

Reactions of the borole complex $\text{CpRh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ with monocationic organometallic fragments

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Received 31 October 2006; accepted 21 December 2006

Available online 13 January 2007

Dedicated to Prof. Piero Zanello on the occasion of his 65th birthday. Mi congratulo con Lie di buon compleanno!

Abstract

The B-phenylborole complex $\text{CpRh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ (**1**) reacts with $[\text{ML}]^+$ fragments to give the arene-type cationic complexes $[\text{CpRh}(\mu\text{-}\eta^5\text{-}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{ML}]^+$ ($\text{ML} = \text{RuCp}^*$ (**3**), $\text{Co}(\text{C}_4\text{Me}_4)$ (**4**), $\text{Rh}(\text{cod})$ (**5**), and $\text{Ir}(\text{cod})$ (**6**)). Cation **4** undergoes a reversible rearrangement into the triple-decker complex $[\text{CpRh}(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Co}(\text{C}_4\text{Me}_4)]^+$ (**7**) under visible light irradiation in CH_2Cl_2 solution. DFT calculations revealed greater stability of arene-type complexes over triple-decker isomers. The structure of $[\text{3}]\text{BF}_4$ was determined by X-ray diffraction.

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Keywords: Boron; Boron heterocycles; Cobalt; Iridium; Rhodium; Ruthenium; Sandwich compounds

1. Introduction

The favorable balance of donor and acceptor properties of the borole ligand $\text{C}_4\text{H}_4\text{BR}$ (4e donor and 2e acceptor) results in much greater stability of μ -borole triple-decker complexes compared with cyclopentadienyl analogues. Herberich et al. have described a lot of such complexes for late transition metals [1].

Electrophilic stacking of sandwich compounds with organometallic fragments $[\text{ML}]^{n+}$ ($n = 1, 2$) proved to be an effective method for the preparation of cationic triple-decker complexes [2]. In particular, using this method, complexes with bridging cyclopentadienyl [2,3] and boratabenzene [4] ligands have been obtained. We have synthesized the μ -borole triple-decker cations $[\text{CpCo}(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_4\text{H}_4\text{BCy})\text{M}(\text{ring})]^{2+}$ [$\text{M}(\text{ring}) = \text{RhCp}^*$, $\text{Ru}(\text{arene})$; $\text{Cy} = \text{cyclohexyl}$] by stacking of $\text{CpCo}(\eta^5\text{-C}_4\text{H}_4\text{BCy})$ with dicationic

$[\text{M}(\text{ring})]^{2+}$ fragments [5]. A similar reaction of B-phenylborole complex $\text{CpRh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ (**1**) with $[\text{CoCp}^*]^{2+}$ affords $[\text{CpRh}(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{CoCp}^*]^{2+}$ [6]. However, reactions of **1** with $[\text{IrCp}^*]^{2+}$ and $[\text{Ru}(\text{arene})]^{2+}$ are complicated by side formation of arene-type complexes; moreover, arene-type complex, $[\text{CpRh}(\mu\text{-}\eta^5\text{-}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{RhCp}^*]^{2+}$ (**2**) was isolated as a sole product from the reaction with the $[\text{RhCp}^*]^{2+}$ fragment (see Chart 1). The rhodacarborane complex $(\eta^5\text{-9-SMe}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10})\text{Rh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ reacts with $[\text{MCp}^*]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) in a similar way [7].

Herein, we report the reactions of **1** with monocationic fragments $[\text{RuCp}^*]^+$, $[\text{Co}(\text{C}_4\text{Me}_4)]^+$, $[\text{Rh}(\text{cod})]^+$, and $[\text{Ir}(\text{cod})]^+$ giving arene-type complexes.

2. Results and discussion

2.1. Synthesis

We found that the reactions of **1** with $[\text{ML}]^+$ fragments ($\text{ML} = \text{RuCp}^*$, $\text{Co}(\text{C}_4\text{Me}_4)$, $\text{Rh}(\text{cod})$, and $\text{Ir}(\text{cod})$) afford

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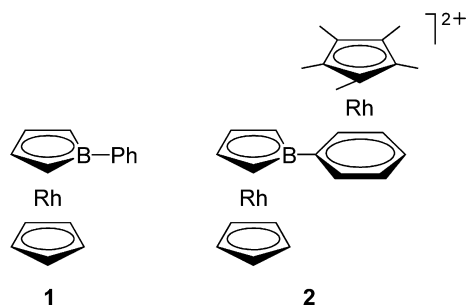
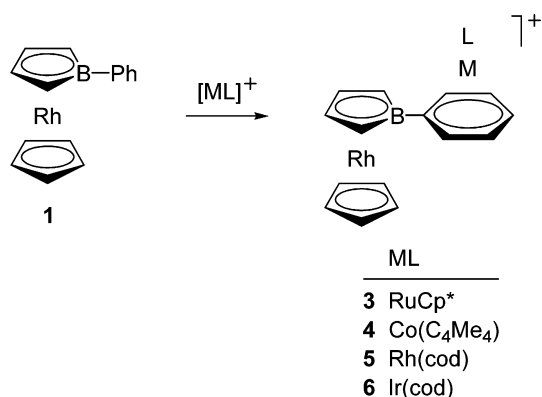


Chart 1.



Scheme 1.

the arene-type complexes $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{ML}]^+$ (**3–6**) rather than the expected triple-decker cations $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{ML}]^+$ (Scheme 1).¹ The $[\text{ML}]^+$ fragments were used in form of labile complexes following to earlier described methods. For example, the $[\text{RuCp}^*]^+$ solvate was generated in situ by treatment of $[\text{Cp}^*\text{RuCl}_2]_2$ with Zn dust and TiBF_4 in THF [8]. The $[\text{Co}(\text{C}_4\text{Me}_4)]^+$ fragment was generated by visible light irradiation of the benzene complex $[(\text{C}_4\text{Me}_4)\text{Co}(\text{C}_6\text{H}_6)]^+$ in CH_2Cl_2 [9]. The solutions of $[\text{M}(\text{cod})]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) solvates were pre-prepared from $[(\text{cod})\text{MCl}]_2/\text{Ag}^+$ in MeNO_2 [4b].

The arene-type complexes **3–6** were characterized by ^1H and ^{11}B NMR spectroscopy (Table 1). The signals of borole ring protons are downfield shifted ($\Delta\delta = 0.1\text{--}0.2$ ppm) and the signals of the boron atoms are upfield shifted ($\Delta\delta = 3.0\text{--}4.0$ ppm) from the corresponding signals for the sandwich compound **1**. The same pattern was observed earlier for the related dicationic arene-type complex **2** [6]. The signals of the Ph ring protons in **3–6** are upfield shifted relative to the starting complex, in accordance with the general tendency for arene complexes.

Noteworthy, in the case of the photochemical reaction of **1** with $[(\text{C}_4\text{Me}_4)\text{Co}(\text{C}_6\text{H}_6)]^+$ (Scheme 2), the colour of the reaction mixture changes from yellow to red during the irradiation but returns back to yellow in a few minutes

after the end of irradiation. Taking into account this observation, we have supposed that the initial electrophilic attack of $[(\text{C}_4\text{Me}_4)\text{Co}]^+$ proceeds at the borole ring with an intermediate formation of the red triple-decker complex **7** which is unstable at room temperature and transforms into the yellow arene-type complex **4**. Unfortunately, we were unable to detect **7** by ^1H NMR spectroscopy, probably owing to its short life time at room temperature. Nevertheless, the initial formation of **7** can be postulated based on analogy with the reaction of **1** with $[\text{Cp}^*\text{Rh}]^{2+}$ giving the arene-type complex **2** via an intermediate formation of the triple-decker cation $[\text{Cp}^*\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhCp}]^{2+}$ detected by ^1H NMR spectroscopy [6] and is additionally confirmed by DFT calculations (vide infra).

Interestingly, the irradiation of pure **4** in CH_2Cl_2 also results in a red solution. UV–Vis spectral measurements at 20°C show that the initial absorption band of **4** ($\lambda = 325$ nm) shifts for 3 nm to red region after 2 h irradiation and turns back within 15 min after the end of irradiation (Fig. 1). Such a small shift may be connected with the low concentration of the triple-decker complex **7** owing to the fact that the rate of its thermal transformation into **4** is considerably higher than the rate of the back photochemical reaction. The concentration of **7** can be increased by irradiation at -80°C apparently due to the slowing down of its thermal transformation into **4** (the rate of photochemical process weakly depends on temperature). The shift of the band in this case is increased up to 25 nm (Fig. 2). It should be emphasized that triple-decker complexes are characterized by strong bathochromic shift relative to corresponding sandwich complexes [6]. Therefore, these data can be considered as an indirect evidence of the initial formation of **7** by the reaction of **1** with the $[(\text{C}_4\text{Me}_4)\text{Co}]^+$ fragment.

2.2. Structure of 3BF_4

The structure of complex **3** BF_4 was determined by X-ray diffraction. Cation **3** consists of two sandwich moieties $\text{CpRh}(\eta^5\text{-C}_4\text{H}_4\text{B})$ and $\text{Cp}^*\text{Ru}(\eta^6\text{-C}_6\text{H}_5)$ connected by the C–B bond (Fig. 3). Selected bond lengths and angles are given in Table 2. The planes of cyclic ligands in each sandwich moiety are almost coplanar (the dihedral angles $\text{Cp}/\text{C}_4\text{H}_4\text{B}$ and $\text{Cp}^*/\text{C}_6\text{H}_5$ are equal to 1.53° and 4.00° , respectively). Noteworthy, the coordination of the $[\text{RuCp}^*]^+$ fragment at the phenyl substituent of **1** does not lead to notable structural changes in the $\text{CpRh}(\eta^5\text{-C}_4\text{H}_4\text{B})$ moiety, similar to the earlier studied complex **2** [6]. For example, the bonds B–C (av. 1.537 Å) and C–C (av. 1.424 Å) in the borole ring are close to the corresponding bonds in the sandwich compound **1** (1.545 and 1.429 Å, respectively).

The C–C bonds within the benzene ring in **3** (av. 1.418 Å) are longer than the corresponding bonds in **1** (av. 1.391 Å). As illustrated in Fig. 4, the C–C bonds in the related (arene)ruthenium complexes depend on the electronic effect of the substituent in the benzene ring. Based on these data, it may be suggested that the effect of the

¹ All the cationic complexes described here were isolated as salts with the BF_4^- or PF_6^- anions (the anions are omitted in the schemes).

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