

# Cationic Triple-Decker Complexes with a Bridging 4-Borataborepine Ligand: Synthesis, Structure, and Bonding

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*Dedicated to Professor Heinrich Nöth on the occasion of his 80th birthday*

**Keywords:** Boron / Bonding analysis / Density functional calculations / Heterocycles / Ruthenium / Triple-decker complexes

Cationic 30 VE triple-decker complexes  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})\text{ML}]^+$  [ $\text{ML} = \text{Co}(\text{C}_4\text{Me}_4)$  (**3a**),  $\text{RuCp}^*$  (**4a**),  $\text{Rh}(\text{cod})$  (**7a**), and  $\text{Ir}(\text{cod})$  (**8a**)] with a bridging hexamethyl-4-borataborepine ligand were obtained by electrophilic stacking of the sandwich compound  $\text{Cp}^*\text{Ru}(\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})$  (**2a**) with  $[\text{ML}]^+$  complex fragments. The reaction of the phenyl-substituted derivative  $\text{Cp}^*\text{Ru}(\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})$  (**2b**) with  $[(\text{C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]^+$  selectively affords the triple-decker complex  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{:}\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})\text{Co}(\text{C}_4\text{Me}_4)]^+$  (**3b**), whereas a similar reaction with  $[\text{Cp}^*\text{RuCl}]_4/\text{TiBF}_4$  produces a 1:3 mixture of cations, the triple-decker  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{:}\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})\text{RuCp}^*]^+$  (**4b**) and the arene-coordinated  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^6\text{:}\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})\text{RuCp}^*]^+$  (**5**). Stacking of  $\text{Cp}^*\text{Ru}(\eta^7\text{-7-PhCH}_2\text{C}_5\text{B}_2\text{Me}_5\text{H})$  (**2c**) with  $[\text{CpRu}(\text{MeCN})_3]^+$  selectively gives the triple-decker complex  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{:}\eta^7\text{-7-PhCH}_2\text{C}_5\text{B}_2\text{Me}_5\text{H})\text{RuCp}]^+$  (**6c**). The dinuclear cations **3–8**

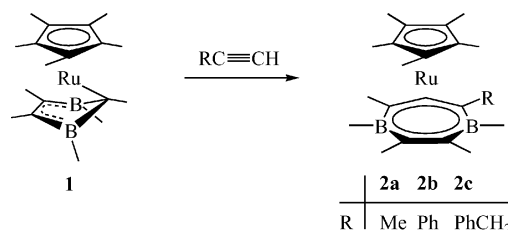
were isolated as deep-colored air-stable salts with  $[\text{BF}_4]^-$  or  $[\text{PF}_6]^-$  anions in moderate to high yields. Structures of **3bPF**<sub>6</sub>, **4aBF**<sub>4</sub>, **7aBF**<sub>4</sub>, and **8aBF**<sub>4</sub> were confirmed by X-ray diffraction studies. Energy decomposition analysis of complexes  $\text{CpRu}(\text{ring})$  and  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$  (ring = Cp,  $\text{C}_5\text{BH}_6$ ,  $\text{C}_5\text{B}_2\text{H}_7$ ) revealed that the insertion of BH units makes the bonding between  $[\text{ring}]^-$  and  $[\text{RuCp}]^+$  more covalent. According to Mulliken population analysis, weakening of  $\pi$ -donation and strengthening of  $\delta$ -back donation occur in the same order. The electrostatic character of the bond and the contribution of  $\sigma$ -donation to the covalent bonding are higher in the case of bifacially bonded rings. The boron-containing triple-decker complexes are considerably more stable than the cyclopentadienyl analog.

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## Introduction

The 2,3-dihydro-1,3-diborolyl ligand of the formally 16 VE ruthenium complex  $\text{Cp}^*\text{Ru}(\text{C}_3\text{B}_2\text{Me}_5)$  (**1**)<sup>[1]</sup> is similarly folded along the B...B line as that of the structurally characterized derivative with  $\text{BCH}_2\text{SiMe}_3$  groups (40.7°).<sup>[2]</sup> Although the folding promotes the metal atom to complete its valence shell, compound **1** possesses a unique reactivity towards various reagents to give classical 18 VE complexes. In particular, it reacts with CO, RNC, and  $\text{RPH}_2$  to yield adducts **1–L** with much less folded diborolyl rings. The incorporation of a BH fragment (from  $\text{BH}_3$ ) as well as a sulfur atom or a phosphaaalkyne leads to ruthenacarboranes.<sup>[3]</sup> Insertion of terminal alkynes into the heterocycle creates complexes **2** with the novel  $\eta^7$ -4-borataborepine ligand

(Scheme 1).<sup>[4]</sup> However, the analogous reaction with internal alkynes, dimethyl- and diethylacetylene, affords the boratabenzene complexes  $\text{Cp}^*\text{Ru}(2,3\text{-R}_2\text{C}_5\text{BMe}_4)$  (R = Me, Et) as a result of the elimination of one BMe unit. Surprisingly, the reaction of **1** with di-*p*-tolylacetylene in  $\text{CH}_2\text{Cl}_2$  gave a small amount of the triple-decker cation  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{:}\eta^7\text{-1,2,3,4,6-Me}_5\text{C}_5\text{B}_2\text{H}_2)\text{RuCp}^*]^+$  having a bridging 4-borataborepine ligand with two CH groups separated by a CMe unit. Its structure has been confirmed by X-ray diffraction; however, details of its formation are unknown.<sup>[5]</sup>



Scheme 1. Preparation of the borataborepine complexes **2a–c**.

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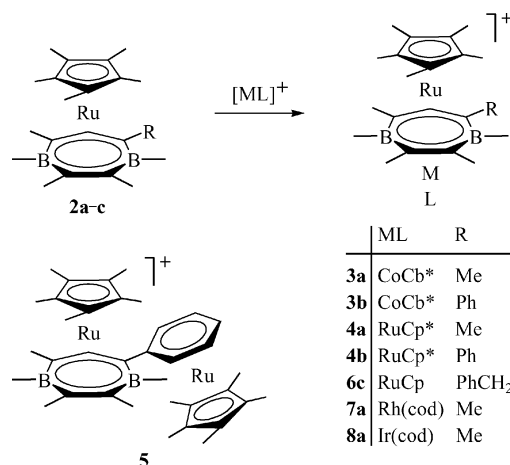
Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

A straightforward synthetic approach to cationic triple-decker complexes is based on the electrophilic stacking of sandwich compounds with  $[ML]^+$  fragments (in form of their labile derivatives).<sup>[6]</sup> In particular, complexes with bridging cyclopentadienyl,<sup>[7]</sup> phospholyl,<sup>[8]</sup> pentaphospholyl,<sup>[9]</sup> borole,<sup>[10]</sup> and boratabenzene<sup>[11]</sup> rings have been synthesized using this way. Herein we report the electrophilic stacking of **2** with  $[ML]^+$  species giving triple-decker complexes with a bridging 4-borataborepine ligand. Their structural and bonding features are also discussed.

## Results and Discussion

### Synthesis

At the beginning of this study, complexes **2b** and **2c** containing phenyl and benzyl substituents in the 7-position of the 4-borataborepine ligand were known. However, the benzene ring of these substituents can be attacked by  $[ML]^+$  species to give arene-coordinated derivatives, thus complicating the formation of triple-decker complexes. Therefore, we first prepared the undecamethyl sandwich **2a** by insertion of propyne into **1** (Scheme 1). The reactions of **2a** with  $[(C_4Me_4)Co(MeCN)_3]^+$  and  $[Cp^*Ru(thf)_3]^+$  (generated in situ from  $[Cp^*RuCl]_4/TIBF_4$  in thf) afford the 30 VE triple-decker cations **3a** and **4a** in high yields (Scheme 2). The analogous reactions with  $[(cod)M(thf)_x]^+$  solvates ( $M = Rh, Ir$ )<sup>[12]</sup> give complexes **7a** and **8a**.



Scheme 2. Synthesis of  $\mu$ -borataborepine triple-decker complexes.

As expected, the reaction of the phenyl-substituted complex **2b** with  $[Cp^*Ru(thf)_3]^+$  produces a mixture of cations, the triple-decker **4b** and the arene-coordinated **5** in 1:3 ratio according to  $^1H$  NMR spectroscopy. However, a similar reaction with  $[(C_4Me_4)Co(MeCN)_3]^+$  selectively affords the triple-decker complex **3b**, which is explained by lower reactivity of the cobalt reagent towards arenes. The reaction of the benzyl-substituted derivative **2c** with  $[CpRu(MeCN)_3]^+$  also gives the triple-decker cation **6c** as a single product.

The dinuclear cations **3–8** were isolated as deep-colored salts with  $BF_4^-$  or  $PF_6^-$  anions in moderate to high yields.

They are air-stable both in the solid state and in solution (acetone,  $CH_2Cl_2$ , or  $MeNO_2$ ) at least for several weeks. All complexes were characterized by  $^1H$  and  $^{11}B$  NMR spectroscopy and elemental analysis. The signals of 4-borataborepine ring protons are downfield shifted ( $\Delta\delta = 0.1$ – $1.6$  ppm), and the signals of boron atoms are upfield shifted ( $\Delta\delta = 12$ – $16$  ppm) as compared to the corresponding signals for the sandwich compounds **2a–c**.

### X-ray Structures

The structures of complexes **3b**PF<sub>6</sub>, **4a**BF<sub>4</sub>, **7a**BF<sub>4</sub>, and **8a**BF<sub>4</sub> were studied by X-ray diffraction. The triple-decker cations (Figures 1, 2, 3, and 4) are formed by three cyclic ligands held together by two metal atoms. In cations **3b** and **4a** the central  $C_5B_2$  ring was found to be disordered. In **3b** disorder is around a pseudo twofold axis perpendicular to the  $Ru \cdots Co$  line and through C1 (refined occupancies of the two sets are 0.55 and 0.45). Cation **4a** has a crystallographic mirror plane, which runs through C7 and the two Ru atoms. In both cases disorder around the (pseudo) symmetry element causes a fairly close superposition of partially occupied, chemically not equivalent central ring atoms (boron and carbon, and differently substituted carbon atoms, respectively, belonging to different sets). During refinement, the corresponding atoms of the two disordered sets had to be constrained to the same positions and anisotropic displacement parameter (ADP) components. Hence, bond lengths and angles involving these atoms are not reliable. Likewise, the individual atoms in the periphery of these seven-membered rings could not be resolved into two dis-

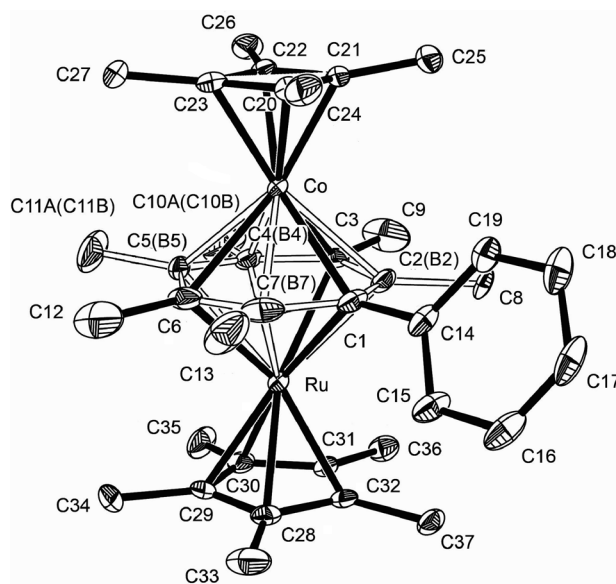


Figure 1. Structure of cation **3b** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Ru–C2/B2 2.364(4), Ru–B7/C7 2.373(4), Ru–B4/C4 2.372(4), Ru–C5/B5 2.451(4), Ru–C6 2.336(4), Ru–C1 2.367(4), Co–C2/B2 2.295(4), Co–B7/C7 2.302(4), Co–B4/C4 2.306(4), Co–C5/B5 2.244(4), Co–C3 2.243(3), Co–C1 2.274(3), Ru $\cdots$ C5 1.797(2), Co $\cdots$ C4 1.716(2), Ru $\cdots$ C5B2 1.670(1), Co $\cdots$ C5B2 1.522(2).

tinct sets and were refined as single atoms (with partial occupations where appropriate). As expected for such a case, ADPs are somewhat larger for these atoms.

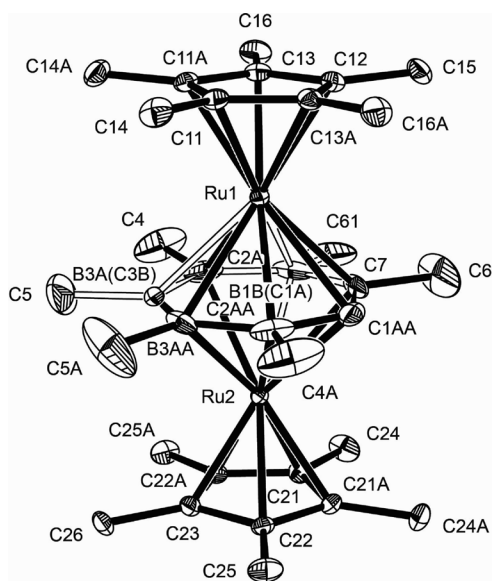


Figure 2. Structure of cation **4a** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Ru1–C2A 2.382(2), Ru1–B1B 2.375(2), Ru1–C7 2.367(3), Ru1–B3A 2.417(2), Ru2–C2A 2.409(2), Ru2–B1B 2.368(2), Ru2–C7 2.393(3), Ru2–B3A 2.389(2), Ru1...C<sub>5</sub> 1.779(1), Ru2...C<sub>5</sub> 1.781(1), Ru1...C<sub>5</sub>B<sub>2</sub> 1.676(1), Ru2...C<sub>5</sub>B<sub>2</sub> 1.678(1).

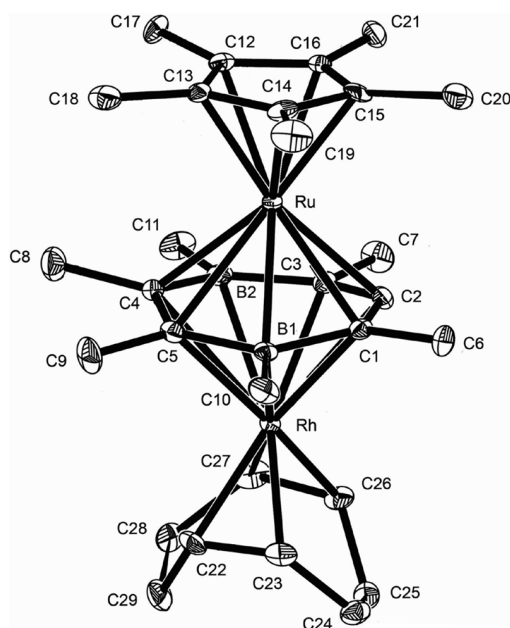


Figure 3. Structure of cation **7a** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Ru–B1 2.440(4), Ru–B2 2.406(4), Ru–C1 2.317(4), Ru–C2 2.263(4), Ru–C3 2.359(4), Ru–C4 2.320(4), Ru–C5 2.415(4), Rh–B1 2.473(4), Rh–B2 2.443(4), Rh–C1 2.532(4), Rh–C2 2.479(4), Rh–C3 2.327(4), Rh–C4 2.603(4), Rh–C5 2.487(4), Ru...C<sub>5</sub> 1.800(2), Ru...C<sub>5</sub>B<sub>2</sub> 1.625(1), Rh...C<sub>5</sub>B<sub>2</sub> 1.791(1).

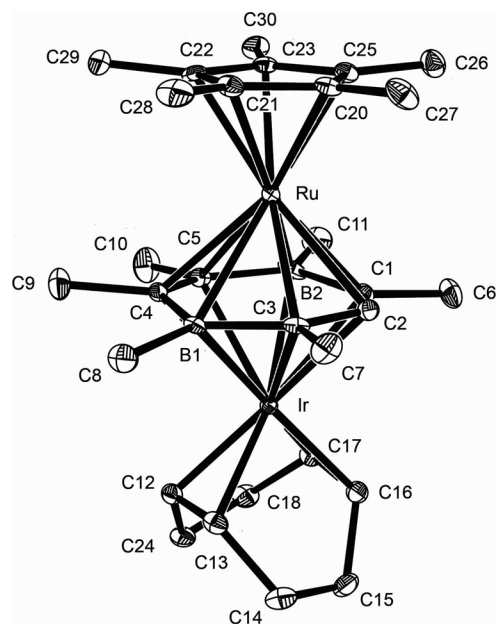


Figure 4. Structure of cation **8a** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances [Å]: Ru–B1 2.420(4), Ru–B2 2.392(5), Ru–C1 2.390(4), Ru–C2 2.309(4), Ru–C3 2.323(4), Ru–C4 2.348(4), Ru–C5 2.450(4), Ir–B1 2.442(4), Ir–B2 2.474(4), Ir–C1 2.316(4), Ir–C2 2.458(4), Ir–C3 2.495(4), Ir–C4 2.510(4), Ir–C5 2.448(4), Ru...C<sub>5</sub> 1.795(2), Ru...C<sub>5</sub>B<sub>2</sub> 1.645(1), Ir...C<sub>5</sub>B<sub>2</sub> 1.748(1).

In all cases, the planes of the ligands are almost coplanar; the dihedral angles are equal to 1.6° (C<sub>5</sub>B<sub>2</sub>/C<sub>5</sub>) and 1.4° (C<sub>5</sub>B<sub>2</sub>/C<sub>4</sub>) for **3b**, 0.3° and 0.8° (C<sub>5</sub>B<sub>2</sub>/C<sub>5</sub>) for **4a**, 1.4° (C<sub>5</sub>B<sub>2</sub>/C<sub>5</sub>) for **7a**, and 0.1° (C<sub>5</sub>B<sub>2</sub>/C<sub>5</sub>) for **8a**. The metal atoms are located above the centers of all the rings. The Ru...Co (3.19 Å), Ru...Ru (3.35 Å), Ru...Rh (3.42 Å), and Ru...Ir (3.39 Å) distances are longer than the corresponding sums of the covalent radii for RuCo (2.78 Å), RuRu (2.98 Å), RuRh (2.83 Å), and RuIr (2.96 Å)<sup>[13]</sup> suggesting the absence of direct metal–metal interactions in all cases. In the triple-decker cations **3b**, **4a**, **7a**, and **8a**, the 4-borataborepine ligand is significantly less folded along the B...B line than in mononuclear sandwich complexes **2** due to its bifacial coordination with two metal atoms. For instance, the folding angles in **7a** (7.0°) and **8a** (1.2°) are smaller than in **2c** (12.1°).<sup>[4]</sup> All bonds in the C<sub>5</sub>B<sub>2</sub> ring of **3b** are longer than in **2b** as a result of loosening of bonds upon bifacial coordination.

## Bonding Analysis

For a better understanding of the borataborepine bonding properties, we compared the related [RuCp]<sup>+</sup> complexes with the cyclopentadienyl (Cp<sup>−</sup>), boratabenzene ([C<sub>5</sub>BH<sub>6</sub>]<sup>−</sup>), and borataborepine ([C<sub>5</sub>B<sub>2</sub>H<sub>7</sub>]<sup>−</sup>) anions using the energy decomposition analysis (EDA), which has proven to be one of the best methods for the analysis of chemical bonding.<sup>[14]</sup> According to this method, the interaction energy between

the bonding fragments  $\Delta E_{\text{int}}$  can be divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

$\Delta E_{\text{elstat}}$  is the electrostatic interaction energy between the fragments with a frozen electron-density distribution,  $\Delta E_{\text{Pauli}}$  presents the repulsive four-electron interactions between occupied orbitals (Pauli repulsion), and  $\Delta E_{\text{orb}}$  is the stabilizing orbital interactions. The ratio  $\Delta E_{\text{elstat}}/\Delta E_{\text{orb}}$  indicates the electrostatic/covalent character of the bond. The bond dissociation energy is:

$$D_e = -(\Delta E_{\text{int}} + \Delta E_{\text{prep}}),$$

$\Delta E_{\text{prep}}$  (the fragment preparation energy) is the energy that is necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state that they have in the optimized structure. This method has already proven its usefulness for the analysis of the nature of metal–ligand bonding in ferrocene and some other sandwich compounds.<sup>[15]</sup>

The EDA data for the mononuclear complexes  $\text{CpRu}(\text{ring})$  in terms of interactions between  $[\text{ring}]^-$  and  $[\text{RuCp}]^+$  are given in Table 1 (Figure S1 in the Supporting Information). The energies of different conformers are very close, suggesting their fast transformation in solution (designations “ecl” and “stg” correspond to conformers having boron atoms in eclipsed and staggered positions relative to the carbon atoms of Cp, respectively). The total bonding energies for the anions  $[\text{C}_5\text{BH}_6]^-$  and  $[\text{C}_5\text{B}_2\text{H}_7]^-$  are very close, being approximately 11 kcal mol<sup>−1</sup> lower than for Cp<sup>−</sup> (the differences between average values for all conformers are cited in the text). Each additional BH group leads to a weakening of the electrostatic attraction by ca. 16 kcal mol<sup>−1</sup>, which correlates with the decrease of the total NBO charge of the ring atoms (−1.86, −1.76, and −1.68; Figure S2 in the Supporting Information). The attractive orbital interactions also decrease, but to a much lower extent (2–3 kcal mol<sup>−1</sup>). However, the resulting destabilizing effect is considerably compensated by the decrease of Pauli repulsion (ca. 8 and 17 kcal mol<sup>−1</sup> on addition of the first and the second BH group, respectively). Most likely, the main reason for the weakening of  $\Delta E_{\text{orb}}$  and  $\Delta E_{\text{Pauli}}$  is the increase of ring size resulting in poorer overlap of its orbit-

als with those of the  $[\text{RuCp}]^+$  fragment. A larger decrease of  $\Delta E_{\text{elstat}}$  compared to  $\Delta E_{\text{orb}}$  results in a slight growth of the covalent contribution (41.4, 42.7, and 43.9% for Cp<sup>−</sup>,  $[\text{C}_5\text{BH}_6]^-$ , and  $[\text{C}_5\text{B}_2\text{H}_7]^-$ ); however, the electrostatic bonding is still playing a main role. Although the total interaction energies for anions  $[\text{C}_5\text{BH}_6]^-$  and  $[\text{C}_5\text{B}_2\text{H}_7]^-$  are very close, the dissociation energy  $D_e$  is lower for borataborepine, which is explained by its larger preparation energy  $\Delta E_{\text{prep}}$  as a result of considerable distortion of this ring upon coordination. This distortion is caused by folding along the B...B line (8–9°) owing to the larger boron covalent radius vs. carbon and considerable bending of hydrogen atoms toward the metal atom as a result of reorientation of the ring  $\pi$ -orbitals for better overlap.<sup>[16]</sup>

Let us now analyze the bonding in the cationic triple-decker complexes  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$ . The energies of different conformers in this case are also very close. Table 2 and Figure S3 in the Supporting Information show the EDA data for these cations using  $[\text{ring}]^-$  and  $[\text{CpRu}\cdots\text{RuCp}]^{2+}$  as interacting fragments. The influence of additional BH units is very similar to that in mononuclear complexes. Strong decrease of electrostatic attraction (ca. 56 and 102 kcal mol<sup>−1</sup> on addition of the first and the second BH) is compensated by decrease of Pauli repulsion (ca. 41 and 129 kcal mol<sup>−1</sup>, respectively). Less considerable change of  $\Delta E_{\text{orb}}$  compared to  $\Delta E_{\text{elstat}}$  results in increase of the covalent character of the Ru–ring bond on insertion of BH fragments. Interestingly, the strongest orbital interactions are observed for the boratabenzene anion.

Table 2. Results of EDA for  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$  complexes with  $[\text{ring}]^-$  and  $[\text{CpRu}\cdots\text{RuCp}]^{2+}$  as interacting fragments (at BP86/TZ2P). Energy values in kcal mol<sup>−1</sup>.

| Ring:                            | Cp           |              | $\text{C}_5\text{BH}_6$ |              | $\text{C}_5\text{B}_2\text{H}_7$ |              |
|----------------------------------|--------------|--------------|-------------------------|--------------|----------------------------------|--------------|
| Conformer:                       | $D_{5h}$ ecl | $D_{5h}$ stg | $C_{2v}$ ecl            | $C_{2v}$ stg | $C_{2v}$ ecl                     | $C_{2v}$ stg |
| $\text{Ru}\cdots\text{Ru}$ [Å]   | 3.695        | 3.696        | 3.510                   | 3.519        | 3.408                            | 3.417        |
| $E_{\text{relative}}$            | 0            | 0.15         | 0.46                    | 0            | 0.66                             | 0            |
| $\Delta E_{\text{int}}$          | −370.8       | −369.9       | −370.5                  | −369.8       | −365.3                           | −365.3       |
| $\Delta E_{\text{Pauli}}$        | 557.6        | 557.1        | 520.5                   | 514.7        | 386.8                            | 383.2        |
| $\Delta E_{\text{elstat}}^{[a]}$ | −611.1       | −610.6       | −557.9                  | −554.4       | −453.2                           | −451.1       |
|                                  | (65.8)       | (65.9)       | (62.6)                  | (62.7)       | (60.3)                           | (60.3)       |
| $\Delta E_{\text{orb}}^{[a]}$    | −317.3       | −316.4       | −333.1                  | −330.2       | −298.9                           | −297.4       |
|                                  | (34.2)       | (34.1)       | (37.4)                  | (37.3)       | (39.7)                           | (39.7)       |
| $\Delta E_{\text{prep}}$         | 71.9         | 72.0         | 73.2                    | 72.9         | 72.2                             | 71.9         |
| $D_e$                            | 298.9        | 297.9        | 297.3                   | 296.9        | 293.1                            | 293.4        |

[a] The values in parentheses give the percentage (%) contribution to the total attractive interactions.

Table 1. Results of EDA for  $\text{CpRu}(\text{ring})$  complexes with  $[\text{ring}]^-$  and  $[\text{RuCp}]^+$  as interacting fragments (at BP86/TZ2P). Energy values in kcal mol<sup>−1</sup>.

| Ring:                            | Cp       |          | $\text{C}_5\text{BH}_6$ |           | $\text{C}_5\text{B}_2\text{H}_7$ |           |
|----------------------------------|----------|----------|-------------------------|-----------|----------------------------------|-----------|
| Conformer:                       | $D_{5h}$ | $D_{5d}$ | $C_s$ ecl               | $C_s$ stg | $C_s$ ecl                        | $C_s$ stg |
| $E_{\text{relative}}$            | 0        | 0.06     | 0                       | 0.64      | 0.03                             | 0         |
| $\Delta E_{\text{int}}$          | −228.5   | −228.4   | −217.5                  | −217.4    | −216.7                           | −217.3    |
| $\Delta E_{\text{Pauli}}$        | 222.4    | 217.2    | 212.1                   | 212.5     | 193.2                            | 193.9     |
| $\Delta E_{\text{elstat}}^{[a]}$ | −264.1   | −261.0   | −246.2                  | −246.3    | −230.1                           | −230.6    |
|                                  | (58.6)   | (58.6)   | (57.3)                  | (57.3)    | (56.1)                           | (56.1)    |
| $\Delta E_{\text{orb}}^{[a]}$    | −186.9   | −184.5   | −183.5                  | −183.6    | −179.8                           | −180.6    |
|                                  | (41.4)   | (41.4)   | (42.7)                  | (42.7)    | (43.9)                           | (43.9)    |
| $\Delta E_{\text{prep}}$         | 4.9      | 5.4      | 7.6                     | 7.6       | 11.7                             | 11.8      |
| $D_e$                            | 223.7    | 223.0    | 209.9                   | 209.8     | 205.0                            | 205.4     |

[a] The values in parentheses give the percentage (%) contribution to the total attractive interactions.

The comparison with mononuclear complexes shows that the electrostatic interaction in the case of bifacial bonding of  $[\text{ring}]^-$  with two  $[\text{RuCp}]^+$  cations is roughly twice of that for the bonding with only one cation in accordance with Coulomb's law. However, the orbital interactions increase to a lesser extent (70, 80, and 65% for Cp<sup>−</sup>,  $[\text{C}_5\text{BH}_6]^-$ , and  $[\text{C}_5\text{B}_2\text{H}_7]^-$ , respectively) since the same ring orbitals are used for the binding with the second  $[\text{RuCp}]^+$  fragment, resulting in lesser overlap populations of the Ru–ring bonds. The greater increase of  $\Delta E_{\text{elstat}}$  compared to  $\Delta E_{\text{orb}}$  results in a larger electrostatic character of the Ru–ring bond in the triple-decker complexes as compared to mononuclear



analogs.<sup>[17]</sup> The total interaction energy increases only by 62–70%. Furthermore, the large preparation energy (72–73 kcal mol<sup>−1</sup>), resulting mainly from a strong electrostatic repulsion of two [RuCp]<sup>+</sup> cations in the [CpRu...RuCp]<sup>2+</sup> unit, makes the dissociation energy of two Ru–ring bonds only 34–43% higher than that of one bond in the mononuclear analogs. In overall, these data indicate strong weakening of the Ru–ring bond on bifacial coordination.

To compare the stability of the triple-decker complexes, we also carried out the EDA analysis using their real precursors and expected decomposition products, CpRu(ring) and [RuCp]<sup>+</sup> (Table 3, Figure S4 in the Supporting Information). The total bonding energy increases by ca. 14 and 5 kcal mol<sup>−1</sup> on addition of the first and the second BH unit, respectively. However, the increasing preparation energy slightly reduces the stabilizing effect, making the boratabenzene and borataborepine complexes more stable than the cyclopentadienyl analog by ca. 11 and 14 kcal mol<sup>−1</sup>, respectively.

It is worth emphasizing that in the triple-decker [CpRu(ring)RuCp]<sup>+</sup> complexes the CpRu(ring) moiety acts as a 6-electron  $\pi$ -ligand toward the [RuCp]<sup>+</sup> cation, similar to benzene in [CpRu(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup>. The bonding character for the CpRu(ring) moiety and benzene is very close (52–54 and 57% covalent, respectively; Table S1 in the Supporting Information). The total bonding energies for the boron-containing CpRu(ring) moieties (ca. −94 and −100 kcal mol<sup>−1</sup>

Table 3. Results of EDA for [CpRu(ring)RuCp]<sup>+</sup> complexes with CpRu(ring) and [RuCp]<sup>+</sup> as interacting fragments (at BP86/TZ2P). Energy values in kcal mol<sup>−1</sup>.

| Ring:                                   | Cp                         |                            | C <sub>5</sub> BH <sub>6</sub> |                            | C <sub>5</sub> B <sub>2</sub> H <sub>7</sub> |                            |
|-----------------------------------------|----------------------------|----------------------------|--------------------------------|----------------------------|----------------------------------------------|----------------------------|
| Conformer:                              | <i>D</i> <sub>5h</sub> ecl | <i>D</i> <sub>5h</sub> stg | <i>C</i> <sub>2v</sub> ecl     | <i>C</i> <sub>2v</sub> stg | <i>C</i> <sub>2v</sub> ecl                   | <i>C</i> <sub>2v</sub> stg |
| $\Delta E_{\text{int}}$                 | −81.0                      | −80.7                      | −94.7                          | −94.3                      | −100.1                                       | −99.6                      |
| $\Delta E_{\text{Pauli}}$               | 189.6                      | 189.1                      | 189.3                          | 187.2                      | 147.7                                        | 152.3                      |
| $\Delta E_{\text{elstat}}^{\text{[a]}}$ | −125.1                     | −124.8                     | −135.6                         | −134.4                     | −114.8                                       | −117.4                     |
|                                         | (46.2)                     | (46.3)                     | (47.8)                         | (47.7)                     | (46.3)                                       | (46.6)                     |
| $\Delta E_{\text{orb}}^{\text{[a]}}$    | −145.5                     | −145.0                     | −148.4                         | −147.1                     | −133.0                                       | −134.5                     |
|                                         | (53.8)                     | (53.7)                     | (52.2)                         | (52.3)                     | (53.7)                                       | (53.4)                     |
| $\Delta E_{\text{prep}}$                | 5.6                        | 5.9                        | 8.5                            | 7.5                        | 12.0                                         | 10.5                       |
| <i>D</i> <sub>c</sub>                   | 75.4                       | 74.8                       | 86.2                           | 86.8                       | 88.2                                         | 89.2                       |

[a] The values in parentheses give the percentage (%) contribution to the total attractive interactions.

for ring = C<sub>5</sub>BH<sub>6</sub> and C<sub>5</sub>B<sub>2</sub>H<sub>7</sub>, respectively) are also very close to that for benzene (ca. −97 kcal mol<sup>−1</sup>).

Figure 5 compares main orbital interactions of the anions Cp<sup>−</sup>, [C<sub>5</sub>BH<sub>6</sub>]<sup>−</sup>, and [C<sub>5</sub>B<sub>2</sub>H<sub>7</sub>]<sup>−</sup> with the [RuCp]<sup>+</sup> cation. Addition of each BH group results in decreasing of energies of  $\pi$  and  $\delta$  [ring]<sup>−</sup> frontier orbitals in accordance with better electron delocalization, whereas the energies of lower lying  $\sigma$ -orbitals remain almost the same. This suggests a decrease of  $\pi$ -donation [ring]<sup>−</sup> → [RuCp]<sup>+</sup> and an increase of  $\delta$ -back donation [RuCp]<sup>+</sup> → [ring]<sup>−</sup> in the same sequence in accordance with better energy matching of interacting orbitals.

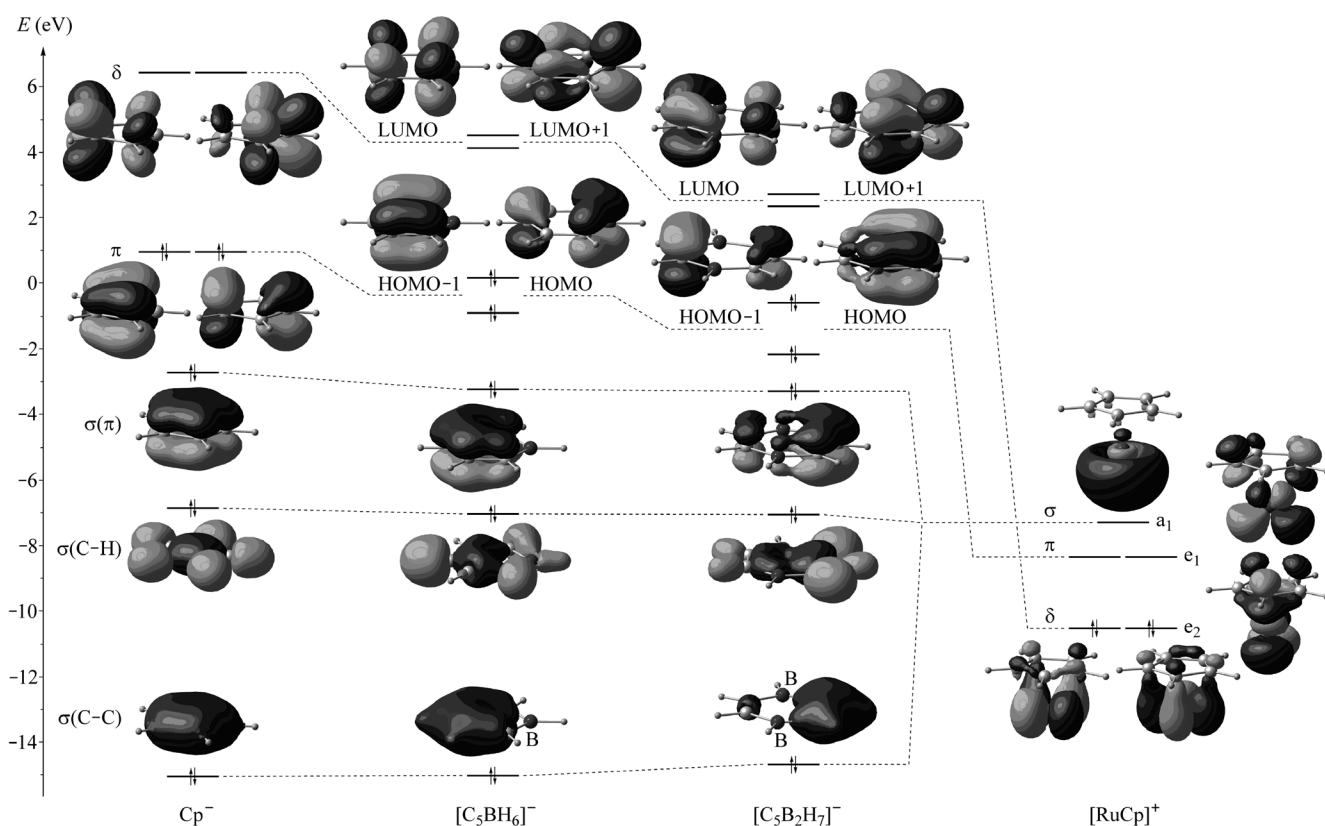


Figure 5. Main orbital interactions of the anions Cp<sup>−</sup>, [C<sub>5</sub>BH<sub>6</sub>]<sup>−</sup>, and [C<sub>5</sub>B<sub>2</sub>H<sub>7</sub>]<sup>−</sup> with [RuCp]<sup>+</sup> at BP86/def2-TZVPP/BP86/TZ2P (MO isodensity surface 0.05).

In order to estimate contributions of  $\pi$ ,  $\sigma$ , and  $\delta$  interactions, we analyzed fragment orbital (FO) occupancies in the complexes determined by Mulliken population analysis. For instance, in ruthenocene the unoccupied  $e_1$  (LUMO, LUMO+1) and  $a_1$  (LUMO+2) FOs of  $[\text{RuCp}]^+$  have 0.276 and 0.155 occupancies, respectively. The occupied  $e_2$  (HOMO, HOMO–1) FOs have 0.911 occupancy in the complex, suggesting that contribution of each of them to the bonding is equal to 0.089. Thus, the contributions of  $\pi$ -,  $\sigma$ -, and  $\delta$ -interactions are estimated to be 62.3, 17.5, and 20.2%, respectively. Similar data for the  $\text{CpRu}(\text{ring})$  and  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$  complexes, determined both from  $[\text{RuCp}]^+$  and  $[\text{ring}]^-$  FO contributions to occupied MOs, are given in Table 4 (Figure S5 in the Supporting Information).

Table 4. Ruthenium NBO charges (a.u.) and the percentage (%) contributions of  $\pi$ -,  $\sigma$ -, and  $\delta$ -interactions for  $\text{CpRu}(\text{ring})$  (normal) and  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$  (*italics*) at BP86/def2-TZVPP/BP86/TZ2P.

| Ring                                               | $q_{\text{Ru}}$ | Contribution (%) |             |             | Comment |
|----------------------------------------------------|-----------------|------------------|-------------|-------------|---------|
|                                                    |                 | $\pi$            | $\sigma$    | $\delta$    |         |
| $\text{Cp}(\text{ecl})^{[a]}$                      | 0.07            | 62.3             | 17.5        | 20.2        | [b]     |
|                                                    |                 | <i>44.9</i>      | <i>33.5</i> | <i>21.6</i> |         |
|                                                    | <i>0.12</i>     | 60.1             | 20.5        | 19.4        | [c]     |
|                                                    |                 | <i>48.4</i>      | <i>31.4</i> | <i>20.2</i> |         |
| $\text{C}_5\text{BH}_6(\text{stg})^{[a]}$          | 0.10            | 66.2             | 13.8        | 20.0        | [d]     |
|                                                    |                 | <i>51.1</i>      | <i>22.5</i> | <i>26.5</i> |         |
|                                                    | <i>0.12</i>     | 56.2             | 18.0        | 25.9        | [b]     |
|                                                    |                 | <i>39.6</i>      | <i>35.4</i> | <i>25.1</i> |         |
| $\text{C}_5\text{B}_2\text{H}_7(\text{stg})^{[a]}$ | 0.15            | 55.9             | 19.9        | 24.2        | [c]     |
|                                                    |                 | <i>44.3</i>      | <i>32.6</i> | <i>23.1</i> |         |
|                                                    | <i>0.15</i>     | 52.1             | 17.0        | 30.9        | [b]     |
|                                                    |                 | <i>37.9</i>      | <i>32.7</i> | <i>29.5</i> |         |
|                                                    |                 | 52.4             | 17.3        | 30.4        | [c]     |
|                                                    |                 | <i>43.1</i>      | <i>29.9</i> | <i>27.0</i> |         |

[a] Orientation of Cp rings relative to a central ring. [b] From the  $[\text{RuCp}]^+$  FO contributions to occupied MOs. [c] From the  $[\text{ring}]^-$  FO contributions to occupied MOs. [d] According to EDA at BP86/TZ2P.

As expected, for the sandwich compounds  $\text{CpRu}(\text{ring})$  the contribution of  $\pi$ -donation decreases, whereas that of  $\delta$ -back donation increases on insertion of BH groups. The role of  $\sigma$ -donation remains almost unchanged. Although  $\pi$  (HOMO, HOMO–1) ring orbitals play the main role in  $\pi$ -donation, a weak interaction of  $\pi(\sigma)$  orbitals (Figure 6 shows such orbitals for the borataborepine anion) with  $e_1$  (LUMO, LUMO+1) of  $[\text{RuCp}]^+$  is also observed (4.6, 6.1, and 8.4% from the total  $\pi$ -donation for  $\text{Cp}^-$ ,  $[\text{C}_5\text{BH}_6]^-$ , and  $[\text{C}_5\text{B}_2\text{H}_7]^-$ , respectively). Main contributions to  $\sigma$ -donation belong to ring orbitals  $\sigma(\pi)$  (66.1, 60.3, and 48.9%) and  $\sigma(\text{C–C})$  (33.4, 34.4, and 29.0%, respectively) (Figure 5). The interaction with the  $\sigma(\text{C–H})$  orbital is negligible for  $\text{Cp}^-$  (0.5%) and becomes significant for the boron heterocycles  $[\text{C}_5\text{BH}_6]^-$  (5.3%) and  $[\text{C}_5\text{B}_2\text{H}_7]^-$  (22.1%).

In the triple-decker complexes  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$ , a central ring ligand is bifacially bonded with two metal atoms forcing it to more effective use of available orbitals. In the first place, it leads to the strengthening of interactions which are weak in mononuclear complexes. In accordance with this tendency, the percentage contribution of  $\sigma$ -

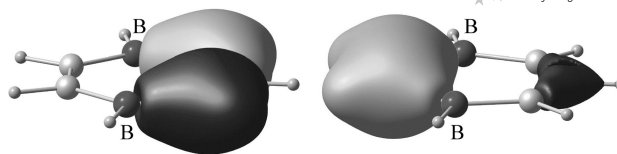


Figure 6.  $\pi(\sigma)$  Frontier orbitals (HOMO–14, HOMO–15) of the  $[\text{C}_5\text{B}_2\text{H}_7]^-$  anion (isodensity 0.05).

donation increases and that of  $\pi$ -donation decreases. Upon addition of BH groups, the strength of  $\pi$ -,  $\sigma$ -, and  $\delta$ -interactions in the triple-decker complexes changes in the same order as in  $\text{CpRu}(\text{ring})$ . The role of  $\pi(\sigma)$  orbitals in  $\pi$ -donation is considerably larger than in mononuclear analogs (13.2, 17.7, and 19.6% for  $\text{Cp}^-$ ,  $[\text{C}_5\text{BH}_6]^-$ , and  $[\text{C}_5\text{B}_2\text{H}_7]^-$ , respectively), being the strongest for the borataborepine anion. The role of orbitals  $\sigma(\text{C–C})$  (50.3, 54.2, and 40%) and  $\sigma(\text{C–H})$  (1.9, 10.6, and 27.2%) in  $\sigma$ -donation also increases.

In the case of highly symmetric cyclopentadienyl complexes, the contributions of  $\pi$ -,  $\sigma$ -, and  $\delta$ -orbitals to the total covalent bonding were also determined by the EDA method (Table 4). In general, these data are in good agreement with those obtained by Mulliken population analysis. However, a considerably larger growth of  $\delta$ -bonding upon bifacial coordination is worth mentioning.

The back donation is stronger for better electron-accepting ligands, and therefore data of Table 4 suggest that the acceptor ability of the ring ligands increases in the following order:  $\text{Cp}^- < [\text{C}_5\text{BH}_6]^- < [\text{C}_5\text{B}_2\text{H}_7]^-$ . The ruthenium NBO charges are in accordance with this conclusion.

## Conclusions

The electrophilic stacking of the ruthenium sandwich compounds **2a–c** with  $[\text{ML}]^+$  fragments has proven to be effective for the preparation of cationic triple-decker complexes with a bridging 4-borataborepine ligand  $[\text{C}_5\text{B}_2\text{RMe}_5\text{H}]^-$ . The metal–ring bonding in two series of the related complexes  $\text{CpRu}(\text{ring})$  and  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$  (ring = Cp,  $\text{C}_5\text{BH}_6$ ,  $\text{C}_5\text{B}_2\text{H}_7$ ) was studied by using energy decomposition scheme and Mulliken population analysis. The attractive interactions between  $\text{Cp}^-$  and  $[\text{RuCp}]^+$  in ruthenocene are 41.4% covalent and 58.6% electrostatic. The covalent bonding increases on incorporation of BH groups ( $[\text{C}_5\text{BH}_6]^-$  42.7%,  $[\text{C}_5\text{B}_2\text{H}_7]^-$  43.9%) and decreases on bifacial coordination of the ring ligand with two metal atoms ( $\text{Cp}^-$  34.2%,  $[\text{C}_5\text{BH}_6]^-$  37.3%,  $[\text{C}_5\text{B}_2\text{H}_7]^-$  39.7%).

In the triple-decker complexes  $[\text{CpRu}(\text{ring})\text{RuCp}]^+$ , the bonding between the  $\text{CpRu}(\text{ring})$  moiety and  $[\text{RuCp}]^+$  is predominantly covalent (52–54%). The bond dissociation energy increases with the acceptor ability of the ring ligand:  $\text{Cp}^- \ll [\text{C}_5\text{BH}_6]^- < [\text{C}_5\text{B}_2\text{H}_7]^-$ , making the boron-containing triple-decker complexes much more stable than the cyclopentadienyl analog.

Both for mono- and dinuclear complexes, the contribution of  $\pi$ -donation to the total covalent bonding decreases, whereas that of  $\delta$ -back donation increases on ad-

dition of BH groups due to a better energy matching of interacting orbitals. The bifacial bonding of the ring ligand is characterized by a higher contribution of  $\sigma$ -donation compared to the monofacial one; however,  $\pi$ -donation is always of primary importance.

## Experimental Section

**General:** All manipulations were performed under dry nitrogen by using standard vacuum-line and Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. Compounds **1**,<sup>[1]</sup> **2b**,<sup>c,[4]</sup>  $[\text{CpRu}(\text{MeCN})_3]\text{PF}_6$ ,<sup>[18]</sup>  $[\text{Cp}^*\text{RuCl}]_4$ ,<sup>[19]</sup>  $[(\text{C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]\text{PF}_6$ ,<sup>[20]</sup>  $[(\text{cod})\text{RhCl}]_2$ ,<sup>[21]</sup>  $[(\text{cod})\text{IrCl}]_2$ ,<sup>[22]</sup> and  $\text{AgBF}_4 \cdot 3\text{dioxane}$ <sup>[23]</sup> were prepared as described in the literature. Propyne was obtained from ABCR GmbH & Co. KG and dried with  $\text{CaCl}_2$  before use. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra were recorded with a Bruker DRX200 spectrometer operating at 200 and 64 MHz, respectively.

**$\text{Cp}^*\text{Ru}(\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})$  (**2a**):** A solution of complex **1** (235 mg, 0.64 mmol) in pentane (5 mL) was treated with propyne at room temperature for 5 min to give immediately a yellow solid. This solid was filtered off, washed with pentane (ca. 1 mL) and dried in vacuo. Yield 210 mg (80%). Complex **2a** is moderately soluble in pentane and thf and can be purified by recrystallization. Column chromatography (silica gel; pentane) cannot be used owing to fast elimination of one BMe unit to give the boratabenzene complex  $\text{Cp}^*\text{Ru}(\text{C}_5\text{BMe}_5\text{H})$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.54 (s, 1 H, CH), 1.94 (s, 6 H, Me), 1.88 (s, 6 H, Me), 1.49 (s, 15 H, Cp\*), 0.62 (s, 6 H, BMe) ppm.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 26.4 (br., BMe) ppm.  $\text{C}_{21}\text{H}_{34}\text{B}_2\text{Ru}$  (409.20): calcd. C 61.64, H 8.38; found C 61.53, H 8.38.

**$[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})\text{Co}(\text{C}_4\text{Me}_4)]\text{PF}_6$  (**3aPF**<sub>6</sub>):** A solution of complex **2a** (42 mg, 0.1 mmol) and  $[(\text{C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]\text{PF}_6$  (44 mg, 0.1 mmol) in thf (5 mL) was stirred overnight. The red precipitate was filtered off, dissolved in acetone and eluted through a short silica gel column (0.5  $\times$  0.5 cm). Evaporation of the solvent gave a red solid which was dried in vacuo. Yield 37 mg (51%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 6.09 (s, 1 H, CH), 2.52 (s, 6 H, Me), 2.22 (s, 6 H, Me), 1.54 (s, 15 H, Cp\*), 1.25 (s, 6 H, BMe), 0.98 (s, 12 H,  $\text{C}_4\text{Me}_4$ ) ppm.  $^{11}\text{B}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 14.1 (br., BMe) ppm.  $\text{C}_{29}\text{H}_{46}\text{B}_2\text{CoF}_6\text{PRu}$  (721.27): calcd. C 48.29, H 6.43; found C 48.21, H 6.38.

**$[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})\text{Co}(\text{C}_4\text{Me}_4)]\text{PF}_6$  (**3bPF**<sub>6</sub>):** This complex was prepared similar to **3aPF**<sub>6</sub> as a red solid by starting from **2b** (47 mg, 0.1 mmol) and  $[(\text{C}_4\text{Me}_4)\text{Co}(\text{MeCN})_3]\text{PF}_6$  (43 mg, 0.1 mmol). Yield 69 mg (88%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 7.76 (d,  $J$  = 7.5 Hz, 2 H, Ph), 7.61 (t,  $J$  = 7.3 Hz, 2 H, Ph), 7.50 (d,  $J$  = 5.6 Hz, Ph), 6.38 (s, 1 H, CH), 2.63 (s, 3 H, Me), 2.34 (s, 6 H, Me), 1.57 (s, 15 H, Cp\*), 1.35 (s, 3 H, Me), 1.22 (s, 3 H, Me), 1.00 (s, 12 H,  $\text{C}_4\text{Me}_4$ ) ppm.  $^{11}\text{B}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 14.3 (br., BMe) ppm.  $\text{C}_{34}\text{H}_{48}\text{B}_2\text{CoF}_6\text{PRu}$  (783.36): calcd. C 52.13, H 6.18; found C 52.20, H 6.21.

**$[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-7-PhCH}_2\text{C}_5\text{B}_2\text{Me}_5\text{H})\text{RuCp}^*]\text{PF}_6$  (**6cPF**<sub>6</sub>):** This complex was prepared similar to **3aPF**<sub>6</sub> as an orange solid by starting from **2c** (48 mg, 0.1 mmol) and  $[\text{CpRu}(\text{MeCN})_3]\text{PF}_6$  (43 mg, 0.1 mmol) in thf (5 mL). Yield 68 mg (86%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 7.68 (d,  $J$  = 3.8 Hz, 2 H, Ph), 7.47–7.30 (m, 3 H, Ph), 6.54 (s, 1 H, CH), 4.44 (d,  $J$  = 12.4 Hz, 1 H,  $\text{CH}_2$ ), 4.05 (s, 5 H, Cp), 3.52 (d,  $J$  = 12.4 Hz, 1 H,  $\text{CH}_2$ ), 2.43 (s, 3 H, Me), 2.38 (s, 6 H, Me), 1.65 (s, 15 H, Cp\*), 1.39 (s, 3 H, Me), 1.19 (s, 3 H, Me) ppm.  $^{11}\text{B}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 15.3 (br., BMe) ppm.

$\text{C}_{32}\text{H}_{43}\text{B}_2\text{F}_6\text{PRu}_2$  (796.56): calcd. C 48.26, H 5.44; found C 48.49, H 5.41.

**$[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})\text{RuCp}^*]\text{BF}_4$  (**4aBF**<sub>4</sub>):** Complex **2a** (42 mg, 0.1 mmol),  $[\text{Cp}^*\text{RuCl}]_4$  (27 mg, 0.025 mmol), and  $\text{TIBF}_4$  (29 mg, 0.1 mmol) were stirred in thf (5 mL) overnight. The orange solid formed was filtered off and extracted with  $\text{CH}_2\text{Cl}_2$ . The clear orange extract was concentrated in vacuo to ca. 0.5 mL, and  $\text{Et}_2\text{O}$  (10 mL) was added to precipitate a yellow solid which was filtered off and washed with  $\text{Et}_2\text{O}$ . The solid was dissolved in acetone and eluted through a short layer of silica gel. The orange band was concentrated to give an orange solid which was dried in vacuo. Yield 56 mg (77%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 5.86 (s, 1 H, CH), 2.42 (s, 6 H, Me), 2.13 (s, 6 H, Me), 1.55 (s, 30 H, Cp\*), 1.13 (s, 6 H, BMe) ppm.  $^{11}\text{B}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 10.4 (br., BMe), –0.9 (s,  $\text{BF}_4$ ) ppm.  $\text{C}_{31}\text{H}_{49}\text{B}_3\text{F}_4\text{Ru}_2 \cdot 0.25\text{CH}_2\text{Cl}_2$  (753.75): calcd. C 49.80, H 6.62; found C 49.73, H 6.58.

**Formation of  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})\text{RuCp}^*]\text{BF}_4$  (**4bBF**<sub>4</sub>) and  $[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^6\text{-}\eta^7\text{-7-PhC}_5\text{B}_2\text{Me}_5\text{H})\text{RuCp}^*]\text{BF}_4$  (**5BF**<sub>4</sub>):** The reaction was carried out similar to the preparation of **4aBF**<sub>4</sub> by starting from **2b** (47 mg, 0.1 mmol),  $[\text{Cp}^*\text{RuCl}]_4$  (27 mg, 0.025 mmol), and  $\text{TIBF}_4$  (29 mg, 0.1 mmol). The yellow solid obtained was found to be a mixture of complexes **4bBF**<sub>4</sub> and **5BF**<sub>4</sub> in a 1:3 ratio. **4bBF**<sub>4</sub>:  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 7.42–7.51 (m, 5 H, Ph), 2.34 (s, 3 H, Me), 1.96 (s, 6 H, Me), 1.42 (s, 30 H, Cp\*), 1.10 (s, 3 H, Me), 1.05 (s, 3 H, Me) ppm. **5BF**<sub>4</sub>:  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 6.28 [t,  $J$  = 5.7 Hz, 1 H, CH (Ph)], 5.68–5.87 (m, 5 H, Ph and CH), 2.16 (s, 3 H, Me), 1.91 (s, 15 H,  $\eta^6\text{-RuCp}^*$ ), 1.85 (s, 3 H, Me), 1.84 (s, 3 H, Me), 1.49 (s, 15 H,  $\eta^7\text{-RuCp}^*$ ), 0.72 (s, 3 H, Me), 0.59 (s, 3 H, Me) ppm.

**$[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})\text{Rh}(\text{cod})]\text{BF}_4$  (**7aBF**<sub>4</sub>):** A mixture of  $[(\text{cod})\text{RhCl}]_2$  (25 mg, 0.05 mmol) and  $\text{AgBF}_4 \cdot 3\text{dioxane}$  (46 mg, 0.1 mmol) was stirred in thf (5 mL) for 1 h. The yellow solution formed (containing the  $[(\text{cod})\text{Rh}(\text{thf})_x]^+$  species) was separated by syringe from the precipitate of  $\text{AgCl}$  and added to a solution of **2a** (42 mg, 0.1 mmol) in thf (5 mL). After stirring overnight, the reaction mixture was concentrated to dryness. The yellow solid was washed with  $\text{Et}_2\text{O}$ , dissolved in acetone and eluted through a short layer of silica gel. The yellow band was concentrated in vacuo to ca. 0.5 mL. Addition of  $\text{Et}_2\text{O}$  (ca. 10 mL) precipitated a yellow solid which was filtered off, washed with  $\text{Et}_2\text{O}$  and dried in vacuo. Yield 61 mg (86%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 7.10 (s, 1 H, CH), 3.79 [br, 4 H, CH (cod)], 2.46 (s, 6 H, Me), 2.27 (s, 6 H, Me), 2.09 [m, 4 H,  $\text{CH}_2$  (cod)], 1.71 [m, 4 H,  $\text{CH}_2$  (cod)], 1.64 (s, 15 H, Cp\*), 0.69 (s, 6 H, BMe) ppm.  $^{11}\text{B}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 13.2 (br., BMe), –0.9 (s,  $\text{BF}_4$ ) ppm.  $\text{C}_{29}\text{H}_{46}\text{B}_3\text{F}_4\text{RhRu}$  (707.09): calcd. C 49.26, H 6.56; found C 49.23, H 6.48.

**$[\text{Cp}^*\text{Ru}(\mu\text{-}\eta^7\text{-}\eta^7\text{-C}_5\text{B}_2\text{Me}_6\text{H})\text{Ir}(\text{cod})]\text{BF}_4$  (**8aBF**<sub>4</sub>):** The complex was prepared similar to **7aBF**<sub>4</sub> by starting from **2a** (42 mg, 0.1 mmol),  $[(\text{cod})\text{IrCl}]_2$  (34 mg, 0.05 mmol), and  $\text{AgBF}_4 \cdot 3\text{dioxane}$  (46 mg, 0.1 mmol). Yield 46 mg (58%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 6.69 (s, 1 H, CH), 3.71 [m, 4 H, CH (cod)], 2.35 (s, 6 H, Me), 2.32 (s, 6 H, Me), 1.88 [m, 4 H,  $\text{CH}_2$  (cod)], 1.63 (s, 15 H, Cp\*), 1.46 [m, 4 H,  $\text{CH}_2$  (cod)], 0.99 (s, 6 H, BMe) ppm.  $^{11}\text{B}$  NMR ( $[\text{D}_6]\text{acetone}$ ):  $\delta$  = 12.1 (br., BMe), –0.9 (s,  $\text{BF}_4$ ) ppm.  $\text{C}_{29}\text{H}_{46}\text{B}_3\text{F}_4\text{IrRu}$  (796.40): calcd. C 43.74, H 5.82; found C 43.75, H 5.84.

**X-ray Crystal Structure Determinations:** Crystals of **3bPF**<sub>6</sub>, **7aBF**<sub>4</sub>, and **8aBF**<sub>4</sub> were obtained by slow diffusion in a two-layer system, an acetone solution of complex/diethyl ether at –30 °C. Crystals of **4aBF**<sub>4</sub> were obtained by slow concentration of an acetone/ $\text{CH}_2\text{Cl}_2$  solution at room temperature. Crystal data and details of the structure determinations are listed in Table 5. Intensity data were collected at 100 K with a Bruker AXS Smart 1000 CCD dif-



Table 5. Crystal data and structure-refinement parameters for **3bPF<sub>6</sub>**, **4aBF<sub>4</sub>**, **7aBF<sub>4</sub>**, and **8aBF<sub>4</sub>**.

|                                                     | <b>3bPF<sub>6</sub></b>                                             | <b>4aBF<sub>4</sub></b>                                                       | <b>7aBF<sub>4</sub></b>                                            | <b>8aBF<sub>4</sub></b>                                            |
|-----------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|
| Empirical formula                                   | C <sub>34</sub> H <sub>48</sub> B <sub>2</sub> CoF <sub>6</sub> PRu | C <sub>31</sub> H <sub>47</sub> B <sub>3</sub> F <sub>4</sub> Ru <sub>2</sub> | C <sub>29</sub> H <sub>46</sub> B <sub>3</sub> F <sub>4</sub> RhRu | C <sub>29</sub> H <sub>46</sub> B <sub>3</sub> F <sub>4</sub> IrRu |
| Formula mass                                        | 783.31                                                              | 730.26                                                                        | 707.07                                                             | 796.36                                                             |
| Crystal size [mm]                                   | 0.10 × 0.10 × 0.10                                                  | 0.25 × 0.25 × 0.15                                                            | 0.10 × 0.10 × 0.03                                                 | 0.20 × 0.15 × 0.10                                                 |
| Crystal system                                      | triclinic                                                           | orthorhombic                                                                  | orthorhombic                                                       | monoclinic                                                         |
| Space group                                         | <i>P</i> <sub>1</sub>                                               | <i>Ama</i> 2                                                                  | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>              | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                 |
| <i>a</i> [Å]                                        | 10.5267(10)                                                         | 15.9985(10)                                                                   | 12.6945(7)                                                         | 12.9275(6)                                                         |
| <i>b</i> [Å]                                        | 12.2670(12)                                                         | 9.9311(6)                                                                     | 13.5925(7)                                                         | 13.7811(7)                                                         |
| <i>c</i> [Å]                                        | 13.2352(13)                                                         | 18.7859(11)                                                                   | 16.4172(9)                                                         | 15.9095(8)                                                         |
| $\alpha$ [°]                                        | 89.346(2)                                                           | 90                                                                            | 90                                                                 | 90                                                                 |
| $\beta$ [°]                                         | 74.048(2)                                                           | 90                                                                            | 90                                                                 | 94.5680(10)                                                        |
| $\gamma$ [°]                                        | 84.158(2)                                                           | 90                                                                            | 90                                                                 | 90                                                                 |
| <i>V</i> [Å <sup>3</sup> ]                          | 1634.5(3)                                                           | 2984.8(3)                                                                     | 2832.8(3)                                                          | 2825.4(2)                                                          |
| <i>Z</i>                                            | 2                                                                   | 4                                                                             | 4                                                                  | 4                                                                  |
| <i>D</i> <sub>calcd.</sub> [g cm <sup>-3</sup> ]    | 1.592                                                               | 1.625                                                                         | 1.658                                                              | 1.872                                                              |
| Absorption coefficient [mm <sup>-1</sup> ]          | 1.077                                                               | 1.058                                                                         | 1.160                                                              | 5.285                                                              |
| <i>F</i> (000)                                      | 804                                                                 | 1488                                                                          | 1440                                                               | 1568                                                               |
| <i>T</i> <sub>max</sub> and <i>T</i> <sub>min</sub> | 0.7455 and 0.5494                                                   | 0.7464 and 0.6635                                                             | 0.7464 and 0.6618                                                  | 0.7464 and 0.6479                                                  |
| $\theta$ range [°]                                  | 2.0–28.7                                                            | 2.2–32.2                                                                      | 2.0–30.5                                                           | 2.0–31.0                                                           |
| Completeness                                        | 99.8                                                                | 97.3                                                                          | 100                                                                | 99.9                                                               |
| Reflections collected                               | 34110                                                               | 37400                                                                         | 68859                                                              | 69697                                                              |
| Independent reflections                             | 8442 ( <i>R</i> <sub>int</sub> = 0.0698)                            | 5190 ( <i>R</i> <sub>int</sub> = 0.0402)                                      | 8665 ( <i>R</i> <sub>int</sub> = 0.0964)                           | 8995 ( <i>R</i> <sub>int</sub> = 0.0792)                           |
| Absolute structure parameter                        | –                                                                   | –                                                                             | –0.04(3)                                                           | –                                                                  |
| Parameters                                          | 433                                                                 | 205                                                                           | 354                                                                | 354                                                                |
| Index ranges                                        | –13 ≤ <i>h</i> ≤ 14<br>–16 ≤ <i>k</i> ≤ 16<br>0 ≤ <i>l</i> ≤ 17     | 0 ≤ <i>h</i> ≤ 23<br>0 ≤ <i>k</i> ≤ 14<br>–27 ≤ <i>l</i> ≤ 27                 | –18 ≤ <i>h</i> ≤ 18<br>0 ≤ <i>k</i> ≤ 19<br>0 ≤ <i>l</i> ≤ 23      | –18 ≤ <i>h</i> ≤ 18<br>0 ≤ <i>k</i> ≤ 19<br>0 ≤ <i>l</i> ≤ 23      |
| <i>R</i> ( <i>F</i> ) (observed)                    | 0.0467                                                              | 0.0213                                                                        | 0.0387                                                             | 0.0334                                                             |
| <i>wR</i> <sub>2</sub> (all data)                   | 0.1140                                                              | 0.0528                                                                        | 0.0813                                                             | 0.0703                                                             |
| GooF                                                | 1.067                                                               | 1.123                                                                         | 1.103                                                              | 1.067                                                              |
| Largest diff. peak/hole [e Å <sup>-3</sup> ]        | 0.947/–1.058                                                        | 0.858/–0.443                                                                  | 1.349/–1.109                                                       | 2.093/–1.645                                                       |

fractometer (Mo-*K*<sub>α</sub> radiation, graphite monochromator,  $\lambda$  = 0.71073 Å). Crystals of **4aBF<sub>4</sub>** were racemic twins. Data were corrected for Lorentz, polarization and absorption effects (semiempirical, SADABS).<sup>[24]</sup> The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors (DIRDIF)<sup>[25]</sup> and refined by full-matrix least-squares methods based on *F*<sup>2</sup>.<sup>[26]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined with a riding model. CCDC-672081 (**3b**), -672082 (**4a**), -672083 (**7a**), and -672084 (**8a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Computational Details:** The geometries have been optimized at the gradient-corrected DFT level of theory by using the exchange functional of Becke<sup>[27]</sup> and the correlation functional of Perdew<sup>[28]</sup> (BP86). Uncontracted Slater-type orbitals were employed as basis functions for the SCF calculations.<sup>[29]</sup> Scalar relativistic effects were considered by using the zero-order regular approximation (ZORA).<sup>[30]</sup> The all-electron ZORA relativistic valence triple- $\zeta$  basis set, augmented by two polarization functions TZ2P, was used. The bonding interactions were studied by means of Morokuma-Ziegler energy decomposition analysis.<sup>[31]</sup> The calculations were carried out by using the ADF 2006.01 program package.<sup>[32]</sup> Fragment orbital occupations were determined by Mulliken population analysis using the AOMix program.<sup>[33]</sup> The input files were obtained from single-point calculations at the BP86/TZ2P-optimized structures with the Gaussian 98 program<sup>[34]</sup> by using the BP86 functional and a basis set of triple- $\zeta$  quality with two polarization functions def2-TZVPP.<sup>[35]</sup> Natural charges were obtained by using

the NBO scheme<sup>[36]</sup> at the same level of theory. The ChemCraft program<sup>[37]</sup> was used for molecular modeling and visualization.

**Supporting Information** (see footnote on the first page of this article): Details of DFT calculations for CpRu(ring) and [CpRu(ring)-RuCp]<sup>+</sup> (ring = Cp, C<sub>5</sub>BH<sub>6</sub>, C<sub>5</sub>B<sub>2</sub>H<sub>7</sub>) complexes as well as free ring ligands and the [RuCp]<sup>+</sup> cation (atomic coordinates for optimized geometry, energy data, fragment orbital contributions to occupied MOs, NBO charges and C–C/C–B distances in ring ligands), extended versions of Tables 2 and 3 (with information for other conformers), diagrams corresponding to Tables 1, 2, 3, and 4, energy decomposition analysis of the [CpRu(C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> complex.

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF AG. We thank Prof. L. Gade for generous support. A. R. K. thanks the Division of General Chemistry and Material Sciences of RAS.

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Received: January 3, 2008  
Published Online: June 13, 2008