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Synthesis and characterization of half-sandwich iridium(III) and rhodium(III) complexes bearing organochalcogen ligands

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ABSTRACT

Reactions of $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Ir, Rh; Cp^* = η^5-pentamethylcyclopentadienyl) with bi- or tri-dentate organochalcogen ligands Mbit (**L1**), Mbpit (**L2**), Mbbit (**L3**) and $[Tm^{Me}]^-$ (**L4**) (Mbit = 1,1′-methylene-bis(3-methyl-imidazole-2-thione); Mbpit = 1,1′-methylene bis (3-*iso*-propyl-imidazole-2-thione), Mbbit = 1,1′-methylene bis (3-*tert*-butyl-imidazole-2-thione)) and $[Tm^{Me}]^-$ (Tm^{Me} = tris (2-mercapto-1-methylimidazolyl) borate) result in the formation of the 18-electron half-sandwich complexes $[Cp^*M(Mbit)Cl]Cl$ (M = Ir, **1a**; M = Rh, **1b**), $[Cp^*M(Mbpit)Cl]Cl$ (M = Ir, **2a**; M = Rh, **2b**), $[Cp^*M(Mbbit)Cl]Cl$ (M = Ir, **3a**; M = Rh, **3b**) and $[Cp^*M(Tm^{Me})]Cl$ (M = Ir, **4a**; M = Rh, **4b**), respectively. All complexes have been characterized by elemental analysis, NMR and IR spectra. The molecular structures of **1a**, **2b** and **4a** 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 [1–12]. The remarkable character of these two kinds of ligands are anionic and softer donor electrons ligands. It can be used as a 4-electron donor if coordinated through two sulfur atoms and a 6-electron donor if coordinated though three sulfur atoms. Whereas the anionic $[S_2]$ and $[S_3]$ ligands are ubiquitous, but the analogous neutral $[S_2]$ ligands are uncommon [13–17].

We were interested in supramolecular complexes based on quasi-octahedral geometries that bear pentamethylcyclopentadienyl group, which was proved to be efficient ancillary ligands in organometallic complexes [18–23]. Although Cp^* stabilize metal centers by tri-dentate coordination in a facial fashion, it is rather difficult to modify the electronic and steric properties of these ligands. If other ligands such as soft $[S_2]$ compounds or *N*-heterocyclic carbene were introduced may change the complexes structures and chemical properties [13,24–26]. Therefore, the synthesis and design of neutral organochalcogen compounds bearing imidazole ring are very attractive from organometallic and application points of view, and complexes containing these functional group strongly bound to late transition metal are of considerable interest.

Interested in further developing neutral organochalcogen coordination chemistry, in this paper we describe the preparation of two new neutral organochalcogen ligands (**L2** and **L3**) and their derivatives with half-sandwich iridium and rhodium fragments. The molecular structures of $[Cp^*Ir(Mbit)Cl]Cl$ (**1a**), $[Cp^*Rh(Mbpit)Cl]Cl$ (**2b**), and $[Cp^*Ir(Tm^{Me})]Cl$ (**4a**) were determined by X-ray crystallography, which also confirmed the ligands configuration (Mbit = 1,1′-methylenebis(3-methyl-imidazole-2-thione); Mbpit = 1,1′-methylene bis (3-*iso*-propyl-imidazole-2-thione), and Tm^{Me} = tris (2-mercapto-1-methylimidazolyl) borate).

2. Results and discussion

The bi-dentate organochalcogen compounds Mbpit and Mbbit analogs of Mbit can be prepared according to the previous literature [13,14]. The synthetic method in this paper is environmentally benign and more economically than that using potassium *tert*-butoxide as base [15]. Both compounds have similar characteristic peaks on NMR spectra, so it is feasible to take Mbpit for an example. The ^1H NMR spectrum of Mbpit show signals at δ 1.36, 5.05, 6.37, 6.67 and 7.68 ppm, which can be assigned to the *i*-Pr, CH_2, and two olefinic protons of Mbpit, respectively. And the ^{13}C NMR spectra show singlet at about δ 162.0 ppm for C=S group of Mbpit, which also prove the formation of the compound.

The reactions of $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$ with two equivalents of neutral bi-dentate organochalcogen compounds Mbit, Mbpit, Mbbit and tri-dentate anionic $[Tm^{Me}]K$ [27] in dichloromethane at ambient

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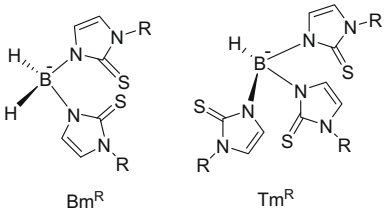
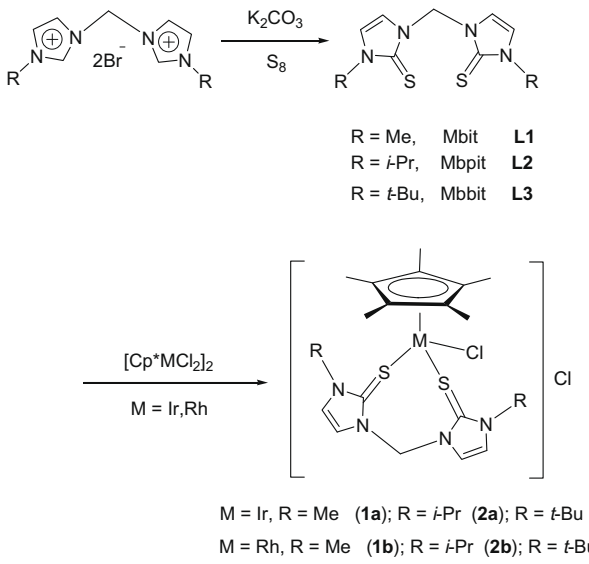


Chart 1.

temperature afford the corresponding half-sandwich iridium complexes formulated as [Cp*Ir(Mbit)Cl]Cl (**1a**), [Cp*Ir(Mbpit)Cl]Cl (**2a**), [Cp*Ir(Mbbit)Cl]Cl (**3a**) and [Cp*Ir(Tm^{Me})]Cl (**4a**), respectively, as red crystals in moderate yields. The analogous products of rhodium complexes **1b**–**4b** were also obtained as dark-red crystals through the same methods (Schemes 1 and 2). These complexes were characterized by NMR, IR spectra as well as elemental analysis.

The ^{1}H NMR spectra of these complexes exhibited signals around δ 1.63–1.71 ppm due to Cp* ring. The ^{1}H NMR spectra also shows that the two bridging methylene backbone protons of the complexes, H_a and H_b, are in magnetically distinct environments for each of the complexes **1–3** (**a**, **b**). The ^{13}C NMR spectra shows the singlet ranged from 153 to 156 ppm for complexes **1**–**4** due to C=S group, which were downfield shifted compared with the organochalcogen compounds. Detailed structures of the complexes were conformed by X-ray analyses.



Scheme 1. Synthesis of half-sandwich iridium and rhodium complexes **1–3** (**a**, **b**).

Crystals of **1a**, **2b** and **4a** suitable for X-ray crystallographic diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in dichloromethane. The crystallographic data for compounds **1b**, **2b** and **4a** are summarized in Table 1, and selected bond lengths and angles are given in Table 2. The molecular structures of **1a**, **2b** and **4a** are shown in Figs. 1–4.

As shown in Fig. 1, the complex **1a** has a three-legged piano-stool geometry and coordinatively saturated metal centers with an eight-membered macrocyclic ring. The iridium–sulfur bond distance (Ir(1)–S(1)) is 2.3862(14) Å, which is compatible with a typical single bond length between the iridium center and the sulfur atom reported in the previous literature [28–31], but longer than that in the complexes with five-membered metalladithiolene ring complexes [32–35]. The structure of **1a** is solved in the orthorhombic space group *pnma* with high asymmetric, while the selenium analog complexes [Cp*Ir(Mbis)Cl]Cl [13] adopt triclinic crystal system and $P\bar{1}$ space group, but the structures of these two complexes are very similar to each other.

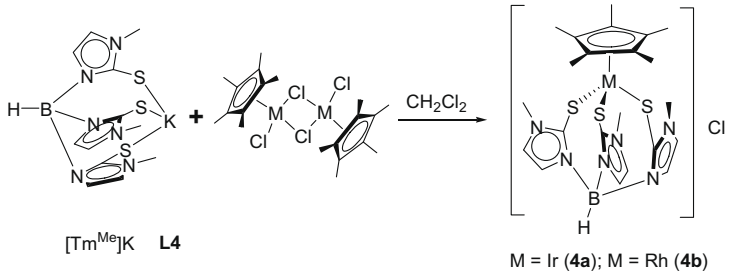
As shown in Fig. 2, complex **2b** have remarkably similar molecular structure to **1a**. Assuming that the Cp* ring serve as three-coordinated ligand, the metal centers of **2b** exist in the three-legged piano-stool conformation with an eight-membered metallocycle formed by coordination of the bi-dentate organochalcogen to the metal center in each case existing in the boat configuration. The average distances Rh–S for **2b** is 2.4031(13) Å, which are longer than the corresponding complexes [Cp*Rh(Mbit)Cl]Cl (2.3967(11) Å) [13] due to the repulsion of bigger substituent group (*i*-Pr) on imidazole ring.

As shown in Fig. 3, there are two kinds of the hydrogen bonds interaction in the unit cell, which are most probably stabilized the molecular structure. The C–H···Cl hydrogen bonds of imidazole with the distance of H···Cl is 2.6458(6) Å and the angle of C–H···Cl is 167.4°; C–H···Cl hydrogen bonds of methyl of Cp* with the distance of H···Cl is 2.7703(9) Å, and the angle of C–H···Cl is 118.5°. Although the force is not strong, which play a crucial role in halogenated molecules in the solid state.

Complex **4a** adopt triclinic crystal system and $P\bar{1}$ space group. Each iridium is coordinated by three sulfur atoms from one ligand and containing three eight-membered macrocyclic rings. The geometry around every iridium center is described as a three-legged piano-stool, which is common in Cp*Ir complexes. The distance between the iridium and sulfur atom is in the range 2.369–2.396 Å, this bond length is compatible with a typical single bond length between the iridium center and the sulfur atom. The distance between B and Ir is 4.1414(17) Å, which indicated there is inexistence of any interaction in complex **4a**.

3. Conclusion

In conclusion, we have reported a series of half-sandwich iridium (III) and rhodium (III) complexes containing bi-dentate organ-



Scheme 2. Synthesis of half-sandwich iridium and rhodium complexes **4** (**a**, **b**).

Table 1
Crystallographic data and structure refinement parameters for complexes **1a**, **2b** and **4a**.

	1a	2b	4a
Empirical formula	$C_{19}H_{27}Cl_2IrN_4S_2$	$C_{23}H_{37}Cl_2N_4ORhS_2$	$C_{22}H_{33}BClIrN_6OS_3$
Formula weight	638.67	623.50	732.18
Crystal system, space group	orthorhombic, *Pnma*	monoclinic, *C2/c*	triclinic, $P\bar{1}$
a (Å)	10.323(4)	27.449(10)	10.450(4)
b (Å)	11.433(4)	9.421(3)	12.154(5)
c (Å)	21.736(8)	27.046(10)	13.380(5)
α (°)	90	90	111.196(6)
β (°)	90	118.638(4)	91.878(6)
γ (°)	90	90	114.833(5)
Volume (Å^3), *Z*	2565.4(16), 4	6139(4), 8	1403.3(9), 2
D_{calc} (mg/m^3)	1.747	1.349	1.733
μ (Mo Kα) (mm^{-1})	5.598	0.887	5.103
F(0 0 0)	1328	2576	724
θ range (°)	1.87 ~ 27.12	1.69~ 27.13	1.67 ~ 25.01
Limiting indices	−12, 13; −14, 14; −24, 27	−32, 34; −12 12; −29, 34	−12,12; −14, 9; −15, 15
Reflections/unique [R_{int}]	12 432/2970[0.0538]	14 451/6606[0.0478]	5855/4854[0.0598]
Completeness to θ (°)	27.12 (99.6%)	27.13 (97.2%)	25.01 (98%)
Data/restraints/parameters	2970/6/164	6606/0/311	4854/1/329
Goodness-of-fit on F^2	1.040	0.846	0.716
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0311, 0.0619	0.0424, 0.0987	0.0458, 0.0737
R_1, wR_2 (all data)	0.0481, 0.0663	0.0743, 0.1040	0.0809, 0.0795
Largest difference peak/hole (e/Å^3)	0.927, −1.317	0.792, −0.398	0.906, −0.886

[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 **1a**, **2b** and **4a**.

Bond distance (Å) in ***1a***			
Ir(1)–S(1)	2.3862(14)	Ir(1)–Cl(1)	2.4102(17)
S(1)–C(1)	1.714(5)		
Bond angle (°) in ***1a***			
S(1)–Ir(1)–S(1A)	89.23(8)	S(1)–Ir(1)–Cl(1)	91.49(4)
Bond distance (Å) in ***2b***			
Rh(1)–S(1)	2.4190(13)	Rh(1)–S(2)	2.3871(13)
Rh(1)–Cl(1)	2.3937(13)	S(1)–C(1)	1.729(4)
S(2)–C(5)	1.706(4)		
Bond Angle (°) in ***2b***			
S(1)–Rh(1)–S(2)	90.45(4)	S(1)–Rh(1)–Cl(1)	93.66(4)
S(2)–Rh(1)–Cl(1)	92.37(3)		
Bond distance (Å) in ***4a***			
Ir(1)–S(1)	2.369(3)	Ir(1)–S(2)	2.396(3)
Ir(1)–S(3)	2.381(2)	S(1)–C(1)	1.715(9)
S(2)–C(5)	1.742(10)	S(3)–C(9)	1.727(10)
Bond Angle (°) in ***4a***			
S(1)–Ir(1)–S(2)	90.40(9)	S(1)–Ir(1)–S(3)	93.44(9)
S(2)–Ir(1)–S(3)	94.32(9)		

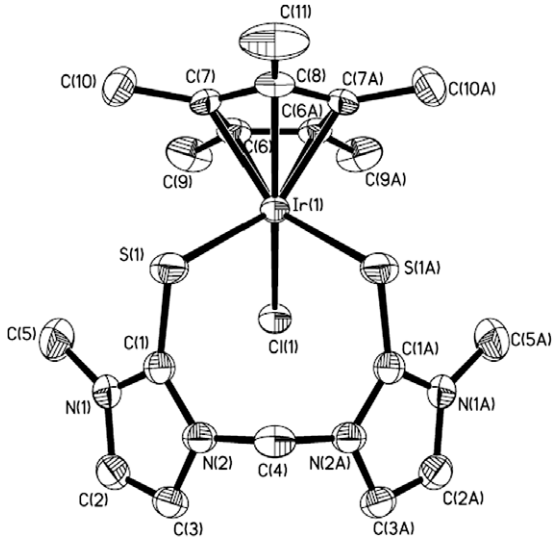


Fig. 1. Molecular structure of **1a** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity.

ochalcogen and tripodal borate ligands. A combination of spectroscopic studies and X-ray crystallographic confirmed the structures of iridium complexes **1a** and **4a**, and rhodium complexes **2b**.

4. Experimental

4.1. General procedures

All manipulations were carried out under nitrogen using standard Schlenk and vacuum-line techniques. All solvent were purified and degassed by standard procedures. The materials, $[Cp^*M(\mu\text{-}Cl)Cl]_2$ (M = Ir, Rh) [36], $[Cp^*M(Mbit)Cl]Cl$ (M = Ir (**1a**), Rh (**1b**)) [13], $[Cp^*M(Tm^{Me})]Cl$ (M = Ir (**4a**), Rh (**4b**)) [37] and 1,1′-diisopropyl-3,3-methylenediimidazolium dibromide, 1,1′-di-*tert*-butyl-3,3-methylenediimidazolium dibromide [38], were synthesized according to the procedures described in the literature. Other chemicals were analytical grade and used as received. The NMR spectra were obtained using ECA-400 spectrophotometer in $CDCl_3$ for complexes using TMS as an internal standard. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer.

4.2. Synthesis of *L2* and *L3*

4.2.1. Mbpit (*L2*)

In a 100 mL Schlenk flask fitted with reflux condenser were placed 1,1′-diisopropyl-3,3-methylenediimidazolium dibromide of 3.93 g (10 mmol), 0.64 g S (20 mmol), 2.0 g K_2CO_3 and 60 mL methanol. The mixture was refluxed for 24 h after which the methanol was removed. The residue was shaken with 2 × 30 mL CH_2Cl_2 and then evaporated. The colorless product **L2** was obtained. Yield: (1.33 g, 45%). *Anal.* Calc. for $C_{13}H_{20}N_4S_2$ (296.45): C, 52.67; H, 6.80; N, 18.90. Found: C, 52.68; H, 6.76; N, 18.86%. ^{1}H NMR (400 MHz, $CDCl_3$): 1.36 (d, *J* = 4.1 Hz, $4CH_3$, 12H), 5.05 (sept, 2CH, 2H), 6.37 (s, CH_2, 2H), 6.67 (d, *J* = 2.3 Hz, imidazole, 2H), 7.68 (d, *J* = 2.3 Hz, imidazole, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 21.8 (CH_3), 49.2

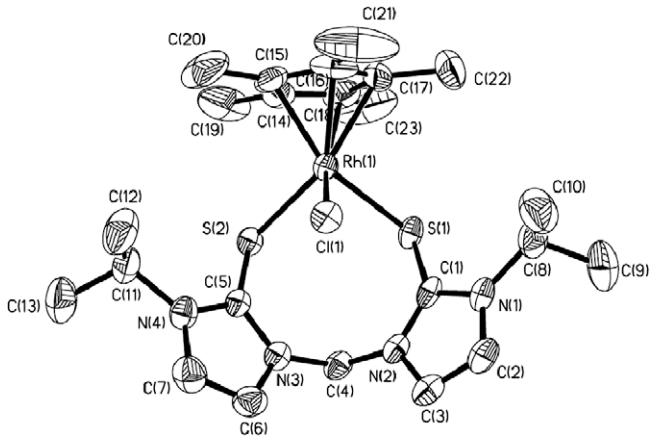


Fig. 2. Molecular structure of **2b** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity.

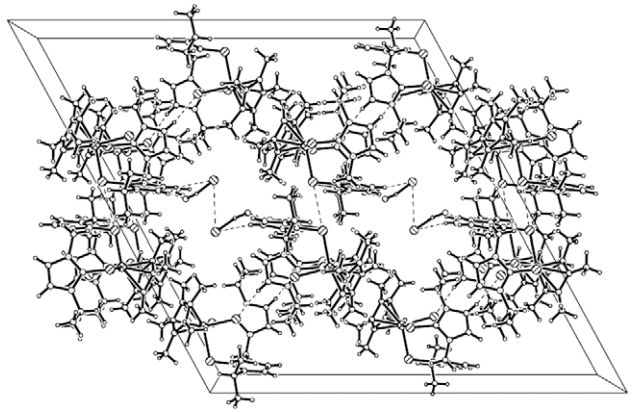


Fig. 3. Packing diagram for complex **2b** along the *b* axis.

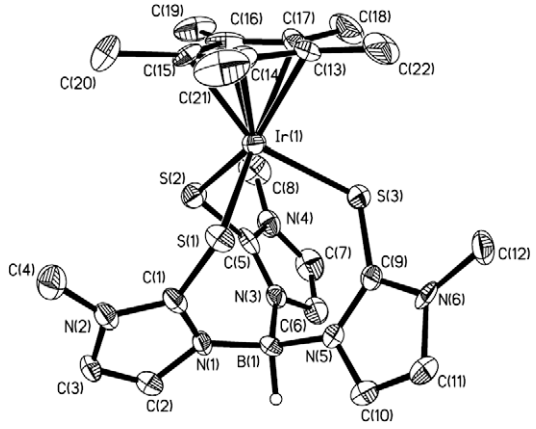


Fig. 4. Molecular structure of **4a** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity.

(*C*H), 55.5 (CH_2), 113.0 (imidazole), 119.3 (imidazole), 162 (*C*=S) ppm. IR (KBr disk): 3151 (m), 3125 (m), 2973 (w), 2934(m), 2868(m) 1656 (w), 1536 (m), 1415 (s), 1347 (s), 1294 (m), 1209 (s), 1131 (m), 1070 (m), 946 (m), 880 (w), 712 (w), 666(m) cm^{-1}.

4.2.2. Mbbit (*L3*)

The procedure was similar to compound **L2**, using 1,1′-di-*tert*-butyl-3,3-methylenediimidazolium dibromide (4.22 g, 10 mmol), S (0.64 g, 20 mmol) and 2.0 g K_2CO_3. Yield: (1.13 g, 35%). *Anal.* Calc. for $C_{15}H_{24}N_4S_2$ (324.50): C, 55.52; H, 7.45; N, 17.27. Found: C, 55.49, H, 7.42, N, 17.29%. ^{1}H NMR (400 MHz, $CDCl_3$): 1.77 (s, $6CH_3$, 18H), 6.39 (s, CH_2, 2H), 6.76 (d, *J* = 2.4 Hz, imidazole, 2H), 7.67 (d, *J* = 2.4 Hz, imidazole, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 28.1 (CH_3), 54.7 (–*C*(CH_3)$_3$), 59.4 (–CH_2–), 114.51 (imidazole), 118.19 (imidazole), 162.29 (*C*=S) ppm. IR (KBr disk): 3176 (m), 3140 (m), 3109 (m), 2971 (w), 2929 (m), 2868 (m), 1638 (w), 1571 (m), 1479 (s), 1421 (m), 1393 (m), 1366 (m), 1327 (s), 1288 (m), 1262 (m), 1209 (s), 1132 (m), 1075 (m), 1029 (m), 960 (m), 928 (m), 812 (w), 746 (w), 714 (w), 674(m) cm^{-1}.

4.3. Synthesis of complexes *2* and *3*

4.3.1. [Cp*Ir(Mbpit)Cl]Cl (*2a*)

[Cp*Ir(μ-Cl)Cl]$_2$ (80 mg, 0.1 mmol) was added to a solution of (Mbpit) (59 mg, 0.2 mmol) in degassed dichloromethane (40 mL) in a Schlenk tube and kept at room temperature to stir for 12 h. The color of the solution changed from orange-yellow to orange-red. The reaction mixture was filtered and filtrate was reduced to about 5 mL under vacuum. Ethyl ether was added slowly in the orange-red solution, giving orange-red solids of **2a** (68 mg, 76%). *Anal.* Calc. for $C_{23}H_{35}N_4IrCl_2S_2$ (694.80): C, 39.76; H, 5.08; N, 8.06. Found: C, 39.57; H, 5.34; N, 8.42%. ^{1}H NMR (400 MHz $CDCl_3$): 1.35 (d, *J* = 6.9 Hz, $2CH_3$, 6H), 1.41 (d, *J* = 6.9 Hz, $2CH_3$, 6H), 1.70 (d, $5CH_3$, 15H), 4.90 (m, CH_2, 2H), 6.84 (d, CH_2, 1H), 6.87 (d, *J* = 1.4 Hz, imidazole, 2H), 7.38 (d, CH_2, 1H), 9.06 (d, *J* = 1.4 Hz, imidazole, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 8.52 (*C*H_3-Cp*), 22.25 (C(*C*H_3)$_2$), 22.80 (C(*C*H_3)$_2$), 51.20 (*C*(CH$_3$)$_2$), 56.0 (*C*H_2), 88.41 (Cp*), 115.56 (imidazole), 123.48 (imidazole), 153.71 (C=S) ppm. IR (KBr disk): 3040 (s), 3037 (w), 2980 (w), 1633 (m), 1568 (m), 1457 (s), 1410 (m), 1373 (m), 1304 (w), 1240 (m), 1199 (s), 1148 (w), 1085 (m), 1028 (m), 882 (w), 749 (m), 618 (w) cm^{-1}.

4.3.2. [Cp*Rh(Mbpit)Cl]Cl (*2b*)

Prepared by the same procedure as described above for **2a**, using [Cp*Rh(μ-Cl)Cl]$_2$ (62 mg, 0.1 mmol) and (Mbpit) (59 mg, 0.2 mmol). Yield: (104 mg 86%). *Anal.* Calc. for $C_{23}H_{35}N_4RhCl_2S_2$ (605.49): C, 45.62; H, 5.83; N, 9.25. Found: C, 45.43; H, 5.76; N, 9.12%. ^{1}H NMR (400 MHz $CDCl_3$): 1.38 (d, *J* = 6.9 Hz, $2CH_3$, 6H), 1.42 (d, *J* = 6.8 Hz, $2CH_3$, 6H), 1.69 (d, $5CH_3$, 15H), 4.92 (m, CH_2, 2H), 6.73 (d, CH_2, 1H), 6.89 (d, *J* = 1.8 Hz, imidazole, 2H), 7.31 (d, CH_2, 1H), 9.00 (d, *J* = 2.0 Hz, imidazole, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 8.98 (*C*H_3–Cp*), 22.21 (C(*C*H_3)$_2$), 22.77 (C(*C*H_3)$_2$), 51.01 (*C*(CH$_3$)$_2$), 55.36 (*C*H_2), 95.76 (Cp*), 115.96 (imidazole), 123.02 (imidazole), 154.19 (C=S) ppm. IR (KBr disk): 3114 (w), 3042 (s), 2982 (m), 1633 (w), 1569 (m), 1447 (s), 1412 (vs), 1373 (s), 1307 (w), 1243 (s), 1198 (s), 1147 (w), 1081 (w), 1022 (m), 884 (w), 749 (m), 623 (w) cm^{-1}.

4.3.3. [Cp*Ir(Mbbit)Cl]Cl (*3a*)

Prepared by the same procedure as described above for **2a**, using [Cp*Ir(μ-Cl)Cl]$_2$ (80 mg, 0.1 mmol) and (Mbbit) (65 mg, 0.2 mmol). Yield: (116 mg 80%). *Anal.* Calc. for $C_{25}H_{39}N_4IrCl_2S_2$ (722.86): C, 41.54; H, 5.44; N, 7.75. Found: C, 41.78; H, 5.57; N, 7.47%. ^{1}H NMR (400 MHz $CDCl_3$): 1.63 (s, $6CH_3$, 18H), 1.77 (d, $5CH_3$, 15H), 6.79 (m, CH_2, 1H), 6.95 (m, CH_2, 1H), 7.04 (d, *J* = 1.7 Hz, imidazole, 2H), 8.86 (d, *J* = 1.6 Hz, imidazole, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 8.98 (*C*H_3–Cp*), 29.24 (C(*C*H_3)$_3$), 53.56 (*C*(CH$_3$)$_3$), 61.03 (*C*H_2), 95.96 (Cp*), 118.30 (imidazole), 122.18 (imidazole), 153.24 (C=S) ppm. IR (KBr disk): 3087 (m), 2981 (m), 1634 (w), 1569 (m), 1455 (s), 1380 (s), 1334 (w), 1225 (w), 1199 (w), 1160 (m), 1081 (w), 1030 (s), 790 (w), 742 (m), 687 (w) cm^{-1}.

4.3.4. [Cp*Rh(Mbbit)Cl]Cl (*3b*)

Prepared by the same procedure as described above for **2a**, using [Cp*Rh(μ-Cl)Cl]$_2$ (62 mg, 0.1 mmol) and (Mbbit) (65 mg,

0.2 mmol). Yield: (93 mg 73%). *Anal.* Calc. for C $C_{25}H_{39}N_4RhCl_2S_2$ (633.54): C, 47.46; H, 6.22; N, 8.86. Found: C, 47.35; H, 6.25; N, 8.59%. ^{1}H NMR (400 MHz $CDCl_3$): 1.65 (s, 6CH_3, 18H), 1.75 (d, 5CH_3, 15H), 6.95 (m, CH_2, 1H), 7.05 (m, CH_2, 1H), 7.11 (d, J = 1.9 Hz, imidazole, 2H), 8.89 (d, J = 2.0 Hz, imidazole, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 8.96 (CH_3–Cp^*), 29.50 (C(CH_3)$_3$), 53.72 (C(CH_3)$_3$), 60.11 (CH_2), 95.80 (Cp^*), 118.23 (imidazole), 122.16 (imidazole), 154.33 (C═S) ppm. IR (KBr disk): 3089 (m), 2983 (m), 1636 (w), 1570 (m), 1449 (s), 1380 (s), 1333 (w), 1226 (w), 1197 (w), 1160 (m), 1081 (w), 1032 (s), 791 (w), 743 (m), 686 (w) cm^{-1}.

4.3.5. [$Cp^*Ir(Tm^{Me})$]Cl (**4a**)

Prepared by the same procedure as described above for **2a**, using [Cp^*Ir(μ-Cl)Cl]$_2$ (80 mg, 0.1 mmol) and [Tm^{Me}]K (78 mg, 0.2 mmol). Yield: (120.1 mg 84%). *Anal.* Calc. for $C_{22}H_{31}BN_6IrClS_3$ (714.19): C, 37.00; H, 4.38; N, 11.77. Found: C, 36.98; H, 4.25; N, 11.68%. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.74 (s, 5CH_3, 15H), 3.73 (s, 3CH_3, 9H), 6.93 (d, J = 1.8 Hz, imidazole, 3H), 7.16 (d, J = 1.8 Hz, imidazole, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 8.8 (CH_3–Cp^*), 35.5 (N–CH_3), 90.9 (Cp^*), 121.3 (imidazole), 124.2 (imidazole), 153.4 (C═S) ppm. IR (KBr disk): 3149 (m), 3075 (m), 2435 (w), 1624 (w), 1558 (w), 1464 (s), 1409 (w), 1375 (s), 1326 (w), 1299 (w), 1210 (vs), 1153 (m), 1123 (w), 1084 (m), 1025 (m), 751 (m) cm^{-1}.

4.3.6. [$Cp^*Rh(Tm^{Me})$]Cl (**4b**)

Prepared by the same procedure as described above for **2a**, using [Cp^*Rh(μ-Cl)Cl]$_2$ (62 mg, 0.1 mmol) and [Tm^{Me}]K (78 mg, 0.2 mmol). Yield: (114 mg 91%). *Anal.* Calc. for $C_{22}H_{31}BN_6RhClS_3$ (624.88): C, 42.29; H, 5.00; N, 13.45. Found: C, 42.09; H, 4.98; N, 13.67%. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.71 (s, 5CH_3, 15H), 3.71 (s, 3CH_3, 9H), 6.86 (d, J = 1.8 Hz, imidazole, 3H), 7.13 (d, J = 1.8 Hz, imidazole, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 9.4 (CH_3–Cp^*), 35.4 (N–CH_3), 97.4 (Cp^*), 121.3 (imidazole), 124.1 (imidazole), 155.8 (C═S) ppm. IR (KBr disk): 3150 (m), 3075 (m), 2435 (w), 1626 (w), 1558 (w), 1462 (s), 1411 (w), 1375 (vs), 1324 (w), 1296 (w), 1210 (vs), 1156 (m), 1125 (w), 1083 (m), 1019 (m), 750 (m) cm^{-1}.

4.4. X-ray crystallography

Diffraction data of **1a**, **2b** and **4a** 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) [39], All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located at calculated positions. All calculations were performed using the Brucker Smart program. Crystal data, data collection parameters and the results of the analyses of complexes **1a**, **2b** and **4a** are listed in Table 1.

5. Supplementary material

CCDC 729942, 729943 and 729944 contain the supplementary crystallographic data for **1a**, **2b** and **4a**. 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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