

半夹心结构有机金属铱和铑化合物 $[\text{Cp}^*\text{M}(\text{Tm}^{\text{Me}})]\text{Cl}$ ($\text{M}=\text{Ir}, \text{Rh}$; $\text{Tm}^{\text{Me}}=\text{三}(2\text{-巯基-1-甲基咪唑})\text{硼酸根}$)的合成与表征

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摘要: 三齿配体三(2-巯基-1-甲基咪唑)硼酸盐 $[\text{Tm}^{\text{Me}}]\text{K}$ 与含有半夹心结构金属铱和铑化合物 $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$ 和 $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$ 反应形成具有 18 电子结构的配合物 $[\text{Cp}^*\text{Ir}(\text{Tm}^{\text{Me}})]\text{Cl}$ (1)和 $[\text{Cp}^*\text{Rh}(\text{Tm}^{\text{Me}})]\text{Cl}$ (2)。所有的化合物都经过 IR, NMR 和 EA 表征,并通过 X-射线衍射单晶结构分析测定了配合物 2 的分子结构。

关键词: 铱; 铑; 半夹心配合物; 合成; 结构

中图分类号: O614.82²; O614.82⁵

文献标识码: A

文章编号: 1001-4861(2008)08-1242-05

Synthesis and Characterization of Half-sandwich Metal Complexes $[\text{Cp}^*\text{M}(\text{Tm}^{\text{Me}})]\text{Cl}$ ($\text{M}=\text{Ir}, \text{Rh}$; $\text{Tm}^{\text{Me}}=\text{tris}(2\text{-mercapto-1-methylimidazolyl})\text{borate radical}$)

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Abstract: The reactions of $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$ or $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$ with tripodal ligand tris (2-mercapto-1-methylimidazolyl) borate ($[\text{Tm}^{\text{Me}}]\text{K}$) lead to formation of the 18-electron complexes $[\text{Cp}^*\text{Ir}(\text{Tm}^{\text{Me}})]\text{Cl}$ (1) and $[\text{Cp}^*\text{Rh}(\text{Tm}^{\text{Me}})]\text{Cl}$ (2). Both complexes have been fully characterized by IR and NMR spectroscopy, as well as elemental analysis. The molecular structures of 2 have been confirmed by X-ray crystal structure analysis. CCDC: 692299, 2.

Key words: iridium; rhodium; half-sandwich complexes; synthesis; structure

The coordination chemistry of the tris(mercaptoimidazolyl)hydroborate (Tm^{R}) analogue ligands system is expanding at an accelerated pace. 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^[1~7]. The remarkable character of this kinds of ligands are anionic and softer donor electrons ligands^[8~12].

We are interested in supramolecular complexes based on quasi-octahedral geometries that bear penta-

methylcyclopentadienyl group and which was proved to be efficient ancillary ligands in organometallic complexes^[13~18]. Although Cp^* stabilize metal centers by tridentate coordination in a facial fashion, it is rather difficult to modify the electronic and steric properties of these ligands. If other ligands such as *N*-heterocyclic carbenes or soft $[\text{S}_3]$ compounds was introduced may change the complexes structures and chemical properties^[19~27]. Therefore, the synthesis of organochalcogen (S) compounds derived from *N*-methylimidazole are very attractive from the organometallic and application

收稿日期:2008-03-13。收修改稿日期:2008-05-27。

国家自然科学基金资助项目(No.20531020,20721063,20771028)。

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points of view, and the complexes containing these functional group strongly bound to late transition metal are of considerable interest.

In this paper, we report the reactions of the half-sandwich iridium and rhodium fragments with tripodal anionic face-capping ligand [Tm^M]*K* to yield the 18-electron complexes [Cp*Ir(Tm^M)]Cl (**1**) and [Cp*Rh(Tm^M)]Cl (**2**). The molecular structure of **2** is determined by X-ray crystal structure analysis.

1 Experimental section

1.1 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 starting materials, [Cp*Ir(μ-Cl)Cl]₂^[28], [Cp*Rh(μ-Cl)Cl]₂^[28] and [Tm^M]*K*^[29] were synthesized according to the procedures described in the literature. Other chemicals were analytical grade and used as received. ¹H and ¹³C NMR spectra were obtained using Bruker DMX-500 spectrophotometer in CDCl₃, for all compounds using TMS as an internal standard. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer.

1.2 Synthesis of complex 1 and 2

[Cp*Ir(Tm^M)]Cl (**1**): [Cp*Ir(μ-Cl)Cl]₂ (80 mg, 0.1 mmol) was added to a solution of [Tm^M]*K* (78 mg, 0.2 mmol) in degassed dichloromethane (40 mL) in a Schlenk tube and kept at room temperature to stir for 10 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 **1** (120.1 mg 84%). Anal. Calcd for C₂₂H₃₁BN₆IrClS₃ (%): C 37.00, H 4.38, N 11.77. Found (%): C 36.98, H 4.25, N 11.68, ¹H NMR (CDCl₃, ppm): δ 1.74 (s, 5CH₃, 15H), 3.73 (s, 3CH₃,

9H), 6.93 (d, imidazole, 3H), 7.16 (d, imidazole, 3H). ¹³C NMR (CDCl₃, ppm): δ 8.8 ((CH₃)₅Cp*), 35.5 (N-CH₃), 90.9 (Cp*), 121.3 (imidazole), 124.2 (imidazole), 153.4 (C=S). IR (KBr cm⁻¹): 3 149 (m), 3 075 (m), 2 435 (w), 1 624 (w), 1 558 (w), 1 464 (s), 1 409 (w), 1 375 (s), 1 326(w), 1 299(w), 1 210(vs), 1 153(m), 1 123(w), 1 084 (m), 1 025 (m), 751 (m).

[Cp*Rh(Tm^M)]Cl (**2**): prepared by the same procedure as described above for **1**, using [Cp*Rh(μ-Cl)Cl]₂ (62 mg, 0.1 mmol) and [Tm^M]*K* (78 mg, 0.2 mmol) Yield: (114 mg 91%). Anal. Calcd for C₂₂H₃₁BN₆RhClS₃ (%): C 42.29, H 5.00, N 13.45. Found (%): C 42.09, H 4.98, N 13.67, ¹H NMR (CDCl₃, ppm): δ 1.71 (s, 5CH₃, 15H), 3.71 (s, 3CH₃, 9H), 6.86 (d, imidazole, 3H), 7.13 (d, imidazole, 3H). ¹³C NMR (CDCl₃, ppm): δ 9.4 ((CH₃)₅Cp*), 35.4(N-CH₃), 97.4(Cp*), 121.3(imidazole), 124.1 (imidazole), 155.8(C=S). IR(KBr cm⁻¹): 3 150 (m), 3 075 (m), 2 435(w), 1 626(w), 1 558(w), 1 462(s), 1 411 (w), 1 375(vs), 1 324(w), 1 296(w), 1 210(vs), 1 156(m), 1 125 (w), 1 083 (m), 1 019 (m), 750 (m).

1.3 Crystal structure determination

The crystal with approximate dimensions 0.10 mm × 0.10 mm × 0.08 mm was selected for the structure analysis. Diffraction data of **2** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ=0.071 073 nm) at room temperature. Absorption corrections were applied to the data with SADABS^[30]. The structures were solved by direct methods using SHELXS-97, the data reduction using SAINTPLUS program^[31], and subsequently refined on *F*² by using full-matrix least-squares techniques (SHELXS)^[31]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. Detailed crystal data and structure refinement parameters of the complex are summarized in Table 1, and the selected bond distances and angles are listed in Table 2.

CCDC: 692299, **2**.

Table 1 Crystallographic data and structure refinement parameters for complex **2**

Empirical formula	C ₂₂ H ₃₃ BClN ₆ ORhS ₃	μ (Mo Kα) / mm ⁻¹	0.952
Formula weight	642.89	<i>F</i> (000)	660
Crystal syst.	Triclinic	θ range / (°)	1.67~27.14
Space group	<i>P</i> $\bar{1}$	Limiting indices	-13, 13; -13, 15; -17, 12

Continued Table 1

a / nm	1.050 3(3)	Reflections / unique (R_{int})	7 152 / 6 030 (0.019 2)
b / nm	1.214 9(4)	Reflections observed [$I > 2\sigma(I)$]	
c / nm	1.339 6(4)	Completeness to $\theta = 27.14^\circ / \%$	96.4
$\alpha / (^\circ)$	110.989(4)	Data / restraints / parameters	6 030 / 1 / 328
$\beta / (^\circ)$	92.129(4)	Goodness-of-fit on F^2	1.004
$\gamma / (^\circ)$	115.211(3)	Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.042\ 7$, $wR_2 = 0.102\ 0$
Volume / nm^3	1.407 0(7)	R indices (all data)	$R_1 = 0.056\ 8$, $wR_2 = 0.108\ 0$
Z	2	Larg. diff. peak / hole / ($\text{e} \cdot \text{nm}^{-3}$)	934, -484
$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.518		

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

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for complex **2**

Rh(1)-S(1)	0.240 1(11)	Rh(1)-S(2)	0.238 9(10)	Rh(1)-S(3)	0.237 3(10)
S(1)-C(1)	0.171 3(4)	S(2)-C(5)	0.171 6(4)	S(3)-C(9)	0.172 1(4)
N(1)-B(1)	0.154 8(6)	N(3)-B(1)	0.154 9(6)	N(5)-B(1)	0.154 5(5)
S(1)-Rh(1)-S(2)	95.24(4)	S(1)-Rh(1)-S(3)	90.95(4)	S(2)-Rh(1)-S(3)	94.09(4)
N(1)-B(1)-N(3)	111.5(3)	N(1)-B(1)-N(5)	113.0(3)	N(3)-B(1)-N(5)	111.8(3)

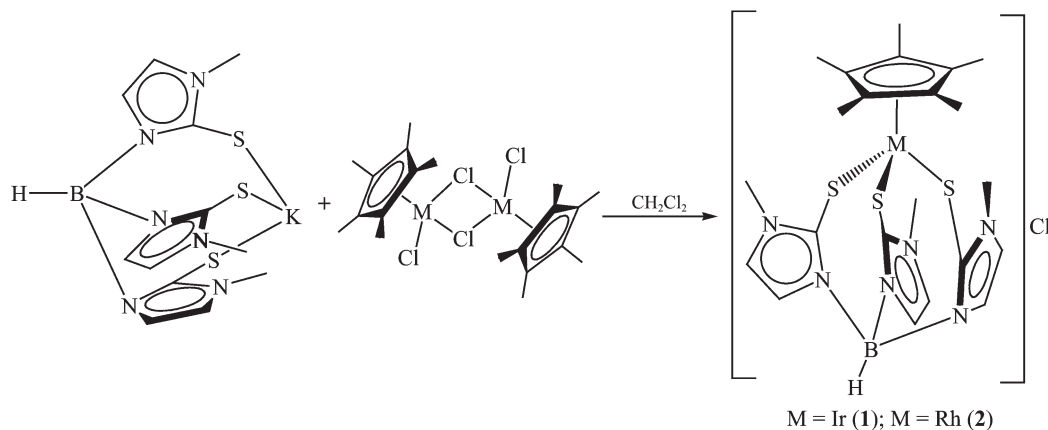
2 Results and discussion

The tripodal borate ligand $[\text{Tm}^{\text{Me}}]\text{K}$ was prepared by established procedures^[29]. The reactions of $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})\text{Cl}]_2$ or $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})\text{Cl}]_2$ with $[\text{Tm}^{\text{Me}}]\text{K}$ leads to formation of the 18-electron complexes $[\text{Cp}^*\text{Ir}(\text{Tm}^{\text{Me}})]\text{Cl}$ (**1**) and $[\text{Cp}^*\text{Rh}(\text{Tm}^{\text{Me}})]\text{Cl}$ (**2**) in good yields, respectively (Scheme 1). Complexes **1** and **2** are moderately air-stable in the solid state, but unstable in the solution. Complexes **1** and **2** exhibit good solubility in polar organic solvents, such as CH_2Cl_2 , CHCl_3 and THF.

Complexes **1** and **2** were characterized by ^1H NMR, ^{13}C NMR, IR spectroscopy as well as elemental analysis. For complex **1**, the ^1H NMR spectrum in

CDCl_3 showed signals at δ 1.74, 3.73, 6.93 and 7.16 ppm, which can be assigned to the Cp^* , methyl, and four olefinic H protons of the Tm^{Me} ligand, respectively, and the ^{13}C NMR spectrum showed the typical signal at 153.4 for C=S groups. The IR spectra of **1** shows intense B-H vibration at about $2\ 435\ \text{cm}^{-1}$.

Molecular structure of complex **2** was determined (Fig.1). Complex **2** adopt triclinic crystal system and $P\bar{1}$ space group. Each rhodium is partially coordinated by three sulfur atoms from one ligand forming three eight-membered macrocyclic rings. The coordination geometry around every rhodium center is described as a three-legged piano-stool, which is common in Cp^*Rh complexes. The distance between the rhodium metal

Scheme 1 Synthesis of complexes **1** and **2**

and sulfur atom is in the range 0.233 7~0.240 1 nm, this bond length is compatible with a typical single bond length between the rhodium center and the sulfur atom reported in previous literature^[3,32-34].

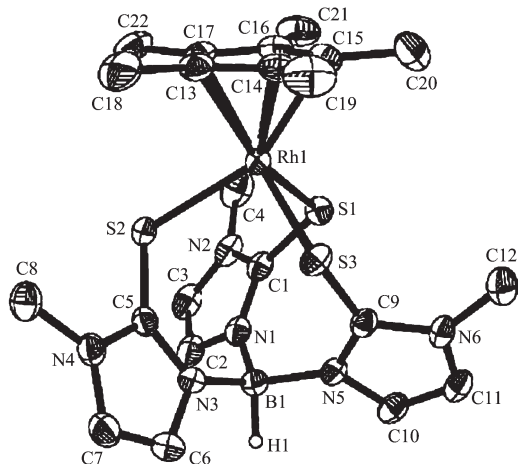


Fig.1 Molecular structure of complex 2

The distance between B and Rh is 0.412 4(55) nm, which indicated there is inexistence of any interaction in complex 2. In the sphere of boron, the boron atom center metal ion adopts a distorted tetrahedron with the follow angles (H(1)-B(1)-N(1) 110.2(16)°, H(1)-B(1)-N(3) 106.2(16)°, H(1)-B(1)-N(5) 103.5(15)°, N(1)-B(1)-N(3) 111.5(3)°, N(1)-B(1)-N(5) 113.0(3)°, N(3)-B(1)-N(5) 111.8(3)°).

As shown in the Fig.2, there are three 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 methyl of imidazole with the distance of H...Cl is 0.273 nm and the angle of C-H...Cl is 150.4°, C-H...Cl hydrogen bonds of imidazole with the average distance of H...Cl is 0.271 nm, and the C-H...S hydrogen bonds of methyl of

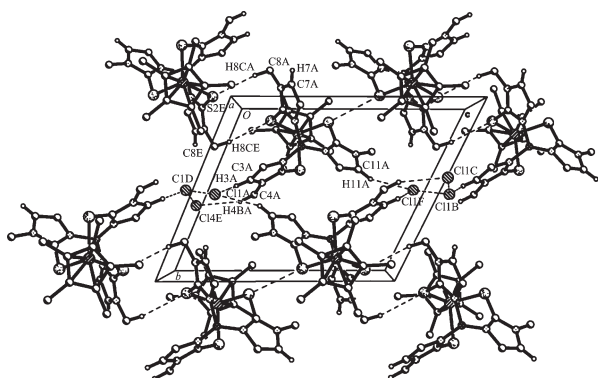


Fig.2 Packing diagram for complex 2 along the c axis

imidazole with the distance of H...S is 0.282 nm and the angle of C-H...S is 158.9°. Although the force is not strong, which play a crucial role in halogenated molecules in the solid state.

In conclusion, we have synthesized the 18-electron half-sandwich iridium (III) and rhodium (III) complexes containing tripodal borate ligand. A combination of spectroscopic studies and X-ray crystallographic confirmed the structures of these half-sandwich complexes. The application research of these complexes are now in progress.

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