

半夹心结构含 1,2-二硫碳硼烷的铑配合物的合成以及结构表征

韩英锋 金国新*

(复旦大学化学系,上海市分子催化和功能材料重点实验室,上海 200433)

摘要: 室温下,18-电子体系的半夹心铑配合物 $\text{Cp}^*\text{Rh}(\text{L})\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$ ($\text{L}=4\text{-ClCH}_2\text{-C}_6\text{H}_4\text{N}$ (**2a**), $4\text{-CH}_3\text{SCH}_2\text{-C}_6\text{H}_4\text{N}$ (**2b**)) 可以通过 16-电子体系的半夹心铑配合物 $[\text{Cp}^*\text{Rh}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]]$ 与吡啶衍生物合成。化合物通过 IR、 ^1H NMR 和元素分析进行了表征,并用 X-射线单晶衍射测定了配合物 **2a** 和 **2b** 的单晶结构。

关键词: 碳硼烷; 硫; 半夹心铑配合物

中图分类号: O614.82*2

文献标识码: A

文章编号: 1001-4861(2008)06-0843-05

Synthesis and Characterization of Half-sandwich Rhodium Complexes Containing 1,2-dithiolato Carborane Ligands

HAN Ying-Feng JIN Guo-Xin*

(Shanghai Key Laboratory of Molecular Catalysis and Innovative Material,
Department of Chemistry, Fudan University, Shanghai 200433)

Abstract: The 18-electron dithiolato carborane complexes $\text{Cp}^*\text{Rh}(\text{L})\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$ ($\text{L}=4\text{-(chloromethyl)pyridine}$ (**2a**), $4\text{-(methylthiomethyl)pyridine}$ (**2b**)) were synthesized from the 16e half-sandwich rhodium complex $[\text{Cp}^*\text{Rh}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]]$ and pyridine derivatives (L) at room temperature. The complexes have been fully characterized by their IR and ^1H NMR spectroscopy, as well as elemental analysis. The molecular structures of **2a** and **2b** were established through X-ray crystal structure analysis. CCDC: 679789, **2a**; 679790, **2b**.

Key words: carborane; sulfur; half-sandwich rhodium

Since the discovery of 1,2-dicarba-closo-dodecaborane, the chemistry of this exceptionally stable carborane and its 1,7- and 1,12-isomers has aroused considerable interest^[1]. The 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolates can serve as the voluminous and chemically robust chelate ligands and react with half-sandwich metal dichloride $\text{Cp}'_2\text{M}_2\text{Cl}_2(\mu\text{-Cl})_2$ to form 16-electron complexes $[\text{Cp}'_2\text{M}_2\{\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]$ ($\text{Cp}'=\eta^5\text{-C}_5\text{Me}_5$, $\eta^5\text{-C}_5\text{H}_5$; $\text{M}=\text{Co}$, Rh , Ir ; $\text{E}=\text{S}$, Se)^[2], which can be stored conveniently and used for further transformations in a controlled way under various conditions. These 16-

electron Cp and Cp^* half-sandwich metal complexes, containing a bidentate 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolato ligand and a “pseudo-aromatic” metalladichalcogenolene five-membered ring, themselves, possess very special features. Bulky ortho-carborane and cyclopentadienyl units can potentially stabilize the 16-electron metal center^[3]. And they can be used as models to study the insertion of alkynes into one of the metal-sulfur bonds^[4], this may lead to the formation of a metal-to-boron bond or substitution of the carborane cage in the positions of B(3)/B(6)^[5], and they

收稿日期:2007-10-15。收修改稿日期:2008-01-03。

国家自然科学基金资助项目(No.20531020,20421303)。

*通讯联系人。E-mail:gxjin@fudan.edu.cn

第一作者:韩英锋,男,27岁,博士研究生;研究方向:碳硼烷化学和有机金属多核化合物的设计与合成。

can also serve as promising precursors for the synthesis of mixed-metal clusters^[6]. During the past decade, considerable attention has been devoted to this kind of complexes.

Aiming at the development of versatile and rational methods for the coordinative saturated 18-electron derivatives, we have extended our study to include the *o*-carborane-1,2-dithiolate rhodium complex [Cp*RhS₂C₂(B₁₀H₁₀)]. Herein, we report the addition reactions of Cp*Rh[S₂C₂(B₁₀H₁₀)] with pyridyl derivatives forms the 18-electron dithiolato carborane complexes Cp*Rh(L)S₂C₂(B₁₀H₁₀) (L=4-(chloromethyl)pyridine (**2a**), 4-(methylthiomethyl)pyridine (**2b**)).

1 Experimental

1.1 Materials and methods

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by M. Braun Solvent Purification System (4464) and collected just before use. Elemental analyses were carried out by Elementar III Vario EI Analyzer. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer, and ¹H NMR (500 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in CDCl₃.

[Cp*RhCl₂]₂^[7] and Cp*Rh[S₂C₂(B₁₀H₁₀)]^[2] were prepared according to the reported procedures, while other chemicals were obtained commercially and used without further purification.

1.2 Synthesis of the complexes

Synthesis of 2a: A solution of **1** (89 mg, 0.2 mmol) in CH₂Cl₂ (30 mL) was added to 4-(chloromethyl)pyridine (25 mg, 0.2 mmol) in CH₂Cl₂ (30 mL). The green-colored mixture was stirred for 24 h, where upon it gradually became dark red. The solvent was then evaporated under vacuum. The residue was washed with toluene to give a red solid of **2a** (93 mg, 82%). Elemental analysis. Calc. for C₁₈H₃₁B₁₀ClNRhS₂ (%): C, 37.79; H, 5.46; N, 2.45. Found (%): C, 37.52; H, 5.54; N, 2.68. IR (KBr): $\nu=2\,555$ ($\nu_{\text{B-H}}$) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, ppm): $\delta=8.73$ (d, 2H), 7.32(d, 2H), 4.59(s, 2H), 1.66(s, 15H, Cp*).

Synthesis of 2b: A solution of **1** (89 mg, 0.2 mmol)

in CH₂Cl₂ (30 mL) was added to 4-(methylthiomethyl)pyridine (28 mg, 0.2 mmol) in CH₂Cl₂ (30 mL). The green-colored mixture was stirred for 24 h, where upon it gradually became dark red. The solvent was then evaporated under vacuum. The residue was washed with toluene to give a red solid of **2b** (102 mg, 87%). Elemental analysis. Calc. for C₁₉H₃₄B₁₀NRhS₃ (%): C, 39.10; H, 5.87; N, 2.40. Found (%): C, 39.52; H, 5.72; N, 2.38. IR (KBr): $\nu=2\,553$ ($\nu_{\text{B-H}}$) cm⁻¹. ¹H NMR (500 MHz, CDCl₃, ppm): $\delta=8.71$ (d, 2H), 7.37(d, 2H), 4.60(s, 2H), 2.23(s, 3H), 1.67(s, 30H, Cp*).

1.3 Crystal structure determination

Diffraction data of crystal **2a** with dimensions of 0.30 mm × 0.20 mm × 0.10 mm and crystal **2b** with dimensions of 0.10 mm × 0.08 mm × 0.06 mm were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda=0.071\,073$ nm) at 293 (2) K. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. A total of 12 622 reflections for **2a** were collected in the range of 1.38° < θ < 25.01° by using an ω scan mode, of which 9 850 were unique with $R_{\text{int}}=0.032\,5$. A total of 13 552 reflections for **2b** were collected in the range of 1.71° < θ < 27.13° by using an ω scan mode, of which 6 040 were unique with $R_{\text{int}}=0.090\,0$. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program^[8]. The structures were solved by direct methods. All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the SHELX-97 program^[9]. Some solvents molecules were unordered, therefore, new data sets corresponding to omission of the unordered solvents molecules were generated with the SQUEEZE algorithm^[10] and the structures were refined to convergence. Crystal data, data collection parameters, and the results of the analyses of compounds **2a** and **2b** are listed in Table 1 and the selected bond distances and angles in Table 2.

CCDC: 679789, **2a**; 679790, **2b**.

Table 1 Crystallographic data for complexes **2a** and **2b**

Complex	2a	2b
Formula	C ₁₈ H ₃₁ B ₁₀ ClRhNS ₂ ·0.5CH ₂ Cl ₂	Cl ₂ C ₁₉ H ₃₄ B ₁₀ NRhS ₃
<i>M</i>	614.48	583.66
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> / nm	1.122 2(3)	2.959 1(7)
<i>b</i> / nm	1.526 2(4)	1.236 0(3)
<i>c</i> / nm	1.878 6(5)	1.874 5(5)
α / (°)	76.546(4)	
β / (°)	76.618(4)	126.462(3)
γ / (°)	82.429(4)	
<i>V</i> / nm ³	3.033 9(14)	5.514(2)
<i>Z</i>	4	8
<i>D_c</i> / (g·cm ⁻³)	1.345	1.406
μ (Mo <i>K</i> α)	0.887	0.858
<i>F</i> (000)	1244	2384
Crystal size / mm	0.30 × 0.20 × 0.10	0.10 × 0.08 × 0.06
Reflections collected / unique (<i>R_{int}</i>)	12 622 / 9 850 (0.032 5)	13 552 / 6 040 (0.090 0)
θ range / (°)	1.38 to 25.01	1.71 to 27.13
Data / restraints / parameters	9 850 / 0 / 653	6 040 / 0 / 323
Goodness-of-fit on <i>F</i> ²	0.853	0.747
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ =0.052 0, <i>wR</i> ₂ =0.104 4	<i>R</i> ₁ =0.048 9, <i>wR</i> ₂ =0.083 3
<i>R</i> indices (all data)	<i>R</i> ₁ =0.088 0, <i>wR</i> ₂ =0.112 6	<i>R</i> ₁ =0.131 4, <i>wR</i> ₂ =0.097 2
Larg. diff. peak and hole / (e·nm ⁻³)	1 211 and -1 138	655 and -665

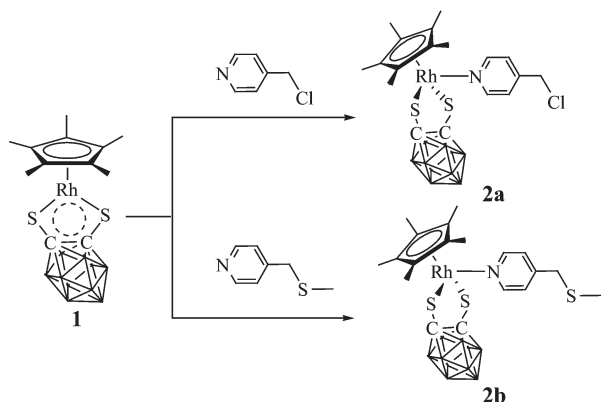
$$^a [I > 2\sigma(I)], R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^2]^{1/2}.$$

Table 2 Selected bond distances (nm) and angles (°) for **2a** and **2b**

2a					
Rh(1)-N(1)	0.214 7(5)	Rh(1)-S(2)	0.235 82(17)	Rh(1)-S(1)	0.236 83(17)
S(1)-C(2)	0.177 8(6)	S(2)-C(1)	0.179 3(6)	Cl(1)-C(8)	0.168 8(9)
N(1)-C(7)	0.133 6(7)	N(1)-C(3)	0.133 8(8)	C(1)-C(2)	0.167 9(8)
B(3)-C(1)	0.172 7(10)				
N(1)-Rh(1)-S(2)	91.17(15)	N(1)-Rh(1)-S(1)	91.80(15)	S(1)-Rh(1)-S(2)	90.38(6)
S(2)-Rh(1)-S(1)	90.38(6)	C(1)-S(1)-Rh(1)	106.5(2)	C(2)-S(2)-Rh(1)	106.7(2)
C(7)-N(1)-Rh(1)	121.6(5)	C(3)-N(1)-Rh(1)	121.6(5)		
2b					
Rh(1)-N(1)	0.214 2(4)	Rh(1)-S(2)	0.235 22(15)	Rh(1)-S(1)	0.235 87(14)
S(1)-C(1)	0.179 0(5)	S(2)-C(2)	0.178 6(5)	S(3)-C(8)	0.175 4(6)
S(3)-C(9)	0.185 7(13)	C(1)-C(2)	0.166 5(6)		
N(1)-Rh(1)-S(2)	90.77(11)	N(1)-Rh(1)-S(1)	90.50(11)	S(2)-Rh(1)-S(1)	90.69(5)
C(1)-S(1)-Rh(1)	106.29(16)	C(1)-S(1)-Rh(1)	106.29(16)	C(2)-S(2)-Rh(1)	106.75(15)
C(8)-S(3)-C(9)	102.6(3)	C(3)-N(1)-C(7)	117.3(5)	C(3)-N(1)-Rh(1)	121.5(4)
C(7)-N(1)-Rh(1)	120.6(3)				

2 Results and discussion

The synthesis route of complexes **2a** and **2b** are shown in Scheme 1. According to the former work^[2], the dilithium carborane dichalcogenolates $\text{Li}_2\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$ react with the half-sandwich rhodium chloro-bridged dimer $[\text{Cp}^*\text{RhCl}_2]_2$ to give the 16-electron complex $\text{Cp}^*\text{RhS}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$ **1**. The corresponding 18-electron complexes $\text{Cp}^*\text{Rh}(\text{L})\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})_2$ ($\text{L}=4\text{-(chloromethyl)pyridine}$ (**2a**), $4\text{-(methylthiomethyl)pyridine}$ (**2b**)) have been prepared by addition of two-electron ligands L ($\text{L}=4\text{-(chloromethyl)pyridine}$, $4\text{-(methylthiomethyl)pyridine}$), respectively. The IR spectra of **2a** and **2b** both show a strong band for B-H vibration at approximately 2555 cm^{-1} . The ^1H spectra for **2a** showed two singlet at $\delta=1.66, 4.59\text{ ppm}$ due to Cp^* and methylene protons and two double resonance at $\delta=7.32, 8.73\text{ ppm}$ due to pyridine ligand protons, that for **2b** had three singlet at $\delta=1.67, 2.23, 4.59\text{ ppm}$ due to Cp^* , methyl and methylene protons and two double resonance at $\delta=7.37, 8.71\text{ ppm}$ due to pyridine ligand protons, respectively.



Scheme 1 Synthesis of **2a**, **2b**

The molecular structures of the 18-electron complexes **2a** and **2b** in the crystal were determined by X-ray crystal structure analyses and the molecular structures of **2a** and **2b** with the atom-numbering scheme are shown in Fig.1 and 2, respectively. In our previous report, the molecule of **1** corresponds to point group symmetry C_{2v} with two perpendicular mirror planes. Addition of ligand pyridyl derivatives ($4\text{-(chloromethyl)pyridine}$, $4\text{-(methylthiomethyl)pyridine}$) into the rhodium of **1** to form the 18-electron complexes **2a** and **2b** lead to C_s symmetry with only one mirror plane left. The rhoda-

dithiolene heterocycle in **1** (which is coplanar with centers of both the Cp^* ring and the ortho-dicarbododecaborane cluster) is bent in **2a** and **2b** with a dihedral angle at $\text{S}\cdots\text{S}$ vector of 172.6° , 179.5° , respectively. Apparently, the ligand pyridyl derivatives destroy the pseudo-aromatic RhS_2C_2 system in **1** slightly. This is particularly evident from the fact that on going from **1** to **2a** and **2b**, the $\text{C}(1)\text{-C}(2)$ bond lengths are 0.168 nm (**2a**), 0.166 nm (**2b**) and the Rh-S bond lengths are 0.236 nm (**2a**), 0.235 nm (**2b**) (av.), while the S-Rh-S angles are $90.38(6)^\circ$ (**2a**), $90.69(5)^\circ$ (**2b**).

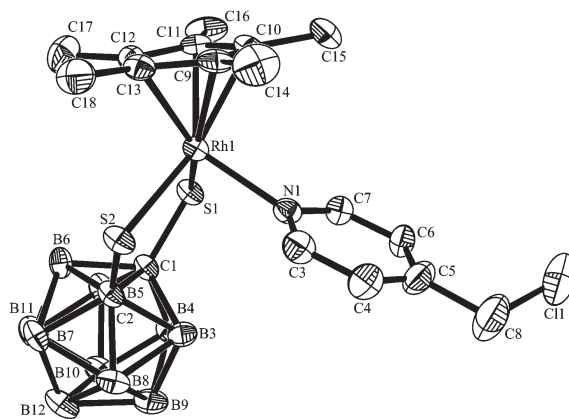


Fig.1 Molecular structure of **2a**

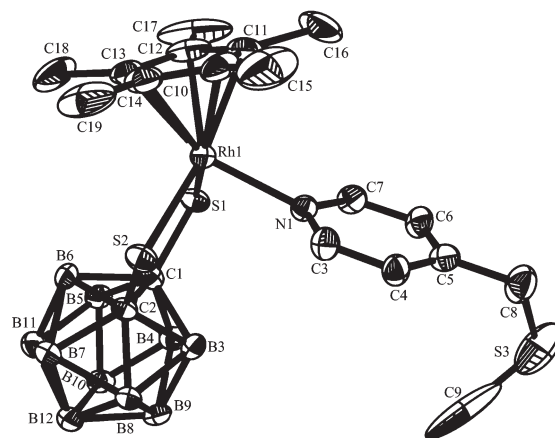


Fig.2 Molecular structure of **2b**

3 Conclusions

In this context work, we carried out the reactions of the mononuclear 16-electron rhodium complex with pyridyl derivatives. Two 18-electron dithiolato carborane complexes were prepared and fully characterized by IR, NMR, and X-ray crystallographic analysis. We anticipate this is a noteworthy approach for the design of a variety of more complex coordination motifs with

novel patterns.

References:

- [1] Jin G X. *Coord. Chem. Rev.*, **2004**,**248**:587~602
- [2] (a)Hou X F, Wang X C., Wang J Q, et al. *J. Organomet. Chem.*, **2004**,**689**:2228~2235
(b)Herberhold M, Jin G X, Yan H, et al. *J. Organomet. Chem.*, **1999**,**587**:252~257
- [3] Liu S, Han Y F, Jin G X. *Chem. Soc. Rev.*, **2007**,**36**:1543~1560
- [4] Herberhold M, Yan H, Milius W, et al. *J. Organomet. Chem.*, **2000**,**604**:170~175
- [5] Herberhold M, Jin G X, Yan H, et al. *Eur. J. Inorg. Chem.*, **1999**:873~875
- [6] (a)KONG Qing-An(孔庆安), JIN Guo-Xin(金国新), LIN Yue-Hua (林永华). *Chem. J. Chin. Univ. (Gaodeng Xuexiao Huaxue Xuebao)*, **2002**,**23**:410~412
(b)KONG Qing-An(孔庆安), JIN Guo-Xin(金国新), CAI Shu-Yi(蔡淑怡), et al. *Chin. Sci. Bull.(Kexue Tongbao)*, **2003**, **48**:783~786
- [7] White C, Yates A, Maitles P M. *Inorg. Synth.*, **1992**,**29**:228~232
- [8] Sheldrick G M. *SADABS* (2.01), *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA, **1998**.
- [9] Sheldrick G M. *SHELXL-97, Program for the Refinement of Crystal Structures*, Universität Göttingen: Germany, **1997**.
- [10]Van der Sluis P, Spek A L. *Acta Crystallogr.*, **1990**,**A46**:194~201