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Rhenium(I) organometallic complexes with novel bis(mercaptoimidazolyl)borates and with hydrotris(mercaptoimidazolyl)borate: chemical and structural studies

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Dedicated to Professor Alberto Romão Dias on the occasion of his 60th birthday in recognition of his friendship and outstanding contribution to inorganic chemistry

Abstract

Lithium salts of novel poly(mercaptoimidazolyl)borate anions $[H(R)B(tim^{Me})_2]^-$ have been synthesised under mild conditions by reaction of the corresponding lithium organoborohydrides with 2-mercapto-1-methylimidazole. Treatment of the Re(I) starting materials $[Re(CO)_5Br]$ or $(NEt_4)_2[Re(CO)_3Br_3]$ with the stoichiometric amount of $Li[H(R)B(tim^{Me})_2]$ (R = Me (**1**), Ph (**2**)) or $Na[HB(tim^{Me})_3]$ gave the tricarbonyl complexes $[Re\{\kappa^3\text{-}R(\mu\text{-}H)B(tim^{Me})_2\}(CO)_3]$ (R = Me (**3**), Ph (**4**)) and $[Re\{\kappa^3\text{-}HB(tim^{Me})_3\}(CO)_3]$ (**5**). These complexes were also prepared under aqueous and aerobic conditions, in almost quantitative yield, using $(NEt_4)_2[ReBr_3(CO)_3]$ as starting material. Compounds **1**–**5** have been characterised by the usual analytical techniques and by X-ray crystallographic analysis in the case of **3**–**5**. The X-ray diffraction analysis of **3**–**5** showed that the rhenium atom adopts a slightly distorted octahedral coordination with a facial arrangement of the carbonyl ligands. In complex **5** the three remaining coordination positions are occupied by the three thione sulphur atoms from the tripodal hydrotris(2-mercapto-1-methylimidazolyl)borate, and in **3** and **4** these positions are occupied by the two thione sulphur atoms and by one hydrogen atom, which is involved in a strong agostic B–H···Re interaction.

Keywords: Rhenium; Carbonyl; Poly(mercaptoimidazolyl)borates; Agostic interaction; X-ray diffraction analysis

1. Introduction

Rhenium(I) carbonyl complexes are one of the most studied class of compounds in organometallic rhenium chemistry. In the past, the interest on these low-valent complexes was driven mainly by their interesting behaviour in different chemical, electrochemical or photochemical processes, including catalytic ones [1]. More recently, studies on the basic coordination chemistry of Tc(I) and Re(I) complexes containing the *fac*-$M(CO)_3$ moieties highlighted the potential relevance of these complexes in the development of radioactive products for diagnostic (^{99m}Tc) and therapeutic ($^{186/188}Re$) medical applications [2]. Recently, these synthons have been successfully applied on the labelling of some biomolecules, such as peptides or serotoninergic receptor ($5HT_{1A}$) antagonists [3]. To further apply these new labelling tools it is of great importance to introduce novel chelator systems and to evaluate their coordinating capability to the *fac*-$M(CO)_3$ cores (M = Re, Tc). By introducing new chelators one can tune the physical–chemical properties of the final complexes (e.g. charge, size and lipophilicity) which determine their potential biological applications.

Recently, the tripodal $[HB(tim^{Me})_3]^-$ and the potentially bidentate $[H_2B(tim^{Me})_2]^-$ (we use the abbreviation tim^{Me}, from the term 'thioimidazolyl', to represent the 2-mercapto-1-methylimidazolyl fragment) have been in-

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troduced and their coordination chemistry studied with a few late transition metals and with ruthenium [4]. These soft ligands were considered as analogues of the ubiquitous poly(pyrazolyl)borates, largely used in organometallic and inorganic chemistry, namely for rhenium [5,6].

As part of our ongoing research on low-valent Tc and Re complexes for biomedical applications, we have recently described the complexes [M{κ³-H(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (M = Re, ^{99}Tc), and we have shown that the analogous ^{99m}Tc complex can be prepared with high radiochemical yield and with high specific activity [7]. An unprecedented and quite robust B–H···M agostic interaction was formed and, consistently, the ^{99m}Tc complex was remarkably stable, even under aqueous and aerobic conditions. These findings indicated that poly(mercaptoimidazoyl)borates features inherent requirements for developing novel radiopharmaceuticals. Moreover, the tuning of the physico-chemical properties of the complexes is facilitated by the easy modification of these ligands and selected biomolecules can be coupled to the chelator framework either by attachment to the imidazole residue or by linkage to the boron atom. Following this approach, our group is currently investigating the chemistry of Re and Tc carbonyl complexes stabilised with poly(mercaptoimidazolyl)borates bearing different substituent groups, including biologically active ones. In this research, it is of crucial importance to acquire knowledge about the influence of the substituents on the coordination chemistry of the ligands. Herein, we report the synthesis and characterisation of the novel [H(R)B(tim^{Me})$_2$]$^-$ (R = Me (**1**), Ph (**2**)) and reactions of Re(I) starting materials with these ligands and with the already available [HB(tim^{Me})$_3$]$^-$. These reactions led to the synthesis of the new complexes [Re{κ³-R(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (R = Me (**3**), Ph (**4**)) and [Re{κ³-HB(tim^{Me})$_2$}(CO)$_3$] (**5**), which are also described in this work.

2. Experimental

The reactions were carried under a N_2 atmosphere using standard Schlenk techniques, unless otherwise indicated. Solvents were dried and distilled prior to use according to described procedures. The starting materials [ReBr(CO)$_5$] [8] and (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] [9], the ligand Na[HB(tim^{Me})$_3$] [4e] and the organoborohydrides Li(RBH$_3$) (R = Me, Ph) [10] were prepared by the literature methods. The other chemicals were used as purchased.

^{1}H- and ^{11}B-NMR spectra were recorded on a Varian Unity 300 MHz spectrometer; ^{1}H and chemical shifts were referenced with the residual solvent resonances relative to Me$_4$Si and the ^{11}B-NMR chemical shifts with external NaBH$_4$ solution. NMR spectra were run in CD$_3$CN or in DMSO-d_6. IR spectra were recorded as KBr pellets on a Perkin–Elmer 577 spectrometer. C, H and N analyses were performed on an EA110 CE Instruments automatic analyser.

2.1. Synthesis of Li[H(Me)B(tim^{Me})$_2$]·THF (1)

To a solution of Li(MeBH$_3$) (174 mg, 4.86 mmol) in THF was added 2-mercapto-1-methylimidazole (1.120 g, 9.81 mmol) dissolved in the minimum volume of THF, and the resulting mixture was stirred at room temperature (r.t.). The course of the reaction was checked by ^{1}H- and ^{11}B-NMR analyses of aliquots from the reaction mixture. After 2 h there was complete conversion of the borohydride and the solvent was removed under vacuum. The solid residue was washed with C$_6$H$_5$CH$_3$ to remove any unreacted 2-mercapto-1-methylimidazole. The recovered white insoluble solid (440 mg, yield = 34%) was formulated as **1** based on IR, ^{1}H- and ^{11}B-NMR spectroscopies.

IR (cm^{-1}): ν(B–H) 2438 w. ^{1}H-NMR (CD$_3$CN, 300 MHz): δ = 0.11 (d, 3H, J_{H-H} = 5.7 Hz, CH_3–B), 3.40 (s, 6H, CH_3–N), 6.64 (d, 2H, J_{H-H} = 2.1 Hz, CH), 6.76 (d, 2H, J_{H-H} = 2.1 Hz, CH). ^{11}B-NMR (CD$_3$CN, 96 MHz): δ = 39.35.

2.2. Synthesis of Li[H(Ph)B(tim^{Me})$_2$]·THF (2)

The preparation and recovery of **2** was done as described above for **1**, except that the reaction mixture was refluxed during 2 h. Starting from 200 mg (2.05 mmol) of Li[PhBH$_3$] were obtained 440 mg of **2** in the form of a microcrystalline white solid (yield: 67%).

IR (cm^{-1}): ν(B–H) 2440 w. ^{1}H-NMR (CD$_3$CN, 300 MHz): δ = 3.48 (s, 6H, CH_3–N), 6.44 (d, 2H, J_{H-H} = 2.1 Hz, CH), 6.72 (d, 2H, J_{H-H} = 2.1 Hz, CH), 6.97–7.13 (br m, 5H, Ph). ^{11}B-NMR (CD$_3$CN, 96 MHz): δ = 41.12.

2.3. Synthesis of [Re{κ³-R(μ-H)B(tim^{Me})$_2$}(CO)$_3$] (R = Me (3), Ph (4))

To solutions of [Re(CO)$_5$Br] (100 mg, 0.25 mmol) in THF were added Li[H(R)B(tim^{Me})$_2$] (R = Me, Ph), at low temperature and in ca. 1:1 molar ratio (10% molar excess). The respective reaction mixtures were slowly warmed to r.t., then refluxed for 2 h. The reaction mixtures were filtered to remove any insoluble materials. The filtrates were concentrated under vacuum; on addition of *n*-hexane pale-yellow microcrystalline solids precipitated which were formulated as **3** (95 mg, yield = 74%) and **4** (144 mg, yield = 76.4%).

Compound **3**. Anal. Found: C, 30.20; H, 2.21; N, 10.71. Calc. for C$_{12}$H$_{14}$N$_4$O$_3$S$_2$BRe: C, 27.53; H, 2.68; N, 10.71%. IR (cm^{-1}): ν(C–O) 1880 s, ν(C–O) 1905 s,

ν(C–O) 2020 s, ν(B–H···Re) 2160 w. ^{1}H-NMR (CD_3CN, 300 MHz): $\delta = -6.36$ (br, 1H, B–*H*), 0.50 (3H, C*H*$_3$–B), 3.50 (s, 6H, C*H*$_3$–N), 6.91 (d, 2H, $J_{H-H} = 2.1$ Hz, C*H*), 7.09 (br m, 2H, C*H*).

Compound **4**. Anal. Found: C, 34.60; H, 2.29; N, 10.25. Calc. for $C_{17}H_{16}N_4BO_3S_2Re$: C, 34.87; H, 2.73; N, 9.57%. IR (cm^{-1}): ν(C–O) 1900 s, ν(C–O) 1970 s, ν(C–O) 2020 s, ν(B–H···Re) 2160 w. ^{1}H-NMR (CD_3CN, 300 MHz): $\delta = -5.20$ (br, 1H, B–*H*), 3.56 (s, 6H, C*H*$_3$–N), 6.74 (d, 2H, $J_{H-H} = 2.1$ Hz, C*H*), 7.13 (d, 2H, $J_{H-H} = 2.1$ Hz, C*H*), 7.29 (br m, 2H, Ph), 7.36 (br m, 3H, Ph).

2.4. Synthesis of [Re{κ^3-HB(tim^{Me})$_3$}(CO)$_3$] (5)

Complex **5** was prepared by reacting [Re(CO)$_5$Br] with Na[HB(tim^{Me})$_3$], as described above for **3** and **4**. The only difference was that in the case of **5** the reaction mixture was refluxed during 6 h. Starting from 100 mg (0.25 mmol) of [ReBr(CO)$_5$] were obtained 120 mg (yield: 72%) of **5**.

Anal. Found: C, 28.64; H, 2.53; N, 13.34. Calc. for $C_{15}H_{16}N_6BO_3S_3Re$: C, 28.98; H, 2.58; N, 13.53%. IR (cm^{-1}): ν(C–O) 1863 s, ν(C–O) 1987 s, ν(B–H) 2470 w. ^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 3.57$ (s, 9H, C*H*$_3$–N), 7.06 (d, 3H, $J_{H-H} = 1.5$ Hz, C*H*), 7.09 (d, 3H, $J_{H-H} = 1.5$ Hz, C*H*).

2.5. X-ray crystallographic analysis

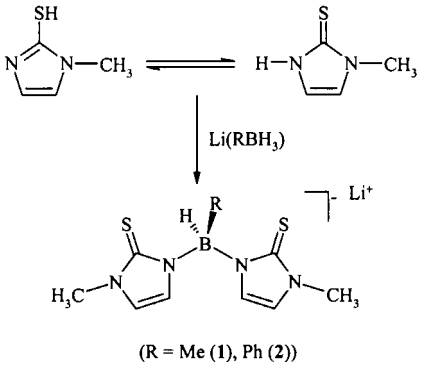
The crystals were obtained by recrystallisation from THF/*n*-hexane (**3** and **4**) or from CH_2Cl_2/*n*-hexane (**5**), and mounted in thin-walled glass capillaries. Data were collected at r.t. on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation, using a ω–2θ scan mode. The crystal data are summarised in Table 1.

The data were corrected [11] for Lorentz and polarisation effects, for linear decay (no decay was found in **5**) and empirically for absorption by Ψ scans. The heavy atom positions were located by Patterson methods using SHELXS-86 [12]. The remaining atoms were located in successive Fourier-difference maps and refined by least-squares refinements on F^2 using SHEXL-93 [13]. For compound **5** on the basis of the systematic absences and of the threefold symmetry expected for the molecule, the possible space groups are $R3$ and $R\bar{3}$. Attempts to solve the structure in $R\bar{3}$ with the Re and B atoms on a crystallographic threefold axis and admitting disorder of the ligands led to unsatisfactory refinement and was unsuccessful. So, the solution of the structure was attempted in the non-centrosymmetric space group $R3$, with two molecules per asymmetric unit, and with the two Re and the two B atoms on a crystallographic threefold axis. The refinement con-

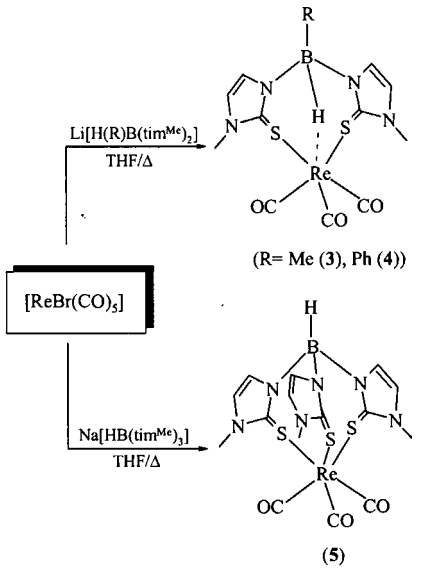
Table 1
Crystallographic data for **3**, **4** and **5**

Compound	**3**	**4**	**5**
Empirical formula	$C_{12}H_{14}BN_4O_3ReS_2$	$C_{17}H_{16}BN_4O_3ReS_2$	$C_{15}H_{16}BN_6O_3ReS_3$
Formula weight	523.40	585.47	621.53
Crystal system	Triclinic	Monoclinic	Trigonal
Space group	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)	$R3$ (no. 146)
Unit cell dimensions			
a (Å)	9.039(1)	13.7441(13)	14.302(2)
b (Å)	9.2910(1)	13.0203(10)	14.302(2)
c (Å)	12.453(1)	22.960(3)	17.956(3)
α (°)	73.84(1)	90	90
β (°)	75.41(1)	105.056(11)	90
γ (°)	61.64(1)	90	120
V (Å^3)	875.0(2)	3967.7(7)	3180.8(8)
Z	2	8	6
D_{calc} (g cm^{-3})	1.987	1.960	1.947
μ(Mo–K$_\alpha$) (cm^{-1})	7.198	6.362	6.055
Reflections collected	3528	4008	3600
Independent reflections	3313 [$R_{int} = 0.0227$]	3905 [$R_{int} = 0.0658$]	3404 [$R_{int} = 0.0299$]
Parameters	209	254	178
Largest difference peak and hole (e Å^{-3})	0.749 and −0.557	1.090 and −1.064	0.623 and −0.759
Goodness-of-fit on F^2	1.058	1.066	1.043
R [a]	0.0389 (0.0608) [b]	0.0803 (0.1968) [b]	0.0341 (0.0523) [b]
wR_2 [a]	0.0632 (0.0813) [b]	0.1050 (0.1829) [b]	0.0671 (0.0879) [b]

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$; [$F_o > 4\alpha(F_o)$].
[b] Based on all data.



Scheme 1.



Scheme 2.

verged consistently to $R_1 = 0.0432$ [for $I > 2\sigma(I)$], with all non-hydrogen atoms refining anisotropically. At this stage the refinement program flagged a possible *racemic* twin. The refinement as a *racemic* twin (including TWIN and BASF parameters) proved to be acceptable, decreasing the wR_2 value from 0.0955 to 0.0672 ($R_1 = 0.0341$). The BASF value converged to 0.60(1). For the structures of **3**–**5** all the non-hydrogen atoms were refined anisotropically; the contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-93 [13]. The drawings were made with ORTEP-II [14a] and ORTEP-3 [14b]; all the calculations were performed on a 3000 Dec α computer.

3. Results and discussion

3.1. Syntheses

The work of Reglinski and coworkers [4a] proved that poly(mercaptoimidazolyl)borate ligands can be easily obtained by reacting alkaline salts of BH_4^- with 2-mercapto-1-methylimidazole, with procedures similar to those used for the related poly(pyrazolyl)borates. Following this approach, we have evaluated the possibility of preparing ligands of the type $[H(R)B(tim^{Me})_2]^-$, starting from the organoborohydrides $Li[RBH_3]$ (R = Me, Ph) which were prepared by reaction of the corresponding boronic acids $RB(OH)_2$ with $LiAlH_4$, according to procedures described in the literature [10]. As shown in Scheme 1, $Li[RBH_3]$ (R = Me, Ph) react readily, in THF, with two equivalents of 2-mercapto-1-methylimidazole, giving $Li[H(R)B(tim^{Me})_2]$ (R = Me (**1**), Ph (**2**)). The kinetics of the reaction depends on the nature of the substituent attached to the boron. Indeed, ligand **1** is easily prepared at r.t. while the preparation of **2** requires reflux in THF. Obviously, this difference reflects the higher basicity of the hydrides in $[MeBH_3]^-$ in comparison with $[PhBH_3]^-$, as a consequence of the electronic withdrawing properties of the phenyl group.

The formation of **1** and **2** is quite efficient, as shown by the follow-up of the respective reaction mixtures by ^{1}H- and ^{11}B-NMR analyses. However, after work-up compounds **1** and **2** are obtained only in moderate to low isolated yield, since the removal of traces of unreacted 2-mercapto-1-methylimidazole is only possible by washing with $C_6H_5CH_3$ and the ligands are also slightly soluble in this solvent.

Ligands **1** and **2** are hygroscopic white solids, which are soluble in most common polar organic solvents and in water and are relatively resistant towards aerobic oxidation and hydrolysis. These characteristics are compatible with their further use in the development of organometallic complexes potentially relevant in biological and biomedical applications that usually involve aqueous medium.

As shown in Scheme 2 reaction of $[Re(CO)_5Br]$ with stoichiometric amounts of $Li[H(R)B(tim^{Me})_2]$ (R = Me (**1**), Ph (**2**)) or $Na[HB(tim^{Me})_3]$, in THF solution and upon reflux, gives $[Re\{\kappa^3\text{-}R(\mu\text{-}H)B(Simz)_2\}(CO)_3]$ (R = Me (**3**), Ph (**4**)) and $[Re\{\kappa^3\text{-}RB(tim^{Me})_3\}(CO)_3]$ (**5**). Compounds **3**–**5** are recovered as pale-yellow (**3** and **4**) or white (**5**) solids in moderate to high yield, upon concentration of the respective reaction mixtures followed by addition of *n*-hexane.

Owing to our interest in biomedical applications, we studied using ^{1}H-NMR the possibility of preparing **3**–**5**, using $(NEt_4)_2[Re(CO)_3Br_3]$ as starting material. In fact this compound in coordinating solvents forms cations of the type $[Re(CO)_3L_3]^+$ (L = solvent molecule), which are analogous to the synthons $[M(CO)_3L_3]^+$ (M = ^{99m}Tc, $^{186/188}$Re) available in radiopharmaceutical preparations [2]. We observed that

$(NEt_4)_2[Re(CO)_3Br_3]$ reacts with $Li[H(R)B(tim^{Me})_2]$ or with $Na[HB(tim^{Me})_3]$ in CD_3CN at 40°C, leading quantitatively to the complexes **3**–**5**, within 15 min.

Compounds **3** and **4** are analogous to the previously described $[Re\{\kappa^3\text{-}H(\mu\text{-}H)B(tim^{Me})_2\}(CO)_3]$ [7] and are relatively rare examples of rhenium complexes which contain B–H···Re agostic interactions. These agostic interactions also remain intact in the presence of coordinating solvents and, therefore, their strength is not affected strongly by the alkyl or aryl groups attached to the boron. The coordinative behaviour of the ligands $[H(R)B(tim^{Me})_2]^-$ (R = H, Me (**1**), Ph (**2**)) towards the electron-rich Re(I) centre markedly contrasts with that previously described for the harder congener $[H_2B(pz)_2]^-$. In fact, when $[Re(CO)_5Br]$ was treated with $Na[H_2B(pz)_2]$ no compound containing a B–H···Re agostic interaction was detected. In this reaction some degradation of the ligand was observed, and the only complex isolated has been $[Re\{H_2B(pz)_2\}(CO)_2(pzH)]$ [15]. It is not clear whether these differences are determined by steric factors or by a better match between the electronic properties of the sulphur donor ligands and the soft d^6 rhenium centre. In fact, in the case of the hydrotris(2-mercapto-1-methylimidazolyl)borate, the isolated complex $[Re\{\kappa^3\text{-}HB(tim^{Me})_3\}(CO)_3]$ (**5**) is analogous to the previously described $[Re\{\kappa^3\text{-}HB(pz)_3\}(CO)_3]$ [16], both tripodal ligands displaying a similar behaviour.

3.2. Spectroscopic data

The IR spectra of $[Re\{\kappa^3\text{-}R(\mu\text{-}H)B(Simz)_2\}(CO)_3]$ (R = Me (**3**), Ph (**4**)) and $[Re\{\kappa^3\text{-}HB(tim^{Me})_3\}(CO)_3]$ (**5**) present very strong bands in the range 1860–2020 cm^{-1}, which were attributed to the ν(C–O) stretching mode. The IR spectra of compound **5** display two bands associated with the E_1 and A_1 vibration modes, in a typical pattern for complexes with the '*fac*-$Re(CO)_3$' moiety in a distorted C_3 environment. In the case of **3** and **4** the IR spectra show three ν(CO) bands, as a consequence of the lower symmetry (C_s) of these complexes [3g]. The values of the carbonyl stretching frequencies in $[Re\{\kappa^3\text{-}HB(tim^{Me})_3\}(CO)_3]$ (1863 and 1987 cm^{-1}) are lower than those previously reported for the congener $[Re\{\kappa^3\text{-}HB(pz)_3\}(CO)_3]$ (1896 and 2020 cm^{-1}) [16b], confirming the better donor capability of $[HB(tim^{Me})_3]^-$. An important feature of the IR spectra of **3** and **4** is the presence of weak to medium intensity bands centred at 2160 cm^{-1}, which were assigned to ν(B–H···Re). These ν(B–H···Re) frequencies are strongly red shifted compared to the ν(B–H) stretching frequency in the free ligands (2438 cm^{-1} for **1** and 2440 cm^{-1} for **2**). These data indicated that we are in the presence of strong ν(B–H···Re) agostic interactions, as previously observed for $[Re\{\kappa^3\text{-}H(\mu\text{-}H)B(tim^{Me})_2\}(CO)_3]$ [7]. This type of interaction is absent in complex **5** which contains a tripodal ligand coordinated through the three thione sulphur atoms. In fact for **5** the ν(B–H) stretching band appears at 2470 cm^{-1}, only slightly shifted from the corresponding band of the free ligand (2480 cm^{-1}). These spectroscopic features are consistent with the molecular structures of complexes **3**–**5** which were determined by X-ray diffraction analysis (see Section 3.3).

The ^{1}H-NMR spectra obtained for **3**–**5** are in accordance with the C_s (**3** and **4**) and C_3 (**5**) symmetries found in the solid state. The most striking feature of the ^{1}H-NMR spectra of complexes **3** and **4** is the presence of highfield shifted resonances at −6.36 and −5.20 ppm, respectively, which are due to the protons involved in the B–H···Re agostic interactions. These results confirm the stability of the agostic interactions in solution, even in coordinating solvents, as previously observed for $[Re\{\kappa^3\text{-}H(\mu\text{-}H)B(tim^{Me})_2\}(CO)_3]$ (δ = −6.40 ppm) [7]. It is interesting to note that the chemical shifts observed for the B–H···Re protons are in the range where the hydrides normally appear in rhenium polyhydride complexes [17], indicating that the coordinated hydrogen has an almost hydridic character.

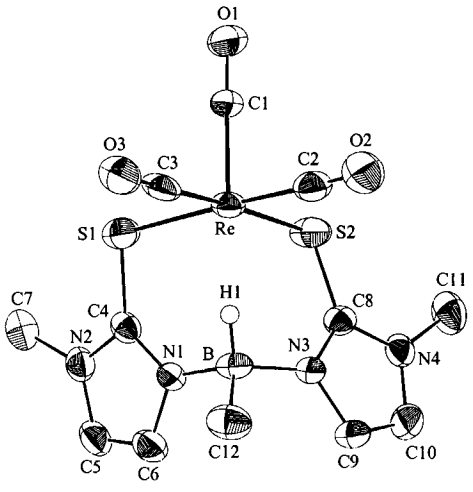


Fig. 1. ORTEP view of **3**. Vibrational ellipsoids are drawn at the 40% probability level.

3.3. Molecular structures of complexes *3*–*5*

The structures of complexes $[Re\{\kappa^3\text{-}R(\mu\text{-}H)B(tim^{Me})_2\}(CO)_3]$ (R = Me (**3**), Ph (**4**)) and $[Re\{\kappa^3\text{-}HB(tim^{Me})_3\}(CO)_3]$ (**5**) consist of discrete mononuclear units with the rhenium atom in a slightly distorted octahedral environment. Complex **5** possesses a crystallographically imposed threefold rotation symmetry, with the Re and the B–H atoms located in the crystallographic axis. There are two molecules per asymmetric unit which are crystallographically independent but chemically equivalent. The ORTEP views of the molecular structures are shown in Figs. 1–3. Fig. 4 presents a

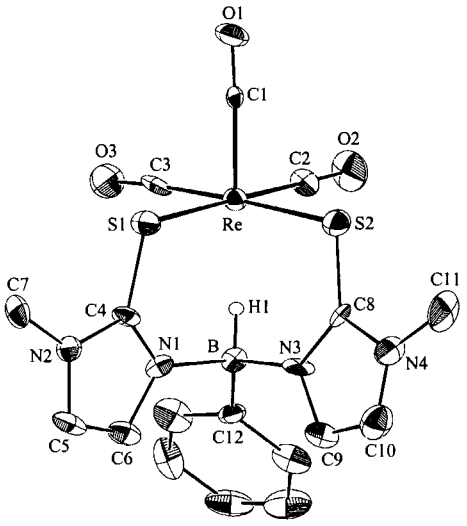


Fig. 2. ORTEP view of **4**. Vibrational ellipsoids are drawn at the 30% probability level.

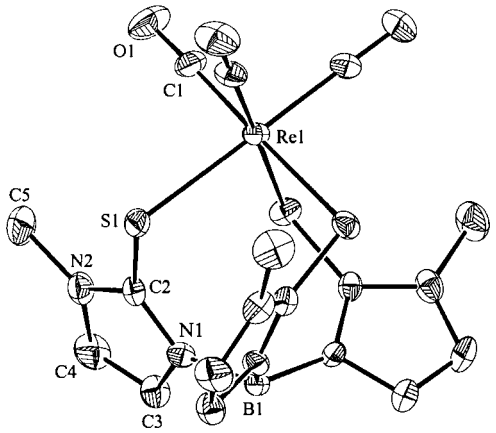


Fig. 3. ORTEP view [14b] of molecule 1 of **5**. Vibrational ellipsoids are drawn at the 30% probability level.

B–Re view of the two independent molecules of **5**. Selected bond distances and angles are given in Tables 2 and 3, respectively.

The carbonyl ligands occupy one face of the coordination polyhedra, with average Re–C distances of 1.902 (10), 1.89 (2) and 1.904(9) Å for **3**, **4** and **5**, respectively. These distances are in the range (1.89–1.94 Å) found for other Re(I) tricarbonyl complexes containing sulphur donor ligands, such as thioethers or thioureas [3g,18]. The three remaining coordination positions are occupied by two thione sulphur atoms and by the hydrogen from the B–H···Re agostic interactions in the case of **3** and **4**, while for **5** those positions are defined by the three thione sulphur atoms of the tripodal ligand. The average Re–S bond distance found in complex **5** (2.516(2) Å) is larger than the values of 2.485(2) and 2.478(6) Å found in complexes **3** and **4**, respectively. This is justified by the greater steric requirements of $[HB(tim^{Me})_3]^-$ due to the presence of a third mercaptoimidazolyl ring. The Re–S distances found for **3**–**5** are in the range reported for Re(I) tricarbonyl complexes with chelating or unidentate thiourea derivatives (2.466–2.536 Å) also coordinated through thione sulphur atoms [18a]. The C–S bond distances span from 1.68 to 1.73 Å, with average values of 1.704(7), 1.71(2) and 1.723(8) Å for **3**, **4** and **5**, respectively. These C–S lengths are intermediate between single and double bonds and indicate a partial reduction of the π-character of the C–S bond if compared with the same bond

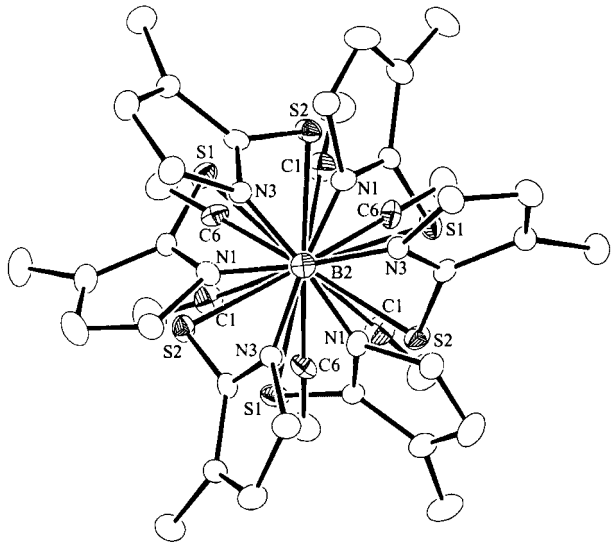


Fig. 4. ORTEP view of the two independent molecules of **5**, down the *c* axis (along the B–Re axis). Vibrational ellipsoids are drawn at the 20% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for **3** and **4**

	3	**4**
Re–C(1)	1.878(7)	1.89(2)
Re–C(2)	1.906(10)	1.87(2)
Re–C(3)	1.921(8)	1.92(2)
Re–S(1)	2.478(2)	2.493(5)
Re–S(2)	2.491(2)	2.462(6)
Re–B	2.908(8)	2.92(2)
C(1)–O(1)	1.162(8)	1.16(2)
C(2)–O(2)	1.148(9)	1.18(2)
C(3)–O(3)	1.149(8)	1.16(2)
C(4)–S(1)	1.711(7)	1.73(2)
C(8)–S(2)	1.696(7)	1.68(2)
C(1)–Re–C(2)	88.1(3)	88.1(9)
C(1)–Re–C(3)	89.6(3)	89.1(10)
C(2)–Re–C(3)	92.1(3)	90.9(8)
C(1)–Re–S(1)	93.3(2)	92.2(7)
C(1)–Re–S(2)	91.9(2)	93.4(7)
C(2)–Re–S(1)	177.7(2)	177.6(6)
C(2)–Re–S(2)	90.3(2)	88.6(6)
C(3)–Re–S(1)	89.7(3)	91.6(6)
C(3)–Re–S(2)	177.2(2)	177.4(7)
S(1)–Re–S(2)	87.85(8)	88.9(2)

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Molecule 1			
Re(1)–C(1)	1.901(9)	Re(1)–S(1)	2.521(2)
Re(1)–B(1)	4.20(1)	C(1)–O(1)	1.146(10)
C(2)–S(1)	1.721(8)		
C(1)–Re(1)–C(1) [a]	89.9(4)	C(1)–Re(1)–S(1)	90.9(3)
C(1)–Re(1)–S(1) [b]	88.7(3)	C(1)–Re(1)–S(1) [a]	178.4(3)
S(1)–Re(1)–S(1) [b]	90.48(7)		
Molecule 2			
Re(2)–C(6)	1.906(8)	Re(2)–S(2)	2.510(2)
Re(2)–B(2)	4.20(1)	C(6)–O(2)	1.145(9)
C(7)–S(2)	1.725(7)		
C(6)–Re(2)–C(6) [a]	90.9(3)	C(6)–Re(2)–S(2)	177.8(3)
C(6)–Re–S(2) [b]	90.1(3)	C(6)–Re(2)–S(2) [a]	87.2(3)
S(2)–Re(2)–S(2) [a]	91.82(7)		

[a] Equivalent atoms generated by the symmetry operation $-x+y$, $-x$, $-z$.
[b] Equivalent atoms generated by the symmetry operation $-y$, $x-y$, z.

distance (1.685(2) Å) in free 2-mercapto-1-methyl-imidazole ($tim^{Me}H$) [19].

The structures of complexes **3** and **4** are analogous to those previously described for $[M\{\kappa^3\text{-}H(\mu\text{-}H)B(tim^{Me})_2\}(CO)_3]$ (M = ^{99}Tc, Re) [7], all presenting 3-centre–2-electron B–H···Re agostic interactions. The B···Re distances of 2.91(1) (**3**) and 2.92(2) Å (**4**) are comparable and slightly longer than the B···M (M = ^{99}Tc, Re) distances of 2.834(12) and 2.832(12) Å found in $[M\{\kappa^3\text{-}H(\mu\text{-}H)B(Simz)_2\}(CO)_3]$ (M = ^{99}Tc, Re) [7]. If this difference should arise from electronic factors we would expect a stronger interaction in **3** but a weaker one in **4**, due to different inductive effects of the methyl (−I) and phenyl (+I) groups. Apparently, these differences reflect mainly the greater steric requirements of the uncoordinated methyl and phenyl groups in comparison with the uncoordinated hydrogen atom.

The analogy between the complex $[Re\{\kappa^3\text{-}HB(tim^{Me})_3\}(CO)_3]$ (**5**) and the previously described $[Re\{\kappa^3\text{-}HB(pz)_3\}(CO)_3]$ gives the opportunity of a direct comparison between these tripodal ligands. The most striking difference is that the pyrazole rings in the latter are almost parallel to the Re–B axis giving approximately C_{3v} symmetry, while in **5** the mercaptoimidazolyl rings lie at an average angle of 60.3° to the B–Re axis, resulting in a lower C_3 symmetry. Additionally, in complex **5** the eight-membered chelating rings are highly asymmetric, presenting two very different Re–S–C and C–N–B angles (avg. values of 107.7(2) and 132.6(7)°). The ligand adopts a 'propeller-like' conformation of the rings with an average Re–S–C–N torsion angle of 73° (62.5° for the imaginary torsion angle S–Re···B–N The Re–B distance found in **5** (avg. 4.20(1) Å) is considerably longer than that reported for the hydrotris(pyrazolyl)borate complex (3.36(3) Å), as a consequence of the increase in size (from six to eight) of the chelate rings upon complexation. In $[Re\{\kappa^3\text{-}HB(pz)_3\}(CO)_3]$ the ligand bite angles are rather less than 90° (avg. N–Re–N: 81.0(7)), while in compound **5** these angles are close to 90° (avg. S–Re–S: 91.15(7)°). These data show the larger flexibility of the hydrotris(mercaptoimidazolyl)borate proportionate to a less distorted octahedral coordination environment.

4. Concluding remarks

The soft poly(mercaptoimidazolyl)borates $[H(R)B(tim^{Me})_2]^-$ (R = H, Me (**1**), Ph (**2**)) and $[HB(tim^{Me})_3]^-$ are remarkably stable ligands which are very efficient in the stabilisation of complexes with the '*fac*-$Re(CO)_3$' moiety. We have demonstrated that the attachment of alkyl or aryl substituent to the boron atom has no notorious effect on the coordination behaviour of the $[H(R)B(tim^{Me})_2]^-$ ligands, which coordinate to the metal through a remarkably robust B–H···Re agostic interaction, retained even in coordinating solvents. By introducing a third mercaptoimidazolyl ring no agostic interaction is formed and the $[HB(tim^{Me})_3]^-$ ligand coordinates in a tripodal fashion through the three thione sulphur atoms. Again, the resulting rhenium tricarbonyl complex is quite resistant towards hydrolysis and aerial oxidation.

Our results indicate that poly(mercaptoimidazolyl)borates are expected to provide new building blocks for the labelling of biomolecules, based on organometallic complexes containing the donor sets κ^3-(H,S_2) or κ_3-(S_3). Noticeably, these ligands can provide easy control of the size and lipophilicity of the complexes, which are very important characteristics in their potential biomedical applications.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 157756, 157757 and 157758 for compounds **3**, **4** and **5**, respectively. 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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