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Pseudo-aromatic bis-*o*-carborane iridium and rhodium complexes

Zi-Jian Yao, Ying-Ying Zhang, Guo-Xin Jin*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, China

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Dedicated to Professor Russ Grimes on the occasion of his 80th birthday.

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A B S T R A C T

Reactions of dilithium salt of 1,1-bis-*o*-carborane with half-sandwich transition metal complexes $[Cp^*MCl_2]_2$ (M = Ir, Rh) in THF at room temperature afforded the C,C-chelated mononuclear metal complexes $Cp^*M(C_2B_{10}H_{10})_2$ (M = Ir (**1**), Rh (**2**), $Cp^* = \eta^5{-}C_5Me_5$) in moderate yields, respectively. They represent the first examples of a new type of 16-electron "*pseudo*-aromatic" bis-*o*-carborane iridium and rhodium complexes. All products were fully characterized by elemental analysis and IR and NMR spectroscopy. The structure of complex **1** was further confirmed by single-crystal X-ray diffraction.

Introduction

As a three-dimensional aromatic analog of its benzene counterpart, 1,2-dicarba-*closo*-dodecarborane-1,2-dichalcogenolates [1] ($C_2B_{10}H_{10}E_2^{2-}$, E = S, Se, Te) have attracted considerable attention during the past few years. These chemical robust ligands were easily prepared by the insertion of elemental chalcogen into the Li–C bonds of dilithium carborane after deprotonation by *n*-butyl lithium. Thus, the versatile reactivity of these ligands with different metal compounds, such as Ti [2], Mo [3], Ni [4], Co [5] and rare earth metals [6], has been widely investigated. Among a number of reports in this field, a unique type of "*pseudo*-aromatic" 16-electron half-sandwich iridium complexes were first synthesized by Herberhold [7]. These complexes were used as the building blocks to form a series of multi-nuclear metal clusters through metal–metal bond formation because of the strong coordination ability of the chalcogenolate element [8–15].

However, the research on *pseudo*-aromatic carborane complex was limited to the dichalcogenolate structure so far (Chart 1). In search of a new ligand to construct the analogous structure, the bidentate chelate bis-*o*-carborane ligand **L** served as a proper substrate (Chart 2), which has been used to synthesize late transition metal complexes in the early 1970s by Hawthorne [16]. Based on the previous results, we herein report a new type of "*pseudo*-aromatic" bis-*o*-carborane complexes $Cp^*M(C_2B_{10}H_{10})_2$ (M = Ir, Rh, $Cp^* = \eta^5{-}C_5Me_5$).

Results and discussion

Synthesis and characterization of complexes ***1*** *and* ***2***

L was first prepared by the reaction of $B_{10}H_{12}\cdot 2X$ (X = Et_2S, CH_3CN) with 1,3-butadiyne developed by Hawthorne [17]. Subsequently, the same group has reported several bis-*o*-carborane chelated late transition metal complexes based on this cage and its derivatives [16]. We used a modified synthetic procedure [18] to prepare this ligand because of difficult purified process of the previous method.

The reaction of the dilithium salt of **L** 1,2-Li_2-bis-*o*-$C_2B_{10}H_{10}$ with 0.5 equiv. of dimeric metal complexes $[(Cp^*MCl_2)_2]$ (M = Ir, Rh) gave, after workup, the novel half-sandwich C, C-chelated iridium and rhodium complexes **1** and **2** as the dark green solids in moderate yields (Scheme 1). (M = Ir (**1**) 38%, Rh (**2**) 33%). The iridium complex is stable in the solid state in air, while the rhodium analogous showed slowly decomposition in a few minutes. They are soluble in CH_2Cl_2 and THF, and slightly soluble in hexane and diethyl ether.

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* Corresponding author. Tel.: +86 21 65643776.
E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).

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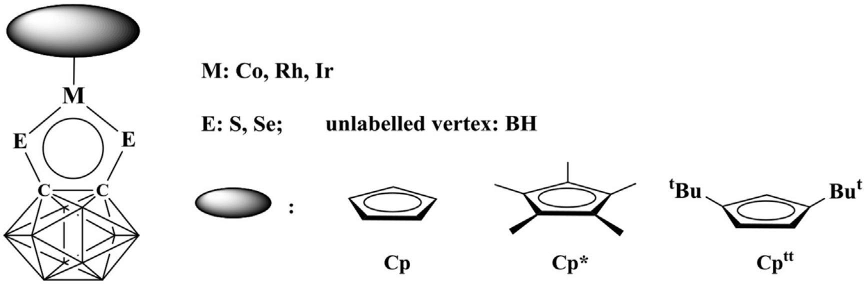


Chart 1. 16-electron half-sandwich *pseudo*-aromatic complexes.

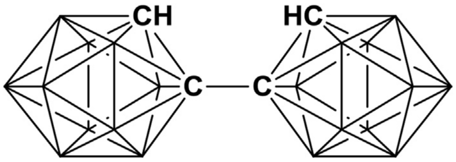


Chart 2. Bis-*o*-carborane ligand **L**.

Complexes **1** and **2** were characterized by various spectroscopic data and elemental analyses. For **1**, The ^{1}H NMR spectrum in $CDCl_3$ shows a sharp peak at δ 1.61, which is assigned to the methyl groups of Cp* ring. The ^{11}B NMR spectrum signals of **1** located in the range of 0 ~ −15 ppm indicated that *closo*-carborane cage was intact after reaction. The IR spectra of **1** and **2** both display a typical strong and broad characteristic B—H absorption at approximately 2560 cm^{-1}, and the removal of the proton in the cage C—H bond was marked by the absence of the typical strong and sharp cage C—H bond absorption at 3040 cm^{-1}. A detailed analysis of the spectroscopic data indicates that the structure of **2** is similar to that of **1**.

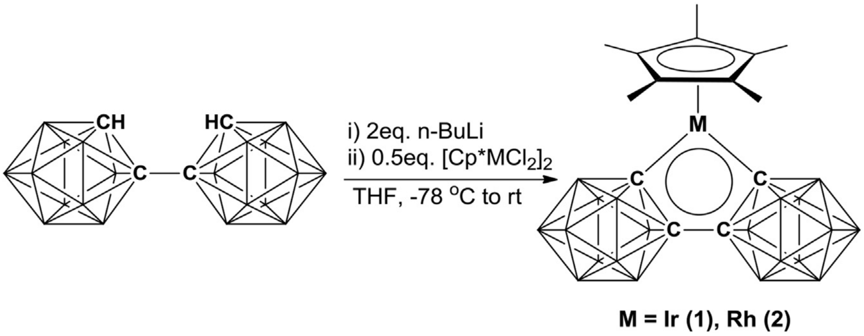
To unambiguously elucidate the structure of **1**, single crystals suitable for X-ray diffraction analyses were obtained by the slow diffusion hexane into their saturated THF solutions. The crystallographic data of **1** was summarized in Table 1. Fig. 1 shows its molecular structure together with selected bond lengths and angles. The structure exhibits a two-legged piano-stool motif and the iridium center is coordinated by two cage carbon atoms and Cp* fragment through η^1 and η^3 modes, respectively. Two Ir—C_c bond lengths are almost identical with each other (2.056(8) Å and 2.074(7) Å), which is similar to those in our previous reported iridium complexes [19–22]. The dihedral angle between C(1)–Ir(1)–C(3) and C(1)–C(2)–C(4)–C(3) planes in the five membered ring is 2.6°, which indicated that the five atoms were nearly in the same plane. The sum of the inner angles of this ring of 539.8° further confirmed the planar geometry of the metal center. This is different from the tetrahedral structure of d$^{7-9}$ transition metal complexes which contained this chelate ligand [23]. So this 16-electron half-sandwich complex was another type of "*pseudo-aromatic*" complex after the dichalcogenolato half-sandwich metal complex was reported.

*Synthesis and characterization of complex **3***

Although the iridium center of *pseudo*-aromatic complex **1** is coordinatively unsaturated, it is very stable probably due to the stabilization ability of both bulky bis-*o*-carborane cage and Cp* ligand. The reactivity of the unsaturated 16-electron complex is of great interest. One of the characteristic reactions is the addition of two-electron ligand to the complex, leading to the formation of saturated 18-electron complex [5]. Reaction of **1** with CO occurred smoothly and the solution of **1** changed gradually from dark green to yellow (Scheme 2). Complex **3** was obtained as yellow crystals in 42% yield after purification. The signals of its ^{1}H and ^{11}B NMR spectra are similar to those of complex **1**. Aim to obtain the single crystal which is suitable for X-ray analysis was failed after many efforts were paid, however, the $[M+H]^+$ ion peak of ESI-MS spectrum at 641.4408 and the elemental analysis of **3** both confirmed the formation of the expected product (Fig. 2), and the vibration at approximately 2050 cm^{-1} in IR spectrum indicated that CO was coordinated to the metal center rather than the insertion of Ir—C bond. Unfortunately, reactions of **1** with other two-electron ligands such as ^{t}BuNC, pyridine or PPh_3 were unsuccessful probably because of the steric effects. We also have explored the reactivity of PMe_3 with the *pseudo*-aromatic complex, however, this reaction gave the unidentified components and black precipitate was formed quickly.

Conclusions

In summary, the present work reports two half-sandwich *pseudo*-aromatic iridium and rhodium complexes through a simple procedure. The 16-electron *pseudo*-aromatic complexes can be



Scheme 1. Synthesis of *pseudo*-aromatic half-sandwich complexes **1** and **2**.