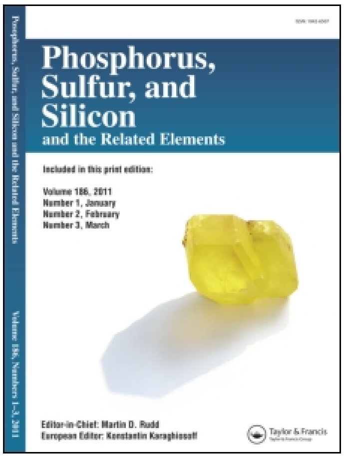


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Aspects of Dithiolene Chemistry of Cyclopentadienyl Ti, Zr and Hf Complexes

Hellfried Balz[a]; Hartmut Köpf[a]; Katharina Lange[a]; Joachim Pickardt[a]
[a] Institut für Anorganische und Analytische Chemie, Technische Universitat, Berlin, Germany

To cite this Article Balz, Hellfried , Köpf, Hartmut , Lange, Katharina and Pickardt, Joachim(1992) 'New Aspects of Dithiolene Chemistry of Cyclopentadienyl Ti, Zr and Hf Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 185 — 188

To link to this Article: DOI: 10.1080/10426509208055349

URL: http://dx.doi.org/10.1080/10426509208055349

Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 185–188

NEW ASPECTS OF DITHIOLENE CHEMISTRY OF CYCLOPENTADIENYL Ti, Zr AND Hf COMPLEXES

HELLFRIED BALZ, HARTMUT KÖPF, KATHARINA LANGE
and JOACHIM PICKARDT
Institut für Anorganische und Analytische Chemie, Technische
Universität, D-1000 Berlin, Germany

Abstract The preparation and ^{1}H n.m.r. data of the new dithiolene type complexes $[Ph_4P]^+[CpTi(1,2\text{-}S_2C_6H_4)_2]^-$ (Cp= η^5-C_5H_5) (**1**) and $[(Cp'_2M)_2(1,2,4,5\text{-}S_4C_6H_2)]$ (Cp'= η^5-$C_5H_4SiMe_3$, M=Ti, **2**; Zr, **3**; Hf, **4**) are presented. The molecular structures of **1**, **2** and **4** have been determined by X-ray diffraction analysis.

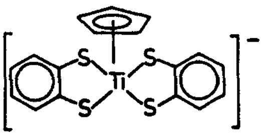
INTRODUCTION

Two different types of chelate complexes of the titanium triad, containing 4,5-benzo-1,3-dithia-2-metallacyclopentane rings, have been investigated: type **A**, comprising one mono(cyclopentadienyl)metal(IV) unit coordinated to two bidentate benzene-1,2-dithiolate ligands in a complex anion, and type **B**, consisting of two bis(cyclopentadienyl)metal(IV) moieties linked to a tetradentate benzene-1,2,4,5-tetrathiolate bridging centre.

PREPARATION OF COMPLEXES

A complex of type **A** was prepared by the reaction of $CpTiCl_3$ with two equivalents of 1,2-$(LiS)_2C_6H_4$ and one equivalent of Ph_4PBr in acetone/pentane (Eq. 1).

$$CpTiCl_3 + 2\ 1,2\text{-}(LiS)_2C_6H_4 + Ph_4PBr \longrightarrow LiBr + 3\ LiCl + [Ph_4P]^+$$



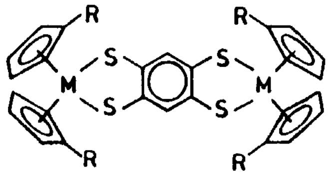
(1)

1

Dark violet crystals of **1** were obtained from CH_2Cl_2/pentane; C, H analysis as well as i.r. and ^{1}H n.m.r. data (CD_2Cl_2, δ= 6.06 ppm, singlet, Cp; 7.02 ppm, AA'BB' multiplet, C_6H_4; 7.65 ppm, multiplet, Ph) were consistent with the formulation of **1** as the proposed complex salt.

Three complexes of type **B** were obtained by the reaction of Cp'_2MCl_2 with tetrasodium-1,2,4,5-tetramercaptobenzene in tetrahydrofuran (thf) (Eq. 2).

$2\ Cp'_2MCl_2 + 1,2,4,5\text{-}(NaS)_4C_6H_2 \longrightarrow 4\ NaCl +$



(2)

R = $SiMe_3$; M = Ti, **2**; Zr, **3**; Hf, **4**.

Compounds **2** (dark green), **3** (orange) and **4** (light red) were recrystallised from $CHCl_3$ and revealed C, H analysis, i.r. and ^1H n.m.r. data (e.g., **2**, thf-d_8, δ = 0.22 ppm, singlet, $SiMe_3$; 6.15 and 6.38 ppm, broad singlets, C_5H_4; 7.52 ppm, singlet, C_6H_2) according to the formula in Eq. (2). Complexes **1** - **4** are air-stable as solids, but are less stable in solution.

STRUCTURE DETERMINATION

The molecular structures of complexes **1** (R = 0.068), **2** (R = 0.107) and **4** (R = 0.069) have been investigated by single crystal X-ray diffraction studies. The structure of the complex anion of **1** (space group $P2_1/c$) is shown in Fig. 1; Fig. 2 represents the structure of **4** which is isostructural with **2** ($P\bar{1}$). Some structural data of **1** and **2** are summarised in Table I.

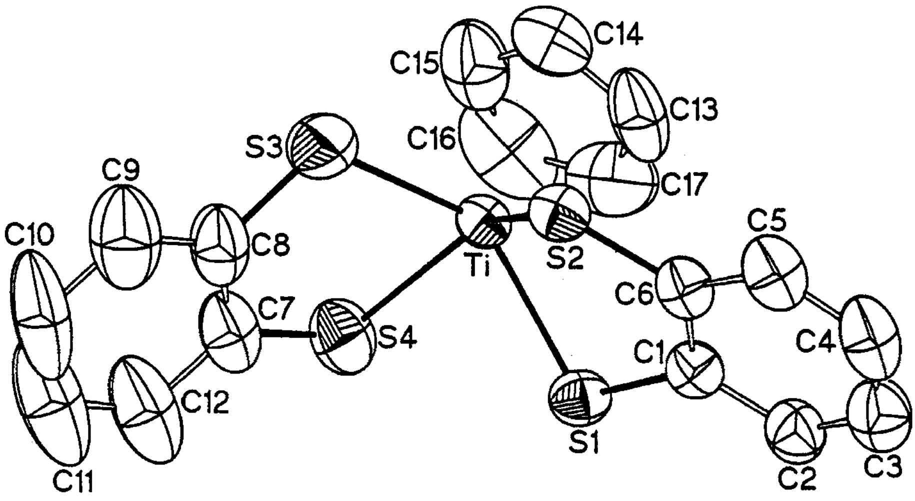


FIGURE 1 ORTEP plot of the anion of **1**, $[\eta^5C_5H_5\text{-}Ti(1,2\text{-}S_2C_6H_4)_2]^-$

TABLE I Selected average bond lengths (pm) and angles (°) for **1** and **2**

		1	**2**
Bond lengths	Ti-S	240.9	242.6
	Ti-C(Cp)	236	239
	Ti-Cp^a	206	207
	S-C^b	174	175
	C-C^b	139	145
	Si-C(Cp)	–	187
Bond angles	S-Ti-S^b	81	81
	Ti-S-C^b	104	97
	S-C-C^b	120	120
	Cp-Ti-Cp^a	–	131
	Dihedral angle^c	30	47

a = centroid of cyclopentadienyl ring; b = bond lengths or angles within chelate rings; c = dihedral angle between S-Ti-S and S-C-C-S planes within the chelate rings.

In the anion of **1** (Fig. 1), the five-coordinate titanium atom is situated in the centre of a tetragonal pyramid. The basal plane of this pyramid is formed by the four sulphur atoms of the two benzene-dithiolate ligands, the apex is occupied by the centre of the Cp ring. The two five-membered TiS_2C_2 chelate rings are folded along the S-S axes by 30° (average value), with one chelate ring plane arranged *exo*, the other *endo* referred to the Cp ligand.

The neutral complexes **2** (M=Ti) and **4** (M=Hf) (Fig. 2) are isostructural with C_i molecular symmetry. The two metal atoms in each binuclear complex are coordinated in the manner of a distorted tetrahedron, formed by the centres of two trimethylsilyl-substituted Cp rings and by the two *ortho*-sulphur atoms of the bridging benzene-tetrathiolate ligand. The $MS_2C_6H_2S_2M$ moieties are in chair-like *trans* conformations with the MS_2 planes inclined by 47° for **2** and 52° for **4** with respect to the $S_2C_6S_2$ plane. This indicates a stronger chelate ring folding in **2** and **4** compared to the bis(chelate) **1**.

As can be seen from Table I, the more pronounced steric overcrowding of the two trimethylsilyl-substituted Cp ligands in **2** compared to the single unsubstituted Cp ring in **1** obviously leads to enhanced Ti-C(Cp), Ti-Cp(centroid) and Ti-S bond lengths in **2**. Similarly, the S-C and C-C distances within the chelate rings of the anionic **1** are contracted in comparison to the bridging chelate rings of the neutral **2**.

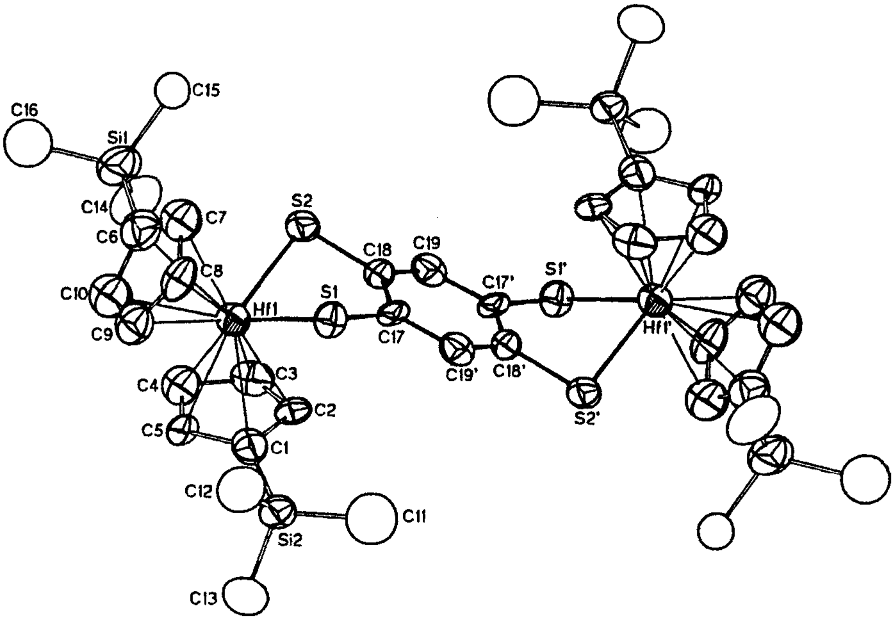


Fig. 2 ORTEP plot of the neutral complex **4**, $[\{\eta^5\text{-}Me_3SiC_5H_4)_2HfS_2\}_2 1,2,4,5\text{-}C_6H_2]$

Whereas the S-Ti-S (81°) and S-C-C (120°) bond angles are equal within the chelate rings of **1** and **2**, the Ti-S-C bond angles differ in **1** and **2**, due to the different chelate ring folding in both complexes.

The complex anion of **1** is related to the neutral species ß-$C_{10}H_{10}TiS_5$ which also reveals tetragonal-pyramidal coordination around titanium(IV)[1]. The chair-like *trans* conformation of the chelate bridge of **2** and **4** is related to the arrangement found in $[(Cp_2TiS_2)_2C_2]$ which, in contrast to the benzene ring in **2** and **4**, contains a central ethylene C_2 unit[2].

REFERENCES

1. D. M. Giolando and T.B. Rauchfuss, J. Am. Chem. Soc., **106**, 6455 (1984).
2. H. A. Harris, A. D. Rae and L. F. Dahl, J. Am. Chem. Soc., **109**, 4739 (1987).