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Stacking reactions of the borole complex $Cp^*Rh(\eta^5\text{-}C_4H_4BPh)$ with the dicationic fragments $[Cp^*M]^{2+}$ (M = Rh or Ir)

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The reaction of the (borole)rhodium iodide complex $[(\eta\text{-}C_4H_4BPh)RhI]_4$ with Cp*Li afforded the sandwich compound $Cp^*Rh(\eta\text{-}C_4H_4BPh)$ (**4**). The reactions of compound **4** with the solvated complexes $[Cp^*M(MeNO_2)_3]^{2+}(BF_4^-)_2$ gave triple-decker cationic complexes with the central borole ligand $[Cp^*Rh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)MCp^*]^{2+}(BF_4^-)_2$ (M = Rh (**5**) or Ir (**7**)). The structure of complex **4** was established by X-ray diffraction.

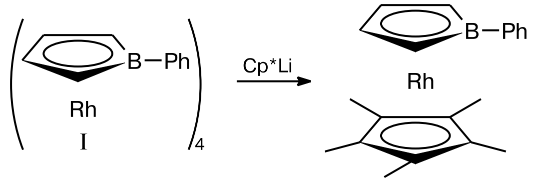
Key words: sandwich compounds, triple-decker complexes, rhodium, iridium.

Electrophilic stacking reactions of sandwich compounds with the $[(ring)M]^{n+}$ fragments are used as the main method for the synthesis of cationic triple-decker complexes.[1] In particular, this method was used for the preparation of compounds with bridging boron-containing heterocycles, such as boratabenzene C_5H_5BR (see Refs 2—4) and borole C_4H_4BR.[5—7] Recently, we have demonstrated[8,9] that in the case of the *B*-phenylborole rhodium complexes $CpRh(\eta\text{-}C_4H_4BPh)$ (**1**) and $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}C_4H_4BPh)$ (**2**), the electrophilic attack occurs on the borole and/or benzene ring. For example, the reaction of **1** with the $[Cp^*Ir]^{2+}$ fragment (Cp* is pentamethylcyclopentadienyl) affords the triple-decker cation $[CpRh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)IrCp^*]^{2+}$ containing the arene-type complex $[CpRh(\mu\text{-}\eta^5\text{:}\eta^6\text{-}C_4H_4BPh)IrCp^*]^{2+}$ as an impurity. To the contrary, the analogous reaction with $[Cp^*Rh]^{2+}$ resulted only in coordination at the benzene ring giving rise to $[CpRh(\mu\text{-}\eta^5\text{:}\eta^6\text{-}C_4H_4BPh)RhCp^*]^{2+}$ (**3**). Unlike complex **1**, the $Cp^*Rh(\eta\text{-}C_4H_4BPh)$ derivative (**4**) contains five methyl groups, whose electron-donating effect leads to an increase in the electron density at the borole ring. Hence, the electrophilic attack on the borole ring would be expected to be more favorable. In the present study, we synthesized sandwich compound **4** and investigated its reactions with the $[Cp^*M]^{2+}$ fragments (M = Rh or Ir).

Results and Discussion

The reaction of the borole iodide complex $[(\eta\text{-}C_4H_4BPh)RhI]_4$ with Cp*Li in tetrahydrofuran produced sandwich complex **4** (Scheme 1). The analogous reaction with the carborane anion $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ has been used earlier[9] for the synthesis of rhodacarborane **2**.

Scheme 1



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The stacking reaction of **4** with the $[Cp^*Rh]^{2+}$ fragment afforded the triple-decker complex $[Cp^*Rh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)RhCp^*]^{2+}$ (**5**) as the only product (Scheme 2).* It should be noted that the pentamethylated analog $[CpRh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)RhCp^*]^{2+}$ (**6**) is unstable at room temperature.[8] To the contrary, complex **5** proved to be very stable. It does not decompose even upon refluxing in nitromethane (100 °C) due apparently to the favorable effect of five additional methyl groups. The analogous stacking reaction of **4** with the $[Cp^*Ir]^{2+}$ fragment gave the $[Cp^*Rh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)IrCp^*]^{2+}$ complex (**7**).

The triple-decker structures of cations **5** and **7** were confirmed by ^1H NMR spectroscopy. Earlier, we have demonstrated that the triple-decker μ-borole complexes $[CpRh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)M(ring)]^{2+}$ are characterized

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* The $[Cp^*M]^{2+}$ fragments (M = Rh or Ir) were generated as the solvated complexes $[Cp^*M(MeNO_2)_3]^{2+}$ by elimination of chloride ions from $[Cp^*MCl_2]_2$ with $AgBF_4$. All resulting cationic complexes were isolated as salts with the BF_4^- anion (the anions are omitted in the schemes).

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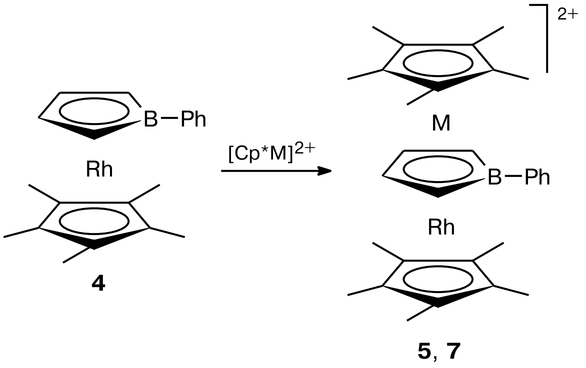
Scheme 2



M = Rh (**5**), Ir (**7**)

by a strong shift of the signals for the protons of the borole ring to lower field ($\Delta\delta$ = 0.7—1.3 ppm) compared to the corresponding signals in the spectrum of sandwich compound **1**, whereas these signals in the spectra of arene-type complexes are shifted in the same direction but to a smaller extent ($\Delta\delta$ = 0.3—0.4 ppm).[8] In the spectra of cations **5** and **7**, the shifts of the signals for the protons of the borole ring relative to the analogous signals for **4** are 1.2—1.3 ppm. In addition, the positions of the signal for the protons of the methyl groups of the Cp* ring in triple-decker (1.8—2.0 ppm) and arene complexes (2.2—2.3 ppm) are also substantially different.[8,9] For cations **5** and **7**, these shifts are 1.9—2.0 ppm. Finally, the ^{1}H NMR spectrum of complex **7** is very similar to that of the pentamethylated analog $[\mathrm{CpRh}(\mu\text{-}\eta^5{:}\eta^5\text{-}\mathrm{C_4H_4BPh})\mathrm{IrCp^*}]^{2+}$, whose structure was established by X-ray diffraction.

Recently, we have developed a procedure for the generation of the unsubstituted $[\mathrm{CpRh}]^{2+}$ fragment and synthesized arene and triple-decker complexes based on this fragment.[4,10] The reaction of **4** with this fragment unexpectedly produced a mixture of triple-decker cation **5** and arene-type complex **3**, which were identified by ^{1}H NMR spectroscopy (Scheme 3). Apparently, this reaction proceeds through the intermediate formation of triple-decker cation **6**. This cation decomposes to form sandwich compound **1** and the $[\mathrm{Cp^*Rh}]^{2+}$ fragment. The attack of the latter on the benzene ring of complex **1** gives rise to complex **3**. The stacking reaction of $[\mathrm{Cp^*Rh}]^{2+}$ with the starting compound **4** gives cation **5**.

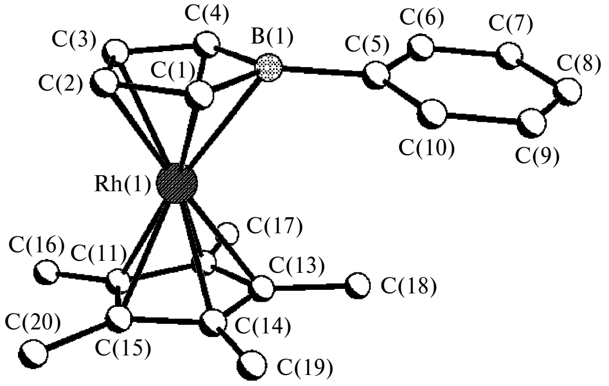


Fig. 1. Structure of complex **4**.

The structure of compound **4** was established by X-ray diffraction. Complex **4** has the expected sandwich structure (Fig. 1). Selected bond lengths and bond angles are given in Table 1. These parameters are very similar to those for nonmethylated analog **1**.[8] The electron-donating effect of five methyl groups in compound **4** would be expected to increase the strength of the bond between the rhodium atom and the borole ligand due to an increase in back donation. However, the distance between the rhodium atom and the borole ring (1.801 Å) is somewhat longer than the analogous distance in compound **1** (1.792 Å). Presumably, this is associated with steric repulsion between the substituents of the borole and pentamethylcyclopentadienyl ligands in the eclipsed conformation.

Therefore, we demonstrated that the electrophilic attack of compound **4** by the dicationic fragments $[(\mathrm{ring})\mathrm{M}]^{2+}$ proceeds exclusively on the borole ring to form triple-decker μ-borole complexes in accordance with

Scheme 3

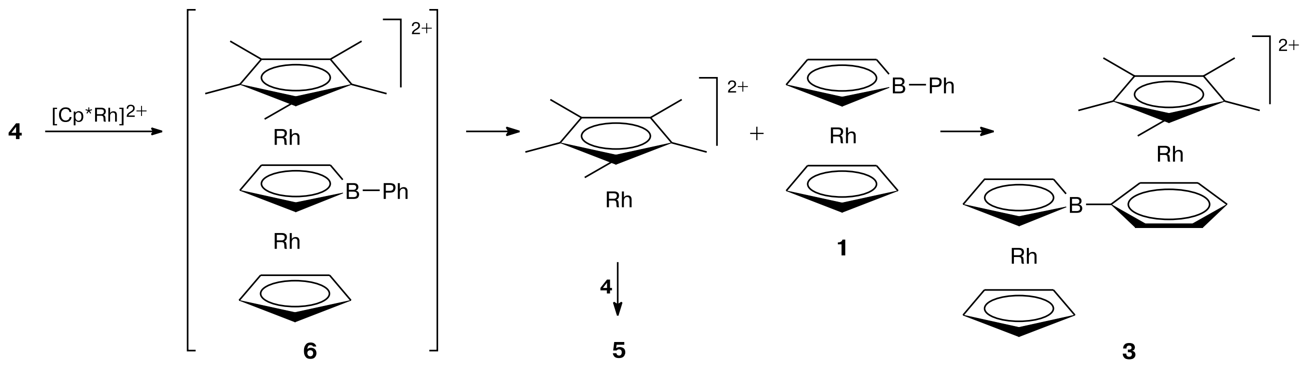


Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **4**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
Rh(1)—B(1)	2.275(6)	Rh(1)—C(14)	2.167(5)
Rh(1)—C(1)	2.193(4)	Rh(1)—C(15)	2.196(5)
Rh(1)—C(2)	2.145(4)	C(1)—C(2)	1.443(7)
Rh(1)—C(3)	2.157(4)	C(2)—C(3)	1.414(8)
Rh(1)—C(4)	2.199(5)	C(3)—C(4)	1.423(7)
Rh(1)—C(11)	2.215(5)	B(1)—C(1)	1.533(8)
Rh(1)—C(12)	2.180(5)	B(1)—C(4)	1.545(6)
Rh(1)—C(13)	2.190(5)	B(1)—C(5)	1.577(8)
Angle	ω/deg	Angle	ω/deg
C(1)—C(2)—C(3)	110.1(4)	C(3)—C(4)—B(1)	108.3(5)
C(2)—C(3)—C(4)	110.5(4)	C(1)—B(1)—C(4)	103.0(5)
B(1)—C(1)—C(2)	108.0(4)		

an increase in the electron density at the borole ring due to the electron-donating effect of five methyl groups.

Experimental

The reactions were carried out under argon with the use of anhydrous solvents prepared according to standard procedures. Operations associated with isolation of the reaction products were carried out in air. The starting compounds $[(\eta\text{-}C_4H_4BPh)RhI]_4$,[11] $[Cp^*RhCl_2]_2$, $[Cp^*IrCl_2]_2$,[12] $[CpRhCl_2]_2$,[13] and $AgBF_4{\cdot}3$dioxane[14] were synthesized according to known procedures. The ^1H and ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz for ^1H and 128.38 MHz for ^{11}B).

(η-Pentamethylcyclopentadienyl)(η-*B*-phenylborole)rhodium, Cp*Rh(η-C_4H_4BPh) (4). A mixture of $[(\eta\text{-}C_4H_4BPh)RhI]_4$ (130 mg, 0.09 mmol) and Cp*Li (61 mg, 0.43 mmol) in tetrahydrofuran (5 mL) was stirred for 24 h. The solvent was removed *in vacuo* and the residue was chromatographed with petroleum ether on a silica gel column (1×10 cm). The yellow fraction was collected, and the solvent was removed *in vacuo*. Complex **4** was obtained as a yellow solid in a yield of 58 mg (44%). Found (%): C, 63.89; H, 6.56. $C_{20}H_{24}BRh$. Calculated (%): C, 63.53; H, 6.40. ^1H NMR ($CDCl_3$), δ: 1.78 (s, 15 H, Cp*); 3.96 (m, 2 H, α-C_4H_4B); 4.90 (m, 2 H, β-C_4H_4B); 7.19 (m, 1 H, *p*-Ph); 7.28 (m, 2 H, *m*-Ph), 7.55 (m, 2 H, *o*-Ph). ^{11}B NMR ($CDCl_3$), δ: 14.2 (br.s, C_4H_4B).

[(η-Pentamethylcyclopentadienyl)rhodium]- (5) and [(η-pentamethylcyclopentadienyl)iridium](μ-η:η-*B*-phenylborole)[(η-pentamethylcyclopentadienyl)rhodium] bis(tetrafluoroborate) (7), $[Cp^*M(\mu\text{-}\eta^5{:}\eta^5\text{-}C_4H_4BPh)RhCp^*](BF_4)_2$. Nitromethane (1 mL) was added to a mixture of the $[Cp^*MCl_2]_2$ complex (0.03 mmol) and $AgBF_4{\cdot}3$dioxane (63 mg, 0.14 mmol), and the reaction mixture was stirred for ~0.5 h. The precipitate of AgCl that formed was removed by centrifugation and the resulting solution was added to complex **4** (25 mg, 0.07 mmol). The reaction mixture was stirred for 2 h, and then diethyl ether (~10 mL) was added. The yellow precipitate that formed was filtered off and twice reprecipitated with diethyl ether from acetone or dichloromethane. Compound 5, the yield was 45 mg (86%). Found (%): C, 44.24; H, 5.07. $C_{30}H_{39}B_3F_8Rh_2$. Calculated (%): C, 45.62; H, 4.98. ^1H NMR (acetone-d_6), δ: 1.90 (s, 30 H, Cp*); 5.19 (m, 2 H, α-C_4H_4B); 6.19 (m, 2 H, β-C_4H_4B); 7.46 (m, 1 H, *p*-Ph); 7.54 (m, 2 H, *m*-Ph); 7.75 (m, 2 H, *o*-Ph). ^{11}B NMR (acetone-d_6), δ: −0.1 (s, BF_4), 12.4 (br.s, C_4H_4B). Compound 7, the yield was 55 mg (95%). Found (%): C, 40.96; H, 4.46. $C_{30}H_{39}B_3F_8RhIr$. Calculated (%): C, 40.98; H, 4.47. ^1H NMR (acetone-d_6), δ: 1.81 (s, 15 H, RhCp*); 1.98 (s, 15 H, IrCp*); 5.21 (m, 2 H, α-C_4H_4B); 6.19 (m, 2 H, β-C_4H_4B); 7.43 (m, 1 H, *p*-Ph); 7.53 (m, 2 H, *m*-Ph); 7.72 (m, 2 H, *o*-Ph). ^{11}B NMR (acetone-d_6), δ: −0.9 (s, BF_4), 7.5 (br.s, C_4H_4B).

Reaction of complex 4 with the $[CpRh]^{2+}$ fragment. Nitromethane (1 mL) was added to a mixture of the $[CpRhCl_2]_2$ complex (16 mg, 0.03 mmol) and $AgBF_4{\cdot}3$dioxane (62 mg, 0.14 mmol), and the reaction mixture was stirred for ~0.5 h. The precipitate of AgCl that formed was removed by centrifugation, and the resulting solution was added to complex **4** (25 mg, 0.07 mmol). The reaction mixture was stirred for 2 h. The addition of diethyl ether (~10 mL) afforded a yellow precipitate (34 mg). According to the ^1H NMR spectroscopic data, the precipitate contained complexes **3** (see Ref. 8) and **5** in a ratio of 2 : 1.

X-ray diffraction study of complex 4. Yellow plate-like crystals of composition $C_{20}H_{28}BRh$, which were grown by slow evaporation of a solution in petroleum ether, are orthorhombic. The unit cell parameters are a = 8.845(2) Å, b = 13.763(3) Å, c = 14.155(3) Å, V = 1723.2(6) Å^3, space group $P2_12_12_1$, Z = 4, d_{calc} = 1.457 g cm^{-3}. A total of 16323 reflections were collected on a Bruker SMART 1000 CCD diffractometer at 140 K (Mo-K_α radiation, $2\theta_{max}$ = 54.00) from a single crystal of dimensions 0.45×0.30×0.05 mm. After merging of equivalent reflections, the data set consisted of 3680 independent reflections (R_{int} = 0.0495), which were used for the structure solution and refinement. An absorption correction (μ = 0.985 mm^{-1}) was applied with the use of the SADABS program (T_{max} and T_{min} are 0.802 and 0.481, respectively). The structure was solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined against F^2_{hkl} with anisotropic displacement parameters. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model with U(H) = nU(C), where U(C) is the equivalent thermal parameter of the corresponding pivot carbon atom, n = 1.2 and 1.5 for the CH and Me groups, respectively. The final R factors were as follows: R_1 = 0.0421 (calculated based on F_{hkl} for 3332 reflections with $I > 2\sigma(I)$), wR_2 = 0.1017 (calculated based on F^2_{hkl} for all 3680 reflections), 199 parameters were refined, GOOF = 1.008. All calculations were carried out using the SHELXTL PLUS 5 program package.[15] The atomic coordinates, displacement parameters, and complete data on geometric parameters were deposited with the Cambridge Structural Database.

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