. Introduction

The chemistry of the group IV metallocenes has been extensively studied with the majority of the work on complexes of titanocene. Complexes containing a bidentate ligand bound to titanium are quite common, with many examples via a pair of chalcogen atoms. These chalcogens can be bridged by groups such as other chalcogen atoms to give a polychalcogen ring [1,2], phosphorus [3], alkyl groups [4] or nitrogen [5]. Titanocene can also give complexes bound to two monodentate ligands which are essentially similar complexes where the two chalcogen atoms are not connected to each other [6]. These have practical uses in that they can be used in ligand transfer to give platinum thiolato complexes [7]. More recently, we have synthesised a series

of titanocene complexes containing a mixture of thiolato, sulfinato and sulfenato ligands [8] linked by an organic aromatic backbone. Dimeric titanocene complexes with two bridging thiolato ligands have been reported [9] and shown to exhibit crown ether like properties, with a silver or copper cation contained in the centre of the structure.

Complexes of zirconocene with a bidentate phosphorus ring [10] or sulfur ring [1], or with two monodentate nitrogen bound ligands have been described [11]. The majority of other chalcogen containing zirconocene complexes contain either two monodentate ligands [12–15] or exist as dimers with two bridging chalcogen atoms [16–18].

Hafnocene is known to exist in a similar complex to zirconocene with two phosphorus atoms bound to the hafnium atom and another phosphorus atom bridging the two to give a four-membered ring [10] and Cp^{*}₂HfH₂ has also been shown to react with RN₃ to give

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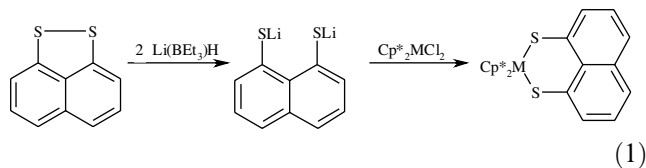
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an interesting complex with a bidentate N_3 ligand which will lose N_2 at 80 °C [19]. Hafnocene complexes with two monodentate ligands bound through carbon [20] which will thermally decompose to give a complex containing one bidentate ligand are known. Similarly to titanocene and zirconocene complexes, hafnocene complexes with two monodentate sulfur bound ligands have also been described [21] while a dimeric structure with two bridging chalcogen atoms has been reported [18].

However, there are very few examples of a homologous series of complexes being produced to allow comparison of all three members of the group. Here, we report the synthesis and X-ray crystal structures of a series of three group IV metallocene complexes containing a bidentate aromatic ligand bound to the metal centre through two sulfur atoms.

2. Results and discussion

The salt elimination reactions of the dilithium salt of naphtho[1,8-*cd*]-1,2-dithiole with the group IV bis(pentamethyl)metallocene dichlorides $Cp_2^*MCl_2$ ($M = Ti, Zr, Hf$) proceed smoothly in tetrahydrofuran at room temperature to give $Cp_2^*TiS_2C_{10}H_6$ (**1**), $Cp_2^*ZrS_2C_{10}H_6$ (**2**) and $Cp_2^*HfS_2C_{10}H_6$ (**3**) in moderate yield (34–64%)



The purification and isolation of these compounds is straightforward; removal of insoluble salts by re-dissolving in toluene and filtering through celite followed by recrystallisation from toluene/hexane gives crystals which are of extremely high purity. The 1H NMR data (CD_2Cl_2) for complexes **1–3** all show the expected peaks, with three separate multiplets in the aromatic region (7.05–7.52 ppm) representing the three pairs of different protons on the naphthalene backbone and a singlet at 1.81, 1.84 and 1.87 ppm, respectively, representing the 10 methyl groups on the cyclopentadienyl rings. No fluxionality was noticed in the 1H NMR spectra of these complexes down to 183 K. The ^{13}C NMR (CD_2Cl_2) are also excellent, each displaying the three quaternary and three non quaternary peaks of the naphthalene backbone plus a peak representing the quaternary carbon atoms of the cyclopentadienyl rings and a single peak at 12.7, 11.6 and 10.5 ppm, respectively, representing the carbon of the ten methyl groups bound to the cyclopentadienyl rings.

Excellent elemental analyses were obtained for all complexes and electrospray mass spectral data were consistent with the proposed structures showing in each case $[M]^+$ and $[M + Na]^+$.

3. Molecular structures

The crystal structures of **1–3** (Fig. 1, Tables 1 and 2) are very similar, indeed they are isomorphous which allows for a comparison of bond lengths and angles which are not influenced by packing effects. All three complexes exist in an envelope conformation folded along the sulfur–sulfur axis. The S–M–S bond angles are in the range 82.40(2)–83.82(4)°; close to previously studied complexes containing a six-membered TiS_2C_3 ring [8]. The other angles in these six-membered rings are also in accord with the literature values. The angle which varies most markedly between the three complexes is the splay angle (the deviation from the two S–C bonds being parallel). The splay angles of complexes **1–3** are 21.0°, 22.8° and 22.9°, respectively. This can be explained by the size of the metal atom which is between the two sulfur atoms, resulting in longer M–S distances and causing the S–C bonds to stray from being parallel. Zirconium has a greater atomic radius than titanium, therefore it forces the sulfur atoms further apart and gives a larger splay angle. Hafnium has a very similar atomic radius to zirconium so has a similar effect on the splay angle. The bond lengths in **1–3** are also very similar and are close to the values in related complexes. The only bond lengths which differ slightly are the M–S and M–Cp bond lengths. The M–S(1) bond lengths of complexes **1–3** are 2.406(2), 2.5033(7) and 2.4832(13) Å, respectively, while the M–S(9) bond lengths are 2.428(2), 2.5107(7) and 2.4901(10) Å. These results are to be expected when the atomic radii of the three metal atoms are considered. The M–S bond lengths are very close to similar complexes [12–14,17,21–25]. This pattern where the Zr–S and Hf–S bond lengths are both very similar and noticeably longer than the Ti–S bond length has been seen before in a series of group IV metallocene complexes [26]. The M–Cp bond lengths show an identical pattern to that previously mentioned for the M–S bond lengths.

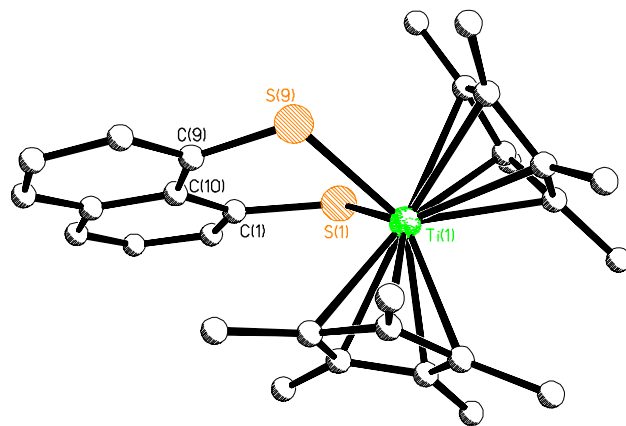


Fig. 1. Molecular structure of $Cp_2^*Ti(S_2C_{10}H_6)$ **1** in the crystal. The structures of **2** and **3** are isomorphous and have been numbered analogously.

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