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Hybrid diborolyl/carbaboranyl triple-decker compounds: [(η^5-pentamethylcyclopentdienyl)ruthenium(μ,η^5-1,3-diborolyl)-rhodiumcarbaboranyl] complexes

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Dedicated to Prof. Sheldon Shore on the occasion of his 70th birthday.

Abstract

Reaction of the violet sandwich [(η^5-C_5Me_5)Ru{η^5-$(CMe)_2(BMe)_2(CMe)$}] with $[(C_2H_4)_2RhCl]_2$ generates the tetranuclear complex [(η^5-C_5Me_5)Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}$RhCl]_2$ (**7**). Treatment of **7** with the *nido*-2,3-$Et_2C_2B_4H_5^{1-}$ anion leads to the violet air-sensitive triple decker complex [(η^5-C_5Me_5)Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}Rh(η^5-2,3-$Et_2C_2B_4H_5$) (**8**), in which the neutral carborane functions as a 5e donor. Its structure is derived from ^1H-, ^{11}B-, ^{13}C-NMR and mass spectral data. The green paramagnetic triple-decker [(η^5-C_5Me_5)Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}Rh($C_2B_9H_{11}$)] (**9**) is obtained from the *nido*-7,8-$C_2B_9H_{12}^{1-}$ carboranyl anion and **7**. Reaction of **7** with the *nido*-6-Me-5,6,9-$C_3B_7H_9^{1-}$ anion yields the green, air-stable triple-decker complexes [(η^5-C_5Me_5)Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}Rh(2-Me-2,3,4-$C_3B_7H_9$)] (**10a**) and [(η^5-C_5Me_5)Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}Rh(4-Me-2,3,4-$C_3B_7H_9$)] (**10b**) having 30 valence electrons. An X-ray structure analysis of **10a** confirms the expected octadecahedral geometry for the *closo*-RhC_3B_7 cluster framework. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carboranes; Diboroles; Ruthenium; Rhodium; Triple-decker complexes

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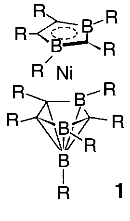
1. Introduction

Metallacarboranes **1**–**3** combine the complex chemistry of the 2,3-dihydro-1,3-diborole heterocycle [1] with that of the tricarbahexaboranyl ligand [2–4]. The extension of this approach led to the syntheses of a number of triple-decker-complexes, e.g. **4**–**6** [5–7] with bridging 1,3-diborolyl and terminal carboranyl ligands. These dinuclear complexes incorporate the 17VE fragment [(η^5-C_5R_5)Co(μ,η^5-$C_3B_2R_5$)] which is derived from the corresponding 18VE sandwich having an acidic axial C–H moiety [1]. Recently, we have reported derivatives of the unusual ruthenium sandwich complex [(η^5-C_5Me_5)Ru(η^5-$C_3B_2R_5$)] which formally have 16VE. However, by an unprecedented folding of the 2,3-dihydro-1,3-diborolyl ligand along the B–B vector (41° in the corresponding iron complex) [8] the metals are able to interact with a combination of σ(B–C) orbitals and thus complete their 18VE shells. Due to its high Lewis acidity, the ruthenium sandwich reacts with $[(C_2H_4)_2RhCl]_2$ to form the tetranuclear compound **7** [9]. With anionic carboranyl ligands it forms stable triple-decker complexes. We here report reactions of **7** with Li^+(*nido*-2,3-$Et_2C_2B_4H_5^{1-}$) [5], Li^+(*nido*-1,2-$C_2B_9H_{12}^{1-}$) [7] and Li^+(*nido*-6-Me-5,6,9-$C_3B_7H_9^{1-}$) [10] leading to the new triple-decker complexes **8**–**10**.



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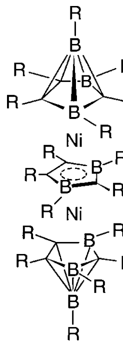

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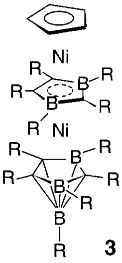

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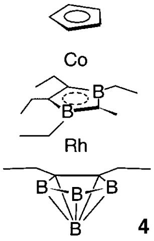

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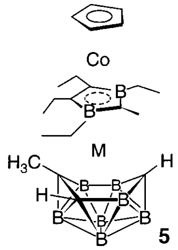

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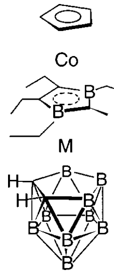

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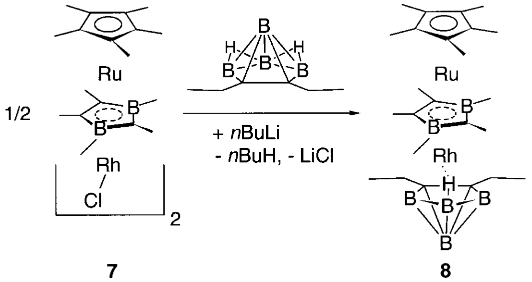
2. Results and discussion

2.1. Synthesis of triple-decker complexes *8*, *9*, and *10*

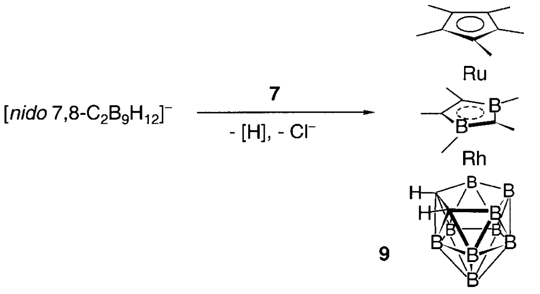
The carborane *nido*-2,3-Et$_2$C$_2$B$_4$H$_6$ was deprotonated with butyllithium at −60°C, and the anion reacted with **7** to give the air-sensitive violet triple-decker **8** (Scheme 1). The compound was isolated in 21% yields following chromatography on silica gel using hexane as eluant. Contact with air results in a brown product of unknown structure.

The solution structure of **8** is derived from its ^{1}H-, ^{11}B-, ^{13}C-NMR spectra and mass spectral data. In the ^{1}H-NMR spectrum only singlets for the methyl substituents and a broad high-field signal at −5.2 ppm are observed. Previous studies of the reactions of the *nido*-2,3-Et$_2$C$_2$B$_4$H$_5^{1-}$ anion with reagents such as CpFe(CO)$_2$I had been found to result in hydrogen transfer to the metal from the carborane ligand to yield products, such as CpFe(H)(2,3-R$_2$C$_2$B$_4$H$_4$), containing a metal hydride [11]. In **8**, the broad −5.2 ppm resonance is at a lower field than that expected for a pure metal-hydride, but higher than that of a normal boron–boron bridging hydrogen. The shift of this resonance coupled with the fact that it does not exhibit any observable ^{103}Rh coupling suggests that it may have significant Rh–H–B bridging interactions. A similar Rh–H–B interaction has previously been crystallographically established in another *closo*-rhodaborane cluster, 1,1-(PMe$_2$Ph)$_2$-1,2-μ-H-2,5-(OMe)$_2$-*isocloso*-1-RhB$_{10}$H$_8$, and the resonance arising from the Rh–H–B bridging proton in this compound was found at a shift (−2.69 ppm) near that observed in **8** (−5.2 ppm) [12].

In contrast to the *nido*-2,3-Et$_2$C$_2$B$_4$H$_5^{1-}$ anion, the *nido*-7,8-C$_2$B$_9$H$_{12}^{1-}$ anion reacts with **7** to yield the paramagnetic triple-decker **9**. The green, air-stable complex was purified by chromatography on SiO$_2$ plates with hexane–CH$_2$Cl$_2$ as eluants. In agreement with its paramagnetism, the exact mass measurements on **9** are consistent with its proposed [(η^5-C$_5$Me$_5$)Ru{μ,η^5-(CMe)$_2$(BMe)$_2$(CMe)}Rh(1,2-C$_2$B$_9$H$_{11}$)] composition in which one additional hydrogen has been lost from the starting carborane ligand. Due to the unpaired electron of the resulting 29VE triple-decker, no signals in the ^{1}H- and ^{13}C-NMR spectra were detected. In the ^{11}B-NMR spectrum, the 1,3-diborolyl ring boron resonances are significantly shifted upfield to −60 ppm, but the carborane cage-boron resonances are found in the normal range expected for diamagnetic complexes derived from the *nido*-7,8-C$_2$B$_9$H$_{11}^{2-}$ ligand, such as



Scheme 1. Synthesis of complex **8**.



Scheme 2. Reaction of 7 with the *nido*-7,8-$C_2B_9H_{12}^{1-}$ carboranyl anion.

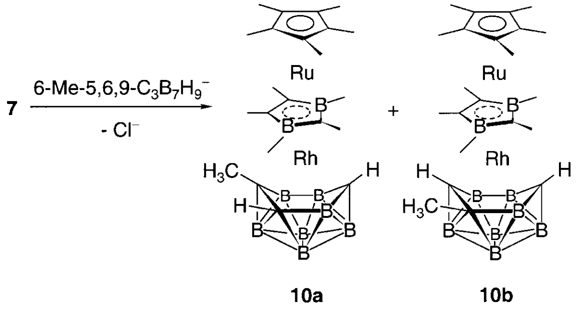
closo-1,2,3,-Cp*$RhC_2B_9H_{11}$ [7,13]. The fact that the diborolyl resonances are significantly shifted, while those of the tricarbaborane cage are not, suggests that the unpaired electron is located in either ruthenium or diborolyl centered orbitals of the complex.

In principle, the reaction of *nido*-7,8-$C_2B_9H_{12}^{1-}$ with **7** (Scheme 2) should have yielded a diamagnetic compound similar to **8** containing one additional hydrogen, i.e. [(η^5-C_5Me_5)Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}-Rh($C_2B_9H_{12}$)], with the extra hydrogen being present, as proposed for **8**, as either a metal-hydride or metal–boron bridging hydrogen, rather than the paramagnetic compound **9** in which one hydrogen has been lost. It is perhaps significant, however, that **8** is readily air-oxidized to form a brown paramagnetic compound (uncharacterized) since this may well be an analog of **9** in which one hydrogen atom is lost. Consistent with this interpretation is the fact that the diamagnetic complex CpFe(H)(2,3-$R_2C_2B_4H_4$) was observed to readily air-oxidize to the paramagnetic complex CpFe(2,3-$R_2C_2B_4H_4$) [11]. The difference in the types of structures and compositions of the final complexes observed from the reactions of **7** with the *nido*-2,3-$Et_2C_2B_4H_5^{1-}$ and *nido*-7,8-$C_2B_9H_{12}^{1-}$ anions may thus simply reflect the relative oxidative stabilities of their initial products.

Unlike the *nido*-2,3-$Et_2C_2B_4H_5^{1-}$ and *nido*-7,8-$C_2B_9H_{12}^{1-}$ anions, the tricarbadecaboranyl *nido*-6-Me-5,6,9-$C_3B_7H_9^{1-}$ anion does not contain any additional bridging hydrogens. Likewise, it has a puckered six-membered open face instead of the five-membered planar face of the two dicarbaborane anions. This anion was reacted with **7** in toluene to give a dark product from which the green, air-stable isomers **10a** (23%) and **10b** (6%) were isolated.

Compound **10a** is separated from **10b** by repeated chromatography on SiO_2 plates with hexane and it crystallizes from a saturated solution of hexane. While the ^1H- and ^{13}C-NMR spectra of **10a** and **10b** exhibit a single resonance for the C_5Me_5 group, both exhibit separate resonances for each methyl group of the diborolyl ring. This indicates that the tricarbadecaboranyl ligand is not symmetrically bonded with respect to the bridging diborolyl ring and that the barrier to rotation is high at room temperature. In the EI mass spectra of both isomers the molecular ion M^+ is found with 100% intensity.

The triple-decker structure of **10a** is confirmed by the crystal structure analysis discussed below. As shown in Scheme 3, the structure of **10b** is proposed to be similar to that of **10a**, with both compounds arising from the insertion of the rhodium atom of the (η^5-C_5Me_5)-Ru{μ,η^5-$(CMe)_2(BMe)_2(CMe)$}Rh fragment into the tricarbadecaboranyl cage to produce an 11-vertex *closo*-rhodatricarbadecaboranyl cluster fragment. The spectral patterns observed for the tricarbadecaboranyl borons in the ^{11}B-NMR spectra of both compounds are similar and consistent with those observed for other 11-vertex *closo*-metallatricarbadecaborane cage systems [6,10b,14]. The two isomers are proposed to differ in that the cage methyl group of the metallatricarbadecaboranyl-cage in **10b** is present at the C4 carbon, rather than at its C2 location in **10a**. Methyl isomerization reactions between the C2 and C4 carbons have frequently been observed during the synthesis of other *closo*-metallatricarbadecaboranyl complexes and the proposed structures for **10a** and **10b** are strongly supported by comparisons of their ^1H-NMR data with known complexes in which the methyl groups are present at the C2 or C4 positions [6,10b,14,15]. Thus, in other 11-vertex *closo*-metallatricarbadecaborane complexes, it has been established that the proton resonances of hydrogens attached to the four-coordinated carbons, i.e. C2 and C3, which are adjacent to the metal atom, appear at low-field (~ 4–6 ppm) while a proton attached to the C4 carbon will appear at higher field (2–0.5 ppm). In agreement with the crystallographically determined structure of **10a** that confirmed the presence of the methyl group at the C2-carbon, its ^1H-NMR spectrum exhibits one cage C–H resonance (C3–H) at low-field (5.13 ppm) and another at high-field (C4–H, 2.06 ppm). On the other hand, the ^1H-NMR spectrum of **10b** shows two C–H resonances (C2–H and C3–H) at low-field (3.97 and 5.29 ppm) strongly indicating that the methyl group is present at the C4 position.



Scheme 3. Formation of the triple-decker complexes **10a** and **10b**.

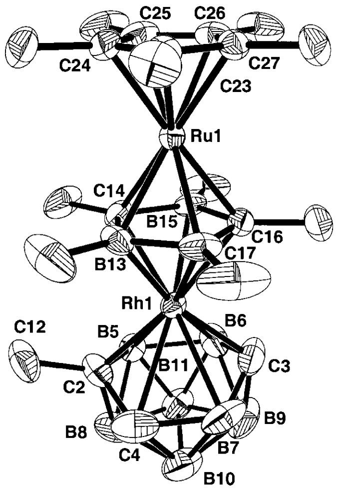


Fig. 1. Molecular structure of **10a** with hydrogen atoms omitted for clarity.

2.2. Crystal structure of **10a**

The structure of **10a** is similar to that of brown **5a** (Fig. 1) [6]. The ligands in **10a** are almost planar and parallel to each other and the 1,3-diborolyl ring does not have the folded structure along the B13–B15 vector that was observed in the isonitrile complex [(η^5-C$_5$Me$_5$)Ru{η^5-(EtC)$_2$(EtB)$_2$(CMe)}CN*t*Bu] [9]. The distances from the ruthenium and rhodium atoms to the 1,3-diborolyl atoms are almost identical. In agreement with its formal cluster electron count, the rhodatricarbadecaboranyl fragment adopts a octadecahedral structure that is similar to that of other 11-vertex *closo*-metallatricarbadecaboranyl complexes. Thus, the rhodium occupies a six-coordinate cage position above the puckered C2–C4–B5–C3–B6–B7 ring with the shortest bond distances to rhodium being found for the two carbons (Rh–C2, 2.143(5) and Rh–C3, 2.046(5) Å) that are out of the ring (Table 1). These two distances are also shorter than the distances observed between the rhodium and the diborolyl carbons (Rh–C14, 2.178(4), Rh–C16, 2.230(5), and Rh–C15, 2.221(5)). The Rh–C2 distance is somewhat longer than the Rh–C3 distance perhaps reflecting steric interactions of the C3 methyl substitute with the diborolyl ring.

The electronic contribution of heteroboranes as ligands in metal complexes has been discussed [16]. When the geometry of a borane ligand in a complex has a *nido* structure the ligand donates 2e to the bonding, an *arachno* geometry donates no electrons and a *hypho* geometry for electron book-keeping is a − 2e donor. In **10**, the *nido*-carboranyl donates 5e (2e from the *nido* framework and 3e from three carbon atoms) to the total number of 30VE ($\pi^5 + d^8 + \pi^3 + d^9 + 5e$).

3. Conclusions

The tetranuclear complex **7** reacts with the *nido*-carboranyl anions *nido*-2,3-Et$_2$C$_2$B$_4$H$_5^{1-}$, *nido*-7,8-C$_2$B$_9$H$_{12}^{1-}$ and *nido*-6-Me-5,6,9-C$_3$B$_7$H$_9^{1-}$ to form stable triple-decker complexes. The C$_2$B$_4$ and the C$_3$B$_7$ carboranes build the diamagnetic 30VE complexes **8** and **10**, while the C$_2$B$_9$ carborane stabilizes the paramagnetic 29VE complex **9**. The crystal structure analysis of **10a** shows the expected *closo*-metallacarbadecaboranyl framework.

4. Experimental

4.1. General

Experiments were carried out under nitrogen or argon, which had been dried and purified before use. Solvents were dried by conventional methods and saturated with nitrogen. NMR spectra were recorded on Bruker AC-200 (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{11}B: 64.21 MHz) and Bruker AC-500 (^{1}H: 500.13 MHz; ^{13}C: 125.76 MHz) in C$_6$D$_6$ as solvent. Chemical shifts are relative to that of TMS and BF$_3$·OEt$_2$. Elemental analyses were performed in the Organisch Chemisches Institut, Universität Heidelberg. The mass spectra were recorded on Varian MAT CH7, Finnigan MAT 8230 and JMS 700 (reference for HRMS is perfluorated Kerosin). Neutral alumina or silica gel used for chromatography had been dried and alumina deactivated by addition of 5% water. The compounds [(η^5-C$_5$Me$_5$)Ru(μ,η^5-C$_3$B$_2$Me$_5$)RhCl]$_2$ [9], Li$^+$(*nido*-6-Me-5,6,9-C$_3$B$_7$H$_9^{1-}$) [10], *nido*-2,3-Et$_2$C$_2$B$_4$H$_6$ [17] and *nido*-7,8-C$_2$B$_9$H$_{13}$ [7] were prepared by previously described methods.

Table 1
Some selected bond distances (Å) and bond angles (°) in **10a**

Ru–C(Cp*)	2.156–2.173(4)	Rh–C4	2.538(6)
Ru–B13	2.241(5)	Rh–B5	2.345(5)
Ru–C14	2.206(5)	Rh–B6	2.361(5)
Ru–B15	2.242(5)	Rh–B7	2.443(6)
Ru–C16	2.203(5)	C2–C4	1.484(8)
Ru–C17	2.234(5)	C2–B5	1.577(7)
B13–C14	1.532(8)	C3–B6	1.582(9)
B13–C17	1.589(8)	C3–B7	1.565(11)
B15–C14	1.599(7)	C4–B7	1.770(11)
B15–C16	1.590(7)	B5–B6	1.873(8)
C16–C17	1.504(8)	Rh–C2	2.143(5)
Rh–B13	2.231(5)	Rh–C3	2.046(5)
Rh–C14	2.178(4)	Rh–C17	2.221(5)
Rh–B15	2.182(5)	Rh–C16	2.230(5)
C14–B13–C17	106.1(4)	C17–C16–B15	109.3(4)
C16–B15–C14	104.6(4)	C16–C17–B13	109.7(4)
B13–C14–B15	110.1(4)		

4.2. (η^5-Pentamethylcyclopentadienyl)ruthenium-(μ,η^5-pentamethyl-2,3-dihydro-1,3-diborolyl)rhodium-(η^5-2,3-diethyl-2,3-dicarbahexaboranyl) ***(8)***

Butyllithium (0.1 ml, 2.5 M in THF) was added dropwise to a solution of 29 mg (0.22 mmol) of *nido*-2,3-$\mathrm{Et_2C_2B_4H_6}$ in THF (30 ml) at −60°C. The reaction mixture was allowed to stir for 15 min and then transferred via canula to a flask containing 110 mg (0.11 mmol) of **7** in 30 ml of THF, cooled to −60°C. After warming up to room temperature (r.t.) and stirring over night, the solvent was removed in vacuum. The dark brown residue was dissolved in hexane and purified by chromatography on silica gel using hexane as eluant. Compound **8** was isolated as a violet solid. Yield: 28 mg (21%). M.p. (dec.) 150°C. ^{1}H-NMR (200.13 MHz, $\mathrm{C_6D_6}$): $\delta = -5.26$ (s, 1H, B–H–B), 1.01 (t, 6 H, $^3J_{\mathrm{HH}} = 7.3$ Hz, $\mathrm{B_4C_2CH_2C}H_3$), 1.18 (s, 6H, $\mathrm{BCH_3}$), 1.41 (s, 15H, $\mathrm{C_5(CH_3)_5}$), 1.83 (m, 2H, $\mathrm{B_4C_2C}H_2\mathrm{CH_3}$), 2.19 (m, 2H, $\mathrm{B_4C_2C}H_2\mathrm{CH_3}$), 2.23 (s, 6H, $=\mathrm{CCH_3}$), 2.25 (s, 3H, $\mathrm{B_2CCH_3}$). ^{11}B-NMR (64.21 MHz, $\mathrm{C_6D_6}$): $\delta = -14.0$ (d, 1B, $^1J_{\mathrm{BH}} = 147$ Hz), −7.2 (d, 1B, $^1J_{\mathrm{BH}} = 146$ Hz), −3.9 (d, 2B, $^1J_{\mathrm{BH}} = 140$ Hz), 16.0 (s, 2B, $\mathrm{C_3B_2}$). ^{13}C-NMR (50.32 MHz, $\mathrm{C_6D_6}$): $\delta = -1.5$ ($\mathrm{BCH_3}$, br), 10.3 ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 14.5 ($\mathrm{B_4C_2CH_2}C\mathrm{H_3}$), 17.7 ($=\mathrm{C}C\mathrm{H_3}$), 21.7 ($\mathrm{B_2C}C\mathrm{H_3}$), 30.2 ($\mathrm{B_4C_2}C\mathrm{H_2CH_3}$), 77.8 ($C_5\mathrm{(CH_3)_5}$), 90.7 ($\mathrm{B_4}C_2\mathrm{CH_2CH_3}$, br), 100.0 ($=C\mathrm{CH_3}$, br), $\mathrm{B_2}C\mathrm{CH_3}$ not observed. MS (EI): m/z (%) = 603 ($\mathrm{M^+}$, 100), 573 ($\mathrm{M^+ - C_2H_5}$, 10), 233 ($\mathrm{Cp^*Ru^+}$−4H, 5). HR MS for $^{12}\mathrm{C}_{24}{}^{1}\mathrm{H}_{45}^{11}\mathrm{B}_6^{102}\mathrm{Ru}^{103}\mathrm{Rh}$: Calc. 603.2228; Found: 603.2236; $\Delta m = 0.8$ mmu.

4.3. (η^5-Pentamethylcyclopentadienyl)ruthenium-(μ,η^5-pentamethyl-2,3-dihydro-1,3-diborolyl)rhodium-(η^5-7,8-dicarbaundecaboranyl) ***(9)***

Butyllithium (0.15 ml, 1.6 M in hexane) was added dropwise to a solution of 31 mg (0.23 mmol) of *nido* 7,8-$\mathrm{C_2B_9H_{13}}$ in glyme (15 ml) at −35°C. The reaction mixture was allowed to stir for 30 min and then transferred via canula to a flask containing 124.1 mg (0.24 mmol) of **7** in 15 ml of glyme, cooled to −50°C. After warming to r.t. and stirring for 36 h the solvent was removed in vacuum. The dark residue was dissolved in 5 ml of hexane. Green air-stable **9** was separated by chromatography on an $\mathrm{SiO_2}$ plate (500 μ, Merck) with hexane–$\mathrm{CH_2Cl_2}$ (1:2). Yield: 26 mg (18%). M.p. 135°C. No paramagnetic ^{1}H-NMR shifts were found. ^{11}B-NMR (64.21 MHz, $\mathrm{C_6D_6}$): $\delta = -59.0$ (2B, $\mathrm{C_3B_2}$), −13.4 (1B, $^3J_{\mathrm{HB}} = 456$ Hz), −6.3 (2B, $^1J_{\mathrm{HB}} = 465$ Hz), −1.1 (3B, $^1J_{\mathrm{HB}} = 370$ Hz), 5.3 (3B, $^1J_{\mathrm{HB}} = 428$ Hz). MS (EI): m/z (%) = 605 ($\mathrm{M^+}$, 100). Anal. Calc. for $\mathrm{C_{20}H_{41}B_{11}RhRu}$: C, 39.70; H, 6.83. Found: C, 39.34; H, 7.03%.

4.4. (η^5-Pentamethylcyclopentadienyl)ruthenium-(μ,η^5-pentamethyl-2,3-dihydro-1,3-diborolyl)rhodium-(η^6-2(4)-methyl-2,3,4-tricarbadecaboranyl) ***(10a,b)***

$\mathrm{Li^+}$(*nido*-6-Me-5,6,9-$\mathrm{C_3B_7H_9^{1-}}$) (0.52 ml, 0.81 M in toluene) was added to a suspension of **7** (216 mg, 0.21 mmol) in 40 ml of toluene and then stirred for 18 h. The solvent was removed in vacuum and the dark residue dissolved in 5 ml of hexane. A mixture of green, air-stable **10a** and **10b** was obtained by chromatography on an $\mathrm{SiO_2}$ plate (500 μ, Merck) with hexane. Compound **10a** can be separated from **10b** by repeated chromatography on $\mathrm{SiO_2}$ plates (500 μ, Merck) with hexane. Green **10a** crystallized from a solution of hexane.

Compound **10a**: Yield: 57.8 mg (23%). M.p. 121°C. ^{1}H-NMR (500.39 MHz, $\mathrm{C_6D_6}$): $\delta = 0.96$, 1.12, 1.97, 1.98, 2.13, 2.17 (6 s, 18H, 2 $\mathrm{BCH_3}$, 2 $=\mathrm{CCH_3}$, $\mathrm{B_2CCH_3}$, $\mathrm{CH_3}$-carb), 1.33 (s, 15H, $\mathrm{C_5(CH_3)_5}$), 2.06 (s, 1H, $\mathrm{C_4H}$-carb), 5.13 (s, 1H, C3H-carb). ^{11}B-NMR (160.55 MHz, $\mathrm{C_6D_6}$): $\delta = -24.5$ (d, 1B, $^1J_{\mathrm{BH}} = 160$ Hz), −19.7 (d, 1B, $^1J_{\mathrm{BH}} = 149$ Hz), −16.2 (d, 1B, $^1J_{\mathrm{BH}} = 148$ Hz), −2.4 (d, 1B, $^1J_{\mathrm{BH}} = 166$ Hz), −1.4 (d, 1B, $^1J_{\mathrm{BH}} = 158$ Hz), −0.5 (d, 1B, $^1J_{\mathrm{BH}} = 158$ Hz), 1.4 (d, 1B, $^1J_{\mathrm{BH}} = 162$ Hz), 20.5 (s, 2B, $\mathrm{C_3B_2}$). ^{13}C-NMR (125.84 MHz, $\mathrm{C_6D_6}$): $\delta = 10.3$ ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 17.3 ($=\mathrm{C}C\mathrm{H_3}$), 18.2 ($=\mathrm{C}C\mathrm{H_3}$), 20.0 ($\mathrm{B_2C}C\mathrm{H_3}$), 27.3 ($C\mathrm{H_3}$–C2carb), 69.5 (br, C4C3-carb), 78.4 ($C_5\mathrm{(CH_3)_5}$), 85.8 (br, C2-carb), $=C\mathrm{CH_3}$, $\mathrm{BCH_3}$ and $\mathrm{B_2}C\mathrm{CH_3}$ not observed. MS (EI): m/z (%) = 608 ($\mathrm{M^+}$, 100), 593 ($\mathrm{M^+ - CH_3}$, 2). HR MS for $^{12}\mathrm{C}_{22}{}^{1}\mathrm{H}_{42}^{11}\mathrm{B}_9^{102}\mathrm{Ru}^{103}\mathrm{Rh}$: Calc. 610.2223; Found: 610.2271; $\Delta m = 4.8$ mmu.

Compound **10b**: Yield: 15 mg (6%). M.p. 121°C. ^{1}H-NMR (500.39 MHz, $\mathrm{C_6D_6}$): $\delta = 0.90$, 1.01, 1.23, 1.94, 1.98, 2.07 (6 s, 18H, 2 $\mathrm{BCH_3}$, 2 $=\mathrm{CCH_3}$, $\mathrm{B_2CCH_3}$, $\mathrm{CH_3}$-carb), 1.36 (s, 15H, $\mathrm{C_5(CH_3)_5}$), 3.97 (s, 1H, $\mathrm{C_2H}$-carb), 5.29 (s, 1H, $\mathrm{C_3H}$-carb). ^{11}B-NMR (160.55 MHz, $\mathrm{C_6D_6}$): $\delta = -21.7$ (s, 1B), −18.2 (s, 1B), −13.1 (s, 1B), −5.7 (s, 1B), −1.4 (s, 3B), 20.5 (s, 2B, $\mathrm{C_3B_2}$). ^{13}C-NMR (125.84 MHz, $\mathrm{C_6D_6}$): $\delta = 10.4$ ($\mathrm{C_5(}C\mathrm{H_3)_5}$), 16.6 ($=\mathrm{C}C\mathrm{H_3}$), 16.7 ($=\mathrm{C}C\mathrm{H_3}$), 18.5 ($\mathrm{B_2C}C\mathrm{H_3}$), 30.2 ($C\mathrm{H_3}$–C2carb), 78.4 ($C_5\mathrm{(CH_3)_5}$), C2-carb, C4C3-carb, $=C\mathrm{CH_3}$, $\mathrm{BCH_3}$ and $\mathrm{B_2}C\mathrm{CH_3}$ not observed. MS (EI): m/z (%) = 608 ($\mathrm{M^+}$, 100), 593 ($\mathrm{M^+ - CH_3}$, 4).

4.5. Crystal structure determinations for ***10a***

Diffraction data were collected on a Rigaku R-AXIS llc area detector [graphite-monochromated Mo–$\mathrm{K_\alpha}$ radiation ($\lambda = 0.71069$)]. Crystal data and details of the measurements are summarized in Table 2. The structure was solved by direct methods (SIR-92) [18] and refined by full-matrix least-squares based on F^2 using SHELXL-93 [19]. All reflections were used during refinement (F^2 values that were experimentally negative were replaced by $F^2 = 0$). Non-hydrogen atoms were refined

Table 2
Crystal and collection parameters for compound **10a**

Empirical formula	$C_{22}H_{42}B_9RuRh$
Formula weight	607.83
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (#19)
Unit cell dimensions	
a (Å)	14.2929(1)
b (Å)	19.4623(1)
c (Å)	9.9135(1)
μ (cm^{-1})	11.56
Volume (Å^3)	2757.79(2)
Z	4
D_{calc} (g cm^{-3})	1.464
F(000)	1232
Crystal size (mm)	0.42 × 0.36 × 0.02
Radiation	Mo–K_α ($\lambda = 0.71069$ Å)
2θ Range (°)	5–50.7
h,k,l collected	$-17 \leq h \leq 17$; $-23 \leq k \leq 23$; $-11 \leq l \leq 11$
No. of reflections measured	18613
No. of unique reflections	5037 ($R_{int} = 0.0309$)
No. of observed reflections	4944 ($F > 4\sigma$)
No. of reflections used in refinement	5037
No. of parameters	299
R indices ($F > 4\sigma$)	$R_1 = 0.0309$, $wR_2 = 0.0753$
R indices (all data)	$R_1 = 0.0319$, $wR_2 = 0.0796$
GoF	1.089
Final difference peaks (e Å^{-3})	+0.380/−0.590

anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 148634. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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