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Synthesis, characterization of novel half-sandwich iridium and rhodium complexes containing pyridine-based organochalcogen ligands

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ABSTRACT

A series of neutral pyridine-based organochalcogen ligands, 2,6-bis(1-methylimidazole-2-thione)pyridine (**Bmtp**), 2,6-bis(1-isopropylimidazole-2-thione)pyridine (**Bptp**), and 2,6-bis(1-*tert*-butylimidazole-2-thione)pyridine (**Bbtp**) have been synthesized and characterized. Reactions of $[Cp^*M(\mu\text{-}Cl)Cl]_2$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl, M = Ir, Rh) with three pyridine-based organochalcogen ligands result in the formation of the complexes $Cp^*M(L)Cl_2$ (M = Ir, L = **Bmtp**, **1a·Cl₂**; M = Rh, L = **Bmtp**, **1b·Cl₂**; M = Ir, L = **Bptp**, **2a·Cl₂**; M = Rh, L = **Bptp**, **2b·Cl₂**; M = Ir, L = **Bbtp**, **3a·Cl₂**; M = Rh, L = **Bbtp**, **3b·Cl₂**), respectively. All compounds have been characterized by elemental analysis, NMR and IR spectra. The molecular structures of **Bbtp**, **1a·Cl₂**, **1b·Cl₂**, **2b·Cl₂** and **3b·Cl₂** have been determined by X-ray crystallography.

1. Introduction

Multidentate ligand systems comprising bis(mercaptoimidazolyl)hydroborate (Bm^R) and tris(mercaptoimidazoly)hydroborate (Tm^R) (Chart 1) have attracted considerable interest in the last decades. A wide variety of complexes with transition and main group metals have been synthesized and characterized due to their potential application in bioinorganic, coordination and organometallic chemistry [1–10].

Whereas the anionic $[S_2]$ and $[S_3]$ ligands are ubiquitous, but the analogous neutral $[S_2]$ ligands are uncommon [11–15]. We previously reported that half-sandwich iridium and rhodium complexes containing neutral bidentate imidazole-2-thione ligands exhibited moderate activities for norbornene addition polymerization [16]. To the best of our knowledge, among these organochalcogen ligands, tridentate pyridine-based ligands incorporating imidazole-2-thione as ancillary pendant arms have probably been the least studied so far. In the case of the pyridine-based organochalcogen ligands, their features are a nitrogen atom as the central binding site and two imidazole-2-thione ancillary groups, although the thione ligand is expected to be bound more strongly to the metal centers [17–22].

Interested in further developing neutral organochalcogen coordination chemistry, in this paper we describe the preparation of three novel tridentate pyridine-based organochalcogen ligands and their complexes with half-sandwich iridium and rhodium fragments. The molecular structures of **Bbtp**, $[Cp^*Ir(\mathbf{Bmtp})]Cl_2$ (**1a·Cl₂**), $[Cp^*Rh(\mathbf{Bmtp})]Cl_2$ (**1b·Cl₂**), $[Cp^*Rh(\mathbf{Bptp})]Cl_2$ (**2b·Cl₂**) and $[Cp^*Rh(\mathbf{Bbtp})]Cl_2$ (**3b·Cl₂**) have been determined by X-ray crystallography. (**Bbtp** = 2,6-bis(1-*tert*-butylimidazole-2-thione)pyridine; **Bmtp** = 2,6-bis(1-methylimidazole-2-thione)pyridine; **Bptp** = 2,6-bis(1-isopropylimidazole-2-thione)pyridine).

2. Results and discussion

2.1. Synthesis of pyridine-based organochalcogen ligands

According to a synthetic method we developed earlier [11,12,16], a series of pyridine-based organochalcogen ligands, **Bmtp** (2,6-bis(1-methylimidazole-2-thione)pyridine), **Bptp** (2,6-bis(1-isopropylimidazole-2-thione)pyridine) and **Bbtp** (2,6-bis(1-*tert*-butylimidazole-2-thione)pyridine) were prepared in one-pot *via* the reactions of pyridine bridged imidazolium dibromide derivatives with sulfur powder in the presence of K_2CO_3 (Scheme 1). The synthetic method is environmentally benign and more economically than that using potassium *tert*-butoxide as base [13,23].

All these compounds were thermally stable and inert toward air and moisture in the solid state, and were soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$ and THF. All the compounds were characterized by NMR, IR spectroscopy as well as elemental analysis.

All these pyridine-based organochalcogen ligands have similar characteristic peaks on NMR spectra, so it is feasible to take **Bmtp** for an example. The ^1H NMR spectrum of **Bmtp** show signals at δ 3.64, 6.80, 7.49, 8.04 and 8.9 ppm, which can be assigned to the methyl, imidazole and pyridyl groups, respectively. And the ^{13}C

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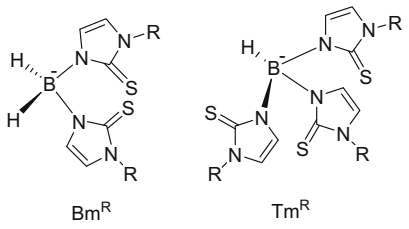
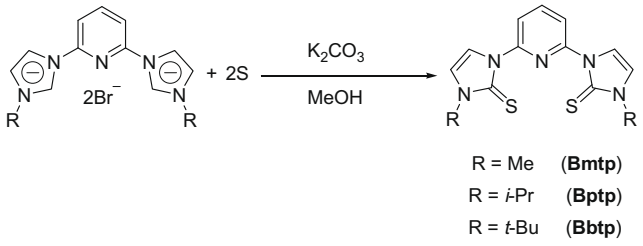


Chart 1.



Scheme 1. Synthesis of pyridine-based organochalcogen ligands.

NMR spectra show singlet at about δ 162.9 ppm for C=S group in **Bmtp**, which also prove the formation of the compound.

Crystal of **Bbtp** suitable for X-ray diffraction was determined (Fig. 1), which suggests the two imidazole-2-thione moieties adopt *trans* conformation to the nitrogen atom of pyridyl group. The bond distance between C and S is 1.679(2) Å and 1.6876(19) Å, respectively, which possess a typical double bond [12].

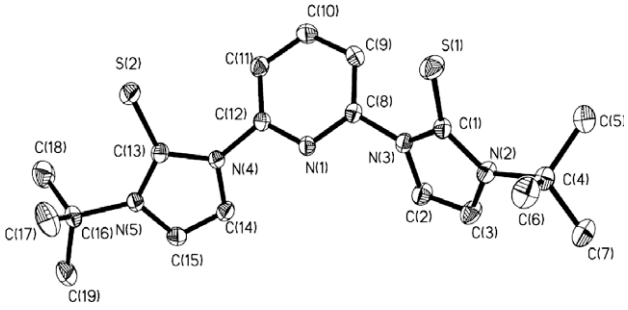


Fig. 1. Molecular structure of **Bbtp** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1) 1.679(2), C(13)–S(2) 1.6876(19); N(1)–C(8)–N(3) 113.94(19), N(1)–C(12)–N(4) 113.19(18).

2.2. Synthesis of half-sandwich iridium(III) and rhodium(III) complexes with pyridine-based organochalcogen ligands

The treatment of $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Ir, Rh) with 1 equivalent of pyridine-based organochalcogen ligands (**Bmtp**, **Bptp** and **Bbtp**) gave $Cp^*M(L)Cl_2$ (**1–3**) as air and moisture-stable crystals in moderate yields, respectively (Scheme 2).

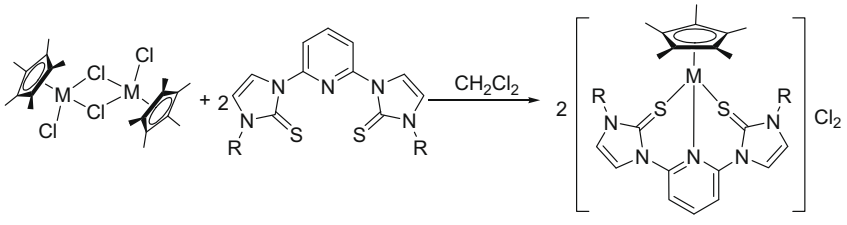
Compounds **1–3** were fully characterized by IR, NMR spectroscopy and elemental analysis. The ^1H NMR spectra of **1–3** in D_2O show singlet resonances due to Cp^* fragment at δ 1.41–1.48 ppm, the pyridyl group appear two resonances at δ 7.74–7.83 and 8.33–8.44 ppm, and the signals of the imidazole rings appear at δ 7.54–7.75 and 7.76–7.89 ppm range. The different substitute alkyl groups in imidazole ring have little effect on the chemical shifts of protons of all half-sandwich iridium and rhodium complexes.

Crystals of **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$** suitable for X-ray crystallographic diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in acetonitrile solution. The crystallographic data for compounds **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$** are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The molecular structures of **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$** are shown in Figs. 2–5.

The half-sandwich iridium and rhodium complexes have remarkably similar molecular structures. Assuming that the Cp^* rings serve as three-coordinated ligand, the metal centers of **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$** exist in the three-legged pianostool conformation with two six-membered chelate rings and one ten-membered chelate ring formed by coordination of the pyridine-based organochalcogen ligands to the metal center, which are common in Cp^*M^{III} (M = Ir, Rh) complexes [24–33].

As shown in Figs. 2 and 3, the complex **1a·Cl$_2$** and **1b·Cl$_2$** have isostructure. As expected, pyridine-based organochalcogen ligand is coordinated to Ir or Rh in a tridentate fashion by the pyridyl nitrogen and two sulfur atoms. The Ir–S distances (2.3850(19), 2.3870(16) Å) in **1a·Cl$_2$**, which are compatible with a typical single bond length between the iridium center and the sulfur atom reported in the previous literature [34,35] but longer than that in the complexes with five-membered metalladithiolene ring complexes [36–38].

The average distance Rh–S for **1b·Cl$_2$** is 2.3848 Å, which is shorter than the corresponding half-sandwich rhodium complex with bidentate organochalcogen ligand $[Cp^*RhMbit]Cl_2$ (Mbit = 1,1′-methylenebis(3-methyl-imidazole-2-thione)) (eight-membered ring 2.3967(11) Å) and $[Cp^*RhEbit]Cl_2$ (Ebit = 1,1′-(1,2-ethanediyl) bis(3-methyl-imidazole-2-thione)) (nine-membered ring 2.4228(11) Å and 2.4470(10) Å) [53], but close to the complex $[Cp^*Rh(Tm^{Me})]Cl$ (av. 2.3848 Å, Tm^{Me} = tris (2-mercapto-1-methyl-imidazolyl)borate), with three eight-membered rings [39].



Scheme 2. Synthesis of half-sandwich complexes with pyridine-based organochalcogen ligands **1–3 (a, b)**.

Table 1
Crystallographic data and structure refinement parameters for complexes **Bbtp**, **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$**.

	Bbtp	**1a·Cl$_2$**	**1b·Cl$_2$**	**2b·Cl$_2$**	**3b·Cl$_2$**
Empirical formula	$C_{19}H_{25}N_5S_2$	$C_{23}H_{32}Cl_2IrN_5O_2S_2$	$C_{23}H_{32}Cl_2N_5O_2RhS_2$	$C_{27}H_{40}Cl_2N_5O_2RhS_2$	$C_{29}H_{48}Cl_2N_5O_4RhS_2$
Formula weight	387.56	737.76	648.47	704.57	768.65
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Orthorhombic, *Pnma*
a (Å)	12.276(3)	13.589(12)	13.604(6)	10.984(9)	12.249(3)
b (Å)	11.261(3)	11.520(10)	11.512(5)	11.509(10)	22.303(5)
c (Å)	29.202(8)	18.116(16)	18.080(7)	13.960(12)	12.992(3)
α (°)	90	90	90	98.578(11)	90
β (°)	90	106.991(11)	106.984(6)	100.164(12)	90
γ (°)	90	90	90	90.147(12)	90
Volume (Å^3), *Z*	4037(2),8	2712(4), 4	2707.9(19), 4	1717(2), 2	3549.3(15), 4
D_{calc} (mg/m^3)	1.275	1.807	1.591	1.363	1.438
μ (Mo Kα) (mm^{-1})	0.277	5.305	1.013	0.805	0.789
F(0 0 0)	1648	1456	1328	728	1600
θ range (°)	139–27.14	166–25.01	166–25.01	1.50–25.01	1.81–25.01
Limiting indices	−10, 15; −14, 14; −37, 28	−16, 16; −13, 13; −21, 10	−16, 15; −13, 8; −21, 21	−13, 5; −13, 13; −16, 16	−14, 14; −22, 26; −13, 15
Reflections/unique [R_{int}]	18484/4419 [0.0722]	10875/4769 [0.0400]	10881/4770[0.0694]	7069/5892 [0.0567]	14075/3227 [0.0994]
Completeness to θ (°)	27.14 (98.7%)	25.01 (99.6%)	25.01 (99.9%)	25.01 (97.6%)	25.01 (100%)
Data/restraints/parameters	4419/0/241	4769/4/339	4770/0/339	5892/2/369	3227/5/224
Goodness-of-fit on F^2	0.721	0.978	0.664	0.863	0.664
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0392, 0.0717	0.0284, 0.0677	0.0370, 0.0507	0.0752, 0.1717	0.0389, 0.0496
R_1, wR_2 (all data)	0.1021, 0.0790	0.0353, 0.0690	0.0756, 0.0545	0.1235, 0.1826	0.0841, 0.0532
Largest difference in peak/hole (e/Å^3)	0.327, −0.243	1.160, −1.825	0.601, −0.592	2.105, −0.961	1.030, −0.692

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Table 2
Selected bond distances (Å) and angles (°) for complexes **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$**.

	1a·Cl$_2$	**1b·Cl$_2$**	**2b·Cl$_2$**	**3b·Cl$_2$**
M–S	Ir(1)–S(1) 2.3850(19) Ir(1)–S(2) 2.3870(16)	Rh(1)–S(1) 2.3866(14) Rh(1)–S(2) 2.3829(12)	Rh(1)–S(1) 2.400(3) Rh(1)–S(2) 2.392(3)	Rh(1)–S(1) 2.3810(11)
M–N	Ir(1)–N(1) 2.174(3)	Rh(1)–N(1) 2.185(3)	Rh(1)–N(1) 2.176(6)	Rh(1)–N(1) 2.126(4)
S–C	S(1)–C(6) 1.696(5) S(2)–C(10) 1.707(4)	S(1)–C(6) 1.687(4) S(2)–C(10) 1.684(4)	S(1)–C(6) 1.696(8) S(2)–C(9) 1.722(8)	S(1)–C(5) 1.696(4)
S1–M–S2	S(1)–Ir(1)–S(2) 86.88(6)	S(1)–Rh(1)–S(2) 87.32(5)	N(1)–Rh(1)–S(2) 85.55(18)	S(1)–Rh(1)–S(1A) 87.15(5)
N–M–S1	N(1)–Ir(1)–S(1) 84.61(10)	N(1)–Rh(1)–S(1) 84.79(9)	N(1)–Rh(1)–S(1) 85.25(18)	N(1)–Rh(1)–S(1) 86.31(9)
N–M–S2	N(1)–Ir(1)–S(2) 85.19(11)	N(1)–Rh(1)–S(2) 86.02(9)	S(1)–Rh(1)–S(2) 88.06(9)	N(1)–Rh(1)–S(1A) 86.31(9)

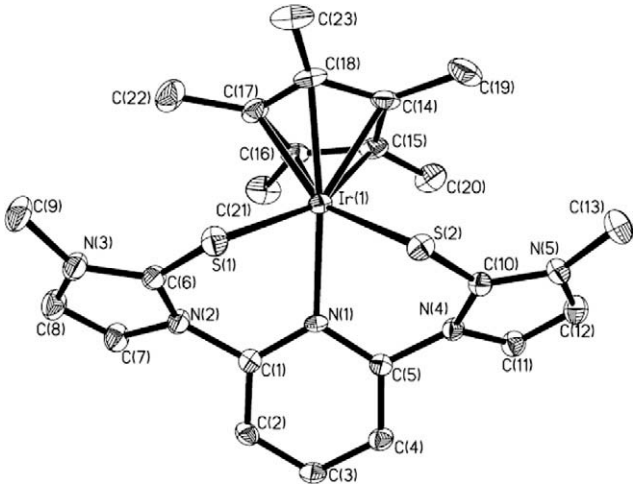


Fig. 2. Molecular structure of **1a·Cl$_2$** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms omitted for clarity.

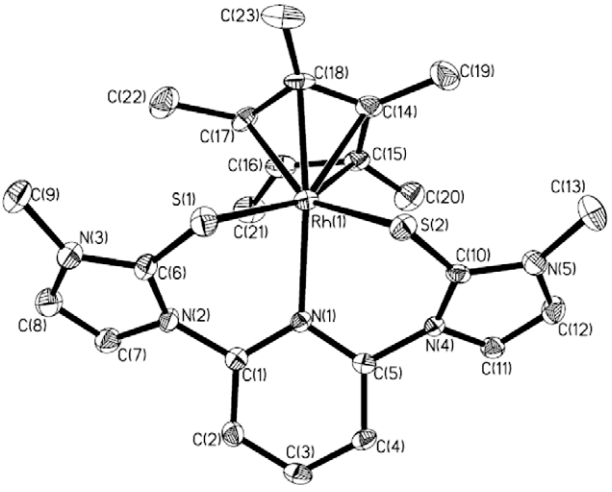


Fig. 3. Molecular structure of **1b·Cl$_2$** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms omitted for clarity.

The molecular structure of half-sandwich rhodium complexes **2b·Cl$_2$** and **3b·Cl$_2$** were shown in Figs. 4 and 5. The average distances Rh–S for **2b·Cl$_2$** and **3b·Cl$_2$** are 2.396(3) and 2.3810(11) Å, respectively. While the different substitute alkyl groups have little effect on Rh–N distances, with the substitute is bigger, the Rh–N distances is shorter. It is also proved that the different substitute alkyl groups in imidazole rings have little effect on molecular structures of Cp*Rh complexes with pyridine-based organochalcogen ligands.

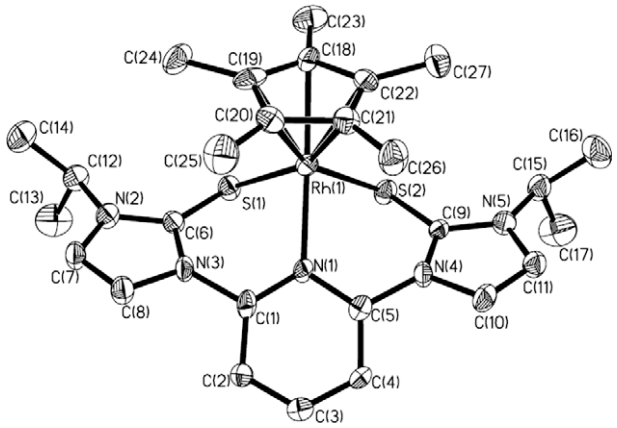


Fig. 4. Molecular structure of **2b·Cl$_2$** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms omitted for clarity.

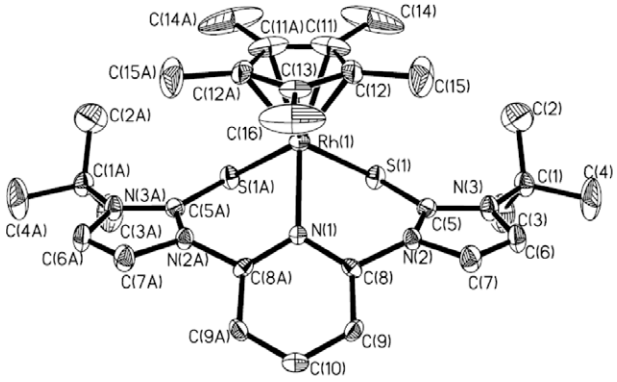


Fig. 5. Molecular structure of **3b·Cl$_2$** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms omitted for clarity.

3. Conclusion

In conclusion, we have reported a series of half-sandwich iridium(III) and rhodium(III) complexes containing neutral pyridine-based organochalcogen ligands. A combination of spectroscopic studies and X-ray crystallographic confirmed the structures of iridium complexes **1a·Cl$_2$** and rhodium complexes **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$**.

3.1. General procedures

All manipulations were carried out under nitrogen using standard Schlenk and vacuum-line techniques. All solvents were purified and degassed by standard procedures. Other chemicals were analytical grade and used as received. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer. The NMR spectra were obtained using ECA-400 spectrophotometer in $CDCl_3$ for ligands using TMS as an internal standard, and D_2O for complexes. The starting materials, $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Ir, Rh) [40], 2,6-bis(1-methylimidazolium)pyridine dibromide [41–44], 2,6-bis(1-isopropylimidazolium)pyridine dibromide [45,46], and 2,6-bis(1-*tert*-butylimidazolium)pyridine dibromide [47,48] were synthesized according to the procedures described in the literature.

3.2. Synthesis of pyridine-based organochalcogen ligands

3.2.1. 2,6-Bis(1-methylimidazole-2-thione)pyridine (*Bmtp*)

In a 100 mL round-bottomed flask fitted with reflux condenser were placed. 2,6-Bis(1-methylimidazolium)pyridine dibromide of 4.01 g (10 mmol), 0.64 g S (20 mmol), 2.8 g K_2CO_3 and 50 mL methanol as solvent. The mixture was allowed to reflux for 8 h after which the methanol was removed with a rotary evaporator. The remaining solid was shaken with 2 × 30 mL CH_2Cl_2 which was then filtered and rotary evaporated. The product was recrystallized from CH_2Cl_2/MeOH to give colorless solid. Yield: (1.91 g 63%) *Anal.* Calc. for $C_{13}H_{13}N_5S_2$ (303.06): C, 51.46; H, 4.32; N, 23.08. Found: C, 51.53; H, 4.24; N, 23.33%. ^{1}H NMR (400 MHz $CDCl_3$): 3.64 (s, 2CH_3, 6H), 6.80 (d, *J* = 2.3 Hz, imidazole, 2H), 7.49 (d, *J* = 2.3 Hz, imidazole, 2H), 8.04 (t, pyridine, 1H), 8.91 (s, pyridine, 1H), 8.93 (s, pyridine, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.3 (CH_3), 115.9 (imidazole), 116.7 (imidazole), 118.6 (pyridine), 140.0 (pyridine), 148.5 (pyridine), 162.9 (C=S) ppm. IR (KBr cm^{-1}): 1143 (m) (C=S).

3.2.2. 2,6-Bis(1-isopropylimidazole-2-thione)pyridine (*Bptp*)

The synthesis procedure was similar to the **Bmtp** to afford the colorless solid **Bptp**, using 2,6-bis(1-isopropylimidazolium)pyridine dibromide (4.65 g, 10 mmol), S (0.64 g, 20 mmol) and 2.8 g K_2CO_3. Yield: (2.69 g 75%) *Anal.* Calc. for $C_{17}H_{21}N_5S_2$ (359.12): C, 56.80; H, 5.89; N, 19.48. Found: C, 56.68; H, 5.74; N, 19.61%. ^{1}H NMR (400 MHz $CDCl_3$): 1.39 (d, *J* = 6.4 Hz, 2((CH_3)$_2$CH), 12H), 5.26 (m, 2(CH$_3$)$_2$C*H*, 2H), 6.85 (d, *J* = 2.7 Hz, imidazole, 2H), 7.44 (d, *J* = 2.7 Hz, imidazole, 2H), 8.02 (t, pyridine, 1H), 8.85 (s, pyridine, 1H), 8.87 (s, pyridine, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7 ((*C*H$_3$)$_2$CH), 48.6 ((CH$_3$)$_2$*C*H), 113.7 (pyridine), 116.8 (imidazole), 117.5 (imidazole), 139.7 (pyridine), 148.6 (pyridine), 161.5 (C=S) ppm. IR (KBr cm^{-1}): 1153 (m) (C=S).

3.2.3. 2,6-Bis(1-tert-butylimidazole-2-thione)pyridine (*Bbtp*)

The synthesis procedure was similar to the ligand **Bmtp** to afford the colorless solid **Bbtp**, using 2,6-bis(1-*tert*-butylimidazolium)pyridine dibromide (4.93 g, 10 mmol), S (0.64 g, 20 mmol) and 2.8 g K_2CO_3. Yield: (2.56 g 66%) *Anal.* Calc. for $C_{19}H_{25}N_5S_2$ (387.16): C, 58.88; H, 6.50; N, 18.07. Found: C, 58.74; H, 6.68; N, 18.32%. ^{1}H NMR (400 MHz $CDCl_3$): 1.87 (s, 2((CH_3)$_3$C), 18H), 6.96 (d, *J* = 2.7 Hz, imidazole, 2H), 7.32 (d, *J* = 2.7 Hz, imidazole, 2H), 7.98 (t, pyridine, 1H), 8.59 (s, pyridine, 1H), 8.61 (d, pyridine, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2 ((*C*H$_3$)$_3$C), 59.9 ((CH$_3$)$_2$*C*H), 115.4 (imidazole), 116.6 (imidazole), 119.2 (pyridine), 138.8 (pyridine), 148.8 (pyridine), 161.7 (C=S) ppm. IR (KBr cm^{-1}): 1137 (m) (C=S).

3.3. Synthesis of complexes *1–3*

3.3.1. [Cp*Ir(*Bmtp*)]Cl$_2$ (*1a·Cl$_2$*)

A solution of $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$ (80 mg, 0.1 mmol) and **Bmtp** (61 mg, 0.2 mmol) in CH_2Cl_2 solution (20 mL) was stirred for 16 h under an atmosphere of nitrogen, resulting in the formation of a red-brown solution and yellow precipitate. The yellow product is obtained by filtration and washed twice with 5 mL of CH_2Cl_2 and dried in vacuo for 15 h. Recrystallization of the product from CH_3CN–Et_2O afforded yellow crystal of **1a·Cl$_2$** (103 mg, 73%). *Anal.* Calc. for $C_{23}H_{28}Cl_2IrN_5S_2$ (701.08): C, 39.37; H, 4.02; N, 9.98. Found: C, 39.46; H, 4.15; N, 9.96%. ^{1}H NMR (400 MHz, D_2O): 1.42 (s, 5CH_3, 15H), 3.96 (s, 2CH_3, 6H), 7.54 (d, *J* = 2.3 Hz, imidazole, 2H), 7.80 (d, *J* = 1.7 Hz, pyridine, 2H), 7.84 (d, *J* = 2.4 Hz, imidazole, 2H), 8.38 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 1158 (m) (C=S).

3.3.2. [Cp*Rh(*Bmtp*)]Cl$_2$ (*1b·Cl$_2$*)

Prepared by the same procedure as described above for **1a·Cl$_2$**, using $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ (62 mg, 0.1 mmol) and **Bmtp** (61 mg, 0.2 mmol). Yield: (100 mg 81%) *Anal.* Calc. for $C_{23}H_{28}Cl_2RhN_5S_2$ (611.02): C, 45.11; H, 4.61; N, 11.44. Found: C, 45.23; H, 4.44; N, 11.49%. ^{1}H NMR (400 MHz, D_2O): 1.42 (s, 5CH_3, 15H), 4.03 (s, 2CH_3, 6H), 7.56 (d, *J* = 2.5 Hz, imidazole, 2H), 7.83 (d, *J* = 1.8 Hz, pyr-

idine, 2H), 7.85 (d, J = 2.4 Hz, imidazole, 2H), 8.44 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 1158 (m) (C=S).

3.3.3. [Cp*Ir(**Bptp**)]Cl_2 (**2a·Cl$_2$**)

Prepared by the same procedure as described above for **1a·Cl$_2$**, using [Cp*Ir(μ-Cl)Cl]$_2$ (80 mg, 0.1 mmol) and **Bptp** (72 mg, 0.2 mmol). Yield: (99 mg 65%) *Anal.* Calc. for $C_{27}H_{36}Cl_2IrN_5S_2$ (757.14): C, 42.79; H, 4.79; N, 9.24. Found: C, 42.64; H, 4.58; N, 9.87%. ^{1}H NMR (400 MHz, D_2O): 1.42 (s, 5CH_3, 15H), 1.45 (d, J = 1.4 Hz, 2(CH_3)$_2$CH, 6H), 1.69 (d, J = 1.5 Hz, 2(CH_3)$_2$CH, 6H), 5.20 (m, 2CH(CH_3)$_2$, 2H), 7.69 (d, J = 2.6 Hz, imidazole, 2H), 7.78 (s, pyridine, 1H), 7.80 (s, pyridine, 1H), 7.84 (d, J = 2.6 Hz, imidazole, 2H), 8.36 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 1155 (m) (C=S).

3.3.4. [Cp*Rh(**Bptp**)]Cl_2 (**2b·Cl$_2$**)

Prepared by the same procedure as described above for **1a·Cl$_2$**, using [Cp*Rh(μ-Cl)Cl]$_2$ (62 mg, 0.1 mmol) and **Bptp** (72 mg, 0.2 mmol). Yield: (114 mg 85%) *Anal.* Calc. for $C_{27}H_{36}Cl_2RhN_5S_2$ (667.08): C, 48.51; H, 5.43; N, 10.48. Found: C, 48.66; H, 5.37; N, 10.24%. ^{1}H NMR (400 MHz, D_2O): 1.41 (s, 5CH_3, 15H), 1.43 (d, J = 1.4 Hz, 2(CH_3)$_2$CH, 6H), 1.70 (d, J = 1.5 Hz, 2(CH_3)$_2$CH, 6H), 5.30 (m, 2CH(CH_3)$_2$, 2H), 7.72 (d, J = 2.6 Hz, imidazole, 2H), 7.80 (s, pyridine, 1H), 7.82 (ds, pyridine, 1H), 7.89 (d, J = 2.7 Hz, imidazole, 2H), 8.43 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 1157 (m) (C=S).

3.3.5. [Cp*Ir(**Bbtp**)]Cl_2 (**3a·Cl$_2$**)

Prepared by the same procedure as described above for **1a·Cl$_2$**, using [Cp*Ir(μ-Cl)Cl]$_2$ (80 mg, 0.1 mmol) and **Bbtp** (78 mg, 0.2 mmol). Yield: (111 mg 70%) *Anal.* Calc. for $C_{29}H_{40}Cl_2IrN_5S_2$ (785.17): C, 44.32; H, 5.13; N, 8.91. Found: C, 44.46; H, 5.24; N, 9.03%. ^{1}H NMR (400 MHz, D_2O): 1.48 (s, 5CH_3, 15H), 1.91 (d, J = 2.2 Hz, 2(CH_3)$_3$C, 18H), 7.65 (d, J = 1.8 Hz, imidazole, 2H), 7.74 (d, J = 2.2 Hz, pyridine, 2H), 7.76 (d, J = 1.8 Hz, imidazole, 2H), 8.33 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 1154 (m) (C=S).

3.3.6. [Cp*Rh(**Bbtp**)]Cl_2 (**3b·Cl$_2$**)

Prepared by the same procedure as described above for **1a·Cl$_2$**, using [Cp*Rh(μ-Cl)Cl]$_2$ (62 mg, 0.1 mmol) and **Bbtp** (78 mg, 0.2 mmol). Yield: (112 mg 80%) *Anal.* Calc. for $C_{29}H_{40}Cl_2RhN_5S_2$ (695.12): C, 50.00; H, 5.79; N, 10.05. Found: C, 49.80; H, 5.65; N, 10.08%. ^{1}H NMR (400 MHz, D_2O): 1.47 (s, 5CH_3, 15H), 1.94 (d, J = 2.3 Hz, 2(CH_3)$_3$C, 18H), 7.67 (d, J = 2.0 Hz, imidazole, 2H), 7.75 (d, J = 2.3 Hz, pyridine, 2H), 7.82 (d, J = 1.8 Hz, imidazole, 2H), 8.40 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 1153 (w) (C=S).

3.4. X-ray crystallography

Diffraction data of **Bbtp**, **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [49], All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located at calculated positions. All the calculations were performed using the BRUCKER SMART program. Crystal data, data collection parameters and the results of the analyses of complexes **Bbtp**, **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$** are listed in Table 1.

4. Supplementary material

CCDC 738855, 738856, 738857, 738858 738859 contains the supplementary crystallographic data for **Bbtp**, **1a·Cl$_2$**, **1b·Cl$_2$**, **2b·Cl$_2$** and **3b·Cl$_2$**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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