Electron-Poor 2,3-Dihydro-1,3-diborolyl Ruthenium Compounds: Synthesis, Complexation, Oxidative Addition, Capping, and Stacking Reactions

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Keywords: Boranes / Ruthenium / Sandwich Complexes / Diboroles / Triple-decker

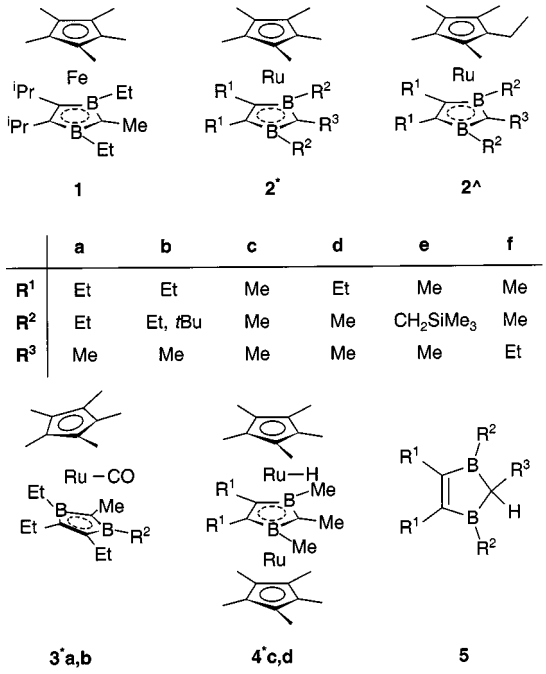
The addition products of lithium alkyls and the pentaalkyl-2,3-dihydro-1,3-diborole derivatives **5a–f** react with $[\{(C_5Me_5)RuCl\}_4]$ and $[\{(C_5Me_4Et)RuCl\}_4]$ to form the violet sandwich compounds **2*c–f** and **2^c**, **f**. These formally 16 VE complexes are in fact electron-poor 18 VE species, because a high-lying combination of σ(B–C) orbitals interacts with the d_{xz} orbital of the Ru atom. Addition of *tert*-butyl isocyanide to **2*a**, or **2*d** leads to the isonitrile complexes **6*a**, and **6*d**, as indicated by the spectroscopic data and X-ray structure analyses. At low temperature the interaction of **2*a**, **c**, or **e** with H_2 yields the classic dihydride complexes **7*a**, **c**, and **e**, respectively, which have been studied by NMR. Oxidative addition of $H_3B{\cdot}THF$ to the ruthenium atom of **2*a** or **c**, followed by a reductive elimination of H_2 and migration of the boranediyl group gives the yellow *closo*-RuC_3B_3 ruthenacarboranes **8*a** and **8*c**, respectively. The reaction of $[(C_2H_4)_2RhCl]_2$ and **2*c** generates the tetranuclear complex **9*c**.

Introduction

Organometallic complexes of the iron triad having less than 18 valence electrons (VE) are of particular interest for catalytic reactions. In the formally 16 VE complexes $[\{(C_5Me_5)Ru(XR)\}_2]$ (X = O, S)[1–3] the Ru atom is coordinatively unsaturated, and the sulfur compounds function as catalysts in the addition of thiols to polar alkynes.[4] Recently, 16 VE $[Ru(C_5Me_5)L_2]^+$ complex cations containing the ligands L_2 = 2,2′-bipyridyl[5a] or a 1,4-diazabutadiene derivative[5b] have been reported.

The formally 16 VE iron complex $[(\eta^5\text{-}C_5Me_5)Fe(\eta^5\text{-}(Ci\text{Pr})_2(BEt)_2CMe)]$ (**1**) has unusual properties.[6] It is thermally stable up to 200°C and shows a folded 1,3-diborolyl ring along the B−B vector by an angle of 41.3°. This unique folding allows a high−lying combination of σ (B−C) orbitals of the 1,3-diborolyl ligand to interact with the empty metal d_{xz} orbital to complete the 18 VE shell.[6] Compound **1** and the isoelectronic Ru complexes **2*a** and **b** are electron-poor, as demonstrated by their reaction with CO. In the case of **1**, a red product of unknown structure is formed, whereas **2*a** and **b** produce the expected monocarbonyl compounds **3*a** and **b**.[6]

Treatment of $[(C_5Me_5)RuCl]_4$ with the less bulky boron heterocycles **5c** and **d** in the presence of an excess of NaH led to the formation of 30 VE triple-decker complexes $[(C_5Me_5)Ru\{\mu,\eta^5\text{-}(CR^1)_2(BR^2)_2CMe\}RuH(C_5Me_5)]$ (**4*c** and **d**) containing a Ru−H bond.[6] The expected sandwich complexes **2*c** and **d** were not obtained. In this paper we describe the synthesis of several ruthenium complexes **2*** (* = pentamethylcyclopentadienyl derivatives) and **2^** (^ = ethyltetramethylcyclopentadienyl derivatives) with less bulky boron heterocycles using lithium methyl as reagent. We report reactions of **2** with *tert*-butylisocyanide, dihydrogen, borane, and the dimer of bisethenerhodium chloride.



	a	b	c	d	e	f
R^1	Et	Et	Me	Et	Me	Me
R^2	Et	Et, *t*Bu	Me	Me	CH_2SiMe_3	Me
R^3	Me	Me	Me	Me	Me	Et

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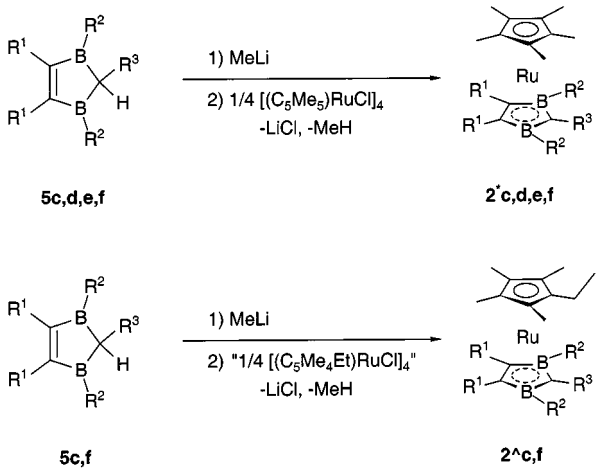
Results and Discussion

Synthesis of Sandwich Complexes 2

The 2,3-dihydro-1,3-diborole derivatives **5c**−**f** are treated with LiMe at −55°C to form addition products, which react with $[(C_5Me_5)RuCl]_4$[7] to give the violet complexes **2*c**, **d**, **e**, and **f** (Scheme 1). In addition to the sandwich compounds **2*c** and **d**, small amounts of the triple-decker compounds **4*c** and **d** are formed, whereas when NaH instead of LiMe is used as base, only the triple-deckers **4*c** and **d** are obtained.[6] The synthesis of the derivatives **2^c** and **f** is achieved by reacting of the boron heterocycle **5c** or **5f** with MeLi and $[(C_5Me_4Et)RuCl]_n$[8] The latter is generated in situ by the reaction of $[(C_5Me_4Et)RuCl_2]_2$ with $[Li(Et_3BH)]$. Isolation and purification of the extremely air-sensitive complexes **2** is achieved by chromatography either on alumina at low temperature or on silica gel at room temperature.

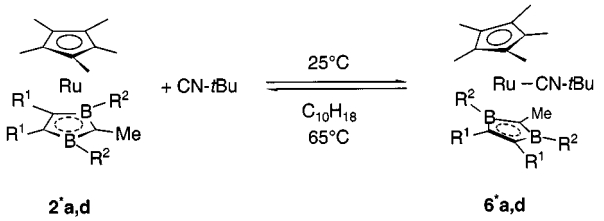


Scheme 1. Formation of complexes **2*** and **2^**

The air-sensitivity of the **2*** and **2** complexes increases with decreasing bulkiness of the ligands. Upon contact with air the color of the complexes changes, and yellow products are formed (see below). Most of the complexes **2*** and **2^** with bulky heterocycle ligands are oily liquids, except for **2*c**, **2*f**, and **2^c**, which are solids. The new compounds are characterized by MS and NMR. In the ^{13}C-NMR spectra, broad signals of the carbon atoms C2 are observed near $\delta = 190$. The following are the C2 shifts for the various complexes: **2*a** $\delta = 191.2$, **2*d** 190.6, **2^f** 190.1, **2^c** 185.8, and **2*c** 185.1. This low-field shift may be the result of a strong interaction between C2 and the ruthenium atom, as it is found in the sandwich **1** [the Fe−C2 distance is 1.899(6) Å, while the Fe−C3,4 distance is 2.116(3) Å][6].

Complexation of 2* with CN*t*Bu

The yellow carbonyl complexes **3*a** and **b** were obtained from the reaction of violet **2*a** and **b** with carbon monoxide.[6] Likewise, with the donor *tert*-butylisocyanide, the yellow complexes **6*a** and **d** are formed (Scheme 2) as crystalline products, which are difficult to purify, because they decompose on a column and during sublimation above 65°C. Their composition was deduced from spectroscopic data and X-ray structure analyses (see below). The ^{13}C-NMR signal for C2 of the isonitrile complex **6*a** appears at $\delta = 70.1$, which is in the range expected for 18 VE compounds. In the ^{11}B-NMR the complexes **6*a**, and **d** exhibit only one signal at $\delta = 29.6$ for **6*a** and 29.4 for **6*d**, whereas **3*b**[6] shows two signals at $\delta = 23.0$ and 36.6. The temperature-dependent ^{11}B-NMR spectra of **6*a** give a relatively sharp signal at 40°C, which gradually broadens at lower temperatures and disappears at −60°C. The ^{1}H- and ^{13}C-NMR spectra of **6*a** and **d** exhibit a double set of signals, which indicates that the isonitrile ligand is not symmetrically bonded with respect to the boron heterocycle, as it is observed for the CO ligand in **3*a** and **b**.[6]

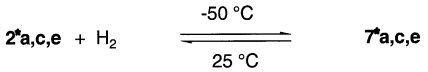


Scheme 2. Addition of CN-*t*Bu to **2*a,d**

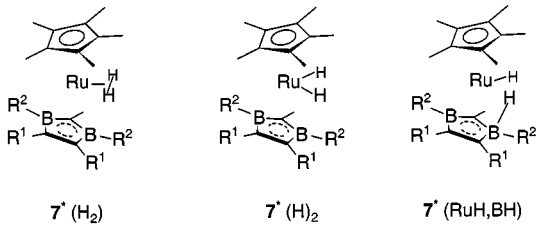
The reactions of CO and CN*t*Bu with **2*a** or **d** occur almost quantitatively. No interaction is observed between **2*** and amines (NH_3, isobutylamine), phosphanes (PEt_3, PPh_3), ethylene, or thiophene. There seems to be a weak interaction between THF and **2***, as indicated by ^{1}H- and ^{11}B-NMR spectra (see Experimental Section).

Oxidative Addition of H_2 to 2*

Addition of hydrogen to **2*a**, **c**, or **e** in hexane, tetrahydrofuran, or toluene, leads to the labile complexes **7*a**, **c**, and **e**, which could not be isolated. The color of the solution is violet at room temperature, but reversibly changes to yellow around −50°C. The weakly bonded hydrogen may be easily removed in vacuum. The complexes decompose after a few hours at room temperature, at −80°C they are stable for days. Three isomers for **7*a**, **c**, and **e** seem possible: the non-classic dihydrogen complex **7***(H_2), the classic dihydride complex **7***$(H)_2$, and the complex **7***(RuH,BH) with one hydrogen at the ruthenium and the other at the boron atom.



Scheme 3. Reaction of **2*** with hydrogen



The solution of the complexes **7*a**, **c**, and **e** have been studied by IR and NMR (^{1}H, ^{11}B, and ^{13}C). IR measurements at 20°C show one strong band after 8 scans: 2977 cm^{-1} for **7*a**, 2975 cm^{-1} for **7*c**, and 2979 cm^{-1} for **7*e**. Unfortunately, the complexes decomposed during the measurements. The ^{1}H-NMR spectra exhibit a high-field signal at $\delta = -12.49$ (**7*a**), -12.24 (**7*c**), and -11.91 (**7*e**), which is in the range for compounds with Ru−H or Ru(H_2) bonds [CpRu(CO)(PCy_3)(H_2)]$^+$: -7.91,[10] $RuH_2(H_2)_2(PCy_3)_2$: -9.1,[11] $Ru_2H_4(H_2)(PCy_3)_4$: -12.5,[11] ($\eta^5C_5Me_5$)Ru(μ-$H)_4$Ru($\eta^5C_5Me_5$): -13.99[12]). A temperature-dependent ^{1}H NMR of **7*c** furnished no information about what happened at −50°C, no shift of the high-field signal at $\delta = -12.24$ occurred (Figure 1).

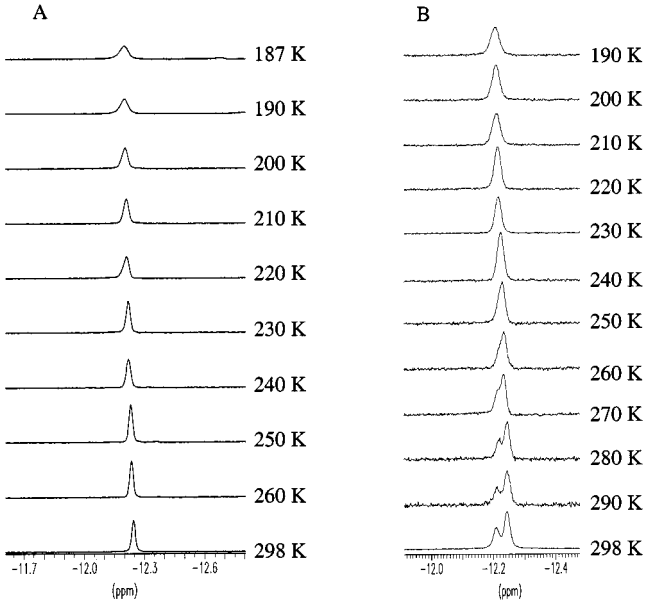


Figure 1. ^{1}H NMR (200.13 MHz, [D_8]THF) at various temperatures after the reaction of **2*c** and H_2 (A) respectively HD (B)

There are two ^{1}H NMR methods to differentiate between the three isomers **7***(H_2), **7***($H)_2$, and **7***(RuH, BH). The first method is the T_1 method, developed by R. H. Crabtree et al.[13] for distinguishing classic hydrides with terminal M−H bonds from non-classic hydrides with H−H as well as M−H bonds. T_1 is a function of the complex structure (dipole−dipole mechanism is the major contributor to this relaxation, a short H−H bond gives small T_1 values down to 3 ms[10]), the magnetic field power, and molecular motion. Molecular motion is dependant on both temperature and solvent, therefore T_1 is measured in dependence of the temperature and a search carried out for the minimum.[14] It is suggested that for $T_{1min} < 40$ ms (250 MHz) a non-classic structure is proposed, and for $T_{1min} > 100$ ms a classic structure is proposed, while values in between are not clearly determinable.[14] Complexes **7*a** and **e** should have small T_{1min} values for a classic and very small T_{1min} values for non-classic structures, because **7*** has a small moment of inertia. In our measurements of **7*a** and **e** no minimum was observed (Figure 2). Unfortunately, the T_1 values (**7*a** = 115 ms and **7*e** = 72) are in the range between a classic and a non-classic complex, therefore we cannot distinguish the two isomers 7*(H_2) and 7*($H)_2$ by this method.

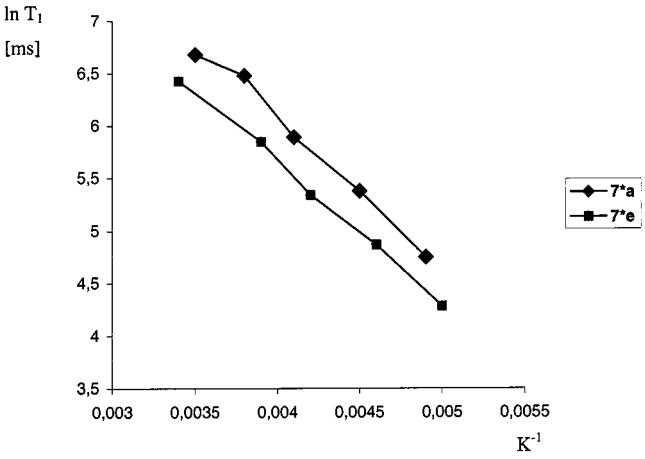


Figure 2. Plot of ln T_1 versus inverse temperature for **7*a**,**e** in [D_8]THF at 200.13 MHz

The second method used to differentiate between classic and non-classic complexes is the H/D exchange. The relationship between the H−D distance and the H−D coupling has been discussed.[15] No coupling is observed when **2*c** is treated with HD (Figure 3, **A**). From this we conclude that no H−D non-classic complex is present. Two signals in **A** of Figure 3 appear at $\delta = -12.21$ and -12.24 in a ratio 1: 1.7. The signal at $\delta = -12.24$ is the same as for **2*c** + H_2 (**C** in Figure 3). When H_2 is bubbled into a solution of **7*c**(HD), the signal at $\delta = -12.21$ decreases and disappears after 10 min (Figure 3).

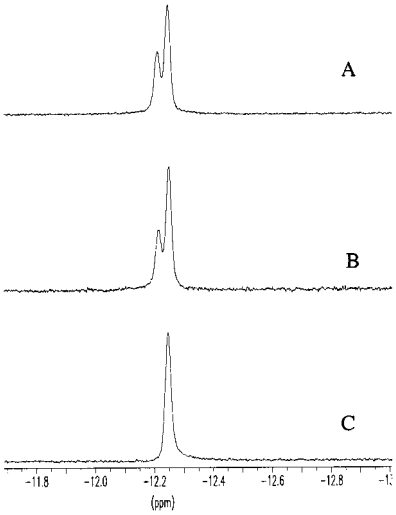


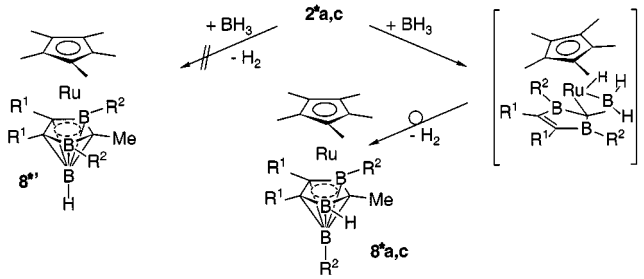
Figure 3. ^{1}H NMR (200.13 MHz, [D_8]THF) of **2*c**, treated with HD and H_2; **A** obtained by bubbling HD into the solution of **2*c**, **B** after H_2 is bubbled for 4 min through the solution of **A**, **C** after H_2 is bubbled for 10 min through the solution of **B**

The temperature-dependent ^{1}H NMR of **2*c** + HD shows that the two signals merge into one another around −50°C (Figure 1) which may parallel the change of the color from violet to yellow. At present we are unable to interpret the findings, in which the compounds **7***(H_2) and

7*(RuH,BH) may be involved. The color change at −50°C is agreement with an adduct formation, as it is observed when complexes **2*** react with a 2e donor such as CO and CN−R. Therefore, we assume that H_2 has added to **2*** to give **7***$(H)_2$ (dihydro complex).

Capping and Stacking Reactions of 2

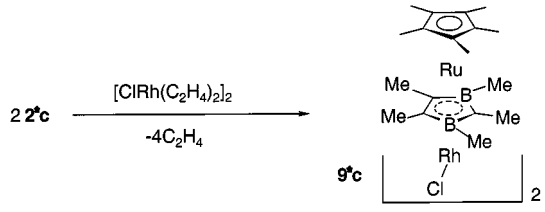
When BH_3·THF is added to **2*a**, or **c** in hexane, the color of the solution changes in a few minutes from violet to yellow, and the tricarbahexaboranyl complexes **8*a** or **8*c** are formed, based on MS, ^{1}H-, ^{11}B-, and ^{13}C-NMR spectra. The isomer **8***′ with BH in the apex position was not detected in the ^{11}B-NMR spectrum as indicated by the absence of a high-field doublet. Three ^{11}B-NMR signals of equal intensity (**8*a**: δ = −0.4, 3.9, 6.6, **8*c**: δ = 1.1, 2.3, 6.0) prove the formation of **8*a** and **8*c**.



Scheme 4. Reaction of **2*a,c** with BH_3

We propose the following mechanism: In the first step an oxidative addition of BH_3 at the ruthenium occurs, followed by the elimination of H_2 to give a transient boranediyl complex, which rearranges with migration of one B−R^2 group into the apex position. Simultaneously, the B−H unit moves into the empty ring position to yield the ruthenacarboranes **8*a** and **c**. According to the cluster rules[16] **8*** has 16 framework electrons and 7 cluster atoms expected for a *closo* structure. Alternatively, **8*** may be described as an 18 VE complex in which the (neutral) 2,3,5-tricarbahexaboranyl ligand supplies 5e for bonding to the metal.[17][18]

When **2*c** is reacted with $[ClRh(C_2H_4)_2]_2$ the diamagnetic tetranuclear complex **9*c** with 56 VE is obtained in 30% yield. The MS and NMR data support the proposed structure of **9*c**, which may be viewed as a pentadecker complex having two bridging chlorine atoms in the central position. It is comparable with the tetranuclear $\{(C_5H_5)Ni[(EtC)_2(BEt)_2CMe]Co(CO)\}_2$ complex having 58 VE.[19]



Scheme 5. Formation of tetranuclear complex **9*c**

Crystal Structures of 6*a, d

The structures of **6*a** and **d** are similar to that of the CO complex **3*b**. The isonitrile group is bonded to the ruthenium, causing a tilt of the Cp* and the 1,3-diborolyl ligands. The best planes through Cp* and 1,3-diborolyl form an angle of 28.6°. The isonitrile is located near one boron atom. The distance B1−C15 is relatively short (2.42 Å) as observed in the CO complex **3*b** (2.41 Å for B1−C17). This weak interaction causes a deviation from linearity of Ru−C≡N*t*Bu (∠ RuCN = 169°), which increases slightly in **3*b** (∠ RuCO = 167°). The 1,3-diborolyl ligand is not planar, but it is less folded along the B1−B3 vector by 16.2° (in **3*a** 19.0°) compared with 41.3° in **1**. The Ru−B distances are significantly larger than those to C, all are in the expected range.

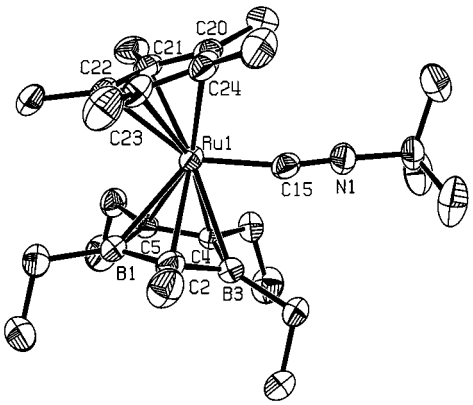


Figure 4. Molecular structure of **6*a** in the crystal

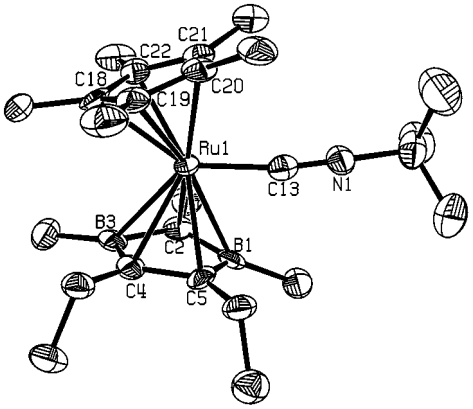


Figure 5. Molecular structure of **6*d** in the crystal

Conclusions

In contrast with our earlier findings,[6] sandwich complexes **2c−f** with less bulky groups may be obtained at low temperature using LiMe instead of NaH as reagent. The electron-poor 18 VE complexes **2*a,** and **c** react with donor ligands such as CO and $CNCMe_3$ to form donor-acceptor compounds, with different stability: CO >> $CNCMe_3$ > H_2 > THF. The complexes **2*a** and **c** activate the B−H bonds

Table 1. Some selected distances [Å] and angles [°] in **6*a**, **d**

Compound	**6*a**	**6*d**
Ru−C(Cp*)	2.215−2.266(2)	2.21−2.27(1)
Ru−C2	2.284(3)	2.29(1)
Ru−C4	2.293(2)	2.33(1)
Ru−C5	2.296(3)	2.27(2)
Ru−B1	2.422(3)	2.40(2)
Ru−B3	2.434(3)	2.44(1)
Ru−C15(C13)	1.944(3)	1.94(1)
B1−C2	1.523(4)	1.51(2)
B3−C2	1.531(3)	1.57(2)
B1−C5	1.559(4)	1.56(2)
B3−C4	1.576(3)	1.54(2)
C4−C5	1.423(3)	1.42(2)
C15(C13)−B1	2.419(3)	2.417(2)
B1−C2−B3	107.4(2)	109.0(13)
C2−B3−C4	105.6(2)	104.0(12)
C2−B1−C5	105.6(2)	104.6(13)
B3−C4−C5	108.6(2)	111(2)
B1−C5−C4	110.1(2)	108.6(13)
Ru−C15(C13)−N1	168.9(2)	168.6(13)
*t*Bu−N1−C15(C13)	170.5(2)	165(2)
γ[a]	28.59(11)	27.5; 29.0(4)
φ[b]	16.7(2)	14.0; 17.1(8)

[a] γ = Angle between the planes C20C21C22C23C24 and B1C5C4B3. − [b] φ = Folding angle between the planes B1B3C4C5 and C2B1B3.

of BH_3 to give with elimination of hydrogen the ruthenacarborane complexes **8*a** and **c**. Reaction of **2*c** $[ClRh(C_2H_4)_2]_2$ leads to the Cl-bridged pentadecker **9*c**

Experimental Section

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_6D_6 as solvent. Chemical shifts are relative to that of TMS and $BF_3{\cdot}OEt_2$. − The mass spectra were recorded on Varian MAT CH7, Finnigan MAT 8230, and JEOL. The MS Station JMS 700 (reference for HRMS is perflourated Kerosin). GC mass spectra were recorded on HP-5890 II gas chromatograph with HP-5971 MSD (column HP-3, 12.5m × 0.25 mm × 0.25 μm). − IR spectra were measured on Bruker IFS 28. Neutral alumina or silica gel used for chromatography had been dried and alumina deactivated by addition of 5% water.

2-Ethyl-1,3-diiodo-4,5-dimethyl-2,3-dihydro-1,3-diborole: 2-Butyne (3.24 g, 60 mmol) was slowly added to a solution of 1,1-bisdiiodoborylpropane (33 g, 60 mmol) in 30 mL of pentane at 0°C. The reaction mixture was allowed to warm to 20°C, stirred for 1 h and then the solvent and iodine were removed in vacuum. 2-Ethyl-1,3-diiodo-4,5-dimethyl-2,3-dihydro-1,3-diborole was isolated by distillation as lightly yellow liquid. Yield 18 g (81%) − b. p. 67°C/10^{-3} Torr. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.00 (br, 1 H, B_2CHCH_2), 1.15 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 1.72 (s, 6 H, = CCH_3), 1.89 (m, 2 H, $CHCH_2CH_3$). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = 15.6 (=CCH_3), 16.9 (CH_2CH_3), 23.2 ($CHCH_2CH_3$), 52.7 (B_2CHCH_2, br), 175.0 (=CCH_3, br). − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 64.8.

2-Ethyl-1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborole (5d): 2-Ethyl-1,3-diiodo-4,5-dimethyl-2,3-dihydro-1,3-diborole (21.5 g, 58 mmol) was dissolved in 40 mL of pentane and cooled to −5°C. 2.78 g (39 mmol) of $AlMe_3$ in 20 mL of pentane were added dropwise within 30 min. After warming to room temp. and stirring over night the solvent was removed in vacuum (80 Torr), and colorless **5d** was distilled. Yield: 6.9 g (79%). − b. p. 20°C/10^{-3} Torr. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.69 (s, 6 H, BCH_3), 2.07 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), 2.42 (t, 1 H, $^3J_{HH}$ = 5.9 Hz, B_2CHCH_2), 2.67 (m, 2 H, $CHCH_2CH_3$), 2.78 (s, 6 H, CCH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = 4.3 (BCH_3, br), 14.3 (=CCH_3), 16.9 (CH_2CH_3), 19.9 ($CHCH_2CH_3$), 51.6 (B_2CHCH_2, br), 173.0 (=CCH_3, br). − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 69.6. − GC-MS: retention time: 2.28 min. − *m/z* (%) = 148 [M^+] (35), 133 [$M^+ - CH_3$] (34), 117 [$M^+ - CH_3, - CH_4$] (33), 41 [$C_3H_5^+$] (100).

2,4,5-Trimethyl-1,3-bis(trimethylsilylmethylene)-2,3-dihydro-1,3-diborole (5e): $LiCH_2SiMe_3$ (40 mL, 1 M in pentane) was added dropwise to a solution of 7.16 g (20 mmol) of 1,3-diiodo-2,4,5-trimethyl-2,3-dihydro-1,3-diborole in 40 mL of pentane at 0°C. The yellow reaction mixture became colorless and a white solid precipitated. After warming to room temp. and stirring over night the precipitate was filtered. The solvent was removed in vacuum (50 Torr) and colorless **5e** was distilled. Yield: 3.5 g (63%). − b. p. 49°C/10^{-3} Torr. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.09 [s, 18, $Si(CH_3)_3$], 1.01 (d, 2 H, $^2J_{HH}$ = 9.5 Hz, BCH_2Si), 1.15 (d, 2 H, $^2J_{HH}$ = 9.5 Hz, BCH_2Si), 1.27 (d, 3 H, $^3J_{HH}$ = 5.2 Hz, $CHCH_3$), 1.32 (q, 1 H, $^3J_{HH}$ = 5.2 Hz, B_2CHCH_3), 1.88 (s, 6 H, =CCH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = 2.4 [$Si(CH_3)_3$], 12.2 (=CCH_3), 15.5 (BCH_2Si, br), 15.9 ($CHCH_3$), 39.2 (B_2CHCH_3, br), 172.0 (=CCH_3, br). − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 68.8. − MS (EI): *m/z* (%) = 278 [M^+] (16), 263 [$M^+ - CH_3$] (7), 190 [$M^+ - CH_2SiMe_3$] (9), 73 [Me_3Si^+] (100). − HRMS calcd. for $C_{14}H_{32}B_2Si_2$: 278.2229, found: 278.2231, Δ*m* = 0.2 mmu.

(η^5-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium (2*c): 1.38 mL (2.2 mmol) of 1.6 M LiMe were added dropwise to a solution of 256 mg (2.2 mmol) of **5c** in THF (35 mL) at −55°C. The reaction mixture was allowed to stir for 15 min and then transferred via canula to a flask containing 600 mg (0.55 mmol) of $[Cp^*RuCl]_4$ in 40 mL of THF, cooled to −55°C. After stirring for 12 h the solvent was removed in vacuum. The violet residue was dissolved in 5 mL of hexane and purified by chromatography, either on Al_2O_3 at −20°C or on silica gel at room temp. using hexane as eluant. **2*c** was isolated as a dark violet solid. Yield: 380 mg (47%). − m.p. 138°C (decomp.). − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.21 (s, 6 H, BCH_3), 1.46 (s, 15 H, $C_5(CH_3)_5$), 2.23 (s, 6 H, =CCH_3), 2.83 (s, 3 H, B_2CCH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = −1.8 (BCH_3, br), 10.6 [$C_5(CH_3)_5$], 16.4 (=CCH_3), 20.9 (B_2CCH_3), 83.8 [$C_5(CH_3)_5$], 118.8 (=CCH_3, br), 185.8 (B_2CCH_3, br) − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 20.6−^{1}H NMR (200.13 MHz, [D$_8$]THF): δ = −0.01 (s, 6 H, BCH_3), 1.61 [s, 15 H, $C_5(CH_3)_5$], 2.25 (s, 6 H, =CCH_3), 2.59 (s, 3 H, B_2CCH_3). − ^{13}C NMR (50.32 MHz, [D$_8$]THF): δ = 11.1 [$C_5(CH_3)_5$], 16.8 (=CCH_3), 20.8 (B_2CCH_3), 84.8 [$C_5(CH_3)_5$], = CCH_3 and B_2CCH_3 not observed. − ^{11}B NMR (64.21 MHz, [D$_8$]THF): δ = 22.6. − MS (EI): *m/z* (%) = 370 [M^+] (88), 351 [$M^+ - CH_3, - 4$ H] (100), 336 [$M^+ - 2\ CH_3, - 4$ H] (74), 301 [$M^+ - C_3H_8, - BCH_3$] (77), 233 [$Cp^*Ru^+ - 4$ H] (77), 41 [$C_3H_5^+$] (89). − HRMS calcd. for $C_{18}H_{30}B_2Ru$: 370.1571, found 370.1563, Δ*m* = 0.8 mmu.

(η^5-4,5-Diethyl-1,2,3-trimethyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium (2*d): Same procedure as for **2*c**. The product, **2*d** was obtained from **5d** (162 mg, 1 mmol), LiMe (0.63 mL, 1 mmol) and $[Cp^*RuCl]_4$ (274 mg, 0.25 mmol) as a dark violet oil. Yield: 147 mg (37%). − b. p. 75°C/10^{-3} Torr. −

^{1}H NMR: δ = 0.26 (s, 6 H, BCH_3), 1.32 (t, 6 H, $^3J_{HH}$ = 7.5 Hz, = CCH_2CH_3), 1.45 [s, 15 H, $C_5(CH_3)_5$], 2.4 (m, 4 H, =CCH_2CH_3), 2.8 (s, 3 H, CCH_3), 3.15 (m, 4 H, =CCH_2CH_3). − ^{13}C NMR: δ = −0.5 (BCH_3, br), 11.7 [$C_5(CH_3)_5$], 15.1 (=CCH_2CH_3), 22.0 (B_2CCH_3), 26.3 (=CCH_2CH_3), 85.1 [$C_5(CH_3)_5$], 123.6 (=CCH_2CH_3, br), 190.6 (B_2CCH_3, br). − ^{11}B NMR: δ = 21. − MS (EI): *m/z* (%) = 397 [M^+ −H] (100), 383 [M^+ − CH_3] (98), 368 [M^+ − C_2H_6] (24), 353 [M^+ − 3 CH_3] (26), 235 [Cp*Ru^+ − H] (60). − HRMS calcd. for $C_{20}H_{34}B_2Ru$: 398.1890, found 398.1889, Δ*m* = 0.1 mmu.

[η^5-2,4,5-Trimethyl-1,3-bis(trimethylsilylmethylene)-2,3-dihydro-1,3-diborolyl](η^5-pentamethylcyclopentadienyl)ruthenium (2*e): Same procedure as for **2*c**. The product, **2*e** was obtained from **5e** (444.6 mg, 1.6 mmol), LiMe (1 mL, 1.6 mmol), and [Cp*RuCl]$_4$ (435 mg, 0.4 mmol) as a dark violet oil. Yield: 334 mg (41%). − b. p. 85°C/10−^{3} Torr. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.01 [s, 18 H. $Si(CH_3)_3$], 0.09 (d, 2 H, $^2J_{HH}$ = 15 Hz, BCH_2Si), 0.43 (d, 2 H, $^2J_{HH}$ = 15 Hz, BCH_2Si), 1.48 [s, 15 H, $C_5(CH_3)_5$], 2.23 (s, 6 H, =CCH_3), 2.74 (s, 3 H, B_2CCH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = 1.2 [$Si(CH_3)_3$], 5.7 [B$CH_2Si(CH_3)_3$, br], 10.7 [$C_5(CH_3)_5$], 16.7 (=CCH_3), 22.1 (B_2CCH_3), 83.4 [$C_5(CH_3)_5$], 118.8 (=CCH_3, br), B_2CCH_3 not observed. − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 21.7. − MS (EI): *m/z* (%) = 514 [M^+] (4), 426 [M^+ − $Si(CH_3)_3$, − CH_3] (4), 233 [Cp*Ru^+ − 4 H] (5), 73 [Me_3Si^+] (100). − HRMS calcd. for $C_{24}H_{46}B_2RuSi_2$: 514.2361, found 514.2357, Δ*m* = 0.4 mmu.

(η^5-2-Ethyl-1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium (2*f): Same procedure as for **2*c**. The product, **2*f** was obtained from **5f** (326 mg, 2.2 mmol), LiMe (1.38 mL, 2.2 mmol) and [Cp*RuCl]$_4$ (590 mg, 0.55 mmol) as a dark violet solid. Yield: 160 mg (19%). − m.p. 148°C (decomp.). − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.25 (s, 6 H, BCH_3), 1.45 (s, 15 H, C_5CH_3), 1.66 (t, 3 H, $^3J_{HH}$ = 7.6 Hz, $B_2CCH_2CH_3$), 2.20 (s, 6 H, =CCH_3), 3.20 (q, 2 H, $^3J_{HH}$ = 7.6 Hz, $B_2CCH_2CH_3$). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = −1.6 (BCH_3, br), 10.9 [$C_5(CH_3)_5$], 16.4 (=CCH_3), 16.8 ($B_2CCH_2CH_3$), 29.7 ($B_2CCH_2CH_3$), 83.8 [$C_5(CH_3)_5$], 118.4 (=CCH_3, br), $B_2CCH_2CH_3$ not observed. − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 21.5. − MS (EI): *m/z* (%) = 384 [M^+] (40), 368 [M^+ − CH_4] (100), 232 [Cp*Ru^+ − 5 H] (15). − HRMS calcd. for $C_{19}H_{32}B_2Ru$: 384.1727, found 384.1723, Δ*m* = 0.4 mmu.

(η^5-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η^5-1-ethyl-2,3,4,5-tetramethylcyclopentadienyl)ruthenium (2^c): Li(Et_3BH) (1.14 mL, 1 M in THF) was added dropwise to a suspension of (Cp^ $RuCl_2$)$_2$ (365 mg, 0.57 mmol) in 40 mL of THF and then stirred for 45 min. In another flask with a cooled solution (−55°C) of **5c** (189 mg, 1.27 mmol) in 40 mL of THF 1.38 mL (2.2 mmol) of 1.6 M LiMe were added dropwise and allowed to stir for 15 min at −55°C. Subsequently the reaction mixture was transferred via canula to the likewise cooled flask of the ruthenium reaction. After stirring for 12 h the solvent was removed in vacuum. The violet residue was dissolved in 5 mL of hexane and purified by chromatography, either on Al_2O_3 at −20°C or on silica gel at room temp. using hexane as eluant. **2^c** was isolated as a dark violet solid. Yield: 88 mg (20%) − m.p. 145°C (decomp.). − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.21 (s, 6 H, BCH_3), 0.84 (t, 3 H, $^3J_{HH}$ = 7.6 Hz, $C_5CH_2CH_3$), 1.43 [s, 6 H, $C_5(CH_3)_4$], 1.50 [s, 6 H, $C_5(CH_3)_4$], 1.89 (q, 2 H, $^3J_{HH}$ = 7.6 Hz, $C_5CH_2CH_3$), 2.23 (s, 6 H, =CCH_3), 2.83 (s, 3 H, B_2CCH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = −2.2 (BCH_3, br), 10.4 and 10.6 [$C_5(CH_3)_4$], 14.8 ($C_5CH_2CH_3$), 16.4 (=CCH_3), 19.1 ($C_5CH_2CH_3$), 21.0 (B_2CCH_3), 83.3, 83.9, and 89,8 ($C_5(CH_3)_4Et$), 118.9 (=CCH_3, br), 185.8 (B_2CCH_3, br). − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 20.7. − MS (EI): *m/z* (%) = 384 [M^+] (39), 243 [Cp Ru^+ − 7 H] (100), 41 [$C_3H_3^+$] (35). − HRMS calcd. for $C_{19}H_{32}B_2Ru$: 384.1727, found 384.1703, Δ*m* = 2.4 mmu.

(η^5-2-Ethyl-1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborolyl)(η^5-1-ethyl-2,3,4,5-tetramethyl cyclopentadienyl)ruthenium (2^f): Same procedure as for **2^c**. The product, **2^f** was obtained from **5f** (250 mg, 1.7 mmol), LiMe (1.06 mL, 1.7 mmol) and [Cp^ $RuCl_2$]$_2$ (543 mg, 0.85 mmol), treated with 1.7 mL (1.7 mmol) of 1 M Li(Et_3BH) as a dark violet oil. Yield: 188 mg (27%). − b.p. 85°C/10^{-3} Torr. − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.25 (s, 6 H, BCH_3), 0.83 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, $C_5CH_2CH_3$), 1.44 [s, 6 H, $C_5(CH_3)_4$], 1.49 [s, 6 H, $C_5(CH_3)_4$], 1.65 (t, 3 H, $^3J_{HH}$ = 7.6 Hz, $B_2CCH_2CH_3$), 1.90 (q, 2 H, $^3J_{HH}$ = 7.4 Hz, $C_5CH_2CH_3$), 2.20 (s, 6 H, =CCH_3), 3.21 (q, 2 H, $^3J_{HH}$ = 7.6 Hz, $B_2CCH_2CH_3$). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = −1.2 (BCH_3, br), 10.8 [$C_5(CH_3)_4$], 10.5 [$C_5(CH_3)_4$], 16.4 (=CCH_3), 16.8 ($B_2CCH_2CH_3$), 14.8 ($C_5CH_2CH_3$), 19.1 ($C_5CH_2CH_3$), 29.8 ($B_2CCH_2CH_3$), 83.3, 84.0, and 89.5 [$C_5(CH_3)_4Et$], 118.6 (=CCH_3, br), 190.1 (B_2CCH_2, br). − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 21.8. − MS (EI): *m/z* (%) = 398 [M^+] (52), 382 [M^+ − CH_4] (100), 368 [M^+ − C_2H_6] (22), 243 [Cp Ru^+ − 8 H] (12), 149 [Cp $^+$] (77), 41 [$C_3H_5^+$] (28). − HRMS cald. for $C_{20}H_{34}B_2Ru$: 398.1890, found 398.1881, Δ*m* = 0.9 mmu.

(η^5-1,3,4,5-Tetraethyl-2-methyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium *tert*-Butylisocyanide (6*a): Compound **2*a** (100 mg, 0.24 mmol) was dissolved in hexane (15 mL) and CNC_4H_9 (19.5 mg, 24 mmol) was added dropwise. The color changed immediately from violet to yellow. After partial removal of the solvent in vacuum **6*a** crystallized at −20°C. Yield: 80 mg (66%) − m.p. 75°C (diss. to the starting materials). − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.17 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, = CCH_2CH_3), 1.24 [s, 9 H, $CNC(CH_3)_3$], 1.34 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, =CCH_2CH_3), 1.38−1.49 (m, 10 H, BCH_2CH_3), 1.51 (s, 3 H, B_2CCH_3), 1.55 [s, 15 H, $C_5(CH_3)_5$], 1.83−2.22 (m, 4 H, = CCH_2CH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = 6.8 (BCH_2CH_3, br), 9.6 [$C_5(CH_3)_5$], 10.5 (BCH_2CH_3, br), 12.2 and 12.9 (BCH_2CH_3), 15.6 (B_2CCH_3), 17.2 and 17.6 (=CCH_2CH_3), 21.5 and 22.6 (=CCH_2CH_3), 31.5 [$CNC(CH_3)_3$], 56.4 [$CNC(CH_3)_3$], 67.5 (B_2CCH_3, br), 90.8 [$C_5(CH_3)_5$], 102.6 and 121.7 (=CCH_2CH_3, br), 166.5 [$CNC(CH_3)_3$]. − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 29.6. − MS (EI): *m/z* (%) = 509 [M^+] (44), 425 [M^+ − $CNC(CH_3)_3$] (53), 396 [M^+ − C_2H_5, − $CNC(CH_3)_3$] (100), 367 [M^+ − 2 C_2H_5, − $CNC(CH_3)_3$] (30), 236 [Cp*Ru^+ − H] (15), 57 [$C_4H_9^+$] (40). − HRMS calcd. for $C_{27}H_{47}B_2NRu$: 509.2938, found 509.2953, Δm = 1.5 mmu. − FT-IR (hexane): $\tilde{\nu}_{CN}$ = 2048 cm^{-1}, 2088 cm^{-1} (weak).

(η^5-4,5-Diethyl-1,2,3-trimethyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium *tert*-Butylisocyanide (6*d): Same procedure as for **6*a**. The product, **6*d** was obtained from **2*d** (95.5 mg, 0.24 mmol) in 15 mL of hexane and 19 mg (0.24 mmol) of $CNC(CH_3)_3$ as yellow crystals. Yield: 76.3 mg (66%) − m.p. 65°C (diss. to the starting materials). − ^{1}H NMR (200.13 MHz, C_6D_6): δ = 0.80 (s, 3 H, BCH_3), 0.84 (s, 3 H, BCH_3), 1.16 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, =CCH_2CH_3), 1.25 [s, 9 H, $CNC(CH_3)_3$], 1.30 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, =CCH_2H_3), 1.47 (s, 3 H, B_2CCH_3), 1.55 [s, 15 H, $C_5(CH_3)_5$], 1.85−2.19 (m, 4 H, = CCH_2CH_3). − ^{13}C NMR (50.32 MHz, C_6D_6): δ = −1.6 (BCH_3, br), 1.9 (BCH_3, br), 10.5 [$C_5(CH_3)_5$], 16.4 (B_2CCH_3), 17.7 (= CCH_2CH_3), 18.4 (=CCH_2CH_3), 22.3 (=CCH_2CH_3), 23.5 (= CCH_2CH_3), 32.5 [$CNC(CH_3)_3$], 57.0 [$CNC(CH_3)_3$], 70.1 (B_2CCH_3, br), 91.6 [$C_5(CH_3)_5$], 109.8 (=CCH_2CH_3, br), 121.9 (=CCH_2CH_3, br), 164.4 [$CNC(CH_3)_3$]. − ^{11}B NMR (64.21 MHz, C_6D_6): δ = 29.4 − MS (EI): *m/z* (%) = 481 [M^+] (40), 397 [M^+ − H, − CN*t*Bu]

(30), 382 [$M^+ - H, - CNtBu, - CH_3$] (100). – HRMS calcd. for $C_{25}H_{43}B_2NRu$: 481.2625, found 481.2650, Δm = 2.5 mmu. – FT-IR (hexane): $\tilde{\nu}_{CN}$ = 2084 cm^{-1}, 2031 cm^{-1} (weak).

(η⁵-1,3,4,5-Tetraethyl-2-methyl-2,3-dihydro-1,3-diborolyl)(η⁵-pentamethylcyclopentadienyl)ruthenium Dihydride (7*a): Complex **2*a** (50 mg, 0.12 mmol) was dissolved in 20 mL of hexane, and H_2 gas was bubbled through the solution for 4 min at a flow rate of 10 mLmin^{-1}. The color changed reversibly at −50°C from violet to yellow. For NMR studies, the deuterated solvents were used instead of hexane. – ^{1}H NMR (200.13 MHz, C_6D_6): δ = −12.49 (s, 2 H, Ru−H), 1.21−1.35 (m, 10 H, BCH_2CH_3), 1.43 (t, 6 H, $^3J_{HH}$ = 8.3 Hz, =CCH$_2$CH_3), 1.53 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.66 (s, 3H, B$_2$CCH$_3$), 1.93 and 2.14 (m, 2H, =CCH_2CH$_3$). – ^{13}C NMR (50.32 MHz, C_6D_6): δ = 5.1 (BCH$_2$CH$_3$, br), 9.7 (BCH$_2$CH$_3$), 10.5 [C$_5$(CH$_3$)$_5$], 13.7 (=CCH$_2$CH$_3$), 22.2 (=CCH$_2$CH$_3$), 30.2 (B$_2$CCH$_3$), 94.6 [C$_5$(CH$_3$)$_5$], 114 (=CCH$_2$CH$_3$, br), B$_2$CCH$_3$ not observed. – ^{11}B NMR (64.21 MHz, C_6D_6): δ = 20.1.

(η⁵-1,2,3,4,5-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η⁵-pentamethylcyclopentadienyl)ruthenium Dihydride (7*c): Same procedure as for **7*a**. The product, **7*c** was formed as a yellow solution from **2*c** (40 mg, 0.11 mmol) in 20 mL of hexane and H_2 gas (10 mLmin^{-1}) at −50°C. – ^{1}H NMR (200.13 MHz, [D$_8$]THF): δ = 0.40 (s, 6 H, BCH$_3$), 1.85 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.62 (s, 6 H, =C−CH$_3$), 1.19 (s, 3 H, B$_2$CCH$_3$), −12.25 (s, 2 H, Ru−H). – ^{13}C NMR (50.32 MHz, [D$_8$]THF): δ = −4.9 (BCH$_3$, br), 10.9 [C$_5$(CH$_3$)$_5$], 14.7 (=CCH$_3$), 31.2 (B$_2$CCH$_3$), 96.7 [C$_5$(CH$_3$)$_5$], =CCH$_3$ and B$_2$CCH$_3$ not observed. – ^{11}B NMR (64.21 MHz, [D$_8$]-THF): δ = 22.9.

(η⁵-1,2,3,4,5-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η⁵-pentamethylcyclopentadienyl)ruthenium Hydride Deuteride [7*c(HD)]: It was obtained from **2*c** (40 mg, 0.11 mmol) in 0.6 mL of [D$_8$]THF and HD gas (10 mLmin^{-1} for 4 min) as a yellow solution at −50°C. – ^{1}H NMR (200.13 MHz, [D$_8$]THF): δ = 0.40 (s, 6 H, BCH$_3$), 1.85 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.63 (s, 6 H, =CCH$_3$), 1.18 (s, 3 H, B$_2$CCH$_3$), −12.21 and −12.24 (s, 1 H, Ru−H). – ^{11}B NMR (64.21 MHz, [D$_8$]THF): δ = 22.8.

[η⁵-2,4,5-Trimethyl-1,3-bis(trimethylsilylmethylene)-2,3-dihydro-1,3-diborolyl](η⁵-pentamethylcyclopentadienyl)ruthenium Dihydride (7*e): Same procedure as for **7*a**. The product, **7*e** was obtained as a yellow solution from **2*e** (50 mg, 0.1 mmol) in 20 mL of hexane and H_2 gas (10 mLmin^{-1}) at −50°C. – ^{1}H NMR (200.13 MHz, C_6D_6): δ = −11.91 (s, 2 H, Ru−H), 0.25 [s, 18 H, Si(CH$_3$)$_3$], 0.64 (d, 2 H, $^2J_{HH}$ = 3.1 Hz, BCH$_2$Si), 0.83 (d, 2 H, $^2J_{HH}$ = 3.1 Hz, BCH$_2$Si), 1.42 (s, 3 H, B$_2$CCH$_3$), 1.53 (s, 15 H, C$_5$(CH$_3$)$_5$), 1.76 (s, 6 H, =CCH$_3$). – ^{13}C NMR (50.32 MHz, C_6D_6): δ = 1.5 [Si(CH$_3$)$_3$], 10.3 [C$_5$(CH$_3$)$_5$], 16.5 (=CCH$_3$), 23.0 (B$_2$CCH$_3$), 96.0 [C$_5$(CH$_3$)$_5$], =CCH$_3$ and B$_2$CCH$_3$ not observed. – ^{11}B NMR (64.21 MHz, C_6D_6): δ = 22.5.

(1,2,3,6-Tetraethyl-5-methyl-4-hydrido-2,3,5-tricarbahexaboranyl)-(η⁵-pentamethylcyclopentadienyl)ruthenium (8*a): BH_3 in THF (0.24 mL, 1 M, 0.24 mmol) was added dropwise to a solution of **2*a** (100 mg, 0.24 mmol) in 40 mL of hexane at room temp. After the yellow reaction mixture had been stirred for 15 min, the solvents were removed in vacuum and the yellow solid was sublimed. Yield: 30 mg (29%). – m.p. 130°C. – ^{1}H NMR (500.13 MHz, C_6D_6): 0.07 (m, 1 H, BCH_2CH$_3$), 0.20 (m, 1 H, BCH_2CH$_3$), 0.83 (t, 3 H, $^3J_{HH}$ = 7.9 Hz, BCH$_2$CH_3), 1.02 (t, 3 H, $^3J_{HH}$ = 7.6 Hz, CCH$_2$CH_3), 1.23−1.34 (m, 5 H, BCH_2CH_3), 1.36 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CCH$_2$CH_3), 1.64 (s, 3 H, B$_2$CCH$_3$), 1.73 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.75−1.89 (m, 3 H, CH_2CH$_3$), 2.14 (m, 1 H, CCH_2CH$_3$). – ^{13}C NMR (125 MHz, C_6D_6): 4.0 (BCH$_2$CH$_3$, br), 8.9 (BCH$_2$CH$_3$, br), 10.6 (B$_2$CCH$_3$), 11.3 [C$_5$(CH$_3$)$_5$], 12.3 (BCH$_2$CH$_3$), 12.7 (BCH$_2$CH$_3$), 14.4 (CCH$_2$CH$_3$), 14.6 (CCH$_2$CH$_3$), 21.0 (CCH$_2$CH$_3$), 21.4 (CCH$_2$CH$_3$), 68.5 (B$_2$CCH$_3$, br), 78.4 (CCH$_2$CH$_3$, br), 80.7 (CCH$_2$CH$_3$, br), 84.4 [C$_5$(CH$_3$)$_5$]. – ^{11}B NMR (64.21 MHz, C_6D_6): −0.4 (1 B, BH, $^1J_{BH}$ = 156 Hz), 3.9 (1 B, BCH$_2$CH$_3$), 6.6 (1 B, BCH$_2$CH$_3$). – MS (EI): *m*/*z* (%) = 438 [M^+] (100), 423 [$M^+ - CH_3$] (10), 235 [Cp*Ru$^+$ − 2 H] (15).

(1,2,3,5,6-Pentamethyl-4-hydrido-2,3,5-tricarbahexaboranyl)(η⁵-pentamethylcyclopentadienyl)ruthenium (8*c): Same procedure as for **8*a**. The complex **8*c** was obtained as a yellow solid from **2*c** (180 mg, 0.49 mmol) in 50 mL of hexane and BH_3 (0.5 mL, 1 M, 0.5 mmol). Yield: 90 mg (48%). – m.p. 110°C. – ^{1}H NMR (200.13 MHz, C_6D_6): δ = −0.55 (s, 3 H, BCH$_3$), 1.44 (s, 3 H, BCH$_3$), 1.73 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.89 (s, 3 H, B$_2$CCH$_3$), 1.99 (s, 3 H, =CCH$_3$), 2.12 (s, 3 H, =CCH$_3$). – ^{13}C NMR (75.46 MHz, C_6D_6): δ = 11.9 [C$_5$(CH$_3$)$_5$], 12.9 (=CCH$_3$), 13.4 (=CCH$_3$), 17.3 (B$_2$CCH$_3$), 83.5 [C$_5$(CH$_3$)$_5$], BCH$_3$, B$_2$CCH$_3$, and =CCH$_3$ not observed. – ^{11}B NMR (64.21 MHz, C_6D_6): δ = 1.1 (1 B, BH, $^1J_{BH}$ = 159 Hz), 2.3 (1 B, BCH$_3$), 6.0 (1 B, BCH$_3$). – MS (EI): *m*/*z* (%) = 382 [M^+] (100), 367 [$M^+ - CH_3$] (20), 233 [Cp*Ru$^+$ − 4 H] (15). – HRMS calcd. for $C_{18}H_{31}B_3Ru$: 381.1761, found 381.1761, Δm = 0.0 mmu.

Dimer of [(η⁵-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η⁵-pentamethylcyclopentadienyl)ruthenium]rhodium Chloride (9*c): To a suspension of μ-dichlorotetraethylenedirhodium (180 mg, 0.46 mmol) in 30 mL of THF 380 mg of **2*c** (1.03 mmol) dissolved in 15 mL of THF was added. After stirring for 12 h the reaction mixture was filtered and the solvent was removed in vacuum. The black residue was purified by chromatography (silica gel, hexane/toluene, 50:50) to give a dark brown solid. Yield: 210 mg (44%). – m.p. 170°C (decomp.). – ^{1}H NMR (200.13 MHz, C_6D_6): δ = 1.28 [s, 15 H, C$_5$(CH$_3$)$_5$], 1.39 (s, 6 H, BCH$_3$), 1.97 (s, 3 H, B$_2$CCH$_3$), 2.23 (s, 6 H, =CCH$_3$). – ^{11}B NMR (64.21 MHz, C_6D_6): δ = 21.8. – MS (EI): *m*/*z* (%) = 1016 [M^+] (100), 779 [M^+ − **2*c**] (4), 509 [M^+ − **2*c** − Rh − Cl] (45), 473 [**2*c**Rh$^+$] (35), 233 [Cp*Ru$^+$ − 4 H] (8).

Table 2. Crystal and collection parameters for compounds **6*a**, **d**

	6*a	**6*d**
Empirical formula	$C_{27}H_{47}B_2NRu$	$C_{25}H_{43}B_2NRu$
Formula weight	508.3	480.3
Crystal system	triclinic	monoclinic
Space group	*P*−1	$P2_1$
Unit cell [Å, °]		
a	9.671(7)	12.035(6)
b	11.115(8)	15.131(8)
c	14.224(10)	14.486(6)
α	72.58(6)	90
β	78.38(6)	95.57(3)
γ	73.13(5)	90
V [Å^3]	1385(2)	2625(2)
Z	2	4
Calcd. density [g/cm^3]	1.22	1.22
Adsorp. coeff. [mm^{-1}]	0.58	0.61
F(000)	540	1016
Crystal size [mm]	0.4 × 0.45 × 0.55	0.2 × 0.25 × 0.45
θ_{max} [°]	25	25
Index range	−11/+11, −12/+13, 0/16	−14/+14, 0/+17, 0/+17
No. of reflections		
unique	4884	4799
observed [$I > 2\sigma(I)$]	4528	3748
Transmission	0.925−1.000	0.763−1.000
Parameters	298	554
Final *R* indices		
*R*1 [$I > 2\sigma(I)$]	0.025	0.063
*wR*2 [all reflections]	0.062	0.165
Largest diff.peak/hole[e/Å^3]	+0.53/−0.53	+1.03/−1.00

Crystal Structure Determinations for 6*a,d: Diffraction data were collected on a Siemens-Stoe AED2 diffractometer (Mo-K_α radiation, graphite monochromator) in the ω-scan mode at −70°C. Crystal data and details of the measurements are summarized in Table 2. The structures were solved by direct methods (SHELXS86)[20] and refined by full-matrix least-squares methods (SHELXL93)[20] based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were added in calculated positions. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-116376 (**6*a**), CCDC-116377 (**6*d**). Copies of the data can be obtained free of charge by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-001; E-mail: deposit@ccdc.cam.ac.uk].

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