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# Rhodium-containing triple-decker complexes with a central borole ligand

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**Abstract**

Triple-decker complexes with a bridging borole ligand $(C_4H_4BPh)Rh(\mu\text{-}C_4H_4BPh)ML$ (ML = RuCp, **2a**; $RuCp^*$, **2b**; $FeCp^*$, **3**; $Co(C_4Me_4)$, **4**; Ir(cod), **5**) were synthesized by stacking reactions of $[Rh(C_4H_4BPh)_2]^-$ (**1**) with cationic $[ML]^+$ fragments. The structures of **2a**,**b** and $(C_4H_4BPh)Rh(\mu\text{-}C_4H_4BPh)Rh(C_4H_4BPh)$ (**6**) were determined by X-ray diffraction.


*Keywords:* Boron; Borole; Rhodium; Sandwich compounds; Triple-decker complexes

## 1. Introduction

The first triple-decker complex, the 34 VE (valence electron) cation $[CpNi(\mu\text{-}Cp)NiCp]^+$, was synthesized in 1972 [1,2]. The quantum-chemical considerations demonstrated that 30 VE complexes should be the most stable [3]. Further progress in this field was mainly achieved due to a wide use of boron-containing heterocyclic ligands. A favorable balance of donor and acceptor properties of these ligands results in their increased ability to bifacial bonding with two metal atoms forming triple-decker complexes. Extensive investigations led to the synthesis of complexes containing one, two or three boron atoms in the ring [4].

A very fruitful approach to the synthesis of 30 VE triple-decker complexes is electrophilic stacking of 18 VE sandwich compounds with coordinatively unsaturated 12 VE half-sandwich fragments [5]. Using this approach, a number of triple-decker complexes with cyclopentadienyl [1,5a,6], phospholyl [7], pentaphospholyl [8], and boratabenzene [9] ligands have been obtained earlier. Electrophilic stacking of borole sandwich complexes $CpM(C_4H_4BR)$ (M = Co, Rh) [10,11], $[CpFe(C_4H_4BPh)]^-$ [10,12] and $[Co(C_4H_4BPh)_2]^-$ [12d,13] has been used to prepare μ-borole triple-decker complexes. Herein we describe synthesis of new complexes of this type by reactions of the anionic rhodium complex $[Rh(C_4H_4BPh)_2]^-$ (**1**) with cationic $[ML]^+$ fragments.

## 2. Results and discussion

### 2.1. Synthesis of triple-decker complexes $(C_4H_4BPh)Rh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)ML$

The choice of appropriate source of 12 VE fragment is a key point in electrophilic stacking reactions. In particular, the ruthenium cations $[(C_5R_5)Ru(MeCN)_3]^+$ (R = H, Me) proved to be good sources of the $[(C_5R_5)Ru]^+$ fragments [14] and have been used earlier for the synthesis of several triple-decker complexes [6a,8c,8e]. We found that stacking reaction of **1** with cations $[(C_5R_5)Ru(MeCN)_3]^+$ (R = H,

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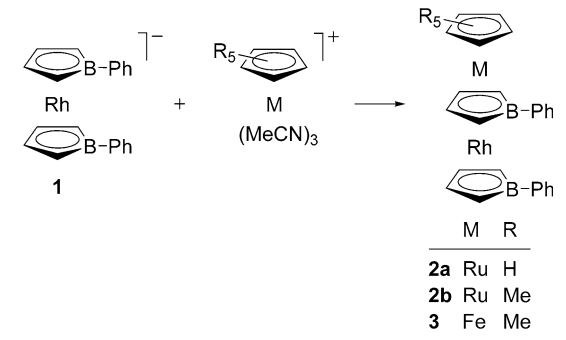
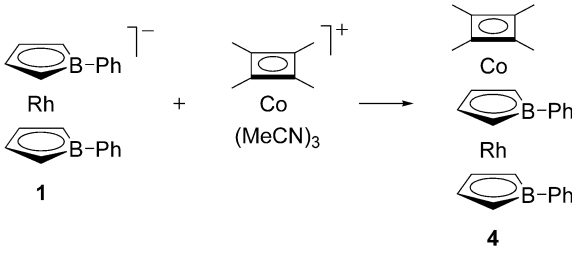
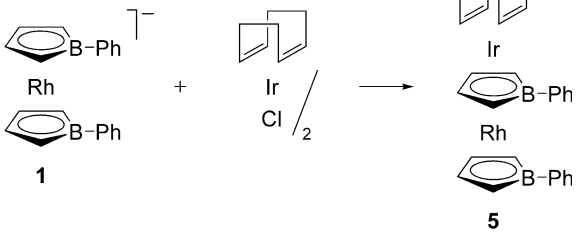



Scheme 1.




Scheme 2.




Scheme 3.

Me) yields the RuRh triple-decker complexes **2a**,**b** (Scheme 1).[1] The reaction proceeds smoothly at room temperature in $CH_2Cl_2$ or THF, affording pure products as orange solids after chromatography. Analogous reaction of **1** with the iron cation $[Cp^*Fe(MeCN)_3]^+$ [15] gives the FeRh triple-decker complex **3**.

Recently, we have described the cobalt complex $[(C_4Me_4)Co(MeCN)_3]^+$ which proved to be very useful synthon of the $[(C_4Me_4)Co]^+$ fragment [16]. In particular, it was successfully used for the synthesis of complexes with 5-electron carbo- and heterocyclic ligands [16b]. Treatment of **1** with the $[(C_4Me_4)Co(MeCN)_3]^+$ cation at room temperature affords the CoRh triple-decker complex **4** as a brick-red solid (Scheme 2).[1]

[1] In the case of the reactions of **1** with $[(C_5R_5)Ru(MeCN)_3]^+$ and $[(C_4Me_4)Co(MeCN)_3]^+$, minor formation of cationic products (2–3%) was also observed. $^1$H NMR spectra suggest that they are formed as a result of coordination of $[(ring)M]^+$ fragment at one of two phenyl rings of primary formed complexes **2a**,**b** and **4**.

Table 1
$^1$H and $^{11}$B NMR spectroscopic data ($\delta$ in ppm) for compounds **2**–**6**

| Complex | $^1$H NMR | | | | | | $^{11}$B NMR | |
|---|---|---|---|---|---|---|---|---|
| | Bridging $C_4H_4BPh$ | | Terminal $C_4H_4BPh$ | | BPh | ML | Bridging $C_4H_4BPh$ | Terminal $C_4H_4BPh$ |
| | α-H | β-H | α-H | β-H | | | | |
| **2a**[a] | 3.80 (m, 2H) | 4.74 (m, 2H) | 4.29 (m, 2H) | 5.37 (m, 2H) | 7.55 (m, 2H), 7.42 (m, 2H), 7.24 (m, 3H), 7.16 (m, 2H), 7.09 (m, 1H) | 4.36 (s) | 7.5 (1B) | 18.4 (1B) |
| **2b**[a] | 3.46 (m, 2H) | 4.42 (m, 2H) | 4.14 (m, 2H) | 5.22 (m, 2H) | 7.50 (m, 2H), 7.32 (m, 2H), 7.20 (m, 5H), 7.10 (m, 1H) | 1.61 (s) | 6.5 (1B) | 17.9 (1B) |
| **3**[a] | 3.26 (m, 2H) | 4.34 (m, 2H) | 3.93 (m, 2H) | 5.03 (m, 2H) | 7.46 (m, 2H), 7.40 (m, 2H), 7.27 (m, 2H), 7.20 (m, 3H), 7.17 (m, 1H) | 1.65 (s) | 6.6 (1B) | 18.0 (1B) |
| **4**[a] | 3.70 (m, 2H) | 4.69 (m, 2H) | 4.07 (m, 2H) | 5.14 (m, 2H) | 7.49 (m, 4H), 7.19 (m, 6H) | 1.18 (s) | 8.7 (1B) | 17.7 (1B) |
| **5**[a] | 3.51 (m, 2H) | 5.15 (m, 2H) | 4.41 (m, 2H) | 5.45 (m, 2H) | 7.49 (m, 4H), 7.20 (m, 6H) | 1.59 (m, 4H, $CH_2$), 1.87 (m, 4H, $CH_2$), 3.91 (m, 4H, $CH$=$CH$) | 10.3 (1B) | 19.4 (1B) |
| **6**[a,b] | 4.01 (m, 2H) | 5.06 (m, 2H) | 4.37 (m, 4H) | 5.28 (m, 4H) | 7.49 (m, 6H), 7.40 (m, 5H), 7.20 (m, 4H) | | 10.3 (1B) | 19.2 (1B) |

[a] In $(CD_3)_2CO$.
[b] Cf. [19].

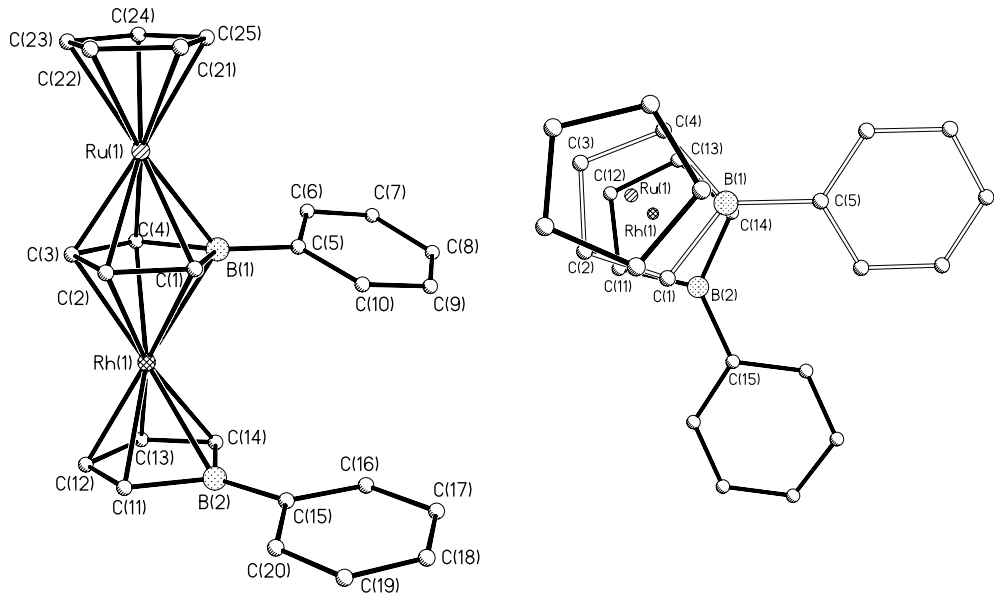



Fig. 1. Molecular structure of compound **2a**. Hydrogen atoms are omitted for clarity.

Earlier, it was shown that the reaction of anion **1** with $[(cod)RhCl]_2$ as a source of the $[(cod)Rh]^+$ cation affords the $Rh_2$ triple-decker complex $(C_4H_4BPh)Rh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)Rh(cod)$ [17]. In our hands similar reaction of **1** with $[(cod)IrCl]_2$ yields the RhIr complex **5** as yellow-orange solid (Scheme 3). Compounds **2**–**5** were isolated in good yields (60–90%). They are stable in air, at least for several hours, both in the solid state and in solution.

### 2.2. NMR spectroscopy

The $^1H$ and $^{11}B$ NMR spectroscopic data for **2**–**5** are given in Table 1. Usually, α- and β-protons of borole ring are observed in $^1H$ spectra as multiplets characteristic of AA′BB′ system [18]. For **2**–**5** there are two such multiplets in 1:1 ratio, corresponding to the terminal and bridging rings. The assignment was made by analogy with the known symmetrical $Rh_2$ complex $(C_4H_4BPh)Rh(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_4H_4BPh)Rh(C_4H_4BPh)$ (**6**) having two multiplets in 1:2 ratio [19]. Sharpness of the signals suggests free rotation of cyclopentadienyl, borole and phenyl rings in **2a**,**b** and **6** in solution.

In the $^{11}B$ NMR spectra of **2**–**5** there are two singlets in 1:1 ratio corresponding to the terminal and bridging borole ligands. The signals are located in the range $\delta$ 6.5–19.4 ppm. Up-field (6.5–10.3 ppm) and down-field (17.7–19.4 ppm) signals were assigned to the bridging and terminal borole rings, respectively, based on comparison with the $^{11}B$ NMR spectrum of **6** [19] having signals of bridging and terminal borole rings at 10.3 and 19.1 ppm. This is in accordance with the common rule [4c] that complexation of a boron ring gives rise to up-field shift of boron signal. In accordance with this rule, the bifacial coordination of borole ligand results in a greater up-field shift as compared with the monofacially coordinated borole ring. Therefore the presence of signals of two different borole ligands in $^1H$ and $^{11}B$ spectra of **2**–**5** is in agreement with their triple-decker structure.

### 2.3. X-ray diffraction study

The structures of **2a**,**b** and **6** determined by X-ray diffraction are shown in Figs. 1–3. Selected bond lengths and angles are given in Table 2. For all three cases the unit cell contains two independent molecules. Generally, average values for bond lengths and angles, quoted in Table 3, are discussed in the text, however individual structural parameters for independent molecules are given if necessary.

Complexes **2a**,**b** and **6** have triple-decker structure formed by three cyclic frames, between which two metal atoms are located. The dihedral angles $C_5R_5/\mu\text{-}C_4H_4B$ and $\mu\text{-}C_4H_4B/C_4H_4B$ in **2a**,**b** (value for the second independent molecule is given in parentheses) are 1.2° (3.2°) and 3.9° (4.4°) (**2a**); 3.3° (2.5°) and 6.9° (5.0°) (**2b**). For **6** the dihedral angles $\mu\text{-}C_4H_4B/C_4H_4B$ are 3.2° (5.5°) and 4.4° (4.8°).

The typical feature of the sandwich borole complexes is folding of the borole ring along the axis $C_\alpha\cdots C_{\alpha'}$, with the B atom being deviated from the $C_4$ plane away from the metal atom. It is connected with the larger covalent radius of boron as compared to carbon. For example, the folding angle[2] and the deviation of B atom from the $C_4$ plane for $(C_4H_4BPh)Fe(CO)_3$ are 6.1° and 0.1 Å, respectively [18]. For **2a** and **6** the central ring is almost planar (average folding angles are 0.8° and 0.9°, respectively), with the B atom being slightly deviated (ca. 0.01 Å) from the $C_4$ plane

[2] Folding angle is dihedral angle between C–B–C and $C_4$ planes of borole ring.

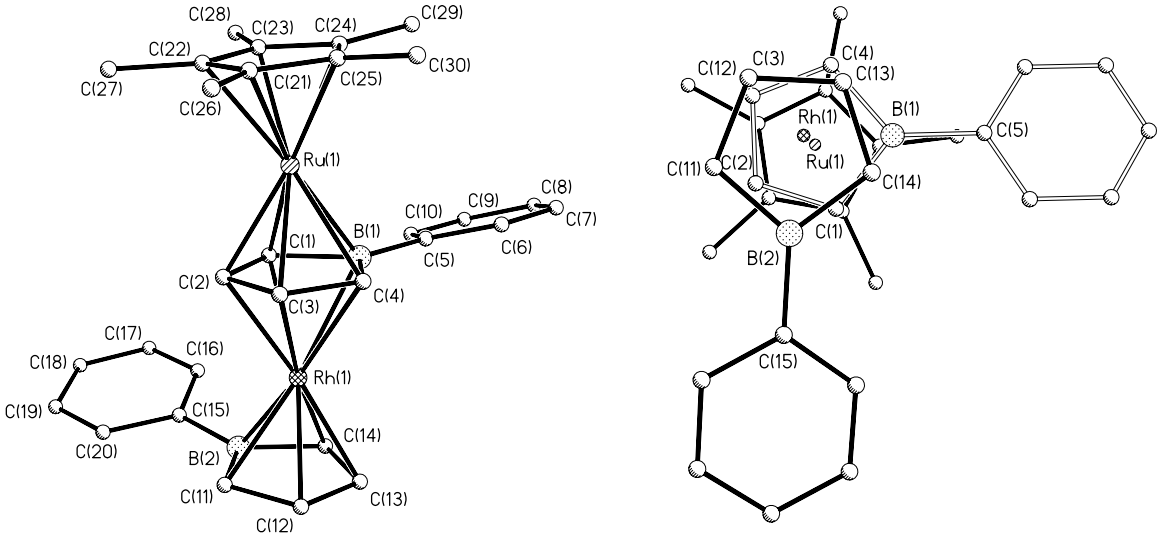



Fig. 2. Molecular structure of compound **2b**. Hydrogen atoms are omitted for clarity.

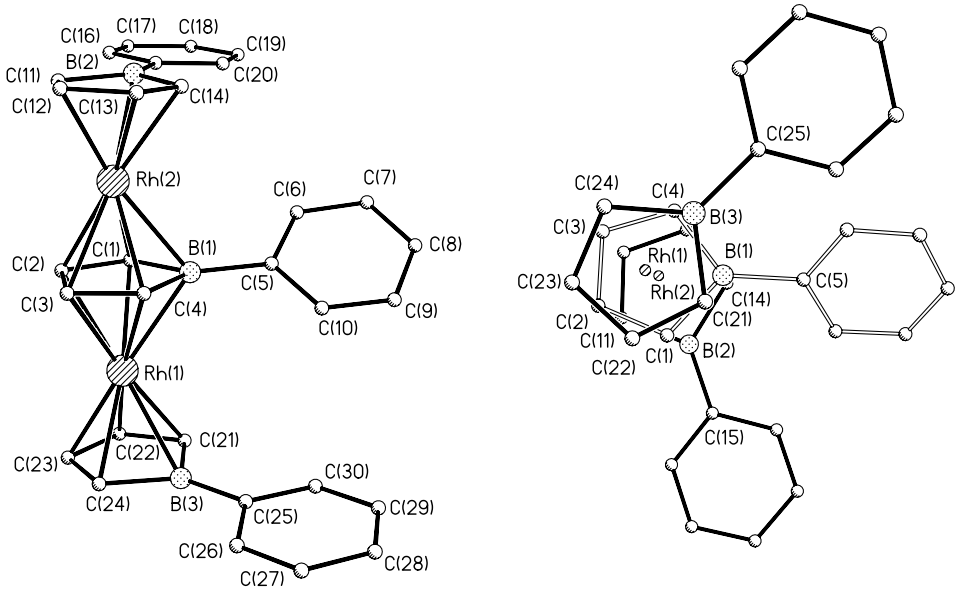



Fig. 3. Molecular structure of compound **6**. Hydrogen atoms are omitted for clarity.

towards the Rh1 atom. The terminal rings in **2a** (3.8°) and **6** (2.5° and 4.9°) are characterized by greater folding angles with the B atom being deviated from the $C_4$ plane for ca. 0.06 Å away from the Rh1 atom. The folding angles of the central (1.8°) and terminal (2.0°) borole rings in **2b** are essentially the same, and the B atoms are deviated in both cases for ca. 0.03 Å but in opposite directions: B1 towards Rh1 atom, and B2 away from it.

Cross-orientation of all five-membered rings in **2a**,**b** and **6** is intermediate between eclipsed and staggered, but more close to eclipsed. The corresponding torsion angles (ring atom)–Ct–Ct′–(ring atom)′[3] for all complexes are within 5–25°, being minimal (5–9°) for the less sterically hindered **2a**. Cross-orientation of the B atoms in two neighbouring borole rings may be described by torsion angles B–Ct–Ct′–B′ which are as follows: 65.4° (65.0°) for **2a**; 94.6° (94.0°) for **2b**; 49.4° (68.8°) and 62.1° (63.0°) for **6**. Phenyl groups at the boron atoms in **2a**,**b** and **6** are not coplanar with the corresponding borole rings, the related dihedral angles being 2.4–35.7°.

Average distances Ru···Rh (3.636 Å for **2a** and 3.645 Å for **2b**) and Rh···Rh (3.674 Å for **6**) are much longer than the corresponding sums of covalent radii Ru–Rh (av. 2.95 Å) and Rh–Rh (av. 2.92 Å) [20] suggesting the absence of direct metal–metal bonds in all cases.

[3] Ct and Ct′ represent the centroids of the corresponding rings.

Table 2
Selected geometric parameters (bond lengths, metal-to-ring distances, metal–metal distances, deviations of **B** atom from the plane (Å) and angles (°)) for complexes **2a**, **2b** and **6** of general formula ($C_4H_4BPh$)–Rh1–(μ-$C_4H_4BPh$)–M–(ring)

| Complex | **2a**[a] | **2b**[a] | **6**[a] |
|---|---|---|---|
| *Bond lengths* | | | |
| Rh1–B1 | 2.281(6); 2.281(6) | 2.297(4); 2.273(4) | 2.274(6); 2.267(6) |
| Rh1–C1 | 2.238(5); 2.206(5) | 2.204(4); 2.202(4) | 2.200(5); 2.216(5) |
| Rh1–C2 | 2.205(5); 2.190(5) | 2.167(4) 2.188(4) | 2.187(5); 2.175(6) |
| Rh1–C3 | 2.232(5); 2.252(5) | 2.209(4); 2.212(4) | 2.238(5); 2.230(6) |
| Rh1–C4 | 2.245(5); 2.257(5) | 2.284(4); 2.261(4) | 2.248(5); 2.217(6) |
| Rh1–B2 | 2.297(6); 2.269(6) | 2.253(5); 2.267(5) | 2.280(7); 2.242(7) |
| Rh1–C11 | 2.198(6); 2.179(5) | 2.194(4); 2.201(4) | 2.156(5); 2.170(6) |
| Rh1–C12 | 2.154(6); 2.136(6) | 2.151(4); 2.134(4) | 2.121(6); 2.142(6) |
| Rh1–C13 | 2.131(6); 2.125(6) | 2.130(4); 2.122(5) | 2.127(6); 2.113(6) |
| Rh1–C14 | 2.149(5); 2.162(5) | 2.149(4); 2.146(5) | 2.151(5); 2.159(6) |
| Rh2–B1 | | | 2.293(6); 2.290(7) |
| Rh2–C1 | | | 2.232(5); 2.212(6) |
| Rh2–C2 | | | 2.229(5); 2.231(6) |
| Rh2–C3 | | | 2.182(6); 2.173(7) |
| Rh2–C4 | | | 2.228(5); 2.218(5) |
| Rh2–B3 | | | 2.314(6); 2.273(7) |
| Rh2–C21 | | | 2.148(6); 2.136(5) |
| Rh2–C22 | | | 2.115(6); 2.128(6) |
| Rh2–C23 | | | 2.132(6); 2.131(6) |
| Rh2–C24 | | | 2.183(5); 2.172(6) |
| Ru1–B1 | 2.278(6); 2.283(5) | 2.309(5); 2.292(5) | |
| Ru1–C1 | 2.208(5); 2.229(5) | 2.204(4); 2.202(4) | |
| Ru1–C2 | 2.186(6); 2.185(6) | 2.168(4); 2.181(4) | |
| Ru1–C3 | 2.170(5); 2.170(6) | 2.191(4); 2.188(4) | |
| Ru1–C4 | 2.205(5); 2.184(5) | 2.228(4); 2.218(4) | |
| B1–C1 | 1.573(8); 1.574(7) | 1.566(6); 1.564(6) | 1.567(8); 1.560(8) |
| B1–C4 | 1.582(7); 1.578(7) | 1.581(6); 1.589(6) | 1.543(8); 1.575(8) |
| B2–C11 | 1.536(9); 1.558(8) | 1.516(7); 1.558(7) | 1.529(8); 1.504(9) |
| B2–C14 | 1.539(9); 1.541(8) | 1.542(7); 1.530(7) | 1.525(8); 1.531(9) |
| B3–C21 | | | 1.537(8); 1.537(8) |
| B3–C24 | | | 1.515(8); 1.503(8) |
| C1–C2 | 1.443(7); 1.455(7) | 1.428(6); 1.444(6) | 1.443(7); 1.431(7) |
| C2–C3 | 1.463(8); 1.463(8) | 1.479(6); 1.459(6) | 1.408(7); 1.431(7) |
| C3–C4 | 1.475(7); 1.460(7) | 1.430(6); 1.434(6) | 1.438(7); 1.417(7) |
| C11–C12 | 1.43(1); 1.431(8) | 1.434(6); 1.420(7) | 1.401(7); 1.398(7) |
| C12–C13 | 1.42(1); 1.417(9) | 1.402(7); 1.408(8) | 1.428(7); 1.399(8) |
| C13–C14 | 1.425(9); 1.420(8) | 1.415(7); 1.428(7) | 1.427(7); 1.441(7) |
| C21–C22 | | | 1.421(8); 1.425(7) |
| C22–C23 | | | 1.416(7); 1.438(8) |
| C23–C24 | | | 1.419(7); 1.429(8) |
| *Metal-to-ring distances* | | | |
| Rh1···(μ-$C_4H_4BPh$) | 1.837(2); 1.834(3) | 1.832(2); 1.826(2) | 1.840(2); 1.829(2) |
| Rh1···($C_4H_4BPh$) | 1.791(3); 1.776(3) | 1.785(2); 1.779(2) | 1.774(2); 1.776(3) |
| M···(μ-$C_4H_4BPh$) | 1.799(2); 1.801(3) (M = Ru1) | 1.818(2); 1.814(2) (M = Ru1) | 1.844(2); 1.833(2) (M = Rh2) |
| M···(ring) | 1.798(2); 1.793(2) (M = Ru1) | 1.787; 1.781 (M = Ru1) | 1.787(3); 1.773(3) (M = Rh2) |
| *Metal–metal distances* | | | |
| Rh1···Rh2 | | | 3.685(2); 3.663(1) |
| Rh1···Ru1 | 3.637(1); 3.635(1) | 3.6504(9); 3.640(1) | |
| *B atom deviations from the $C_4$ plane* | | | |
| B1···(C1–C4) | 0.017; 0.008 | 0.034; 0.028 | 0.003; 0.017 |
| B2···(C11–C14) | 0.080; 0.050 | 0.034; 0.036 | 0.060; 0.024 |
| B3···(C21–C24) | | | 0.088; 0.076 |
| *Folding angles of borol ring* | | | |
| C1–C4/C1B1C4 | 1.0; 0.5 | 2.0; 1.6 | 0.5; 1.2 |
| C11–C14/C11B2C14 | 4.7; 2.9 | 2.0; 2.1 | 3.5; 1.5 |
| C21–C24/C21B3C24 | | | 5.2; 4.6 |

(*continued on next page*)

Table 2 (*continued*)

| Complex | **2a**[a] | **2b**[a] | **6**[a] |
|---|---|---|---|
| *Dihedral angles between borole ring and phenyl substituent* | | | |
| (μ-$C_4H_4B1$)/Ph | 23.2; 31.0 | 13.9; 13.9 | 35.7; 18.0 |
| ($C_4H_4B2$)/Ph | 7.9; 12.1 | 13.3; 10.7 | 2.4; 20.4 |
| ($C_4H_4B3$)/Ph | | | 5.8; 17.1 |

[a] For two independent molecules.

Table 3
Selected average bond lengths (Å) for complexes **2a**,**b** and **6**

| Complex | **2a** | **2b** | **6** |
|---|---|---|---|
| Rh–B terminal | 2.283 | 2.263 | 2.282 |
| Rh–B bridging | 2.281 | 2.287 | 2.284 |
| Rh–$C_\alpha$ terminal | 2.172 | 2.172 | 2.175 |
| Rh–$C_\alpha$ bridging | 2.237 | 2.238 | 2.227 |
| Rh–$C_\beta$ terminal | 2.137 | 2.136 | 2.131 |
| Rh–$C_\beta$ bridging | 2.220 | 2.193 | 2.219 |
| Ru–B | 2.281 | 2.302 | |
| Ru–$C_\alpha$ | 2.207 | 2.213 | |
| Ru–$C_\beta$ | 2.178 | 2.186 | |
| Ru–$C_{Cp}$ | 2.166 | 2.158 | |
| B–$C_\alpha$ terminal | 1.544 | 1.533 | 1.536 |
| B–$C_\alpha$ bridging | 1.577 | 1.578 | 1.573 |
| $C_\alpha$–$C_\beta$ terminal | 1.426 | 1.426 | 1.422 |
| $C_\alpha$–$C_\beta$ bridging | 1.458 | 1.433 | 1.446 |
| $C_\beta$–$C_\beta$ terminal | 1.419 | 1.408 | 1.421 |
| $C_\beta$–$C_\beta$ bridging | 1.463 | 1.473 | 1.453 |
| $C_{Cp}$–$C_{Cp}$ | 1.424 | 1.425 | |

Bonding situation in triple-decker complexes [3] implies that population of bonds relevant to the bridging ring is noticebly weaker than for the terminal one. It should result in elongation of all bonds for a bridging ligand as compared with terminal. It was confirmed by the structures of [CpNi(μ-η:η-Cp)NiCp]$BF_4$ [2], [$Cp^*$Ru(μ-η:η-$Cp^*$)RuCp*]$PF_6$ [6b], $Cp^*$Co(μ-η:η-$Cp^*$)Co$Cp^*$ [21], [$Cp^*$Ru(μ-η:η-$Cp^*$)Mn(CO)$_3$]$PF_6$ [22], and (1,3,5-$C_6H_3Me_3$)Cr(μ-η:η-1,3,5-$C_6H_3Me_3$)Cr(1,3,5-$C_6H_3Me_3$) [23] having identical carbocyclic ligands both in the bridging and terminal positions. For these complexes the elongation of all M···ring, M–C and C–C distances related to the bridging carbocyclic ligand is observed (usually ca. 0.04–0.07 Å). The corresponding distances in **2a**,**b** and **6** for the bridging borole ligand are also longer (ca. 0.01–0.07 Å) than for the terminal one (see Table 3). Similarly, the Rh–B bond for the terminal ring in **2b** is shorter than for the bridging one (ca. 0.025 Å). However, in other cases the elongation of the Rh–B bond for the bridging borole ligand is compensated by a greater folding of the terminal ring. For instance, the Rh–B bonds in **2a** and **6** are almost equal for the terminal and bridging rings (see Table 3). In the case of ($C_4H_4BMe$)Co(μ-$\eta^5$:$\eta^5$-$C_4H_4BMe$)Co($C_4H_4BMe$) [13] the Co–B distances for the terminal ring are even longer than for bridging ones (ca. 0.03–0.04 Å). The Rh–B bonds (2.242–2.297 Å) in **2a**,**b** and **6** are the shortest among the structurally characterized (borole)rhodium complexes: ($C_4H_4BPh$)Rh($PPh_3$)$_2$Cl (2.400 Å) [24], ($C_4H_4BMe$)$_2$RhI (2.367 Å) [25], [($C_4H_4BPh$)RhI]$_4$ (av. 2.325 Å) [25], and ($C_4H_4BPh$)Rh(μ-I)$_3$Rh$Cp^*$ (2.296 Å) [26]. The Ru–B distances in **2a**,**b** (av. 2.281 and 2.302 Å, respectively) are shorter than in the half-sandwich complex ($C_4H_4BPh$)Ru($PPh_3$)$_2$HCl (2.366 Å) [24].

## 3. Conclusion

General approach based on stacking reactions of sandwich compounds with $[ML]^+$ fragments proved to be very effective for the synthesis of rhodium-containing triple-decker complexes with a bridging borole ligand. X-ray diffraction study of such compounds revealed lower folding of the bridging borole ring as compared with the terminal one.

## 4. Experimental

### 4.1. General

The reactions were carried out under an inert atmosphere in dry solvents. The isolation of products was conducted in air. Starting materials Cs[($C_4H_4BPh$)$_2$Rh] (Cs[**1**]) [27], ($C_4H_4BPh$)Rh(μ-$\eta^5$:$\eta^5$-$C_4H_4BPh$)Rh($C_4H_4BPh$) (**6**) [19], [Cp-Ru(MeCN)$_3$]$PF_6$ [14a], [$Cp^*$Ru(MeCN)$_3$]$PF_6$ [14d], [$Cp^*$-Fe(MeCN)$_3$]$PF_6$ [15], [($C_4Me_4$)Co(MeCN)$_3$]$PF_6$ [16b], and [(cod)IrCl]$_2$ [28] were prepared as described in the literature. $^1$H and $^{11}$B{$^1$H} NMR spectra were recorded on a Bruker AMX-400 spectrometer ($^1$H 400.13; $^{11}$B 128.38 MHz) relative to residual protons of acetone-$d_6$ ($^1$H) or $BF_3 \cdot Et_2O$ ($^{11}$B, external standard).

### 4.2. Synthesis of triple-decker complexes ($C_4H_4BPh$)Rh(μ-$\eta^5$:$\eta^5$-$C_4H_4BPh$)ML (2–5)

$CH_2Cl_2$ (10 ml) was added to a mixture of Cs[**1**] (104 mg, 0.2 mmol) and [(ring)M(MeCN)$_3$]$PF_6$ (0.2 mmol) or [(cod)IrCl]$_2$ (0.1 mmol). The reaction mixture was stirred for 12 h and then evaporated. The residue was chromatographed on alumina column (2 × 10 cm) by mixture hexane/$CH_2Cl_2$ (7:1). The intensively colored band (dark-green in the case of (ring)M = $Cp^*$Fe, yellow or orange in all other cases) was collected and evaporated in vacuum to dryness. The product was recrystallized from petroleum ether/ethanol.

#### 4.2.1. Complex **2a**

Orange. Yield: 94 mg (86%). Anal. Calc. for $C_{25}H_{23}B_2RhRu$: C, 54.69; H, 4.22. Found: C, 54.70; H, 4.34%.

#### 4.2.2. Complex **2b**

Orange. Yield: 100 mg (81%). Anal. Calc. for $C_{30}H_{33}B_2RhRu$: B, 3.49; C, 58.19; H, 5.37. Found: B, 3.42; C, 58.05; H, 5.37%.

#### 4.2.3. Complex **3**

Dark-green. Yield: 73 mg (64%). Anal. Calc. for $C_{30}H_{33}B_2FeRh$: C, 62.78; H, 5.80. Found: C, 62.96; H, 5.87%.

#### 4.2.4. Complex **4**

Brick-red. Yield: 81 mg (74%). Anal. Calc. for $C_{28}H_{30}B_2CoRh$: B, 3.93; C, 61.15; H, 5.50. Found: B, 3.91; C, 61.11; H, 5.67%.

#### 4.2.5. Complex **5**

Yellow-orange. Yield: 93 mg (68%). Anal. Calc. for $C_{28}H_{30}B_2IrRh$: B, 3.16; C, 49.22; H, 4.43. Found: B, 3.05; C, 49.44; H, 4.57%.

### 4.3. X-ray crystallography

The crystals of **2a**,**b** and **6**, suitable for X-ray study, were obtained by slow evaporation of hexane solutions of corresponding compounds at room temperature. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector (for **2a** and **6**) or with CAD4 Enraf-Nonius (for **2b**). Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow $N_2$ gas cryostat. Reflection intensities were integrated using SAINT software [29]. The adsorption correlation was carried out using a semi-empirical method SADABS [30]. Reflection intensities were integrated using XCAD4 software [31].

Table 4
Summary of crystallographic data for **2a**,**b** and **6**

| Complex | **2a** | **2b** | **6** |
|---|---|---|---|
| Empirical formula | $C_{25}H_{23}B_2RhRu$ | $C_{30}H_{33}B_2RhRu$ | $C_{30}H_{27}B_3Rh_2$ |
| Molecular weight | 549.03 | 619.16 | 625.77 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ |
| Crystal color, habit | Red, plate | Orange, plate | Yellow-orange, plate |
| Crystal size (mm) | $0.4\times0.3\times0.1$ | $0.4\times0.3\times0.2$ | $0.4\times0.3\times0.1$ |
| $a$ (Å) | 10.832(3) | 12.358(3) | 17.186(7) |
| $b$ (Å) | 10.906(3) | 15.549(3) | 20.876(8) |
| $c$ (Å) | 35.281(8) | 15.884(3) | 13.954(6) |
| $\alpha$ (°) | 90 | 68.16(3) | 90 |
| $\beta$ (°) | 98.822(5) | 89.46(3) | 94.631(9) |
| $\gamma$ (°) | 90 | 74.10(3) | 90 |
| $V$ (Å$^3$) | 4118.3(17) | 2710.1(9) | 4990(3) |
| $Z$ | 8 | 4 | 8 |
| $D_{calc}$ (g cm$^{-3}$) | 1.771 | 1.518 | 1.666 |
| Temperature (K) | 140(2) | 293(2) | 153(2) |
| Radiation | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ |
| $\mu$ (cm$^{-1}$) | 15.43 | 11.82 | 13.41 |
| $2\theta_{max}$ (°) | 60.02 | 21.97 | 56.00 |
| Scan method | $\phi$ and $\omega$ | $\theta$-5/3$\theta$ | $\phi$ and $\omega$ |
| Absorption correction | Semi-empirical | None | Semi-empirical |
| $T_{max}/T_{min}$ | 0.862/0.209 | | 0.492/0.368 |
| Number of measured, independent and observed reflections | 33214, 11994, 9030 | 5942, 5563, 4953 | 51256, 12037, 5265 |
| $R_{int}$ | 0.0749 | 0.0178 | 0.0855 |
| Completeness to $\theta$ (%) | 99.6 | 84.2 | 99.9 |
| Number of parameters used in refinement | 523 | 613 | 631 |
| $R_1$ (on $F$ for observed reflections)[a] | 0.0674 | 0.0262 | 0.0526 |
| $wR_2$ (on $F^2$ for all reflections)[b] | 0.1667 | 0.0762 | 0.0813 |
| Weighting scheme | $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$, where $P=1/3(F_o^2+2F_c^2)$ | | |
| $A$ | 0.1000 | 0.0585 | 0.0010 |
| $B$ | – | 1.5601 | 1.015 |
| $F$(000) | 2176 | 1248 | 2496 |
| Goodness-of-fit | 1.010 | 0.992 | 0.942 |
| $\Delta\rho_{max}/\Delta\rho_{min}$ (e Å$^{-3}$) | 2.142/−1.224 | 0.657/−0.528 | 1.174/−0.830 |

[a] $R_1=\sum\|F_o|-|F_c\|/\sum(F_o)$ for observed reflections.
[b] $wR_2=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$ for all reflections.

The structures were solved by direct method and refined by the full-matrix least-squares against $F^2$ in anisotropic (for non-hydrogen atoms) and isotropic (for H atoms) approximation. The positions of hydrogen atoms were calculated from the geometrical point of view and were included in the final refinement using a rigid model. The crystallographic data, procedures for collecting experimental data, and characteristics of structure refinement are listed in Table 4. All calculations were performed on an IBM PC/AT using the SHELXTL software [32].

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## Appendix A. Supplementary data

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 278926 for **2a**, CCDC 278927 for **2b** and CCDC 2789288 for **6**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.032.

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