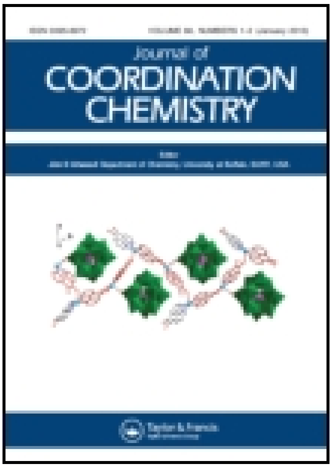

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Boron chlorination on a Cp*Rh-coordinated bis(2-mercapto-1-arylimidazolyl)borate $[H_2B(tim^{Ar})_2]^-$: $[Cp^*Rh\{\kappa^2\text{-}S,S'\text{-}ClHB(tim^{Ar})_2\}Cl]$ and $[Cp^*Rh\{\kappa^3\text{-}H,S,S'\text{-}ClHB(tim^{Ar})_2\}][BF_4]\cdot H_2O$

Fang-Fang Fan[a], Qing Ma[a], Ai-Quan Jia[a], Xiang-Hong Huang[b] & Qian-Feng Zhang[a]
[a] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, PR China
[b] College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou, PR China

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Boron chlorination on a Cp*Rh-coordinated bis(2-mercapto-1-arylimidazolyl)borate $[H_2B(tim^{Ar})_2]^-$: [Cp*Rh{κ^2-*S*,*S′*-ClHB(tim^{Ar})$_2$}Cl] and [Cp*Rh{κ^3-*H*,*S*,*S′*-ClHB(tim^{Ar})$_2$}][BF$_4$]·H$_2$O

FANG-FANG FAN†, QING MA†, AI-QUAN JIA†, XIANG-HONG HUANG‡ and QIAN-FENG ZHANG*†

†Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma’anshan, PR China
‡College of Biology and Environmental Engineering, Zhejiang Shuren University, Hangzhou, PR China

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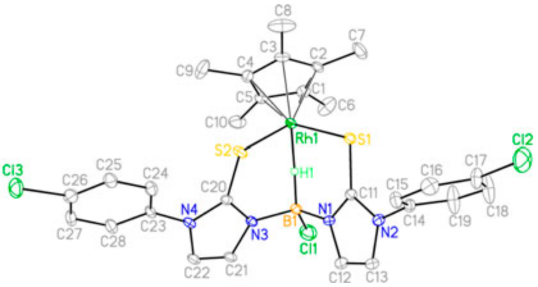

Two rhodium(III) complexes [Cp*Rh{κ^2-*S*,*S*’-ClHB(tim^{Ar})$_2$}Cl] and [Cp*Rh{κ^3-*H*,*S*,*S*’-ClHB(tim^{Ar})$_2$}][BF$_4$]·H$_2$O with the terminal B−Cl bonds were isolated by reaction of boron-chlorination and structurally characterized by X-ray crystallography.

Interaction of [Cp*Rh(μ-Cl)Cl]$_2$ with two equiv. of Na[H$_2$B(tim^{Ar})$_2$] (tim^{Ar} = 1-(4-chloro-phenyl)-imidazole-2-thione) in THF afforded [Cp*Rh{κ^2-*S*,*S′*-H$_2$B(tim^{Ar})$_2$}Cl] (**1**). Treatment of **1** with AgBF$_4$ in THF gave [Cp*Rh{κ^3-*H*,*S*,*S′*-H$_2$B(tim^{Ar})$_2$}][BF$_4$] (**2**) with an agostic B–H···Rh bond, whereas **1** in a stirring CHCl$_3$ solution led to isolation of [Cp*Rh{κ^2-*S*,*S′*-ClHB(tim^{Ar})$_2$}Cl] (**3**) with a B–Cl bond. Similarly, treatment of **3** with AgBF$_4$ in THF gave the cationic complex [Cp*Rh{κ^3-*H*,*S*,*S′*-ClHB(tim^{Ar})$_2$}][BF$_4$]·H$_2$O (**4**·H$_2$O) with both agostic B–H···Rh and terminal B–Cl bonds, isolated from the solution of **2** in CHCl$_3$. All complexes were spectroscopically characterized and structures of **3** and **4**·H$_2$O have been established by X-ray crystallography.

Keywords: Rhodium complex; Dihydrobis(mercaptoimidazolyl) borate ligand; Agostic B–H···Rh bond; B–Cl bond; Boron chlorination; Crystal structure

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*Corresponding author. Email: zhangqf@ahut.edu.cn

1. Introduction

Since the first report of the hydrotris(pyrazolyl)borate (Tp) in 1967 by Trofimenko [1], inorganic and organometallic complexes of poly(pyrazolyl)borates have been extensively explored due to their applications in biological and catalytic systems [2–4]. As sulfur-donor scorpionate analogs, the anionic ligands $[H_xB(tim)_{4-x}]^-$ introduced by Reglinski ($x = 1$) [5] and Parkin ($x = 2$) [6] present either three or two soft sulfur donors, with delocalized anionic charge on the thioimidazole groups (tim^R). Hill and coworkers explored later transition metal complexes supported by $[HB(tim^R)_3]^-$ and $[H_2B(tim^R)_2]^-$ [7], while the groups of Rabinovich, Tatsumi, Parkin, and Connelly reported first-row transition metal complexes with this class of ligands [8–12]. As part of our ongoing studies of ruthenium–sulfur complexes, we recently reported ruthenium complexes with related ligands containing thioimidazoles, such as neutral 1-R-imidazole-2-thione ($Htim^R$) and anionic $[HB(tim^R)_3]^-$, and $[H_2B(tim^R)_2]^-$ (R = methyl, 4-substitute-phenyl) [13–17]. Compared with the ruthenium congeners, relatively few rhodium–$[H_xB(tim)_{4-x}]$ complexes have been synthesized [18–20]. Examples of structurally characterized rhodium–$[H_xB(tim)_{4-x}]$ complexes are $[Rh_2[B(tim^{Me})_3]_2\{\kappa^2\text{-}S,S'\text{-}HB(tim^{Me})_3\}]Cl$ [18], $[Rh(\eta^4\text{-cod})\{\kappa^3\text{-}H,S,S'\text{-}H_2B(tim^{Me})_2]$ (cod = 1,5-cyclooctadiene) [19], $[Rh(\eta^4\text{-cod})\{\kappa^2\text{-}S,S'\text{-}HB(tim^{Me})_3]$, $[Rh(CO)(PPh_3)\{\kappa^2\text{-}S,S'\text{-}HB(tim^{Me})_3]$, $[Rh(CO)\text{-}(P(NMe_2)_3)\{\kappa^2\text{-}S,S'\text{-}HB(tim^{Me})_3]$, and $[Rh(PPh_3)\{\kappa^4\text{-}S,S',S''B\text{-}B(tim^{Me})_3\}][PF_6]$ [20] with Rh(I) species.

Several metals such as ruthenium, rhodium, nickel, and iron have a proven track record in the activation of B–H bonds of $[H_xB(tim^R)_{4-x}]^-$ ligands, which resulted in isolations of the metallaboratrane complexes with M–B bonds, typical M···H–B complexes with the 3c–2e B–H···M interactions, and the M-$[H_xB(tim)_{4-x}]$ complexes with Cl–B bonds. A number of the metallaboratrane [7, 21, 22] and typical M···H–B complexes [18, 19, 23] have already been synthesized, however, examples of the cleanly isolated and fully characterized imidazolyl–borate complexes with Cl–B bonds have been reported by Hill and Parkin *et al.* [24–26]. We previously reported two organoruthenium complexes $[(\eta^6\text{-}p\text{-cymene})Ru\{\kappa^3\text{-}S,S',S''\text{-}ClB(tim^{Me})_3]$ and $[Cp^*Ru\{\kappa^3\text{-}S,S',S''\text{-}ClB(tim^{Me})_3]$ (Cp* = pentamethyl cyclopentadienyl) with Cl–B bonds [13]. In this article, we report boron chlorination on a Cp*Rh-coordinated bis(2-mercapto-1-arylimidazolyl)borate $[H_2B(tim^{Ar})_2]^-$ ligand, $[Cp^*Rh\{\kappa^2\text{-}S,S'\text{-}ClHB(tim^{Ar})_2\}Cl]$, and $[Cp^*Rh\{\kappa^3\text{-}H,S,S'\text{-}ClHB(tim^{Ar})_2\}][BF_4]\cdot H_2O$.

2. Experimental

2.1. *General*

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. $AgBF_4$ was purchased from Alfa Aesar Ltd and used without purification. $Na[H_2B(tim^{Ar})_2]$ [15] and $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ [27] were prepared according to literature methods. NMR spectra were recorded on a Bruker ALX 400 Plus spectrometer operating at 400 MHz for ^1H. Chemical shifts (δ, ppm) are reported with reference to $SiMe_4$ (^1H). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with pressed KBr pellets and positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. *Synthesis of [Cp*Rh{κ²-S,S′-H₂B(timᴬʳ)₂}Cl] (1)*

A mixture of [Cp*Rh(μ-Cl)Cl]$_2$ (61.4 mg, 0.10 mM) and Na[H$_2$B(tim^{Ar})$_2$] (91.1 mg, 0.20 mM) in THF (20 mL) was stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue was washed with hexane. The red solid was extracted with diethyl ether (10 mL × 5) and the volume of the extraction solution was reduced to be ca. 10 mL. Dark red block crystals of [Cp*Rh{κ^2-*S*,*S*′-H$_2$B(tim^{Ar})$_2$}Cl] (**1**) were isolated after storage at −20 °C for three days. Yield: 120 mg, 85%. ^{1}H NMR (400 MHz, C$_6$*D*$_6$): δ (ppm) 1.73(s, 15H), 6.62, 6.63, 6.77, 6.81 (s × 4, 4H), 7.11, 7.34 (d × 2, $^3J_{HH}$ = 8.4 Hz, 8H), IR (KBr disk, cm^{-1}): 2385(ν_{BH}), 1493(s), 1433(m), 1380(s), 1273(m), 1086(s), 813 (m), 692(s). MS(FAB): *m*/*z* 706 [M$^+$], 669 [M$^+$–Cl], 534 [M$^+$–Cl–Cp*]. Anal. Calcd for C$_{28}$H$_{29}$BCl$_3$N$_4$S$_2$Rh: C, 47.65; H, 4.14; N, 7.94%. Found: C, 47.32; H, 4.10; N, 7.83%.

2.3. *Synthesis of [Cp*Rh{κ³-H,S,S′-H₂B(timᴬʳ)₂}][BF₄] (2)*

To a solution of **1** (70.6 mg, 0.10 mM) in THF (10 mL) was added a solution of AgBF$_4$ (19.5 mg, 0.10 mM) in THF (5 mL). The mixture was stirred for 2 h at room temperature. The solvent was removed *in vacuo* and the residue was washed with diethyl ether and further recrystallized from acetone/hexane at room temperature. Dark red crystalline product [Cp*Rh{κ^3-*H*,*S*,*S*′-H$_2$B(tim^{Ar})$_2$}][BF$_4$] (**2**) was obtained in three days. Yield: 58 mg, 76%. ^{1}H NMR (400 MHz, C$_6$*D*$_6$): δ (ppm) 1.66 (s, 15H), 6.62, 6.64, and 6.73, 6.81 (s × 4, 4H), 7.16 and 7.35 (d × 2, $^3J_{HH}$ = 8.4 Hz, 8H). IR (KBr disk, cm^{-1}): 2372(ν_{BH}), 2190(ν_{BHRh}), 1493(s), 1431(m), 1380(s), 1273(m), 1084(s), 815(m), 691(s). MS (FAB): *m*/*z* 669 [M$^+$–BF$_4$], 534 [M$^+$–BF$_4$–Cp*]. Anal. Calcd for C$_{28}$H$_{29}$B$_2$Cl$_2$F$_4$N$_4$S$_2$Rh: C, 44.42; H, 3.86; N, 7.40%. Found: C, 44.32; H, 3.84; N, 7.42%.

2.4. *Synthesis of [Cp*Rh{κ²-S,S′-ClHB(timᴬʳ)₂}Cl] (3)*

1 (75.7 mg, 0.10 mM) was dissolved in CHCl$_3$ (8 mL) and then the solution was stirred for 2 h at room temperature. The filtrate was layered with hexane (20 mL) and dark red crystals of [Cp*Rh{κ^2-*S*,*S*′-ClHB(tim^{Ar})$_2$}Cl] (**3**) suitable for X-ray diffraction were obtained in a week. Yield: 48 mg, 65%. ^{1}H NMR (400 MHz, C$_6$*D*$_6$): δ (ppm) 1.75 (s, 15H), 6.66, 6.69, 6.79, and 6.85 (s × 4, 4H), 7.19 and 7.38 (d × 2, $^3J_{HH}$ = 8.4 Hz, 8H). IR (KBr disk, cm^{-1}): 2382(ν_{BH}), 969(w), 1496(s), 1433(m), 1383(s), 1276(m), 1089(s), 818(m), 694(s). MS (FAB): *m*/*z* 740 [M$^+$], 705 [M$^+$–Cl], 571 [M$^+$–Cl–Cp*]. Anal. Calcd for C$_{28}$H$_{28}$BCl$_4$N$_4$S$_2$Rh: C, 45.43; H, 3.81; N, 7.57%. Found: C, 45.32; H, 3.74; N, 7.53%.

2.5. *Synthesis of [Cp*Rh{κ³-H,S,S′-ClHB(timᴬʳ)₂}][BF₄]·H₂O (4·H₂O)*

The method was similar to that used for **2**, employing **3** (70.6 mg, 0.10 mM) instead of **1**. Yield: 58 mg, 77%. ^{1}H NMR (400 MHz, C$_6$*D*$_6$): δ (ppm) 1.65 (s, 15H), 6.63, 6.66, 6.75, and 6.86 (s × 4, 4H), 7.17 and 7.37 (d × 2, $^3J_{HH}$ = 8.4 Hz, 8H). IR (KBr disk, cm^{-1}): 3452 (mbr), 2192(ν_{BHRh}), 968(w), 1494(s), 1432(m), 1381(s), 1270(m), 1083(s), 814(m), 692(s). MS (FAB): *m*/*z* 705 [M$^+$–BF$_4$], 570 [M$^+$–BF$_4$–Cp*]. Anal. Calcd for C$_{28}$H$_{28}$B$_2$Cl$_3$F$_4$N$_4$S$_2$Rh·(H$_2$O): C, 41.54; H, 3.74; N, 6.92%. Found: C, 41.38; H, 3.72; N, 6.91%. This complex was also synthesized by stirring **2** in CHCl$_3$ (8 mL). Dark red block crystals of **4** were obtained in 83% yield. Elemental analyses and cell dimension

Table 1. Crystallographic data and experimental details for [Cp*Rh{κ^2-*S*,*S′*-ClHB(tim^{Ar})$_2$}Cl] (**3**) and [Cp*Rh{κ^3-*H*,*S*,*S′*-ClHB(tim^{Ar})$_2$}][BF$_4$]·H$_2$O (**4**·H$_2$O).

Complex	**3**	**4**·H$_2$O
Empirical formula	$C_{28}H_{28}N_4BCl_4S_2Rh$	$C_{28}H_{30}N_4B_2OF_4Cl_3S_2Rh$
Formula weight	740.18	809.56
Crystal system	Monoclinic	Monoclinic
a (Å)	8.8580(2)	12.886(6)
b (Å)	18.3614(4)	22.535(10)
c (Å)	19.3443(5)	12.427(6)
β (°)	96.842(2)	109.173(11)
V (Å^3)	3123.85(13)	3408(3)
Space group	P_21/n	P_21/c
Z	4	4
D_{Calcd} (g cm^{-3})	1.574	1.578
Temperature (K)	173(2)	296(2)
F (0 0 0)	1496	1632
μ(Mo Kα) (mm^{-1})	9.023	0.911
Total refln.	17224	21495
Independent refln.	5527	7551
Parameters	366	415
R_{int}	0.0693	0.1083
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0377, 0.0815	0.0737, 0.1833
R_1, wR_2 (all data)	0.0489, 0.0870	0.1613, 0.2369
GoF[c]	0.997	0.966

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.
[c] $\mathrm{GoF} = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

determination showed that the complex was identical to **4** prepared by reaction of **3** and AgBF$_4$ in THF.

2.6. *X-ray crystallography*

A summary of crystallographic data and experimental details for **3** and **4**·H$_2$O are summarized in table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The collected frames were processed with SAINT [28]. The data were corrected for absorption using SADABS [29]. Structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL software package [30, 31]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogens were generated geometrically (C_{sp3}–H = 0.96 and C_{sp2}–H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or oxygen before the final cycle of least-squares refinement. The hydrogens on the hydrate of **4**·H$_2$O were not found from subsequent difference Fourier electronic density maps, but two hydrogen atoms have been calculated in the formula of **4**·H$_2$O.

3. Results and discussion

The reactions between Na[H$_2$B(tim^{Ar})$_2$] ligand and the starting rhodium compound [Cp*Rh(μ-Cl)Cl]$_2$ along with reactivity of the rhodium–[H$_2$B(tim^{Ar})$_2$] complexes are illustrated in scheme 1. Reaction of [Cp*Rh(μ-Cl)Cl]$_2$ with two equiv. Na[H$_2$B(tim^{Ar})$_2$] in THF at room temperature afforded [Cp*Rh{κ^2-*S*,*S′*-$H_2B(tim^{Ar})_2$}Cl] (**1**). One bridging chloride of [Cp*Rh(μ-Cl)Cl]$_2$ was substituted by $[H_2B(tim^{Ar})_2]^-$ to result in a mononuclear Rh(III) complex, **1**, in 85% yield. Treatment of **1** with an equivalent of $AgBF_4$ in THF gave a cationic Rh(III) complex [Cp*Rh{κ^3-*H*,*S*,*S′*-$H_2B(tim^{Ar})_2$}][BF_4] (**2**). One terminal chloride in **1** dissociated and a new agostic B–H···Rh bond formed to maintain the six-coordinate structure. As a result, $[H_2B(tim^{Ar})_2]^-$ coordinated to the rhodium center with a κ^3-*H*,*S*,*S′* coordination mode. Treatment of **1** in $CHCl_3$ at room temperature led to isolation of [Cp*Rh{κ^2-*S*,*S′*-ClHB$(tim^{Ar})_2$}Cl] (**3**) with a B–Cl bond. Previously, it is found that chloride substitution took place at B–H of [(η^6-*p*-cymene)Ru{κ^3-*S*,*S′*,*S″*-HB$(tim^{Me})_3$}]Cl and [Cp*Ru{κ^3-*S*,*S′*,*S″*-HB$(tim^{Me})_3$}] in refluxing $CHCl_3$ to produce the corresponding B–Cl complexes [13]. This substitution reaction was also found in [$MCl_3(\eta^5-C_5H_5)$]{κ^2-*S*,*S′*-ClHB$(tim^{Me})_2$}] (M = Nb, Ta), by reactions of [$MCl_4(\eta^5-C_5H_5)$] with Ph_3Sn[HB((tim^{Me})$_3$)] [24]. Similarly, reactions of **3** with $AgBF_4$ in THF gave the cationic [Cp*Rh{κ^3-*H*,*S*,*S′*-ClHB$(tim^{Ar})_2$}][BF_4]·H_2O (**4**·H_2O) with both agostic B–H···Rh and terminal B–Cl bonds. Perhaps, formation of **4**·H_2O with one water during re-crystallization was due to wet chloroform. Interaction of **2** in $CHCl_3$ also led to isolation of the expected **4**, evidenced by cell dimension determination.

IR spectra of **1–4** clearly show absorptions of both B–H···Rh (around 2190 cm^{-1}) and terminal B–H (about 2380 cm^{-1}) stretches [19]. Similarly, the proton resonances of Cp* were found as one singlet at 1.70 ppm, the imidazole moieties were shown as four singlets at 6.70 ppm and *p*-ClC_6H_4 were displayed as two doublets at 7.25 ppm with coupling constant $^3J_{HH}$ about 8.4 Hz. The positive ion FAB mass spectra of **1** and **3** display the expected peaks corresponding to the molecular ions [(M^+), (M^+–Cl), or (M^+–Cl–Cp*), while cationic **2** and **4** exhibit the expected peaks corresponding to the molecular ions [M^+–BF_4] and [M^+–BF_4–Cp*], with the characteristic isotopic distribution patterns.

The structures of **3** and **4**·H_2O have been established by X-ray crystallography. As shown in figure 1, the central rhodium in **3** is in an octahedral coordination environment, assuming Cp* functions as a three-coordinate ligand. The $[ClHB(tim^{Ar})_2]^-$ ligand in **3** is κ^2-*S*,*S′* coordination. The Rh–S bond lengths in **3** are 2.4323(9) and 2.4063(8) Å, which are compared with those in [Rh(cod){κ^3-*H,S,S′*-$H_2B(tim^{Me})_2$}] (2.3799(8) and 2.4425(13) Å) [19] and (2.432(1)

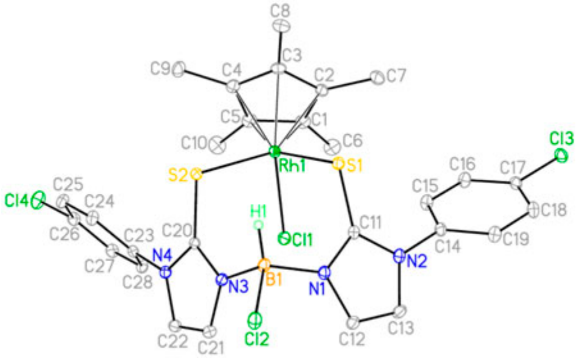


Figure 1. Molecular structure of [Cp*Rh{κ^2-*S*,*S′*-ClHB$(tim^{Ar})_2$}Cl] (**3**). Selected bond lengths (Å) and angles (°): Rh(1)–S(1) 2.4323(9), Rh(1)–S(2) 2.4063(8), Rh(1)–Cl(1) 2.4072(9), B(1)–H(3) 1.0000, B(1)–Cl(2) 1.871(4), C(11)–S(1) 1.723(3), C(20)–S(2) 1.717(3), N(3)–B(1) 1.556(5), N(1)–B(1) 1.558(5); S(2)–Rh(1)–S(1) 93.63(3), Cl(1)–Rh(1)–S(1) 93.61(3), S(2)–Rh(1)–Cl(1) 92.36(3), N(3)–B(1)–N(1) 107.5(3), N(3)–B(1)–Cl(2) 108.3(2), N(1)–B(1)–Cl(2) 108.1(2), N(3)–B(1)–H(1) 110.9, N(1)–B(1)–H(1) 110.9, Cl(2)–B(1)–H(1) 110.9.

and 2.351(2) Å) [20]. The S–Rh–S bond angle of 93.63(3)° in **3** is similar to those in [Rh(cod){κ^3-*H,S,S′*-$H_2B(tim^{Me})_2$}] (92.31°) [19] and [Rh(cod){κ^2-*S,S′*-$HB(tim^{Me})_3$}] (95.18(6)°) [20]. The Rh–Cl bond length of 2.4072(9) Å in **3** is in agreement with that of 2.404(9) Å in [$Cp^*{}_2Rh_2$(k^4-*N*-*O*-dppd)Cl_2][PF_6] (dppdH = 1,3-di(2-pyridyl)propane-1,3-dione) [32]. The terminal B–Cl bond length is 1.871(4) Å in **3**, a little longer than that in [Cp*Ru{κ^3-*S,S′,S′′*-$ClB(tim^{Me})_3$}] (1.820(7) Å), but well within the range of other related complexes (1.863–1.893 Å) [24–26]. The coordination environment around boron is slightly distorted tetrahedron (107.5(3)°–110.9°). The terminal B–H bond length is 1.000 Å in **3**, near to those in [$NbCl_3$(η^5-C_5H_5){κ^2-*S,S′*-$ClHB(tim^{Me})_2$}] (1.012 Å) and [$TaCl_3$(η^5-C_5H_5){κ^2-*S,S′*-$ClHB(tim^{Me})_2$}] (1.031 Å) [24]. The molecular structure of cationic part of [Cp*Rh{κ^3-*H,S,S′*-$ClHB(tim^{Ar})_2$}][BF_4]·H_2O (**4**·H_2O) is displayed in figure 2. The geometry around rhodium is *pseudo*-octahedral with an agostic B–H···Rh bond. The Rh–S bond lengths in **3** are 2.363(2) and 2.378(2) Å, a little shorter than those in neutral **3** (2.4323(9) and 2.4063(8) Å). The terminal B–Cl bond length of 1.724(9) Å in **4**·H_2O is shorter than that of 1.871(4) Å in **3** and those in other related compounds containing B–Cl bonds [24–26]. The S–Rh–S bond angle of 91.60(9)° in **4**·H_2O is near to that of 93.63(3)° in **3**. Similarly, a slightly distorted tetrahedral geometry is found for [$ClHB(tim^{Ar})_2$]$^-$ (106(3)°–111.1(7)°). The B–$H_{agostic}$ bond length is 1.28(8) Å for **4**·H_2O with corresponding Rh–$H_{agostic}$–B angle of 140(6)°; these bond parameters are compared with corresponding values of 1.14(1) Å and 134(2)° in [Rh(cod){κ^3-*H,S,S′*-$H_2B(tim^{Me})_2$}] [19]. The Rh–$H_{agostic}$ bond length of 1.69(7) Å in **4**·H_2O is obviously shorter than that of 2.13(3) Å in [Rh(COD){κ^3-*H,S,S′*-$H_2B(tim^{Me})_2$}] [19].

In summary, a series of rhodium complexes with dihydrobis(mercaptoimidazolyl) borate [$H_2B(tim^{Ar})_2$]$^-$ were synthesized and characterized. The neutral complex [Cp*Rh{κ^2-*S,S′*-$H_2B(tim^{Ar})_2$}Cl] (**1**) converted to the cationic complex [Cp*Rh{κ^3-*H,S,S′*-$H_2B(tim^{Ar})_2$}][BF_4] (**2**) with an agnostic B–H···Rh bond, in the presence of $AgBF_4$. **1** easily transformed to its corresponding boron chloride complex [Cp*Rh{κ^2-*S,S′*-$ClHB(tim^{Ar})_2$}Cl] (**3**) in chloroform at room temperature. Similar substitution reaction occurred on **2** to produce the cationic [Cp*Rh{κ^3-*H,S,S′*-$ClHB(tim^{Ar})_2$}][BF_4] (**4**) with both agnostic B–H···Rh and terminal B–Cl bonds, while **4** could be also obtained by treatment of **3** with $AgBF_4$.

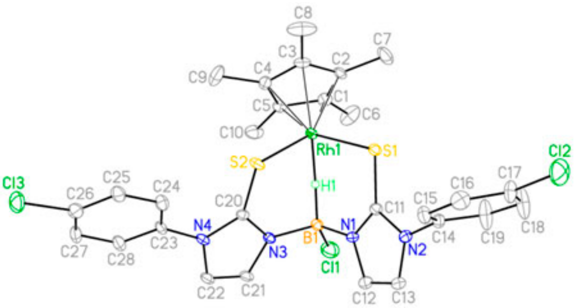
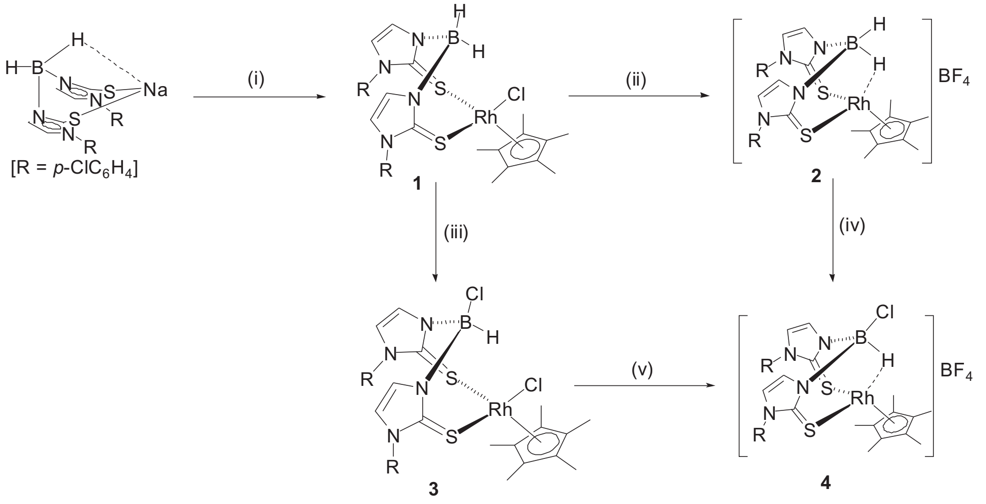


Figure 2. Molecular structure of the cationic [Cp*Rh{κ^3-*H,S,S′*-$ClHB(tim^{Ar})_2$}]$^+$ in **4**. Selected bond lengths (Å) and angles (°): Rh(1)–S(1) 2.363(2), Rh(1)–S(2) 2.378(2), Rh(1)–H(1) 1.69(7), Cl(1)–B(1) 1.724(9), C(11)–S(1) 1.705(8), C(20)–S(2) 1.703(7), N(3)–B(1) 1.545(11), N(1)–B(1) 1.525(11), B(1)–H(1) 1.28(8); S(2)–Rh(1)–S(1) 91.60(9), H(1)–Rh(1)–S(1) 90(3), H(1)–Rh(1)–S(2) 91(3), N(1)–B(1)–N(3) 111.1(7), N(1)–B(1)–Cl(1) 110.0(6), N(3)–B(1)–Cl(1) 110.5(6), N(1)–B(1)–H(1) 111(3), N(3)–B(1)–H(1) 108(3), Cl(1)–B(1)–H(1) 106(3).



Scheme 1. Reagents and conditions for the boron chlorination: (i) $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$, THF, r.t.; (ii) $AgBF_4$, THF, r.t.; (iii) $CHCl_3$, r.t.; (iv) $CHCl_3$, r.t.; and (v) $AgBF_4$, THF, r.t.

Supplementary material

Crystallographic data for **3** and **4**·H_2O have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 813248 and 813249, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1233 336 033; E-mail: deposit@ccdc.cam.ac.uk].

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