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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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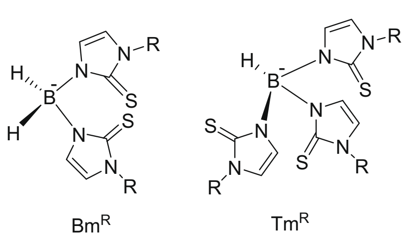
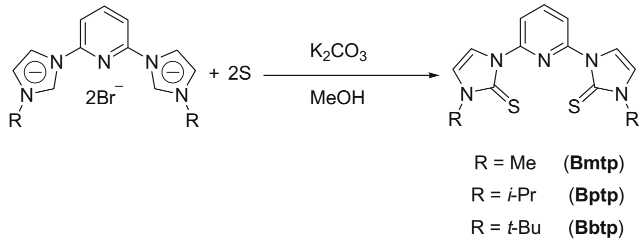


Chart 1.



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].

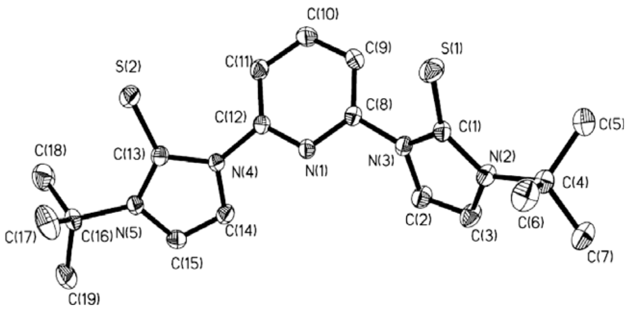


Fig. 1. Molecular structure of **Bbtp** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–S(1) 1.679(2), C(13)–S(2) 1.6876(19); N(1)–C(8)–N(3) 113.94(19), N(1)–C(12)–N(4) 113.19(18).

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).

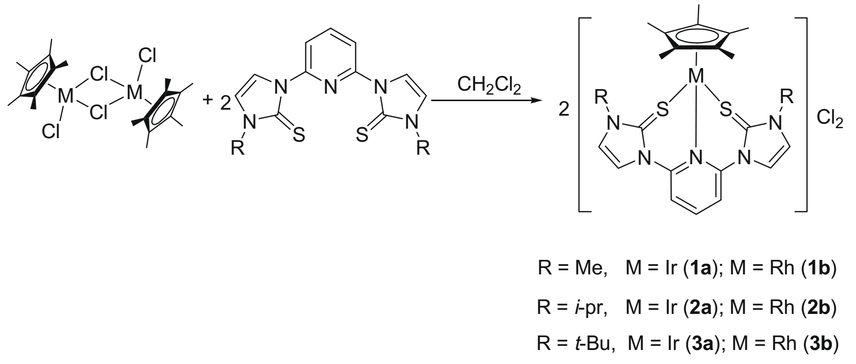
Compounds **1–3** were fully characterized by IR, NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **1–3** in D_2O show singlet resonances due to Cp* fragment at δ 1.41–1.48 ppm, the pyridyl group appear two resonances at δ 7.74–7.83 and 8.33–8.44 ppm, and the signals of the imidazole 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 piano-stool 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)**.