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# Reaction of bromopentacarbonylrhenium(I) with ferrocenylcarbaldehyde thiosemicarbazones: the first X-ray diffraction studies of metal carbonyl complexes containing bidentate thiosemicarbazone ligands

Rosa Carballo<sup>a</sup>, José S. Casas<sup>b</sup>, Emilia García-Martínez<sup>a</sup>, Gumersindo Pereiras-Gabián<sup>a</sup>, Agustín Sánchez<sup>b</sup>, José Sordo<sup>b</sup>, Ezequiel M. Vázquez-López<sup>a,\*</sup>, Juan C. Garcia-Monteaudo<sup>c</sup>, Ulrich Abram<sup>d</sup>

<sup>a</sup> Departamento de Química Inorgánica, Facultad de Ciencias-Química, Universidade de Vigo, E-36200 Vigo, Galicia, Spain

<sup>b</sup> Departamento de Química Inorgánica, Facultad de Farmacia, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Galicia, Spain

<sup>c</sup> Departamento de Química Física, Facultad de Farmacia, Universidade de Santiago de Compostela, E-15782, Santiago de Compostela, Galicia, Spain  
<sup>d</sup> Institut für Chemie-Radiochemie, Freie Universität Berlin, D-14195 Berlin, Germany

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## Abstract

The reactions of  $[\text{ReBr}(\text{CO})_5]$  with ferrocenylcarbaldehyde thiosemicarbazones HL with different groups attached to the amide nitrogen ( $\text{R} = \text{H}, \text{Me}, \text{Ph}$ ) yielded complexes  $[\text{ReBr}(\text{CO})_3(\text{HL})]$  (**1**) in which, according to X-ray studies of **1a**· $\{(\text{CH}_3)_2\text{CO}\}$  and **1b**· $1/2\{(\text{CH}_2\text{Cl}_2)\}$ , the thiosemicarbazone is *N,S*-bidentate and the geometry around the metal *fac*-octahedral. Compounds of formula  $[\text{ReL}(\text{CO})_3]_2$  (**2**) were then prepared by reaction of the corresponding adduct **1** with NaOMe in acetone. A complex of formula  $[\text{ReL}^2(\text{CO})_3]_2$  (**2b'**) was also obtained as a dissolvate by slow concentration of a solution of **1b** in acetone. Single crystals of **2a** and **2b** obtained from the mother liquors are composed of centrosymmetric dimers formed by Re–S–Re bridges, where S is the thiolic sulfur of an *N,S*-bidentate thiosemicarbazonato ligand. Although **2b**· $2\{(\text{CH}_3)_2\text{CO}\}$  and **2b'**· $2\{(\text{CH}_3)_2\text{CO}\}$  have similar coordination spheres, they differ as regards the configuration of the thiosemicarbazonato ligand about the azomethine bond and certain bond lengths (notably Re–N); it seems likely that the configuration of  $\text{L}^{2-}$  determines how close the rhenium can approach the N atom of the ligand, and hence the delocalization of the  $\pi$  electrons in the C–N–N fragment of the thiosemicarbazide chain. The mass, IR and UV–vis spectra of the complexes, and their electrochemical behavior, are also discussed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Ferrocene; Thiosemicarbazone; Rhenium(I); Carbonyl complexes

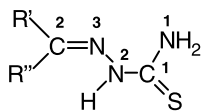
## 1. Introduction

Compounds incorporating chromophore and redox units in a single molecule have been widely studied because of their potential as chemical sensors. When the state of the redox unit determines some property of a part or the whole of the molecule, then the molecule (or

supramolecule) behaves as a molecular switch [1]. In metal complexes of this kind, interaction between the redox unit and the metal via a chromophore has been explored as regards the effect of the state of the redox unit on the spectroscopic properties and reactivity of the metal [2]. Ligands equipped for this purpose with redox units such as ferrocene include pyridine [3], phosphines [2,4] and more complicated molecules such as macrocycles [5] or porphyrins [6]. In many such systems, however, there is in fact no communication between the two units (see for instance Ref. [3a]).

\* Corresponding author. Tel.: +34-986-812319; fax: +34-986-812556

E-mail address: ezequiel@uvigo.es (E.M. Vázquez-López).



Thiosemicarbazones (TSCs) are very versatile ligands. They can co-ordinate to metals as neutral molecules or, after deprotonation, as anionic ligands, and can adopt a variety of different co-ordination modes [7]. The possibility of their being able to transmit electronic effects between a redox unit and a metal centre is suggested by the delocalization of the  $\pi$  bonds in the thiosemicarbazide chain, which is especially marked when the substituent on carbon C(2) is aromatic [8].

As part of our studies of thiosemicarbazone complexes of metal carbonyl compounds, in this work we reacted  $[\text{ReBr}(\text{CO})_5]$  with HL, which has known electrochemical properties [9] but largely unknown co-ordination chemistry [10], and we investigated the reactivity of the resulting complexes and the capacity of the TSCs to communicate the ferrocene and metal centres.

## 2. Results and discussion

### 2.1. Synthesis of the thiosemicarbazone derivatives

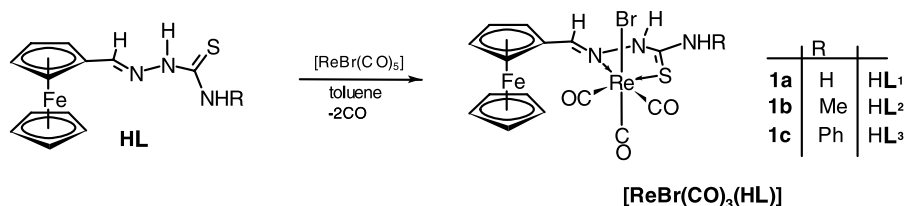
Adducts  $[\text{ReBr}(\text{CO})_3(\text{HL})]$  were obtained in good yields by reacting the corresponding free ligand HL with  $[\text{ReBr}(\text{CO})_5]$  in refluxing toluene (Scheme 1). Red solids that were stable in air, moderately soluble in dichloromethane and highly soluble in acetone were isolated from the reaction mixture.

The stoichiometry shown in Scheme 1 was established by elemental analysis and mass spectrometry. All the mass spectra contain signals corresponding to the molecular ions, although the most intense peak corresponding to a metallated species is always  $[\text{M}-\text{Br}]^+$  (whereas for  $[\text{ReBr}(\text{CO})_3\text{L}_2]$  (L = a phosphonite or phosphite ligand) [11] this signal is weak). *Fac* geometry around the rhenium atom is suggested by the three strong  $\nu(\text{CO})$  IR bands in the range  $2030\text{--}1900\text{ cm}^{-1}$  in the spectra of **1a** and **1b** (the lowest-energy vibration is a shoulder), and was confirmed by the X-ray study of single crystals of **1a** and **1b** obtained by slow concentration of solutions in acetone and dichloromethane, respectively (vide infra). Few thiosemicarbazone com-

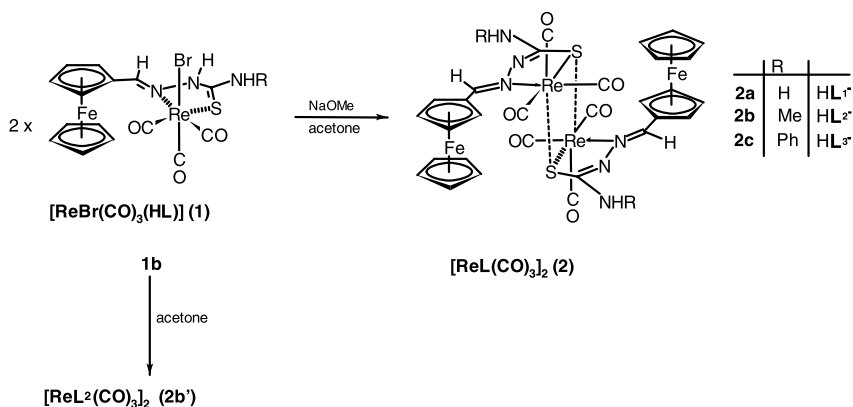
plexes of metal carbonyl compounds have been fully identified [7a,7b] and as far as we know the structures of only three compounds of W and Fe have been studied by X-ray diffraction [12], all of which contain neutral *S*-monodentate TSCs. These complexes were all obtained from acceptor species containing a relatively labile group such as  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{O}$  or acetone as well as CO groups, or by reactions involving the presence of decarboxylating reagents such as trimethylamine *N*-oxide.

Slow concentration of a solution of **1b** in acetone gave two types of crystal with different solubilities in this solvent. X-ray diffractometry showed only the less soluble to possess internal order. Crystallographic analysis showed it to be the complex  $[\text{ReL}^2(\text{CO})_3]_2 \cdot 2\{(\text{CH}_3)_2\text{CO}\}$  (**2b'**  $\cdot 2\{(\text{CH}_3)_2\text{CO}\}$ , vide infra), in which the TSC ligands are deprotonated and the bromine atom in the co-ordination sphere of the metal in **1b** has been replaced by the sulfur atom of the other monomer. The formation of **2b'** suggests that in acetone solution **1b** is subject to deprotonation equilibrium, and shows the lability of the co-ordination sphere of the metal. The behavior of **1b** contrasts with that of *fac*- $[\text{ReBr}\{\text{Ph}_2\text{PCH}_2\text{-C}(\text{O})\text{R}\}(\text{CO})_3]$  (R = Ph, Fc), which gives the anionic complex *fac*- $[\text{ReBr}(\text{Ph}_2\text{PCH}_2\text{-C}(\text{O})\text{R})(\text{CO})_3]^-$  when the co-ordinated ketophosphinic ligand is deprotonated [4]. However, hypothesizing that it was indeed deprotonation of **1b** that initiated the formation of **2b'**, we treated acetone solutions of compounds **1** with sodium methanolate. As expected, this afforded moderate yields of the dimeric complexes  $[\text{ReL}(\text{CO})_3]_2$  (**2**, Scheme 2), which were isolated as orange crystalline solids that were stable in air, poorly soluble in dichloromethane and acetone, and soluble but unstable in DMSO. Performing the same reaction in toluene gave solids with mass spectra and elemental analyses indicating the presence of impure dimeric complexes.

The mass spectra of compounds **2** show signals corresponding to the dimeric molecular ions  $[\text{M}]^+$ . Furthermore, the spectra of **2a** and **2c** also show peaks at  $m/z = 557$  and  $633$ , respectively, the isotopic patterns of which are similar to that of  $[\text{M}]^+$ , suggesting that they are due to  $[\text{M}/2]^+$  species resulting from the symmetric cleavage of the dimeric molecule rather than to the species  $[\text{M}]^{2+}$ . The fact that the IR spectra do not differ significantly from those of the correspond-



Scheme 1.



Scheme 2.

ing precursors **1** suggests that compounds **2** also have *fac* geometry around the rhenium atom, and for **2a** and **2b** this was confirmed by X-ray studies.

## 2.2. Structures of $[\text{ReBr}(\text{CO})_3(\text{HL})]$ : **1a**· $\{(\text{CH}_3)_2\text{CO}\}$ and **1b**· $1/2\{\text{CH}_2\text{Cl}_2\}$

Fig. 1 shows the molecular structures of the two compounds **1** studied by X-ray diffractometry. The chief bond lengths and angles around the rhenium atom are listed in Table 1, and those of the ligand fragment in Table 2. In both compounds, the rhenium atom is octahedrally co-ordinated to three carbonyl carbon atoms in *fac* arrangement, a bromine atom, and the N(3) and S atoms of the TSC ligand, with which the metal forms a five-membered chelate ring. As far as we know, these are the first thiosemicarbazone complexes of rhenium, and the first complexes of any metal carbonyl with a bidentate thiosemicarbazone, to have been characterized structurally by X-ray diffractometry. The Re–Br and Re–C distances are close to those found in *fac*- $[\text{ReBr}(\text{CO})_3(\text{NHR}_2)_2]$  (R = Me, Et) [13] and the former is shorter than that observed in Re complexes with bidentate phosphorus ligands [14]. The Re–N(3)

distance is also similar to that found in amine [13] and imine [15] adducts.

The co-ordination of HL to rhenium modifies the thiosemicarbazide chain [16], changing the configuration about the C(1)–N(2) bond from *E* to *Z* to facilitate N(3),S-co-ordination. There are also small changes in the bond lengths around the azomethine nitrogen, N(3). However, the C–S distance is hardly altered (1.690(3) Å in HL<sup>1</sup>; 1.672(4), 1.674(5) Å in HL<sup>2</sup>) [16], suggesting that the thione form persists in both complexes. The configuration about the C(2)–N(3) bond is *E* in **1a** and *Z* in **1b** [C(11)–C(2)–N(3)–N(2) = 174.9(13) in **1a** and  $-3.6(18)^\circ$  in **1b**]. The angle between the cyclopentadienyl ring bound to C(2) and the least-squares plane of the thiosemicarbazide chain is 40.0(1)° in **1a** and 36.2(5)° in **1b**. The bromine atom is *anti* to the iron atom (Scheme 3), although the presence of two sets of thiosemicarbazide and ferrocene signals in the <sup>1</sup>H-NMR spectra suggests that the *anti* and *syn* diastereomers are probably both present in acetone solution.

Hydrogen bonds are present in both compounds (Fig. 2). In **1a**, the bond between the N(1)H<sub>2</sub> group and the bromine atom of a neighbouring molecule (N(1)–H(1B)···Br<sup>i</sup> = 0.86, 2.61, 3.465(13) Å, 173.9°, *i* =  $-x +$

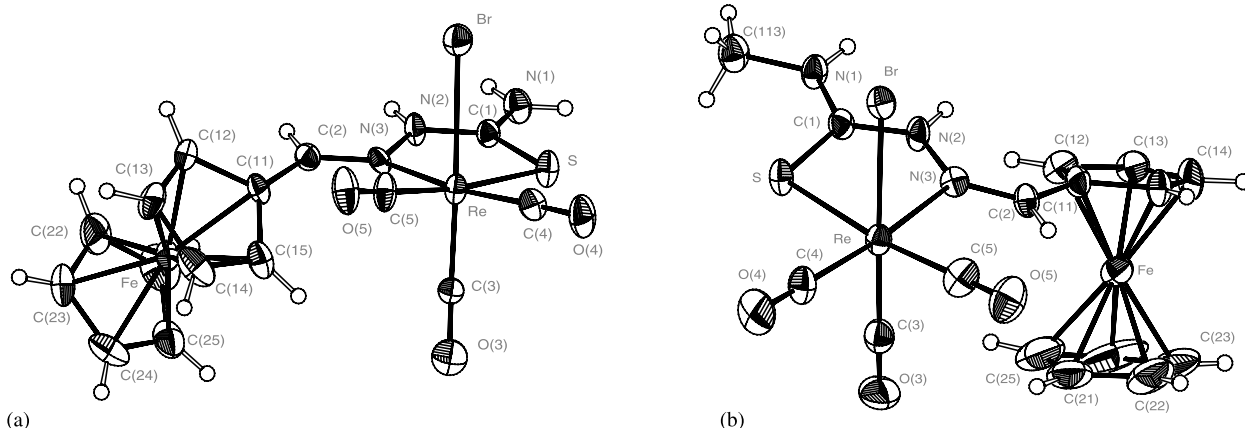


Fig. 1. Molecular structures of **1a**· $\{(\text{CH}_3)_2\text{CO}\}$  (a) and **1b**· $1/2\text{CH}_2\text{Cl}_2$  (b), showing the atomic numbering schemes. The thermal ellipsoids represent 30% occupancy.

Table 1  
Main bond lengths and angles in the co-ordination sphere around the rhenium atom <sup>a</sup>

	<b>1a</b> · {(CH <sub>3</sub> ) <sub>2</sub> CO}	<b>1b</b> · 1/2CH <sub>2</sub> Cl <sub>2</sub>	<b>2a</b> <sup>b</sup>	<b>2b</b> · 2{(CH <sub>3</sub> ) <sub>2</sub> CO} <sup>b</sup>	<b>2b'</b> · 2{(CH <sub>3</sub> ) <sub>2</sub> CO} <sup>b</sup>
<i>Bond lengths</i>					
Re–C(3)	1.816(14)	1.913(14)	1.868(17)	1.913(8)	1.983(7)
Re–C(4)	1.902(17)	1.925(13)	1.924(13)	1.879(9)	1.807(5)
Re–C(5)	1.906(16)	1.941(15)	1.901(14)	1.898(8)	1.927(6)
Re–N(3)	2.214(11)	2.208(8)	2.210(9)	2.213(5)	2.067(4)
Re–S	2.455(4)	2.455(3)	2.465(3)	2.4760(18)	2.4697(13)
Re–X <sup>a</sup>	2.6481(17)	2.6483(12)	2.537(4)	2.5409(18)	2.6706(13)
Re–Re <sup>i</sup>			3.7943(11)	3.8049(5)	3.7804(4)
C(3)–O(3)	1.187(16)	1.134(15)	1.162(16)	1.137(9)	1.205(7)
C(4)–O(4)	1.162(17)	1.138(13)	1.135(14)	1.179(10)	1.087(6)
C(5)–O(5)	1.166(16)	1.134(15)	1.159(15)	1.169(9)	1.178(7)
<i>Bond angles</i>					
C(3)–Re–C(4)	90.3(6)	87.6(5)	90.3(6)	89.4(3)	84.9(2)
C(3)–Re–C(5)	93.9(7)	90.5(6)	88.7(6)	88.7(3)	93.8(2)
C(4)–Re–C(5)	88.3(6)	90.5(5)	91.1(5)	85.2(3)	91.3(2)
C(3)–Re–N(3)	94.0(5)	92.0(4)	91.3(5)	91.0(3)	95.31(19)
C(4)–Re–N(3)	170.8(5)	173.1(5)	171.7(4)	174.5(3)	176.8(2)
C(5)–Re–N(3)	99.5(5)	96.4(4)	97.1(4)	100.2(3)	91.90(2)
C(3)–Re–S	93.0(4)	94.3(4)	90.8(5)	90.9(2)	91.36(17)
C(4)–Re–S	91.8(5)	93.2(4)	94.1(4)	96.5(2)	93.11(19)
C(5)–Re–S	173.2(5)	174.0(4)	174.8(4)	178.2(2)	173.46(16)
N(3)–Re–S	79.8(3)	79.9(3)	77.8(3)	78.04(13)	83.66(12)
C(3)–Re–X <sup>a</sup>	177.3(4)	177.2(4)	172.0(4)	171.6(2)	176.69(17)
C(4)–Re–X <sup>a</sup>	92.4(5)	95.1(4)	91.5(4)	94.8(2)	95.91(18)
C(5)–Re–X <sup>a</sup>	86.4(5)	90.3(4)	99.0(5)	98.9(2)	89.35(17)
N(3)–Re–X <sup>a</sup>	83.3(3)	85.2(2)	85.8(3)	84.16(14)	83.68(11)
S–Re–X <sup>a</sup>	86.75(11)	84.75(8)	81.34(12)	81.36(6)	85.39(5)
Re–X–Re <sup>i</sup> <sup>a</sup>			98.66(12)	98.64(6)	94.61(5)
C(1)–S–Re	98.4(5)	98.7(4)	95.4(4)	94.2(2)	91.11(19)
C(2)–N(3)–Re	131.7(9)	123.6(7)	130.0(8)	132.6(4)	125.1(3)
N(2)–N(3)–Re	114.8(8)	116.0(6)	116.4(7)	117.4(4)	114.5(3)

<sup>a</sup> X = Br in **1**, S<sup>i</sup> in **2**.

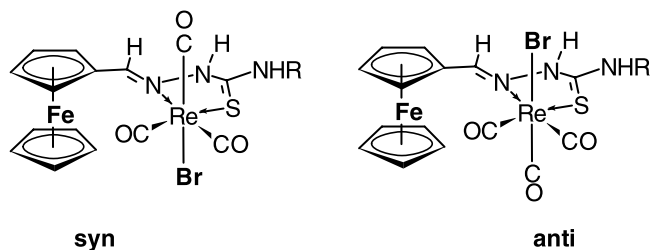
<sup>b</sup> Symmetry codes: **2a**,  $i = -x+1, -y+1, -z+1$ ; **2b**,  $i = -x+2, -y+1, -z+1$ ; **2b'**,  $i = -x+1, -y, -z+1$ .

3/2,  $y+1/2, -z+1/2$ ) links the monomers in chains, and the acetone molecule forms strong hydrogen bonds with the N(1)H<sub>2</sub> and N(2)H groups of the TSC (N(1)–H(1A)···O(6) = 0.86, 2.18, 2.937(1) Å, 147.0°; N(2)–

H(2)···O(6) = 0.84(13), 2.17(13), 2.946(17) Å, 143(13)°). In **1b**, however, the solvent molecule forms no hydrogen bonds, and the molecules are associated in dimers by hydrogen bonds between the bromine atom

Table 2  
Bond lengths (Å) and angles (°) in the thiosemicarbazone fragments

	<b>1a</b> · {(CH <sub>3</sub> ) <sub>2</sub> CO}	<b>1b</b> · 1/2CH <sub>2</sub> Cl <sub>2</sub>	<b>2a</b>	<b>2b</b> · 2{(CH <sub>3</sub> ) <sub>2</sub> CO}	<b>2b'</b> · 2{(CH <sub>3</sub> ) <sub>2</sub> CO}
<i>Bond lengths</i>					
S–C(1)	1.700(14)	1.696(11)	1.783(12)	1.785(7)	1.684(5)
N(1)–C(1)	1.343(17)	1.312(13)	1.342(15)	1.346(9)	1.313(7)
N(2)–C(1)	1.321(18)	1.337(13)	1.281(15)	1.290(8)	1.340(7)
N(2)–N(3)	1.403(15)	1.394(12)	1.408(13)	1.416(7)	1.366(6)
N(3)–C(2)	1.291(16)	1.292(13)	1.274(15)	1.309(8)	1.364(6)
C(2)–C(11)	1.397(18)	1.447(13)	1.410(17)	1.424(9)	1.374(7)
<i>Bond angles</i>					
C(1)–N(2)–N(3)	122.0(12)	121.9(9)	116.9(10)	115.4(5)	120.4(4)
C(2)–N(3)–N(2)	112.7(11)	119.5(9)	112.7(10)	109.3(5)	120.4(4)
N(2)–C(1)–N(1)	118.3(12)	116.2(10)	120.1(11)	119.7(6)	123.9(5)
N(2)–C(1)–S	123.0(11)	121.4(9)	124.5(10)	126.3(5)	126.7(4)
N(1)–C(1)–S	118.6(11)	121.4(9)	115.3(9)	114.0(5)	109.4(4)
N(3)–C(2)–C(11)	124.7(13)	129.8(11)	133.9(12)	131.0(6)	132.8(5)



Scheme 3.

and both the N(1)HMe and N(2)H groups of the partner (N(1)–H(1)···Br<sup>i</sup> = 0.86, 2.51, 3.349(9) Å, 164.2°; N(2)–H(2A)···Br<sup>i</sup> = 0.86, 2.76, 3.529(9) Å, 148.8°; *i* =  $-x+1/2$ ,  $-y+1/2$ ,  $-z+1$ ).

### 2.3. Structure of the dimeric thiosemicarbazonato complex [ReL<sup>i</sup>(CO)<sub>3</sub>]<sub>2</sub> (**2a**)

Single crystals of **2a** were obtained by slow evaporation of the mother liquor produced in the synthesis of the compound (see Section 3). Its molecular structure is shown in Fig. 3. The interaction of the rhenium atom with the sulfur atom of a neighbouring molecule at the position occupied by the Br ligand of **1a** creates centrosymmetric dimers. The rhenium atom retains its octahedral co-ordination, but now interacts with two sulfur atoms, and the sulfur belonging to the partner in the dimer (S<sup>i</sup>, Fig. 3), placed *syn* to the iron atom of ferrocene, is farther away than its 'own' sulfur. The Re–S<sup>i</sup>–Re<sup>i</sup> bridge is in fact more asymmetric than in either the dithiophosphinato Re complex [Re<sub>2</sub>(μ-S<sub>2</sub>PET<sub>2</sub>)<sub>2</sub>(CO)<sub>6</sub>] (Re–S = 2.535(8) and 2.570(11) Å) **17a** or the trithiocarbonate [Re<sub>4</sub>(S<sub>3</sub>C)(CO)<sub>11</sub>] (Re–S = 2.487 and 2.514 Å) **17b**. The planar Re<sub>2</sub>S<sub>2</sub> diamond, in which the Re–Re distance is too long for means any significant

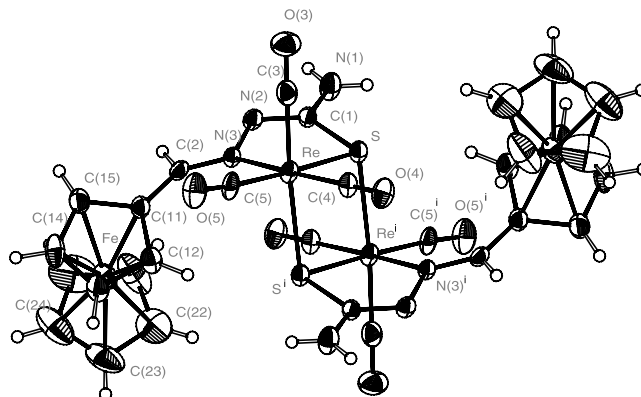


Fig. 3. Molecular structure of **2a**, showing the atomic numbering scheme. The thermal ellipsoids represent 30% occupancy (symmetry code *i* =  $-x+1$ ,  $-y+1$ ,  $-z+1$ ).

bonding interaction (Table 1), has bond angles close to 90°.

The Re–N(3) and Re–S distances are similar to those of **1a**, but C(1)–S is longer than in this adduct or the free ligand, suggesting a predominantly thiol character (Scheme 4). This conclusion is reinforced by the shortening of N(2)–C(1) (1.333(4) Å in HL, 1.321(18) Å in **1a** and 1.281(15) Å in **2a**). As in **1a** the configuration around this latter bond is *Z* (because of the N(3),S chelation to the rhenium) and the configuration with respect to C(2)–N(3) is *E* (C(11)–C(2)–N(3)–N(2) = 177.0(14)°), though the angle between the thiosemicarbazide plane and the plane of the cyclopentadienyl ring is now only 21.9(2)°. This arrangement facilitates a hydrogen bond between the un-substituted Cp ring and the sulfur atom of the partner in the dimer (C(12)–H(12)···S<sup>i</sup> = 0.93, 2.69, 3.504(15) Å, 146.5°; *i* =  $-x+1$ ,  $-y+1$ ,  $-z+1$ ). There are also between-dimer hydro-

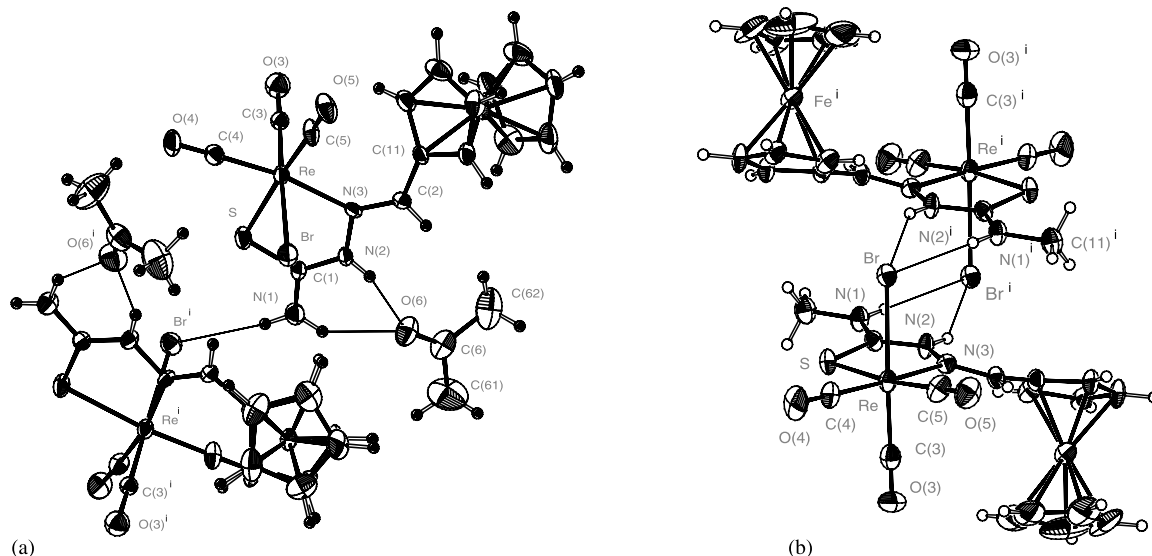
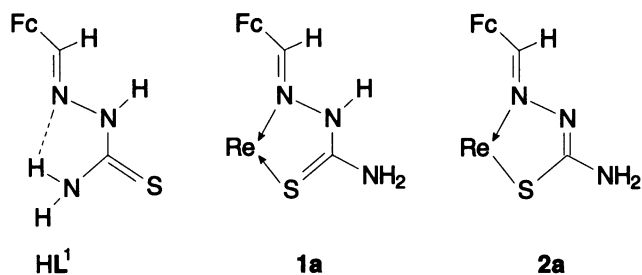


Fig. 2. ZORTEP plots showing the hydrogen bonds in crystals of **1a**·{(CH<sub>3</sub>)<sub>2</sub>CO} (a) and **1b**·1/2CH<sub>2</sub>Cl<sub>2</sub> (b). The thermal ellipsoids represent 30% occupancy.



Scheme 4.

gen bonds between the N(1)H<sub>2</sub> group and N(2) and O(5) atoms (N(1)–H(1A)···N(2)<sup>ii</sup> = 0.86, 2.29, 3.152(14) Å, 175.6°; N(1)–H(1B)···O(5)<sup>iii</sup> = 0.86, 2.46, 3.303(16) Å, 167.8°; ii =  $-x+2, -y+1, -z+1$ , iii =  $x, y-1, z$ ).

#### 2.4. The structures of the two isomers of [ReL<sup>2</sup>(CO)<sub>3</sub>]<sub>2</sub> (**2b**, **2b'**)

As described above, single crystals of composition [ReL<sup>2</sup>(CO)<sub>3</sub>]<sub>2</sub>·2{(CH<sub>3</sub>)<sub>2</sub>CO} were obtained in two different ways: slow concentration of the acetone solution from which **2b** had previously been isolated (**2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO}), and of an acetone solution of the adduct **1b** (**2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO}); see Scheme 2. In the two crystals the molecular dimer lies on the inversion centre but the thiosemicarbazonato ligand has two different configurations with respect to the C(2)–N(3) bond, *E* in **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} and *Z* in **2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO} (C(11)–C(2)–N(3)–N(2) = 179.9(6) and  $-4.7(9)^\circ$ , respectively; Fig. 4).

The structure of **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} resembles that of **2a** (Tables 2 and 3). The L<sup>2-</sup> chelates the rhenium via the N(3) and S atoms, and the C(1)–S distance suggests a predominantly thiol character. Hydrogen bonds (Fig. 5) bind two acetone molecules to the dimer via the N(1)HMe group (N(1)–H(1)···O(51) = 0.86, 2.08, 2.924(8) Å, 166.5°).

In **2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO} the dimerizing Re–S bonds are similar in length to those of **2a** and **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO}, and the Re–Re<sup>i</sup> distance continues to be too long to suggest bonding, but the C(1)–S bond is nevertheless shorter, the Re–N(3) and N(2)–N(3) bonds are much shorter, and the C(2)–N(3) bond is longer. Also, the acetone is bound more weakly to N(1) (Fig. 5) than in **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} (N(1)–H(1)···O(51) = 0.86, 2.22, 3.021(7) Å, 155.4°).

It seems likely that the differences between **2b** and **2b'** all derive from their being formed from ligands differing in their configuration with respect to the C(2)–N(3) bond, and hence in the degree of the steric hindrance exerted by the ferrocene group. The *Z* configuration in **2b'** holds the ferrocene moiety away from N(3), which can thus induce redistribution of the π electrons in the TSC (especially in the C(11)–C(2)–N(3)–N(2) section; Scheme 4 does not represent the electronic structure of **2b'** adequately), and thereby give rise to structural changes. The fact that whether **2b** or **2b'** was isolated depended on whether deprotonation of **1b** was induced or spontaneous suggests that both these complexes are formed once the ligand is deprotonated, and that the isolation of one or the other is determined solely by the solubilities of each in the different reaction media.

#### 2.5. UV–vis and electrochemical studies

The main features of the diffuse reflectance spectra of the ligands and complexes are described in Table 3. In all cases, the spectrum is dominated by the ferrocene bands, which have been discussed by John et al. [18].

The preliminary results of cyclic voltammetry studies are also listed in Table 3. These studies were limited by deposition of the oxidized phase on the electrode. Although voltammograms were recorded at the stability limit of the supporting electrolyte (ca. 1.6 V), they only show waves attributable to the ferrocene centre. A comparison with results obtained for the free ligands

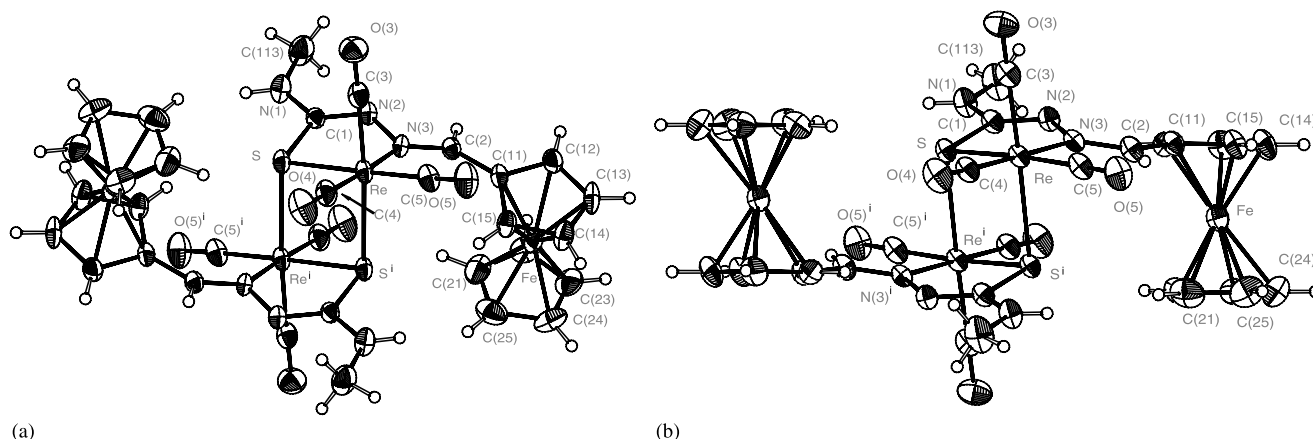


Fig. 4. Molecular structures of **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} (a) and **2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO} (b) showing the atomic numbering schemes. The thermal ellipsoids represent 30% occupancy (symmetry codes: **2b**, i =  $-x+2, -y+1, -z+1$ ; **2b'**, i =  $-x+1, -y, -z+1$ ).

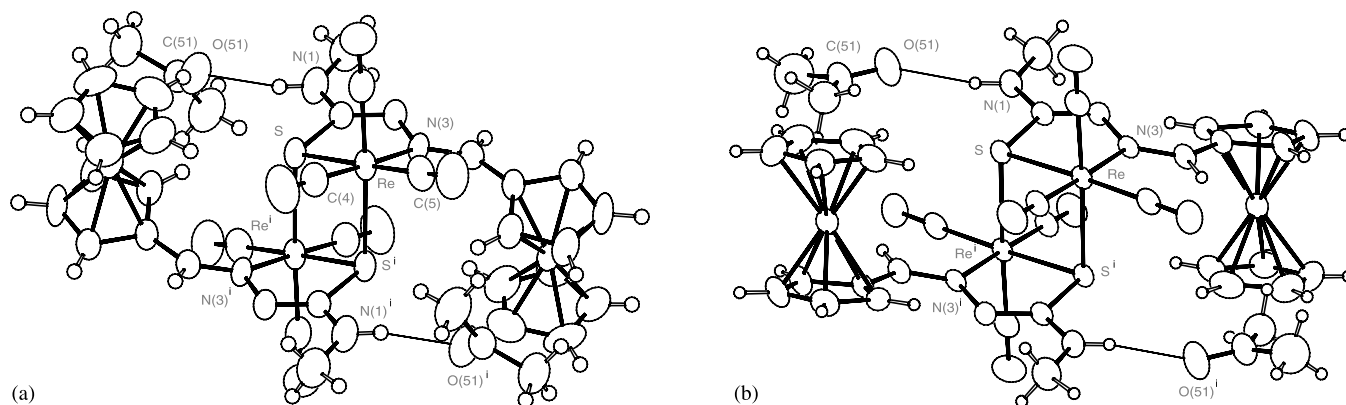


Fig. 5. ZORTEP plots showing the hydrogen bonding of acetone molecules in **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} (a) and **2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO} (b). The thermal ellipsoids represent 30% occupancy.

in acetonitrile by Graúdo et al. [9] shows that the solvent has little influence on the redox process.

Since the separation between the waves corresponding to the anodic and cathodic processes is larger for the rhenium adducts than the free ligands, the oxidation is electrochemically irreversible. As in the case of the free ligands in acetonitrile [9], the nature of R has little effect on the electrochemical behavior. However, the fact that oxidation is always easier for the complexes (especially compounds **2**) than for the free ligands (Fig. 6) suggests that there is back-donation of charge from the Re(CO)<sub>3</sub> fragment to the ferrocene by TSC chain. In this respect, the difference between compounds **1** and **2** has a precedent in the difference between *fac*-[Re-Br{Ph<sub>2</sub>PCH<sub>2</sub>-C(O)Fc}(CO)<sub>3</sub>] and its anion *fac*-[Re-Br{Ph<sub>2</sub>PCH-C(O)Fc}(CO)<sub>3</sub>] [4].

The voltammograms of **2a** and **2c** reflect only one electrochemical process. This shows that there is no electronic communication between the two ferrocene

fragments via the Re<sub>2</sub>S<sub>2</sub> diamond. Although the voltammogram of **2b** presents two oxidation and reduction waves, it seems likely, bearing in mind the scant effect of R on electrochemical behavior, that this is an artifact due to problems at the interface with the electrode deriving from deposition of the species **2b**<sup>2+</sup>.

In search of correlation between redox potential (which increases upon co-ordination of the ligand) and the bathochromic shift of the lowest-energy spin-allowed d–d band (at ca. 450 nm) and the simultaneous increase in absorption intensity by increasing the MLCT character of this band [19], we recorded the UV–vis spectra of the ligands and complexes in solution. For all the ligands, bands appeared at positions similar to those reported previously [20]. Co-ordination caused bathochromic shifts and an accompanying increase in absorption in the lowest-energy band, but unlike redox response these parameters do not seem to be sensitive to whether the ligand is neutral or anionic. This suggests

Table 3  
Electrochemical and spectroscopic data

Compound	$E_{ap}$ (V) <sup>a</sup>	$E_{cp}$ (V) <sup>a</sup>	Solvent	Diffuse reflectance, $\lambda$ (assignment) <sup>b</sup>	Solution, $\lambda$ ( $\epsilon$ ) <sup>b,c</sup>
HL <sup>1</sup>	0.66 0.57	0.50 0.50	CH <sub>2</sub> Cl <sub>2</sub> CH <sub>3</sub> CN <sup>d</sup>	289, 363, 464	313 (24.6), 461 (0.9)
<b>1a</b>	0.66	−0.19	CH <sub>2</sub> Cl <sub>2</sub>	295, 391, 492	344 (3.3), 493 (1.8)
<b>2a</b>	0.22	−0.25	CH <sub>2</sub> Cl <sub>2</sub> /acetone		331 (16.8), 485 (3.0)
HL <sup>2</sup>	0.68	0.46	CH <sub>2</sub> Cl <sub>2</sub> CH <sub>3</sub> CN <sup>d</sup>	289, 368, 464	313 (26.6), 456 (1.3) 258 (11.8), 303 (42.0), 448 (1.1) <sup>e</sup>
<b>1b</b>	0.46	−0.16	CH <sub>2</sub> Cl <sub>2</sub>	289, 357, 486	351 (8.0), 486 (2.3)
<b>2b</b>	0.80 0.22	−0.21 −0.17	CH <sub>2</sub> Cl <sub>2</sub> /acetone		332 (13.6), 472 (3.0)
HL <sup>3</sup>	0.70 0.57	0.57 0.51	CH <sub>2</sub> Cl <sub>2</sub> CH <sub>3</sub> CN <sup>d</sup>	295, 379, 481	317 (26.0), 457 (1.7) 272 (15.1), 314 (27.8), 390 (1.1) <sup>a</sup>
<b>1c</b>	0.46	−0.16	CH <sub>2</sub> Cl <sub>2</sub>	289, 385, 503	355 (10.7), 483 (2.7)
<b>2c</b>	0.17	−0.22	CH <sub>2</sub> Cl <sub>2</sub> /acetone		342 (12.9), 486 (3.0)

<sup>a</sup>  $E_{ap}$ , anodic peak potential;  $E_{cp}$ , cathodic peak potential.

<sup>b</sup> Wavelengths in nm.

<sup>c</sup> Data obtained from ca. 10<sup>−4</sup> M CH<sub>2</sub>Cl<sub>2</sub> solutions. Between parentheses:  $\epsilon \times 10^{-3}$  dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>.

<sup>d</sup> Data obtained from Ref. [9].

<sup>e</sup> Data in CH<sub>3</sub>CN obtained from Ref. [20].

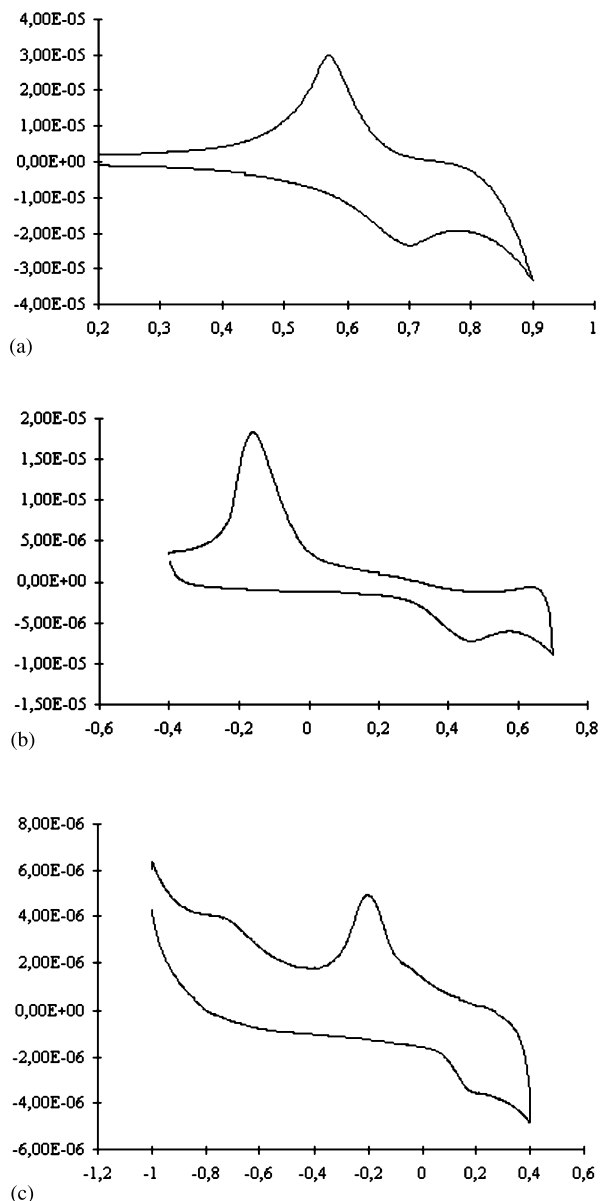


Fig. 6. Cyclic voltammograms of HL<sup>3</sup> (a), 1c (b) and 2c (c).

that other factors (e.g. Cp ring tilt [21a], Cp ring rotation [21b] and iron–metal interactions [21c]) must dominate both redox and chromogenic effects [22].

### 3. Experimental

All operations were carried out under an atmosphere of dry Ar using standard Schlenk techniques. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled in an Ar atmosphere [23].

Re<sub>2</sub>(CO)<sub>10</sub> (ABCR) and ferrocenylformaldehyde (Aldrich) were used as supplied, without any further purification. Ferrocenylcarbaldehyde thiosemicarbazone (HL<sup>1</sup>), <sup>1</sup>N-methyl-ferrocenylcarbaldehyde thio-

micarbazone (HL<sup>2</sup>), <sup>1</sup>N-phenyl-ferrocenylcarbaldehyde thiosemicarbazone (HL<sup>3</sup>) and [ReBr(CO)<sub>5</sub>] were synthesized by reported methods [20,24].

Elemental analyses were carried out on a Fisons EA-1108. Melting points (m.p.) were determined on a Gallenkamp MFB-595 and are uncorrected. Mass spectra were recorded on a Micromass spectrometer operating under FAB conditions (nitrobenzyl alcohol matrix). IR spectra were recorded from KBr pellets on a Bruker Vector 22FT spectrophotometer. <sup>1</sup>H-NMR spectra were obtained from C<sub>3</sub>H<sub>6</sub>O-*d*<sub>6</sub> solutions on a Bruker AMX 400 spectrometer; chemical shifts are referred to internal Me<sub>4</sub>Si.

Cyclic voltammograms were recorded at 298 K in dry CH<sub>2</sub>Cl<sub>2</sub> (1) or 1:1 C<sub>3</sub>H<sub>6</sub>O–CH<sub>2</sub>Cl<sub>2</sub> (2) with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte using a PAR Model 273 potentiostat/galvanostat, a saturated calomel reference electrode, a Pt wire as counter electrode and a Pt disc as working electrode. A Shimadzu UV-3101 PC spectrophotometer was used to obtain electronic spectra in the region 900–350 nm in the solid state. UV–vis spectra of CH<sub>2</sub>Cl<sub>2</sub> solutions were recorded in a CECIL CE2021 apparatus.

#### 3.1. Synthesis of [ReBr(CO)<sub>3</sub>(HL)] (1)

The following synthesis of 1a was typical. A mixture of [ReBr(CO)<sub>5</sub>] (200 mg, 0.49 mmol) and HL (150 mg, 0.52 mmol) in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> (10 ml) was refluxed for 1 h. The red precipitate formed was then filtered out and vacuum dried.

##### 3.1.1. Data for 1a (R = H)

Yield: 307 mg (99.8%). M.p. 200 °C (dec.). Anal. Found: C, 28.6; H, 2.2; N, 6.6; S, 5.2. C<sub>15</sub>H<sub>13</sub>BrFeN<sub>3</sub>O<sub>3</sub>ReS requires: C, 28.3; H, 2.1; N, 6.6; S, 5.0%. Mass spectrum [*m/z* (%): [M]<sup>+</sup> 637(9), [M–Br]<sup>+</sup> 557(34). IR (cm<sup>-1</sup>): 3452m, 3181w, 2985w ν(NH); 2023s, 1918s,b, 1898 sh ν(CO); 1608w, 1592w, 1541w δ(NHR)+ν(CN); 825w ν(CS). <sup>1</sup>H-NMR (ppm): 4.37s, 4.47s [5H, C(Cp)–H]; 4.75m, 4.78m, 4.84m [2H, C(12,15)–H]; 5.05m, 5.20m, 5.31m [2H, C(13,14)–H]; 8.35s, 8.57s [1H, C(2)–H]; 7.79s, 8.47s [2H, N(1)–H]; 11.02s, 12.03s,b [1H, N(2)–H]. Red single crystals of 1a·{(CH<sub>3</sub>)<sub>2</sub>CO} suitable for X-ray diffraction were obtained by slow concentration of an C<sub>3</sub>H<sub>6</sub>O solution of the complex.

##### 3.1.2. Data for 1b (R = Me)

Yield: 278 mg (87.1%). M.p. 200 °C (dec.). Anal. Found: C, 29.7; H, 2.3; N, 6.5; S, 5.2. C<sub>16</sub>H<sub>14</sub>BrFeN<sub>3</sub>O<sub>3</sub>ReS requires: C, 29.5; H, 2.3; N, 6.5; S, 4.9%. Mass spectrum [*m/z* (%): [M]<sup>+</sup> 651(4), [M–Br]<sup>+</sup> 572(16). IR (cm<sup>-1</sup>): 3441m, 3196w, 3023w ν(NH); 2020s, 1911s,b, 1894 sh ν(CO); 1591w, 1521w δ(NHR)+ν(CN); 828w ν(CS). NMR (ppm): 3.13s, 3.15s, 3.19s,b [3H, N(1)–CH<sub>3</sub>]; 4.36s, 4.45s [5H, C(Cp)–H]; 4.74m, 4.76m,



4.79m [2H, C(12,15)–H]; 5.04m, 5.06b, 5.19s,b, 5.29s,b [2H, C(13,14)–H]; 8.29s, 8.79s [1H, C(2)–H]; 8.07s,b, 8.58s [2H, N(1)–H]; 10.81s, 11.69s,b [1H, N(2)–H]. Red single crystals of **1b**·1/2CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray diffraction were obtained by slow concentration of a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. Crystallization from C<sub>3</sub>H<sub>6</sub>O yielded single crystals of **2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO}.

### 3.1.3. Data for **1c** (*R* = Ph)

Yield: 225 mg (63.7%). M.p. 205 °C (dec.). Anal. Found: C, 35.7; H, 2.1; N, 6.0; S, 4.4. C<sub>21</sub>H<sub>17</sub>BrFeN<sub>3</sub>O<sub>3</sub>ReS requires: C, 35.5; H, 2.4; N, 5.9; S, 4.5%. Mass spectrum [*m/z* (%): [M]<sup>+</sup> 713(6), [M–Br]<sup>+</sup> 634(17). IR (cm<sup>-1</sup>): 3344m, 3108w, 3001w ν(NH); 2024s, 1917s,b ν(CO); 1566w, 1541w, 1494w δ(NHR)+ν(CN); 825w ν(CS). NMR (ppm): 7.61–7.54m [2H, C(Ph)–H<sub>o</sub>]; 7.52–7.48m [2H, C(Ph)–H<sub>m</sub>]; 7.47–7.34m [1H, C(Ph)–H<sub>p</sub>]; 4.36s, 4.44s [5H, C(Cp)–H]; 4.78m, 4.81m [2H, C(13,14)–H]; 5.01m, 5.20m, 5.26m, 5.88b [2H, C(12,15)–H]; 8.39s, 8.64s [1H, C(2)–H]; 10.00s,b, 10.55s [1H, N(1)–H]; 10.84s, 11.94s [1H, N(2)–H].

## 3.2. Synthesis of [ReL(CO)<sub>3</sub>]<sub>2</sub> (**2**)

To a solution of 200 mg of the adduct [Re–Br(CO)<sub>3</sub>(HL)] (3.14 mmol of **1a**, 3.07 mmol of **1b**, 2.8 mmol of **1c**) in 5 ml of C<sub>3</sub>H<sub>6</sub>O was added the corresponding equimolar amount of NaOMe (17 mg for **2a**, 17 mg for **2b**, 15 mg for **2c**) and the mixture was stirred for 1 h at r.t. The orange solid formed was filtered out, washed with water and vacuum dried over CaCl<sub>2</sub>.

### 3.2.1. Data for **2a** (*R* = H)

Yield: 26.3 mg (15.1%). M.p. 200 °C (dec.). Anal. Found: C, 32.5; H, 2.3; N, 7.5; S, 5.9. C<sub>30</sub>H<sub>24</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>6</sub>Re<sub>2</sub>S<sub>2</sub> requires: C, 32.3; H, 2.2; N, 7.6; S, 5.8%. Mass spectrum [*m/z* (%): [M]<sup>+</sup> 1112(16), [M/2]<sup>+</sup> 557(11). IR (cm<sup>-1</sup>): 3471s, 3355m, 3171m ν(NH); 2016s, 1923s, 1894s ν(CO); 1605m, 1586m, 1561m δ(NHR)+ν(CN); 822w ν(CS). Orange single crystals of **2a** suitable for X-ray diffraction were obtained by slow concentration of the mother liquor.

### 3.2.2. Data for **2b** (*R* = Me)

Yield: 50.9 mg (28.9%). M.p. 200 °C (dec.). Anal. Found: C, 34.0; H, 2.4; N, 7.4; S, 5.4. C<sub>32</sub>H<sub>28</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>6</sub>Re<sub>2</sub>S<sub>2</sub> requires: C, 33.7; H, 2.5; N, 7.4; S, 5.6%. Mass spectrum [*m/z* (%): [M]<sup>+</sup> 1142(6). IR (cm<sup>-1</sup>): 3453s, 3365m, 3232m ν(NH); 2016s, 1923s, 1892s ν(CO); 1605m, 1561m δ(NHR)+ν(CN); 826w ν(C=S). Orange single crystals of **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} suitable for X-ray diffraction were obtained by slow concentration of the mother liquor.

### 3.2.3. Data for **2c** (*R* = Ph)

Yield: 12.9 mg (14.5%). M.p. 200 °C (dec.). Anal. Found: C, 39.8; H, 2.5; N, 6.5; S, 5.1. C<sub>42</sub>H<sub>32</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>6</sub>Re<sub>2</sub>S<sub>2</sub> requires: C, 39.9; H, 2.6; N, 6.6; S, 5.1%. Mass spectrum [*m/z* (%): [M]<sup>+</sup> 1265(24), [M/2]<sup>+</sup> 633(29). IR (cm<sup>-1</sup>): 3404s, 3345m, 3232m ν(NH); 2016s, 1921s, 1894s ν(CO); 1585m, 1559m, 1518m δ(NHR)+ν(CN); 824w ν(C=S).

Table 4  
Crystal data, data collection and refinement

	<b>1a</b> ·{(CH <sub>3</sub> ) <sub>2</sub> CO}	<b>1b</b> ·1/2CH <sub>2</sub> Cl <sub>2</sub>	<b>2a</b>	<b>2b</b> ·2{(CH <sub>3</sub> ) <sub>2</sub> CO}	<b>2b'</b> ·2{(CH <sub>3</sub> ) <sub>2</sub> CO}
Chemical formula	C <sub>18</sub> H <sub>19</sub> BrFeN <sub>3</sub> O <sub>4</sub> ReS	C <sub>16.5</sub> H <sub>16</sub> BrClFeN <sub>3</sub> O <sub>3</sub> ReS	C <sub>30</sub> H <sub>24</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>6</sub> Re <sub>2</sub> S <sub>2</sub>	C <sub>38</sub> H <sub>40</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>8</sub> Re <sub>2</sub> S <sub>2</sub>	C <sub>38</sub> H <sub>40</sub> Fe <sub>2</sub> N <sub>6</sub> O <sub>8</sub> Re <sub>2</sub> S <sub>2</sub>
Formula weight	695.38	693.79	1112.77	1256.98	1256.98
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> (Å)	10.6491(9)	30.608(3)	9.5748(10)	12.2580(8)	11.2697(8)
<i>b</i> (Å)	10.1254(8)	10.6489(12)	9.6924(10)	13.9451(10)	19.0939(13)
<i>c</i> (Å)	20.4636(16)	13.1567(14)	11.4245(12)	12.6639(9)	10.4016(7)
$\alpha$ (°)			91.133(2)		
$\beta$ (°)	91.113(2)	90.460(2)	105.565(2)	90.6410(10)	100.5490(10)
$\gamma$ (°)			111.200(2)		
<i>V</i> (Å <sup>3</sup> )	2206.1(3)	4288.2(8)	944.13(17)	2164.6(3)	2200.4(3)
<i>Z</i>	4	8	1	2	2
$\rho$ (g ml <sup>-3</sup> )	2.094	2.149	1.957	1.929	1.897
$\mu$ (mm <sup>-1</sup> )	8074	8524	7299	6383	6279
Reflections measured	9099	12 371	6046	13 005	14 275
Independent reflections	3115 (0.0873)	4839 (0.0821)	4170 (0.0493)	5035 (0.0632)	5243 (0.0497)
<i>R</i> factors	<i>R</i> <sub>1</sub> = 0.0600,	<i>R</i> <sub>1</sub> = 0.0546,	<i>R</i> <sub>1</sub> = 0.0562,	<i>R</i> <sub>1</sub> = 0.0458,	<i>R</i> <sub>1</sub> = 0.0366,
[ <i>I</i> > 2σ( <i>I</i> )]	<i>wR</i> <sub>2</sub> = 0.1374	<i>wR</i> <sub>2</sub> = 0.1162	<i>wR</i> <sub>2</sub> = 0.1383	<i>wR</i> <sub>2</sub> = 0.0997	<i>wR</i> <sub>2</sub> = 0.0886
<i>R</i> factors (all data)	<i>R</i> <sub>1</sub> = 0.0883,	<i>R</i> <sub>1</sub> = 0.1118,	<i>R</i> <sub>1</sub> = 0.0909,	<i>R</i> <sub>1</sub> = 0.0713,	<i>R</i> <sub>1</sub> = 0.0560,
	<i>wR</i> <sub>2</sub> = 0.1463	<i>wR</i> <sub>2</sub> = 0.1433	<i>wR</i> <sub>2</sub> = 0.1477	<i>wR</i> <sub>2</sub> = 0.1073	<i>wR</i> <sub>2</sub> = 0.0971

### 3.3. X-ray data collection, structure determination and refinement

Crystallographic data collection and refinement parameters are listed in Table 4. All crystallographic measurements were performed on a Bruker Smart CCD apparatus at CACTI (Universidade de Vigo). The data were corrected for absorption effects using the program SADABS [25a].

Structure analyses were carried out by direct methods [25b]. Least-squares full-matrix refinements on  $F^2$  were performed using the program SHELXL-97. One of the carbonyl groups [C(3)–O(3)] in **1a** and the un-substituted ring of the ferrocene group of **2a** exhibited some disorder, which was modelled by isotropical refinement of the group in **1a** or using structural restraints (AFIX 59 label) [25b] in **2a**. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for Crystallography [26]. Graphics were obtained with ZORTEP [27].

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 176615–176619 for compounds **1a**·{(CH<sub>3</sub>)<sub>2</sub>CO}, **1b**·1/2CH<sub>2</sub>Cl<sub>2</sub>, **2a**, **2b**·2{(CH<sub>3</sub>)<sub>2</sub>CO} and **2b'**·2{(CH<sub>3</sub>)<sub>2</sub>CO}. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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