

# [CpTi( $\mu_3$ -S) $_3$ {Rh(tfbb)} $_3$ ]: An early–late heterometallic complex as molecular model for the deactivation of metal sulphide catalysts

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## Abstract

The heterotetranuclear complex [CpTi( $\mu_3$ -S) $_3$ {Rh(tfbb)} $_3$ ] (1) (tfbb = tetrafluorobenzobarrelene) has been prepared in moderate yield by reacting Cp $_2$ Ti(SH) $_2$  with [Rh( $\mu$ -MeO)(tfbb) $_2$ ] in toluene at room temperature, and its structure has been determined by an X-ray diffraction study. Crystals of 1 are monoclinic, space group  $P2_1/a$ , with cell parameters  $a = 19.975(4)$ ,  $b = 27.352(6)$ ,  $c = 8.186(3)$  Å,  $\beta = 97.15(2)^\circ$  and  $Z = 4$ . The complex displays an incomplete distorted cubane-type structure, involving the four metals and the three triple-bridging sulphur atoms. The metals exhibit usual pseudotetrahedral (Ti) and distorted square-planar (Rh) environments. This molecular structure could be considered as a molecular analogue for the understanding of poisoning of commercial metal sulphide catalysts. The direct bonding of titanium with sulphur atoms and the intermetallic Ti–Rh interactions, 2.912–2.940(3) Å, could be involved in these undesirable processes. Replacement reactions of the diolefin ligands in 1 by CO and PPh $_3$  occur with retention of the structure and nuclearity giving [CpTi( $\mu_3$ -S) $_3$ {Rh(CO) $_2$ } $_3$ ] (2) and [CpTi( $\mu_3$ -S) $_3$ {Rh(CO)(PPh $_3$ )} $_3$ ] (3), showing the remarkable stability of the incomplete cubane framework containing early and late transition metals bridged by sulphido ligands.

**Keywords:** Ti; Rh; X-ray structure; Heterometallic complex; Cubane structure

## 1. Introduction

There is increasing interest in transition metal–sulphur chemistry due to its relevance to the petroleum and/or coal refining industry, especially associated with the prominent use of sulphide catalysts in hydrotreatment reactions (HTRs), particularly hydrodesulphurization [1]. The usual catalysts for these processes imply the commonly designated cobalt or nickel molybdenum supported catalysts. Unfortunately, the presence of small amounts of early transition metals in the raw materials (vanadium in heavy petroleum fractions and titanium in coal) causes significant deactivation of the active sites. In that sense, it has been reported that the formation of vanadium sulphides has deleterious consequences on the activity and life time of the heterogeneous Co/Mo/S

catalysts currently used [2] and that titanium is one of the major constituents of the metal deposits responsible for deactivation of liquefied coal hydrotreatment catalysts [3]. Knowledge of the poisoning metal–sulphide catalyst interaction could be useful to understand the deactivation mechanism.

Furthermore, it has been confirmed that Group VIII metal sulphides exhibit greater activity than the related molybdenum or tungsten analogues [4]. Thus, the preparation of heterometallic complexes of these more active Group VIII metals and early transition metals, which act as poisons in some instances, is interesting both in itself and to rationalise the interactions of sulphur with early transition metals such as titanium. We herein report the synthesis and structure of an unusual heterotetranuclear complex, showing interesting structural features, to be considered as a molecular analogue for the modelization of titanium deposition on metal (rhodium) sulphide catalyst.

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## 2. Results and discussion

In the course of our research on heteropolynuclear rhodium metal complexes tailored through sulphur-containing ligands [5], we have explored the ability of the bis-hydrosulphido titanium complex  $\text{Cp}_2\text{Ti}(\text{SH})_2$  to act as metalloligand and then as synthon for early-late heterometallic complexes. We have found that the reaction of  $\text{Cp}_2\text{Ti}(\text{SH})_2$  with  $[\text{Rh}(\mu\text{-OMe})(\text{tfbb})_2]$  (tfbb = tetrafluorobenzobarrelene) in toluene at room temperature gives bright yellow microcrystals (**1**) and a red-brown solution. Spectral data of the solid (see Experimental section) are not in agreement with the expected trinuclear compound  $[\text{Cp}_2\text{Ti}(\mu_3\text{-S})_2(\text{Rh}(\text{tfbb}))_2]$  resulting from the protonation of the methoxide bridges in the dinuclear rhodium complex by the hydrosulphido ligands and formation of the sulphido-bridged complex. On the contrary, its mass spectrum indicates the formation of a tetranuclear  $[\text{TiRh}_3]$  complex, since the molecular ion at 1197 could be in accordance with either the fragment  $[\text{Cp}_2\text{Ti}(\mu\text{-S})(\text{Rh}(\text{tfbb}))_3]^+$  or the species  $[\text{CpTi}(\mu_3\text{-S})_3(\text{Rh}(\text{tfbb}))_3]^+$ . In addition, its  $^1\text{H}$  NMR spectrum shows a fluxional behaviour associated to the diolefinic ligands, since their resonances are relatively broad and featureless, and supports the second formula-

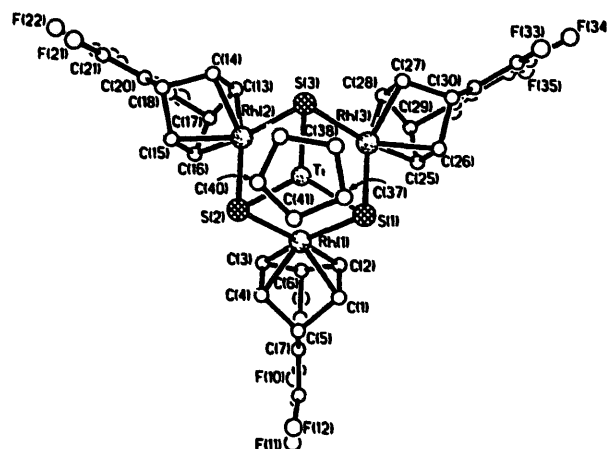


Fig. 1. View of the molecular structure of the complex  $[\text{CpTi}(\mu_3\text{-S})_3(\text{Rh}(\text{tfbb}))_3]$  (**1**) along the Ti–Cp(centroid) direction with the atom numbering scheme.

tion since the Cp:tfbb observed ratio is just 1:3. In order to confirm the loss of a cyclopentadienyl ligand during the reaction and to ascertain the structural features of **1** an X-ray diffraction study was undertaken.

The molecular structure of **1** is shown in Fig. 1 and the significant bond distances and angles are collected

Table 1

Selected bond distances (Å) and angles (°) for the complex  $[\text{CpTi}(\mu_3\text{-S})_3(\text{Rh}(\text{tfbb}))_3]$  (**1**)<sup>a</sup>

Ti–S(1)	2.290(4)	Rh(1)···Ti	2.919(3)
Ti–S(2)	2.298(4)	Rh(1)–S(1)	2.324(4)
Ti–S(3)	2.297(5)	Rh(1)–S(2)	2.338(4)
Ti–C(37)	2.350(18)	Rh(1)–C(1)	2.089(15)
Ti–C(38)	2.289(18)	Rh(1)–C(2)	2.147(16)
Ti–C(39)	2.371(15)	Rh(1)–C(3)	2.155(15)
Ti–C(40)	2.371(15)	Rh(1)–C(4)	2.078(16)
Ti–C(41)	2.330(17)	Rh(3)···Ti	2.912(3)
Rh(2)···Ti	2.940(3)	Rh(3)–S(1)	2.311(4)
Rh(2)–S(2)	2.336(4)	Rh(3)–S(3)	2.331(4)
Rh(2)–S(3)	2.329(4)	Rh(3)–C(25)	2.092(19)
Rh(2)–C(13)	2.135(17)	Rh(3)–C(26)	2.096(17)
Rh(2)–C(14)	2.131(14)	Rh(3)–C(27)	2.111(18)
Rh(2)–C(15)	2.118(15)	Rh(3)–C(28)	2.118(18)
Rh(2)–C(16)	2.163(15)	C(3)–C(4)	1.352(25)
C(1)–C(2)	1.348(24)	C(15)–C(16)	1.336(23)
C(13)–C(14)	1.334(21)	C(27)–C(28)	1.318(27)
C(25)–C(26)	1.346(27)		
S(1)–Ti–S(2)	102.4(2)	S(1)–Rh(1)–S(2)	100.2(1)
S(1)–Ti–S(3)	102.6(2)	S(1)–Rh(1)–M(1)	94.1(5)
S(1)–Ti–G	114.2(5)	S(1)–Rh(1)–M(2)	162.7(5)
S(2)–Ti–S(3)	102.2(2)	S(2)–Rh(1)–M(1)	163.4(5)
S(2)–Ti–G	117.3(5)	S(2)–Rh(1)–M(2)	94.5(5)
S(3)–Ti–G	116.0(5)	M(1)–Rh(1)–M(2)	70.2(6)
S(2)–Rh(2)–S(3)	100.1(1)	S(1)–Rh(3)–S(3)	100.9(1)
S(2)–Rh(2)–M(3)	162.1(5)	S(1)–Rh(3)–M(5)	92.9(5)
S(2)–Rh(2)–M(4)	94.4(5)	S(1)–Rh(3)–M(6)	161.4(5)
S(3)–Rh(2)–M(3)	95.5(5)	S(3)–Rh(3)–M(5)	161.1(5)
S(3)–Rh(2)–M(4)	163.0(4)	S(3)–Rh(3)–M(6)	95.1(5)
M(3)–Rh(2)–M(4)	68.9(6)	M(5)–Rh(3)–M(6)	69.5(7)

<sup>a</sup> M(1), M(2), M(3), M(4), M(5) and M(6) are the midpoints of the olefinic bonds C(1)–C(2), C(3)–C(4), C(13)–C(14), C(15)–C(16), C(25)–C(26) and C(27)–C(28) respectively. G represent the centroid of the cyclopentadienyl ligand.

in Table 1. The complex is tetranuclear with one titanium and three rhodium atoms engaged through three alternated triple-bridging sulphur atoms, each connecting two rhodiums to the titanium centre. The titanium exhibits a pseudotetrahedral environment (three-legged piano stool geometry) joined to the sulphur atoms and to an  $\eta^5$ -cyclopentadienyl ligand. Each rhodium centre is bonded to two sulphide atoms, and completes a distorted square-planar coordination linked to a tfbb molecule, interacting in an  $\eta^2$ -fashion through the two olefinic bonds. Excepting the cyclopentadienyl ligand, the whole molecule shows an approximate  $C_{3v}$  symmetry (Fig. 1), with the three-fold axis along the Ti–Cp(centroid) direction.

Interestingly, the central  $TiRh_3S_3$  core exhibits an incomplete cubane-type structure, with one vacant site close to the three rhodium atoms (Fig. 2a). The internal bond angles in this cubane cluster deviate slightly (max.  $13.2^\circ$ ) from the ideal value of  $90^\circ$  (S–Ti–S  $102.2$ – $102.6(2)^\circ$ ; S–Rh–S  $100.1$ – $100.9(1)^\circ$ ; Ti–S–Rh  $78.0$ – $78.9(1)^\circ$ ; Rh–S–Rh  $96.2$ – $103.2(1)^\circ$ ). Remarkably, this type of heterometallic cubane structure has already been associated to the promotion of hydrodesulphurization activity by the addition of 3d late transition metals (Ni or Co) to the 4d early transition metal-based catalysts (Mo or W) [6].

All the Ti–S bond distances are statistically identical ( $2.290$ – $2.298(4)$  Å), and significantly shorter than those observed in related thiolate-bridged heterometallic CpTi/Rh complexes [CpTi(SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>Rh(nbd)] ( $2.397$ – $2.541(3)$  Å) or [CpTi(SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>(Rh(nbd))<sub>2</sub>] ( $2.466$ – $2.496(7)$  Å), even considering the value for a terminal thiolate ligand ( $2.380(3)$  Å) [7]. This fact characterises the titanium–sulphur bonds as strong ones, conferring apparently to the whole Ti–S<sub>3</sub> unit a relatively high stability, in agreement with the reactivity explored (vide infra). Opposite to the sulphur atoms, the titanium is linked to the carbon atoms of the Cp ligand with slightly different Ti–C bond distances,  $2.29$ –

$2.37(2)$  Å, probably due to the different symmetry of this group compared with that of the rest of the molecule, *trans* disposed to the cyclopentadienyl ring. The S–Ti–Cp(centroid) angles are in the range expected for a pseudotetrahedral coordination,  $114.2$ – $117.3(5)^\circ$ .

The distortions in the square-planar coordination around the rhodium atoms are evidenced by the dihedral angles between the two halves of the square-planes (SRhS vs. MRhM',  $10.7(5)$ ,  $10.6(5)$  and  $14.0(5)^\circ$  for Rh(1), Rh(2) and Rh(3), respectively where M and M' represent the midpoints of the olefinic bonds), which are tilted probably to lengthen the interatomic separations of the tfbb molecules. The Rh–S bond lengths span a narrow range from  $2.311(4)$  to  $2.338(4)$  Å and are at the lower end of the bond distance range reported for the binary sulphide Rh<sub>2</sub>S<sub>3</sub> ( $2.311$ – $2.404$  Å) [8]. They are also slightly shorter than those detected in related polynuclear Rh(I)–thiolate complexes, where triple-bonded sulphur atoms are *trans* situated to a tfbb diolefin, as in [Rh<sub>3</sub>( $\mu_3$ -C<sub>7</sub>H<sub>4</sub>NS<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-(tfbb)]<sup>+</sup>,  $2.374$ – $2.383(6)$  Å [9a] or [Rh( $\mu$ -SC<sub>5</sub>H<sub>4</sub>N)-(tfbb)]<sub>2</sub>,  $2.339$ – $2.349(2)$  Å [9b]. Similar Rh–S bond distances have been observed ( $2.299$ – $2.328(3)$  Å) in the related sulphido complex [Rh<sub>3</sub>( $\mu_3$ -S)<sub>2</sub>( $\mu$ -H)(cod)]<sub>3</sub>, where the sulphur atoms bridge both faces of an Rh<sub>3</sub> triangle [10].

The Rh–Ti separations in **1** are in the range  $2.912$ – $2.940(3)$  Å. These distances, clearly above the values reported for direct Ti–Rh metal–metal bonds found in Ti/Rh alloys ( $2.68$  Å) or in highly reduced rhodium on titania ( $2.55$  Å) [11], together with the values of the Ti–S–Rh angles ( $78.0$ – $78.9(1)^\circ$ ), are consistent with a weak dative interaction— $\sigma$  bonding in character—from the electron rich d<sup>8</sup> metal to the acid d<sup>0</sup> titanium centre [12]. An analogous situation has been described for [CpTi(SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S)<sub>2</sub>Rh(nbd)], where the two metals, maintained in proximity by a triple thiolate bridge, are separated by a comparable distance,  $2.915(2)$  Å [7]. Similar intermetallic separations in the range  $2.827$ –

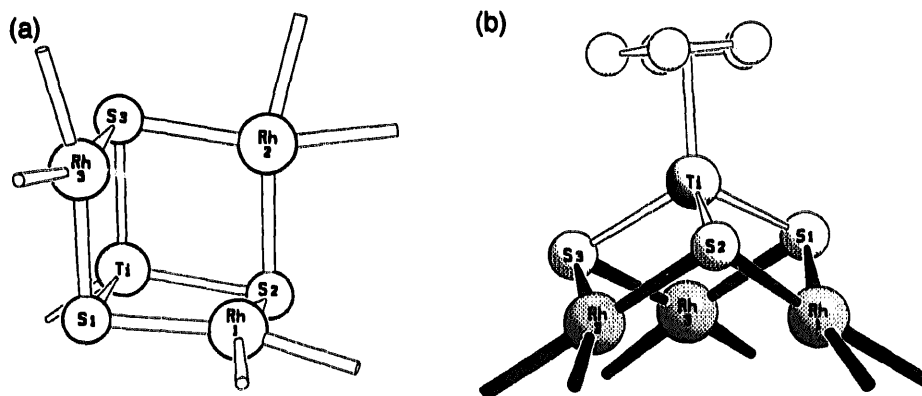


Fig. 2. Schematic view of the central core of complex **1** showing (a) the incomplete cubane-type cluster structure and (b) the analogy of the TiCp moiety deposited on the molecular portion 'Rh<sub>3</sub>S<sub>3</sub>'.

2.986 have also been observed in related methylene-bridged Ti–Rh complexes, and in all these cases have been considered indicative of a dative interaction [13].

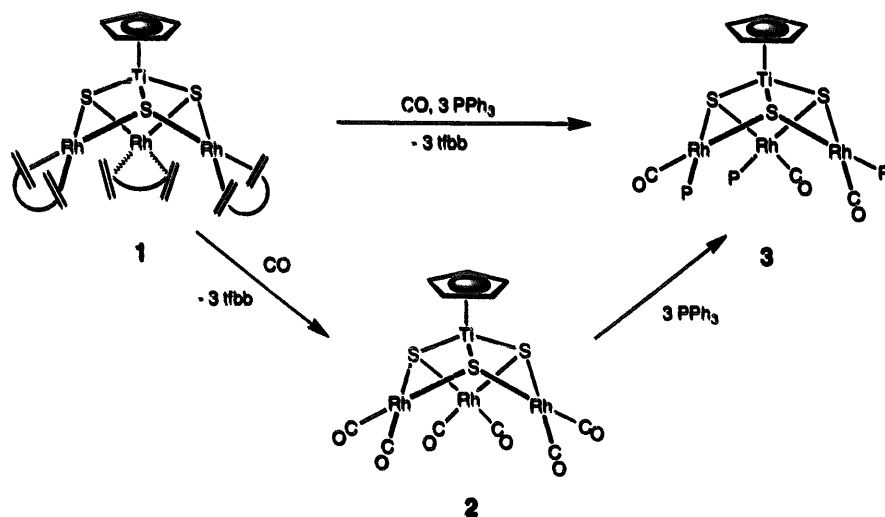
From a structural point of view, the 'Rh<sub>3</sub>S<sub>3</sub>' skeleton resembles the layered structure of active catalytic transition metal sulphides like that of molybdenum or, although distorted, rhodium, where layers of metal and sulphur atoms alternate in the solid. In that sense, the structure of **1** could be seen as originated from the attachment of the TiCp moiety to the 'Rh<sub>3</sub>S<sub>3</sub>' surface portion (Fig. 2(b)). This resemblance, together with the structural features associated with the short-distance Rh–S or Ti–S bonds and the dative intermetallic interactions, and the high stability for further reaction of the 'Ti-(μ<sub>3</sub>-S)<sub>3</sub>-Rh<sub>3</sub>' framework (vide infra), lead us to suggest that this type of structure (and interactions) could be involved in the deactivation of hydrotreatment catalysts.

While this work was in progress a related oxoderivative of formula [Cp\*Ti(μ<sub>3</sub>-O)<sub>3</sub>(Rh(cod))<sub>3</sub>], with an isostructural molecular structure has been communicated [14]. However, in this case a monocyclopentadienyl complex of formula Cp\*TiMe<sub>3</sub> is specifically used as the titanium source. It reacts with [(Rh(μ-OH)(cod))<sub>2</sub>] to yield the oxoheteronuclear derivative. As suggested for **1**, this complex has also been proposed to contain direct rhodium–titanium interactions (Rh–Ti 2.731(2) and 2.760(1)°).

In solution complex **1** maintains its integrity and the structure found in the solid state. Thus, two resonances for the olefinic protons are observed in the <sup>1</sup>H NMR spectrum of **1** at room temperature, as expected from the structure of C<sub>3v</sub> symmetry, assuming the free rotation of the Cp ring. The broadening of these resonances should be associated to a kind of non-rigidity of the whole framework, giving the averaged highly symmetrical species. The nature of **1**, as well as the rela-

tively low yield obtained (55% based on rhodium), indicates that its formation is a consequence of a rather complex pathway. Obviously a Cp ring is removed in the reaction and three sulphur atoms end up in the final product. Attempts to isolate other products from the mother liquor were unsuccessful; for example, chromatography of the solution on silica-gel only led to an extra amount of **1** but not to other titanium complexes. Probably, the formation of the expected trinuclear complex occurs at the first steps of the reaction and then the methanol formed upon protonation of the methoxide bridges is responsible for the breaking of one of the Cp–Ti bonds. In fact, removal of one Cp ring from Cp<sub>2</sub>TiCl<sub>2</sub> by alcohols to give monocyclopentadienylalkoxo titanium complexes is a well-documented reaction [15]. Nevertheless, the protonation of the Cp ligand can take place on a possible dinuclear complex [Cp<sub>2</sub>Ti(μ-S)(μ-SH)Rh(tfbb)] assuming a stepwise protonation of the methoxide bridges. In any case, the coordinatively unsaturated titanium centre formed after this process should still undergo a further reaction to pick up the third sulphur atom and an Rh(tfbb) fragment present in the final product.

Carbonylation of [CpTi(μ<sub>3</sub>-S)<sub>3</sub>{Rh(tfbb)}<sub>3</sub>] (**1**) at atmospheric pressure produces the full replacement of the diolefinic ligands on the rhodium atoms by CO giving rise to the complex [CpTi(μ<sub>3</sub>-S)<sub>3</sub>{Rh(CO)<sub>2</sub>}<sub>3</sub>] (**2**) in 70% yield (Scheme 1). Complex **2** is an air-stable dark-brown dichroic microcrystalline solid giving orange solutions. This colour change is indicative of intermolecular metal–metal interactions in the solid state, as we have frequently observed in some di- and trinuclear rhodium complexes [16]. Spectroscopic data indicate that the nuclearity and structure of the starting material are maintained upon the reaction. Indeed, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2** is fully in accordance with these observations. All the carbonyl ligands are equiva-



Scheme 1. Ligand-replacement reactions on the Ti/Rh complexes.

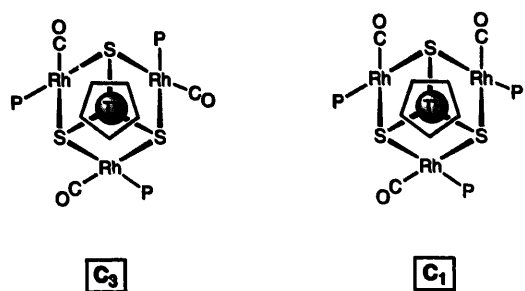


Fig. 3. Possible isomers of complex 3. (Their enantiomers are not drawn and free rotation of the Cp ring is assumed in the symmetry assignment.)

lent, as expected for a molecule of  $C_{3v}$  symmetry similar to that found for **1** in the solid state, and all of them are bonded to the Rh atoms as terminal ligands since they give a single doublet due to the coupling with the Rh active nucleus. Complex **2** reacts with triphenylphosphine, replacing one carbonyl ligand on each rhodium centre to give the tricarbonyl complex  $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{CO})(\text{PPh}_3)\}_3]$  (**3**). The preparation of **3** can be accomplished in one-pot synthesis starting from **1** (Scheme 1). Complex **3** is an air-stable crystalline solid, giving a doublet in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum indicative of the equivalence of the triphenylphosphine ligands. This reaction is selective since the most symmetrical ( $C_3$ , assuming the free rotation of the Cp ring) of two possible isomers (Fig. 3) is isolated although, in fact, both have the corresponding enantiomer. It is noteworthy that the above replacement reactions occur on the rhodium centres presumably through 18e intermediates, showing the stability of the titanium–rhodium framework supported by three bridging sulphido ligands. Further work to advance the knowledge of Ti/S/Rh chemistry and catalytic properties is in progress.

### 3. Experimental

#### 3.1. General

All the reactions were performed under dry nitrogen atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on Varian UNITY 300 and Bruker ARX 300 spectrometers, operating at 299.95 and 300.13; 75.42 and 75.47; 121.42 and 121.49 MHz respectively. Chemical shifts are reported in parts per million and referenced to  $\text{Me}_4\text{Si}$  using the signal of the deuterated solvent ( $^1\text{H}$  and  $^{13}\text{C}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) as external references respectively. IR spectra were recorded on a Nicolet Magna-IR<sup>TM</sup> System 550 spectrometer using Nujol mulls between polyethylene

sheets or in solution in NaCl windows. Elemental analyses were performed with a Perkin-Elmer 240-C micro-analyzer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the  $\text{FAB}^+$  mode. Ions were produced with the standard  $\text{Cs}^+$  gun at ca. 30 Kv, 3-nitrobenzyl alcohol (NBA) was used as matrix. The starting materials  $[\text{Cp}_2\text{Ti}(\text{SH})_2]$  [**17**] and  $[\text{Rh}(\mu\text{-OMe})(\text{tfbb})_2]$  [**18**] were prepared following the literature procedures.

#### 3.2. Synthesis of $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{tfbb})\}_3]$ (**1**)

$[\text{Cp}_2\text{Ti}(\text{SH})_2]$  (0.068 g, 0.277 mmol) was added to a yellow suspension of  $[\text{Rh}(\mu\text{-OMe})(\text{tfbb})_2]$  (0.200 g, 0.277 mmol) in toluene (5 ml) to give immediately a brown–red solution. A yellow microcrystalline solid began to precipitate after stirring for 5 min. The suspension was stirred for 30 min, and filtered to give the complex as yellow microcrystals which were washed with cold toluene and dried under vacuum (0.123 g, 55% based on Rh). Anal. Found: C, 41.15; H, 1.89; S, 7.93  $\text{C}_{41}\text{H}_{23}\text{F}_{12}\text{Rh}_3\text{S}_3\text{Ti}$ . Calc. C, 41.16; H, 1.94; S, 8.04. MS ( $\text{FAB}^+$ ,  $\text{CH}_2\text{Cl}_2$ ,  $m/z$ ): 1197 ( $\text{M}^+$ , 100%), 971 ( $\text{M}^+ - \text{tfbb}$ , 22%), 744 ( $\text{M}^+ - 2\text{tfbb}$ , 16%), 518 ( $\text{M}^+ - 3\text{tfbb}$ , 32%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 20°C):  $\delta$  5.68 (s, 5H, Cp), 5.28 (br s, 6H, CH), 4.42 (br s, 6H, =CH), 4.04 (br s, 6H, =CH).

#### 3.3. Synthesis of $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{CO})_2\}_3]$ (**2**)

Carbon monoxide was bubbled through a solution of complex **1** (0.100 g, 0.083 mmol) in dichloromethane (5 ml) for 5 min to give a yellow–orange solution. Bubbling was maintained in order to concentrate the solution. Addition of hexane (10 ml) and concentration under carbon monoxide to ca. 2 ml gave the complex as dark-brown dichroic microcrystals which were filtered, washed with cold hexane and vacuum dried. (0.040 g, 70%) Anal. Found: C, 19.14; H, 0.92; S, 13.30.  $\text{C}_{11}\text{H}_5\text{O}_6\text{Rh}_3\text{S}_3\text{Ti}$ . Calc. C, 19.26; H, 0.73; S, 14.02. MS ( $\text{FAB}^+$ ,  $\text{CH}_2\text{Cl}_2$ ,  $m/z$ ): 686 ( $\text{M}^+$ , 13%), 658 ( $\text{M}^+ - \text{CO}$ , 15%), 630 ( $\text{M}^+ - 2\text{CO}$ , 9%), 602 ( $\text{M}^+ - 3\text{CO}$ , 6%), 574 ( $\text{M}^+ - 4\text{CO}$ , 7%), 518 ( $\text{M}^+ - 6\text{CO}$ , 7%);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 20°C):  $\delta$  6.05 (s, Cp);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 20°C):  $\delta$  183.0 (d,  $J_{\text{Rh-C}} = 72.2$  Hz, CO), 105.0 (Cp). IR ( $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ),  $\nu(\text{CO})$ : 2090(s), 2065 (m), 2030 (s).

#### 3.4. Synthesis of $[\text{CpTi}(\mu\text{-S})_3\{\text{Rh}(\text{CO})(\text{PPh}_3)\}_3]$ (**3**)

A solution of triphenylphosphine (0.069 g, 0.262 mmol) in dichloromethane (2 ml) was added to a solution of complex **2** (0.060 g, 0.087 mmol) in dichloromethane (5 ml). Stirring for 30 min gave an orange–brown solution after carbon monoxide evolu-

Table 2

Atomic co-ordinates ( $\times 10^4$ ;  $\times 10^5$  for Rh and Ti atoms) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for the complex  $[\text{CpTi}(\mu_3\text{-S})_3(\text{Rh}(\text{tbb}))_3]$ 

Atom	x	y	z	$U_{\text{eq}}^a / U_{\text{iso}}$
Rh(1)	75875(6)	7711(4)	-5893(14)	62(1)
Rh(2)	85857(5)	1540(4)	25346(14)	58(1)
Rh(3)	83852(6)	14810(4)	25655(15)	70(1)
Ti	90410(12)	8850(9)	2808(32)	59(1)
S(1)	8236(2)	1478(1)	-280(5)	61(1)
S(2)	8438(2)	179(1)	-340(4)	58(1)
S(3)	9198(2)	872(1)	3108(5)	64(1)
F(9)	4763(6)	519(5)	84(15)	142(4)
F(10)	3849(7)	412(6)	-2638(18)	171(5)
F(11)	4213(7)	493(6)	-5672(18)	183(6)
F(12)	5520(6)	632(5)	-6064(15)	140(4)
F(21)	9399(4)	-1665(3)	5728(11)	86(3)
F(22)	8619(5)	-2113(4)	7647(13)	105(3)
F(23)	7403(5)	-1714(3)	8231(12)	103(3)
F(24)	6996(5)	-876(3)	6785(12)	97(3)
F(33)	8853(7)	3308(5)	6000(19)	175(6)
F(34)	8009(8)	3657(6)	7939(21)	202(7)
F(35)	6828(7)	3183(6)	8229(19)	184(6)
F(36)	6556(6)	2332(5)	6666(16)	144(4)
C(1)	6806(7)	1146(6)	-1993(21)	72(4)
C(2)	6631(8)	1118(6)	-458(19)	74(4)
C(3)	6755(7)	273(5)	-532(20)	70(4)
C(4)	6936(8)	315(6)	-2064(22)	79(5)
C(5)	6585(9)	717(7)	-3174(26)	99(6)
C(6)	6208(7)	658(6)	-243(20)	74(5)
C(7)	5813(7)	650(6)	-3184(18)	79(5)
C(8)	5636(8)	621(6)	-1694(20)	93(5)
C(9)	4929(8)	557(8)	-1429(21)	117(7)
C(10)	4521(9)	539(9)	-2878(22)	136(8)
C(11)	4688(10)	557(11)	-4285(24)	164(10)
C(12)	5311(8)	641(7)	-4617(20)	99(6)
C(13)	8398(8)	-5(6)	4990(21)	78(5)
C(14)	9002(7)	-183(5)	4779(17)	63(4)
C(15)	8523(8)	-619(6)	2560(22)	78(5)
C(16)	7909(8)	-453(5)	2762(17)	65(4)
C(17)	7809(8)	-362(5)	4566(20)	73(4)
C(18)	8984(7)	-712(5)	4195(19)	67(4)
C(19) <sup>a</sup>	7976(7)	-827(5)	5489(17)	67(4)
C(20)	8578(6)	-1008(5)	5278(17)	62(4)
C(21)	8810(6)	-1468(5)	5999(17)	61(4)
C(22)	8369(7)	-1668(5)	6937(18)	72(4)
C(23)	7824(7)	-1487(5)	7234(19)	76(4)
C(24)	7574(7)	-1074(5)	6561(18)	66(4)
C(25)	7609(10)	1981(6)	2783(18)	82(5)
C(26)	8174(9)	2231(6)	2591(22)	84(5)
C(27)	8721(10)	1835(7)	4810(23)	94(6)
C(28)	8166(10)	1592(6)	5004(21)	82(5)
C(29)	7521(11)	1876(7)	4483(30)	128(8)
C(30)	8594(9)	2366(6)	4237(21)	87(5)
C(31)	7582(9)	2368(7)	5509(24)	106(6)
C(32)	8144(9)	2599(7)	5368(25)	111(6)
C(33)	8314(9)	3061(7)	6240(24)	116(7)
C(34)	7825(9)	3207(7)	7131(27)	133(8)
C(35)	7318(9)	2982(6)	7336(25)	111(6)
C(36)	7133(10)	2560(7)	6619(27)	132(8)
C(37)	9651(8)	1383(7)	-1347(21)	81(5)
C(38)	10025(8)	1304(7)	142(23)	87(5)
C(39)	10218(7)	780(6)	261(18)	70(4)
C(40)	9917(6)	566(5)	-1117(18)	61(4)
C(41)	9578(7)	911(6)	-2085(21)	71(4)

<sup>a</sup>  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup> From this atom downwards isotropic displacement parameters are expressed.

tion. Concentration of the solution under vacuum and slow addition of hexane gave the complex as a dark-orange microcrystalline solid which was filtered, washed with hexane and vacuum dried. (0.095 g, 78%). Anal. Found: C, 52.81; H, 3.25; S, 6.74.  $C_{62}H_{50}O_3P_3Rh_3S_3Ti$ . Calc.: C, 53.62; H, 3.63; S, 6.92. MS(FAB<sup>+</sup>,  $CH_2Cl_2$ ,  $m/z$ ): 1389 (M<sup>+</sup>, 15%), 1361 (M<sup>+</sup>-CO, 4%), 1333 (M<sup>+</sup>-2CO, 8%), 1304 (M<sup>+</sup>-3CO, 16%), 1098 (M<sup>+</sup>-CO-PPh<sub>3</sub>, 44%), 1070 (M<sup>+</sup>-2CO-PPh<sub>3</sub>, 36%), 1042 (M<sup>+</sup>-3CO-PPh<sub>3</sub>, 16%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 20°C): δ 7.56 (m, 18H, PPh<sub>3</sub>), 7.30 (m, 27H, PPh<sub>3</sub>), 5.69 (s, 5H, Cp). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 20°C): δ 35.2 (d, <sup>1</sup>J<sub>Rh-P</sub> = 168 Hz); IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>), ν(CO): 1977 (s).

### 3.5. X-ray crystallography study of [CpTi(μ<sub>3</sub>-S)<sub>3</sub>{Rh(tfbb)}<sub>3</sub>] (1)

#### 3.5.1. Crystal data

$C_{41}H_{23}F_{12}Rh_3S_3Ti$ ;  $M = 1196.4$ ; monoclinic, space group  $P2_1/a$ ;  $a = 19.975(4)$ ,  $b = 27.352(6)$ ,  $c = 8.186(3)$  Å,  $\beta = 97.15(2)^\circ$ ,  $V = 4438(3)$  Å<sup>3</sup>,  $Z = 4$ ;  $D_c = 1.791$  mg m<sup>-3</sup>;  $F(000) = 2328$ ;  $\lambda(Cu K\alpha) = 1.54178$  Å;  $\mu = 12.38$  mm<sup>-1</sup>;  $T = 295$  K.

#### 3.5.2. Data collection and processing

A Siemens AED diffractometer with nickel-filtered Cu K $\alpha$  radiation was used. A yellow needle-shaped crystal  $0.126 \times 0.184 \times 0.632$  mm<sup>3</sup> was mounted on a glass fibre. A total of 9198 reflections were collected ( $6^\circ \leq 2\theta \leq 140^\circ$ ); from 8391 independent reflections 2857 unique with  $I \geq 1.5\sigma(I)$  were considered observed and used in the analysis. Cell parameters were obtained by least-squares refinement from the  $2\theta$  values of 30 accurately centred reflections in the  $2\theta$  range  $22-74^\circ$ . One standard reflection was monitored to check the crystal and instrument stability. Intensities were corrected for Lorentz and polarization effects. Absorption was taken into account using the XABS2 program (correction factors 0.640–1.495) [19].

#### 3.5.3. Structure solution and refinement

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, first with isotropic and then with anisotropic thermal parameters for sulphurs and metals, and for all carbon atoms bonded to them. Hydrogen atoms were included in calculated positions and refined riding on their carbon atoms with a fixed thermal parameter. A weighting scheme  $w^{-1} = [\sigma^2(F_o)^2 + (0.0949P)^2 + 11.87P]$ , with  $P = \max((0, F_o^2) + 2(F_c^2))/3$ , was used in the final stages of the refinement. All calculations were performed using SHELXTL-PLUS and SHELX-93 packages [20]. Final agreement indices were  $R = 0.0464$  and  $wR^2 = 0.1275$  for 391 refined parameters. Atomic scattering factors, corrected for anomalous dispersion, were taken

from Ref. [21]. Final atomic co-ordinates are given in Table 2.

## 4. Supplementary material available

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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