

# Synthesis and structural studies of rhenium(I) tricarbonyl complexes with thione containing chelators

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## Abstract

Sodium dihydrobis(2-mercaptothiazolyl)borate,  $\text{Na}[\text{H}_2\text{B}(\text{tiaz})_2]$ , reacts with  $(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  in water to afford *fac*- $[\text{Re}\{\kappa^3\text{-H}(\mu\text{-H})\text{B}(\text{tiaz})_2\}(\text{CO})_3]$  (**1**). In a similar manner, treatment of the same Re(I) starting material with bis(2-mercaptoimidazolyl)methane,  $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$ , yields *fac*- $[\text{ReBr}\{\kappa^2\text{-H}_2\text{C}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3]$  (**2**). The organometallic complexes **1** and **2** have been characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and also by X-ray crystallographic analysis. X-ray diffraction analysis revealed the presence of a short  $\text{B-H}\cdots\text{Re}$  interaction in the case of **1**, and the absence of  $\text{C-H}\cdots\text{Re}$  interactions in the crystal structure of **2**. For both compounds the rhenium atom adopts a slightly distorted octahedral coordination with a facial arrangement of the carbonyl ligands. The three remaining coordination positions are occupied by the two thione sulfur atoms from the anchor ligands, and by an agostic hydride (**1**) or a bromide ligand (**2**). Compound **1** is highly stable either in the solid state or in solution. In particular, its  $\text{B-H}\cdots\text{Re}$  interaction is retained in solution, even in coordinating solvents, namely acetonitrile, dimethylsulfoxide and tetrahydrofuran. Unlike **1**, compound **2** is only moderately stable in acetonitrile, undergoing a slow release of the bis(2-mercaptoimidazolyl)methane.

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## 1. Introduction

Our research on the chemistry of Tc(I) and Re(I) tri(carbonyl) complexes anchored by bis(2-mercaptoimidazolyl)borates has shown that these soft scorpionates act as powerful ( $\kappa^3\text{-S, S', H}$ ) chelators towards the *fac*- $[\text{M}(\text{CO})_3]^+$  moiety ( $\text{M} = \text{Re, Tc}$ ), forming quite robust  $\text{B-H}\cdots\text{Re}$  or  $\text{B-H}\cdots\text{Tc}$  interactions (Chart 1A) [1]. Most relevantly, this type of complexes could be even prepared with  $^{99\text{m}}\text{Tc}$ , the radionuclide of choice in diagnostic Nuclear Medicine, under the conditions required in the preparation of radiopharmaceuticals, i.e. in aqueous medium and in the presence of a huge excess of coordinating anions, such as chloride [1d]. Our findings emphasized the well recognized tendency of bridgehead B–H hydrides of bis(2-mercaptoimidazolyl)borates to form three-center-

two-electron ( $3\text{c-}2\text{e}$ ) interactions with d- or f-transition metals [2–5].

Within our interest on the chemistry of soft scorpionate rhenium(I) and technetium(I) tricarbonyl complexes, aimed at further application in radiopharmaceutical development, we have decided to extend our studies to a dihydroborate ligand with 2-mercaptothiazoline (tiazH) and to the bis(2-mercaptoimidazolyl)methane ( $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$ ) ligand [6a]. The main goal of this work was to check if the use of other type of cyclic thiones would not compromise the formation of  $\text{B-H}\cdots\text{Re}$  interactions, and to verify if the replacement of the central boron by a carbon atom will still allow the formation of stable compounds with  $\text{C-H}\cdots\text{Re}$  interactions (Chart 1B). We must mention that with  $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$  some studies have been reported with representative and late transition metals [6,7]. However, to the best of our knowledge, its use in the chemistry of d-transition elements is very recent and limited to the work of Hill and co-workers on low valent Rh complexes [2f].

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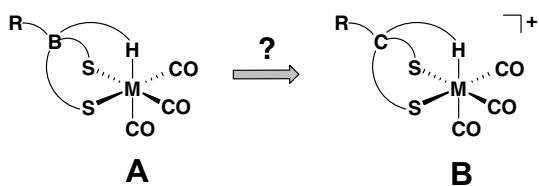
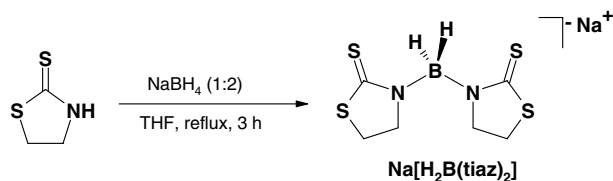


Chart 1. Schematic drawing of complexes with the *fac*-[M(CO)<sub>3</sub>]<sup>+</sup> (M = Re, Tc) moiety anchored on bis(mercaptoazoly)borate (A) and bis(mercaptoimidazoly)methane (B) ligands.



Scheme 1.

In this contribution we report on the synthesis and characterization of sodium dihydrobis(2-mercaptothiazoly)borate, Na[H<sub>2</sub>B(tiaz)<sub>2</sub>], as well as on the evaluation of its coordination capability towards the *fac*-[Re(CO)<sub>3</sub>]<sup>+</sup> moiety, under aqueous conditions. These studies were also extended to the neutral congener H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub>, allowing the synthesis and structural characterization of *fac*-[Re{κ<sup>3</sup>-H(μ-H)B(tiaz)<sub>2</sub>}(CO)<sub>3</sub>] (**1**) and *fac*-[ReBr{κ<sup>2</sup>-H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub>}(CO)<sub>3</sub>] (**2**), which are also described in here.

## 2. Experimental

Chemicals and solvents were of reagent grade and were used without further purification, unless stated otherwise. The ligand H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub> and the organometallic precursor (NEt<sub>4</sub>)<sub>2</sub>[Re(CO)<sub>3</sub>Br<sub>3</sub>] were prepared according to published methods [6a,8]. <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced with the residual solvent resonances relative to tetramethylsilane, and the <sup>11</sup>B NMR chemical shifts with an external NaBH<sub>4</sub> solution. IR spectra were recorded as KBr pellets on a Perkin–Elmer 577 spectrometer. Carbon, hydrogen and nitrogen analysis were performed on a EA110 CE Instruments automatic analyser.

### 2.1. Synthesis of Na[H<sub>2</sub>B(tiaz)<sub>2</sub>]

To a mixture of solid NaBH<sub>4</sub> (100 mg, 2.65 mmol) and 2-mercaptothiazoline (660 mg, 5.55 mmol) were added 15 mL of distilled THF, and the resulting suspension was refluxed for 3 h. After cooling to room temperature, the solvent was removed under vacuum and the residue redissolved in CHCl<sub>3</sub>. After filtration to remove any insoluble material, *n*-hexane was then added to the CHCl<sub>3</sub> solution. After cooling in the refrigerator, the compound Na[H<sub>2</sub>B(tiaz)<sub>2</sub>] precipitates as a white and highly hygroscopic solid,

which was recovered by filtration and drying under vacuum. Yield: 60% (435 mg, 1.60 mmol).

IR (cm<sup>-1</sup>): 2340 s ν(B–H). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 3.07 (4H, tr, *J*<sub>H–H</sub> = 8.3 Hz, CH<sub>2</sub>), 4.25 (4H, tr, *J*<sub>H–H</sub> = 8.0 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 29.8 (S–CH<sub>2</sub>), 67.5 (N–CH<sub>2</sub>), 193.4 (C=S). <sup>11</sup>B NMR (DMSO-*d*<sub>6</sub>, δ): 32.3 (br).

### 2.2. Synthesis of *fac*-[Re{κ<sup>3</sup>-H(μ-H)B(tiaz)<sub>2</sub>}(CO)<sub>3</sub>] (**1**)

To a solution of (NEt<sub>4</sub>)<sub>2</sub>[Re(CO)<sub>3</sub>Br<sub>3</sub>] (130 mg, 0.17 mmol) in distilled water (5 mL) was added Na[H<sub>2</sub>B(tiaz)<sub>2</sub>] (62 mg, 0.23 mmol) dissolved in the minimum volume of water, and the mixture was stirred for 2 h at room temperature. Compound **1** precipitates as a pale yellow microcrystalline solid which was further purified by silica-gel flash chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Yield: 41% (36 mg, 0.07 mmol).

Analysis calculated for C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S<sub>4</sub>BrRe: C, 20.81%; H, 1.93%; N, 5.39%. Found: C, 20.97%; H, 1.82%; N, 5.27%. IR (KBr, ν/cm<sup>-1</sup>): 2409 (m) ν(B–H); 2119 (m) ν(B–H···Re); 2017 (s) and 1899 (vs) ν(CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -7.35 (1H, br, B–H···Re), 3.61–3.76 (4H, m, CH<sub>2</sub>), 4.07–4.27 (4H, m, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 35.9 (S–CH<sub>2</sub>), 60.4 (N–CH<sub>2</sub>), 190.0 (CO), 191.6 (CO), 203.4 (C=S). <sup>11</sup>B NMR (CDCl<sub>3</sub>): 36.1 (br).

### 2.3. Synthesis of *fac*-[ReBr{κ<sup>2</sup>-H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub>}(CO)<sub>3</sub>] (**2**)

To a solution of (NEt<sub>4</sub>)<sub>2</sub>[Re(CO)<sub>3</sub>Br<sub>3</sub>] (100 mg, 0.13 mmol) in distilled water (5 mL) was added solid H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub> (35 mg, 0.15 mmol), and the resulting suspension refluxed for 3 h. Compound **2** precipitates as a white microcrystalline solid, which was collected by filtration, washed with water and dried under vacuum. Yield: 91% (70 mg, 0.12 mmol).

Analysis calculated for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>BrRe: C, 24.41%; H, 2.05%; N, 9.49%. Found: C, 24.76%; H, 1.94%; N, 9.27%. IR (KBr, ν/cm<sup>-1</sup>): 2010 (s), 1894 (vs) and 1865 (vs) ν(CO). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>C=O): 3.72 (6H, s, N–CH<sub>3</sub>), 6.36 (1H, d, *J*<sub>AB</sub> = 13.5 Hz, CH<sub>2</sub>), 7.02 (1H, d, *J*<sub>AB</sub> = 13.5 Hz, CH<sub>2</sub>), 7.35 (2H, d, *J* = 2.4 Hz, CH), 7.81 (2H, d, *J* = 2.4 Hz, CH). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>C=O): 37.8 (N–CH<sub>3</sub>), 59.9 (N–CH<sub>2</sub>), 121.3 (N–CH), 123.6 (N–CH), 156.0 (C=S), 196.9 (CO), 199.7 (CO).

### 2.4. X-ray crystallographic analysis

Crystals of compounds **1** and **2** were obtained by recrystallization from dichloromethane/*n*-hexane and acetone, respectively. Crystallography cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured at room temperature on an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å) and operating in the ω–2θ mode Empirical absorption correction (ψ-scans) and data reduction were performed with the WINGX [9] suite of programmes. The structures were solved by

Table 1  
Crystallographic data for **1** and **2**

Compound	<b>1</b>	<b>2</b>
Chemical formula	C <sub>9</sub> H <sub>10</sub> BN <sub>2</sub> O <sub>3</sub> S <sub>4</sub> Re	C <sub>12</sub> H <sub>12</sub> BrN <sub>4</sub> O <sub>3</sub> S <sub>2</sub> Re
Formula weight	519.44	590.49
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	9.1328(19)	13.280(3)
<i>b</i> (Å)	9.1965(13)	9.448(2)
<i>c</i> (Å)	11.564(3)	14.551(3)
$\alpha$ (°)	112.148(15)	90
$\beta$ (°)	90.425(18)	108.345(19)
$\gamma$ (°)	118.935(15)	90
<i>V</i> (Å <sup>3</sup> )	765.4(3)	1732.9(6)
<i>Z</i>	2	4
<i>T</i> (K)	293(2)	293(2)
$\rho$ (calc.) (g cm <sup>-3</sup> )	2.254	2.263
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	8.487	9.576
$\theta$ range for data collection (°)	1.30–28.03	1.62–28.06
<i>n</i> <sup>o</sup> of data	3677	4186
<i>n</i> <sup>o</sup> of parameters	189	208
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0710 <i>wR</i> <sub>2</sub> = 0.0928	<i>R</i> <sub>1</sub> = 0.0865 <i>wR</i> <sub>2</sub> = 0.1190
<i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0455 <i>wR</i> <sub>2</sub> = 0.0870	<i>R</i> <sub>1</sub> = 0.0523 <i>wR</i> <sub>2</sub> = 0.1048
GOF	1.005	1.094

direct methods with SIR97 [10] and refined by full-matrix least-squares analysis with SHELXL97 [11]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms linked to the boron atom, in the structure of **1**, were located in the difference Fourier map and refined isotropically, whereas all the other H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP3 [12]. A summary of the crystal data, structure solution and refinement parameters are given in Table 1.

### 3. Results and discussion

The cyclic thione 2-mercaptothiazoline has been already used to synthesize sodium hydrotris(2-mercaptothiazolyl)borate (Na[HB(tiaz)<sub>3</sub>]) and potassium tetrakis(2-mercaptothiazolyl)borate (K[B(tiaz)<sub>4</sub>]), by reaction with the corresponding borohydride salt in melt at 160–165 °C [13,14]. As depicted in Scheme 1, the synthesis of the bis-substituted congener, Na[H<sub>2</sub>B(tiaz)<sub>2</sub>], has been achieved

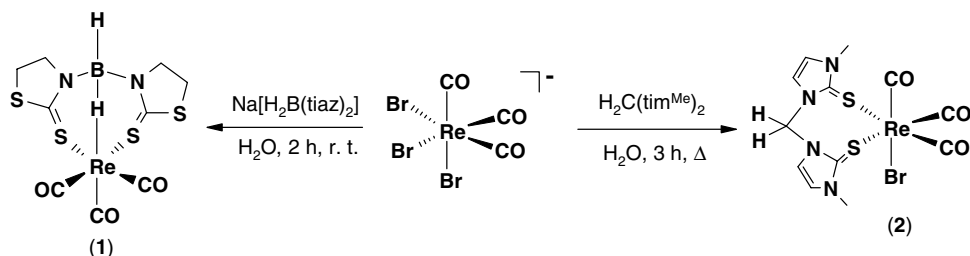
by reacting NaBH<sub>4</sub> with 2-mercaptothiazoline in refluxing THF, using a 1:2 molar ratio.

Compound Na[H<sub>2</sub>B(tiaz)<sub>2</sub>] (60% isolated yield) is a white microcrystalline solid, highly hygroscopic, soluble in polar organic solvents and in water. <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B NMR spectroscopy has shown that the product was sufficiently pure to be used in the synthesis of Re complexes.

The reaction of Na[H<sub>2</sub>B(tiaz)<sub>2</sub>] with (NEt<sub>4</sub>)<sub>2</sub>[Re(CO)<sub>3</sub>Br<sub>3</sub>] in water proceeded with the formation of *fac*-[Re{ $\kappa^3$ -H( $\mu$ -H)B(tiaz)<sub>2</sub>}(CO)<sub>3</sub>] (**1**), which has been isolated in moderate yield (41%), after purification by column chromatography (Scheme 2). Compound **1** is a pale yellow microcrystalline solid, stable towards aerial oxidation in the solid state or in solution. Like the bis(2-mercaptoimidazolyl)borate Re(I) congeners, previously reported by our group [1], complex **1** displays a B–H···Re agostic interaction which resists to water and to other coordinating solvents, such as acetonitrile, tetrahydrofuran and dimethylsulfoxide.

As shown in Scheme 2, (NEt<sub>4</sub>)<sub>2</sub>[Re(CO)<sub>3</sub>Br<sub>3</sub>] also reacts smoothly with H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub> affording *fac*-[ReBr{ $\kappa^2$ -H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub>}(CO)<sub>3</sub>] (**2**) almost quantitatively (91% isolated yield). Whereas the characterization of **1** by <sup>1</sup>H NMR and X-ray diffraction analysis has proved the presence of a B–H···Re interaction, the spectroscopic and structural data obtained for **2** did not corroborate the presence of any C–H···Re interaction, either in the solid state or in solution (see below). Compound **2** was also treated with silver triflate, in a non-coordinating solvent (CH<sub>2</sub>Cl<sub>2</sub>), to abstract the bromide ligand and to see whether the weaker donor triflate would facilitate the formation of a C–H···Re interaction. This was not the case, since the <sup>1</sup>H NMR data of the solid recovered from the supernatant, after removal of AgBr, were consistent with a bidentate coordination mode for H<sub>2</sub>C(tim<sup>Me</sup>)<sub>2</sub> [15].

These results have shown that the dihydrobis(2-mercaptothiazolyl)borate replaces promptly the halide and/or H<sub>2</sub>O ligands yielding compound **1**, which contains the ancillary ligand coordinated in a ( $\kappa^3$ -S, S', H) fashion. In contrast, the bis(2-mercaptoimidazolyl)methane ligand acts as bidentate ( $\kappa^2$ -S, S') without formation of a C–H···Re agostic interaction, either in the presence of bromide or triflate. These differences certainly reflect electronic factors, namely the reversed polarity of the C–H<sup>δ+</sup> and B–H<sup>δ-</sup> bonds which makes the borohydride hydrogen atoms better electron donors.



Scheme 2.

Examples of complexes of d-transition metals with the bis(2-mercaptoimidazolyl)methane ligand are scarce, being limited to the Rh(I) complexes recently reported by Hill and co-workers [2f]. These authors demonstrated that in the solid state the  $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$  ligand coordinates to Rh(I) in a tridentate ( $\kappa^3\text{-S, S', H}$ ) fashion. However, even for those compounds the  $\text{C-H}\cdots\text{Rh}$  interactions are relatively weak and did not persist in solution [2f]. The formation of such  $\text{C-H}\cdots\text{Rh}$  interactions in the solid state could be accounted by the specific topology of 2-mercaptoimidazolyl-based chelators, which may favor the approach of the bridgehead  $\text{A-H}$  ( $\text{A} = \text{B, C}^+$ ) protons to the metal center. However, electronic factors play an important role on the hapticity ( $\kappa^2\text{-S, S'}$  vs.  $\kappa^3\text{-S, S', H}$ ) of this type of ligands, as shown by the results described in this work for Re(I) tricarbonyl complexes.

The X-ray diffraction analysis of compounds **1** and **2** confirmed, respectively, the ( $\kappa^3\text{-S, S', H}$ ) and ( $\kappa^2\text{-S, S'}$ ) coordination modes for the corresponding anchor ligands, as shown in Figs. 1 and 2. For both complexes, the rhenium atoms display a distorted octahedral coordination environment with a facial arrangement for the three CO ligands. Table 2 summarizes selected bond distances and angles for **1** and **2**.

In the case of complex **1**, the presence of the  $\text{B-H}\cdots\text{Re}$  interaction was corroborated by the relatively short  $\text{Re-B}$  distance (2.826(7) Å) which appears within the range (2.79–2.92 Å) that we have found for a series of Tc(I) and Re(I) tricarbonyl complexes anchored by bis(mercaptoimidazolyl)borate chelators acting as ( $\kappa^3\text{-S, S', H}$ ) donors [1]. The hydrogen atoms linked to the boron were

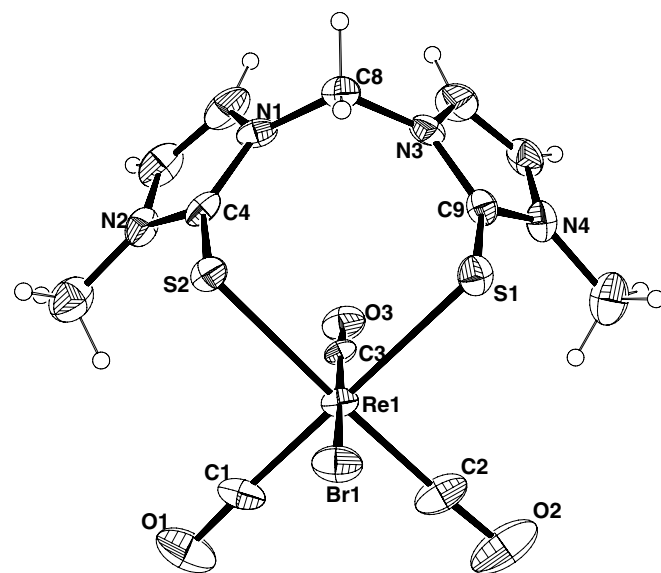


Fig. 2. ORTEP view of **2**. Vibrational ellipsoids are drawn at the 30% probability level.

Table 2  
Selected bond lengths (Å) and angles (°) for **1** and **2**

Complex 1			
Re(1)–C(1)	1.928(10)	Re(1)–C(2)	1.900(9)
Re(1)–C(3)	1.914(8)	Re(1)–S(1)	2.479(2)
Re(1)–S(3)	2.467(2)	Re(1)–H	1.87(7)
Re(1)–B(1)	2.826(7)	C(1)–O(1)	1.142(11)
C(2)–O(2)	1.154(10)	C(3)–O(3)	1.150(9)
C(1)–Re(1)–C(2)	88.9(4)	C(1)–Re(1)–C(3)	91.9(4)
C(2)–Re(1)–C(3)	89.0(4)	C(1)–Re(1)–S(1)	91.2(3)
C(1)–Re(1)–S(3)	177.6(3)	C(1)–Re(1)–H	93(3)
C(2)–Re(1)–S(1)	93.3(3)	C(2)–Re(1)–S(3)	93.5(3)
C(2)–Re(1)–H	175(3)	C(3)–Re(1)–S(1)	176.2(3)
C(3)–Re(1)–S(3)	88.3(3)	C(3)–Re(1)–H	86(2)
S(1)–Re(1)–S(3)	88.49(7)	S(1)–Re(1)–H	92(2)
S(3)–Re(1)–H	85(3)		
Complex 2			
Re(1)–C(1)	1.892(12)	Re(1)–C(2)	1.889(11)
Re(1)–C(3)	1.947(10)	Re(1)–S(1)	2.548(3)
Re(1)–S(2)	2.529(2)	Re(1)–Br(1)	2.6215(11)
Re(1)–C(8)	4.205(10)	C(1)–O(1)	1.152(14)
C(2)–O(2)	1.149(14)	C(3)–O(3)	1.052(11)
C(1)–Re(1)–C(2)	91.1(6)	C(1)–Re(1)–C(3)	89.5(5)
C(2)–Re(1)–C(3)	92.2(4)	C(1)–Re(1)–S(1)	178.0(4)
C(1)–Re(1)–S(2)	92.7(4)	C(1)–Re(1)–Br(1)	93.5(4)
C(2)–Re(1)–S(1)	89.5(4)	C(2)–Re(1)–S(2)	173.0(4)
C(2)–Re(1)–Br(1)	91.5(3)	C(3)–Re(1)–S(1)	92.4(3)
C(3)–Re(1)–S(2)	93.7(2)	C(3)–Re(1)–Br(1)	175.2(2)
S(1)–Re(1)–S(2)	86.51(8)	S(1)–Re(1)–Br(1)	84.51(6)
S(2)–Re(1)–Br(1)	82.41(6)		

located directly, allowing the determination of a short  $\text{Re}\cdots\text{H-B}$  distance of 1.87(7) Å, which is comparable to the values reported for the bridging hydrides in  $[\text{Re}(\text{CO})(\text{P-Me}_3)_3(\kappa^2\text{-BH}_4)]$  (1.80(6) and 1.93(6) Å) [16]. This short  $\text{Re-H}$  bond distance is consistent with the coordination of the agostic hydride, in agreement with the IR data obtained for **1**. The IR spectrum of compound **1** shows a band of medium intensity centered at  $2119\text{ cm}^{-1}$ , due to  $\nu(\text{B-H}\cdots\text{Re})$

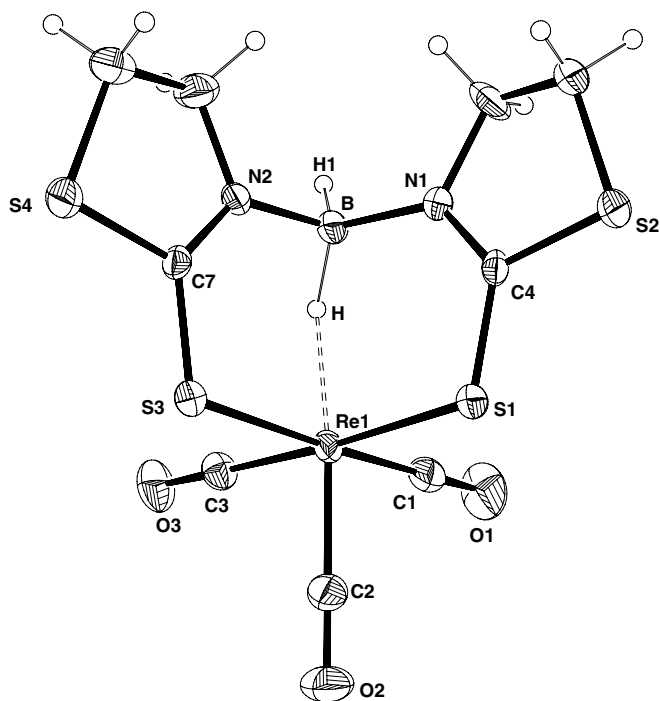


Fig. 1. ORTEP view of **1**. Vibrational ellipsoids are drawn at the 30% probability level.

[1]. As expected, this frequency is strongly red shifted compared to the B–H stretching frequency in the free ligand ( $2340\text{ cm}^{-1}$ ) or to  $\nu(\text{B–H})_{\text{term}}$  in compound **1** ( $2409\text{ cm}^{-1}$ ).

For complex **2**, the coordination environment around the metal is defined by the three carbonyl ligands, the two thione sulfur atoms and the bromide co-ligand. The bidentate  $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$  defines a  $[\text{C}_3\text{N}_2\text{S}_2\text{Re}]$  chelating ring in a chair conformation, exhibiting a long  $\text{Re}(1)\text{–C}(8)$  distance ( $4.205(10)\text{ \AA}$ ) for the bridgehead carbon atom.

Complex **1** shows Re–S bond distances shorter than the ones presented by **2** (**1**,  $2.467(2)$  and  $2.479(2)\text{ \AA}$ ; **2**,  $2.529(2)$  and  $2.548(3)\text{ \AA}$ ). This trend is certainly due to the presence of the B–H...Re interaction, which promotes the shortening of the Re–S bonds and obliges the dihydroborate chelator to assume a boat conformation. The Re–S bond distances found for **1** are within the range ( $2.462(6)\text{–}2.493(5)\text{ \AA}$ ) that we previously reported for  $\text{fac}[\text{Re}\{\kappa^3\text{-R}(\mu\text{-H})\text{B}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3]$  ( $\text{R} = \text{H, Me, Ph}$ ) [1a], while those of complex **2** compare well with the Re–S bond distances ( $2.525\text{–}2.548(3)\text{ \AA}$ ) determined for  $\text{fac}[\text{Re}\{\kappa^2\text{-H}_2\text{B}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3(\text{L})]$  ( $\text{L} = \text{PPh}_3, \text{imzH, NMe}_2\text{py, C}_6\text{H}_{11}\text{-NC}$ ) [17].

The most striking feature of the  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  is the presence of a highfield shifted broad resonance centered at  $-7.35\text{ ppm}$ , which is typical for bridging B–H...Re protons [1]. The terminal B–H appears as a broad signal between 3 and 4 ppm, overlapping with some resonances due to the methylenic protons of the thiazolyl rings. These protons originate two sets of complex multiplets integrating each for four protons, in the range  $3.61\text{–}3.76\text{ ppm}$  and  $4.07\text{–}4.27\text{ ppm}$ , due to the occasional overlapping of the diastereotopic  $\text{CH}_2$  vicinal protons. The  $^{13}\text{C}$  NMR spectrum of **1** has only two resonances for the  $\text{CH}_2$  carbons at  $35.9$  and  $60.4\text{ ppm}$ , showing that the two thiazolyl rings are magnetically equivalent.

For **2**, the two mercaptoimidazolyl rings are also magnetically equivalent and the respective C–H protons originate two well defined doublets at  $7.35$  and  $8.81\text{ ppm}$ , while the N– $\text{CH}_3$  protons appears as a unique singlet at  $3.72\text{ ppm}$ . The presence of two doublets of the AB type for the *exo* and *endo* protons of the bridgehead methylenic group, integrating each for one proton and resonating at  $6.36$  and  $7.02\text{ ppm}$ , is consistent with a bidentate coordination for  $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$ . The same pattern has been observed in the  $^1\text{H}$  NMR spectrum of the compound formed upon treatment of **2** with  $\text{AgCF}_3\text{SO}_3$ , cautiously formulated as “ $\text{fac}[\text{Re}(\text{OTf})\{\kappa^2\text{-H}_2\text{C}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3]$ ” [15]. For this species it was found a large gap between the chemical shifts of the two carbon bridgehead C–H protons ( $\Delta\delta = 1.4\text{ ppm}$ ). However, the chemical shift of the more shielded C–H ( $5.78\text{ ppm}$ ) does not justify the presence of any C–H...Re interaction [2f].

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data collected for **1** and **2** have shown that these complexes are not undergoing fluxional processes, presenting in solution a structure which agrees with the one found in the solid state.

Complexes **1** and **2** present a quite different behaviour in acetonitrile solution, as indicated by  $^1\text{H}$  NMR spectroscopy.

**1** does not undergo any transformation when kept in  $\text{CD}_3\text{CN}$  at room temperature, at least during 24 h, as previously found for complexes with bis(2-mercaptoimidazolyl)borates [1]. By contrast, complex **2** slowly releases the ancillary ligand  $\text{H}_2\text{C}(\text{tim}^{\text{Me}})_2$  in  $\text{CD}_3\text{CN}$ . After 24 h at room temperature, only 75% of complex **2** remains intact. Nevertheless, **2** is stable in acetone, a less coordinating solvent with a poor affinity for the  $\text{fac}[\text{Re}(\text{CO})_3]^+$  moiety. The presence of a unique eight-membered chelating ring in **2** and of two six-membered chelating rings in **1** certainly explains the highest thermodynamic stability of **1**.

#### 4. Concluding remarks

The first d-transition metal complex with a (2-mercaptothiazolyl)borate ligand,  $\text{fac}[\text{Re}\{\kappa^3\text{-H}(\mu\text{-H})\text{B}(\text{tiaz})_2\}(\text{CO})_3]$  (**1**), has been prepared and fully characterized. The stability of **1** in coordinating solvents indicates that dihydrobis(2-mercaptothiazolyl)borates are a class of ligands that may also be interesting for radiopharmaceutical research based on the organometallic approach, as previously shown for dihydrobis(2-mercaptoimidazolyl)borates [1].

The ligand bis(2-mercaptoimidazolyl)methane forms the complex  $\text{fac}[\text{ReBr}\{\kappa^2\text{-H}_2\text{C}(\text{tim}^{\text{Me}})_2\}(\text{CO})_3]$  (**2**), which is not a promising compound for the design of radiopharmaceuticals, since the ancillary ligand is replaceable by coordinating solvents. This might indicate a high probability for the occurrence of *trans*-chelation processes with endogenous biomolecules, compromising the in vivo stability of **2**, an important feature for biomedical applications.

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#### Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC no 609567 for compound **1** and CCDC no 609568 for compound **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.07.032.

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- [15] To a suspension of complex **2** (10 mg, 0.017 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added solid AgCF<sub>3</sub>SO<sub>3</sub> (4.4 mg, 0.017 mmol) and the resulting suspension was stirred overnight in the dark. The AgBr formed was removed by filtration and the solvent from the supernatant was evaporated under vacuum, yielding a white solid which was analysed by <sup>1</sup>H NMR and IR spectroscopy. The collected <sup>1</sup>H NMR and IR data indicate the formation of “*fac*-[Re(OTf){κ<sup>2</sup>-H<sub>2</sub>C-(tim<sup>Me</sup>)<sub>2</sub>}(CO)<sub>3</sub>]”. IR (KBr, ν/cm<sup>-1</sup>): 2012 (s) and 1896 (vs) ν(CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.81 (6H, s, N-CH<sub>3</sub>), 5.78 (1H, d, J<sub>AB</sub> = 14.0 Hz, CH<sub>2</sub>), 6.99 (2H, d, J = 2.4 Hz, CH), 2H, d, J = 2.4 Hz, CH), 7.18 (1H, d, J<sub>AB</sub> = 14.0 Hz, CH<sub>2</sub>).
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