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Syntheses and ligand properties of 1,3-di*t*-butyl-2,3-dihydro-1,3-diboroles. Rhodium-(η^5-2,3-dihydro-1,3-diborole) and rhodium-(η^5-2,3-dihydro-1,3-diborolyl) complexes

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Dedicated to Professor Peter Paetzold, on the occasion of his 65th birthday.

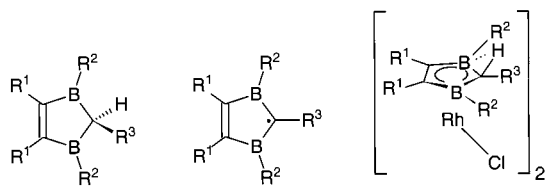
Abstract

Of the new 1,3-di*t*-butyl-2,3-dihydro-1,3-diboroles (**1a**,**b**), the pentaalkyl derivative **1b** reacts with $[(C_2H_4)_2RhCl]_2$ to give the Cl-bridged dimer **2b**. The single crystal structure analysis of **2b** reveals that the hydrogen atoms H2 and H22 in the two-positions are located on the opposite side of the dihydrodiborole rings than the rhodium atoms, with formation of 3c/2e C–H⇀B bonds. The chlorine bridges in **2b** are cleaved with MeLi in toluene to give the arenediborolylrhodium sandwich **3b**. The tetraalkyl-1,3-diborole (**1a**) reacts with MeLi or KH and then $[(C_2H_4)_2RhCl]_2$ in toluene to give the sandwich **3a**. Treatment of **2b** with MeLi in the presence of the 1,3-diborole (**1b**) provides the 16 VE 1,3-diborolyl-1,3-diborolrhodium complex **4b**. With CpNa **2b** forms the 1,3-diborole sandwich **6b**, which has a 3c/2e C–H⇀B bond, whereas with Cp*Li the hydrido complex **7b** with a Rh–H bond is obtained. © 2001 Elsevier Science B.V. All rights reserved.

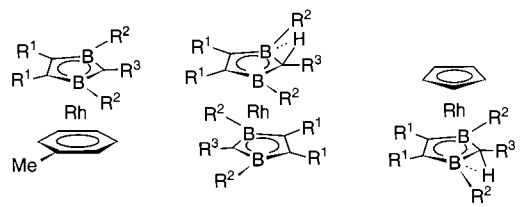
Keywords: Diboroles; Sandwich compounds; Rhodium

1. Introduction

1,2,3,4,5-Pentaalkyl-2,3-dihydro-1,3-diboroles (**1**) function as 4e donor ligands in complexes of the types **2**, **4**, and **6** or, after elimination of a hydrogen atom, as 2,3-dihydro-1,3-diborolyl ligands **1**(-H•), which are 3e donors in complexes **3**, **4**, and **7**. Attempts to synthesize analogous complexes with a 1,3,4,5-tetraalkyl-2,3-dihydro-1,3-diborole ligand (**1**, $R^3 = H$) failed due to the high reactivity of the axial and equatorial hydrogen atoms of the B–CH_2–B group in **2** ($R^3 = H$). In order to increase the stability of tetraalkyl-substituted complexes **2** we have prepared sterically hindered 1,3-diboroles with *t*-butyl substituents at the boron atoms, which are expected to protect the hydrogen atoms at C2. The ligand tetraalkyl-2,3-dihydro-1,3-diborolyl **1a**(-H•) was unexpectedly detected in sandwich **3a** (R^1 = Me, R^2 = *t*-Bu, $R^3 = H$), which was obtained from **1** ($R^1 = R^2$ = Me, $R^3 = H$), *t*-BuLi, and $[(C_2H_4)_2RhCl]_2$ in toluene [1a,c]. We report here the syntheses of the 2,3-dihydro-1,3-diboroles (**1a**,**b**) and the rhodium complexes **2b**–**4b**, **6b**, and **7b**.



1 **1(-H•)** **2**



3 **4** **6**

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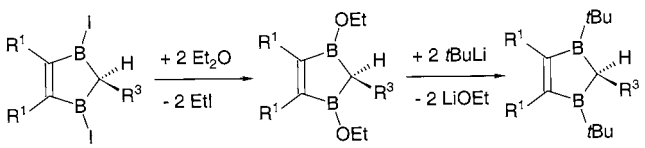
2. Results and discussion

2.1. Syntheses and spectra of 2,3-dihydro-1,3-diboroles (1a,b)

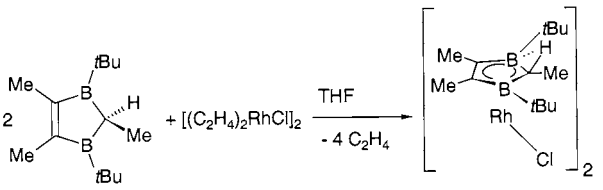
Direct alkylation of 1,3-diiodo-2,3-dihydro-1,3-diboroles with *t-Bu*Li to form the corresponding *t*-butyl derivatives (**1a**,**b**) failed because of the high Lewis acidity of the B–I groups. Instead, isomerization of the *t*-butyl substituents with formation of the 2-butyl derivatives was observed [2,3]. Treatment of the corresponding 1,3-di(ethoxy) derivatives with *t*-BuLi in pentane at 0°C provides the 1,3-di*t*-butyl-2,3-dihydro-1,3-diboroles (**1a**,**b**) in moderate yields. Cleavage of the B–OR bonds is analogous to that in the known reaction with alkyllithium reagents [4–6]. The ^{1}H-, ^{11}B-, ^{13}C-NMR and MS data of the compounds **1a**,**b** are in agreement with the proposed structures.



1	a	b
R^1	Me	Me
R^3	H	Me

2.2. Formation and structure of 2b

Yellow–brown **2b** is synthesized in nearly quantitative yield from **1b** and $[(C_2H_4)_2RhCl]_2$, whereas in the reaction of $[(C_2H_4)_2RhCl]_2$ with **1a** decomposition is observed. Apparently, the steric shielding of the *t*-butyl groups is not sufficient to stabilize **2a**. The new complex **2b** shows an ^{11}B-NMR shift at 30.6 ppm, which is similar to that of pentaalkyl derivatives [1,7]; the ^{1}H-NMR signals are observed in the expected regions. A high-field doublet of quartets pattern at $\delta = -7.87$ with the coupling constants $^{3}J_{HH} = 4.2$ and $^{2}J_{RhH} = 7.2$ Hz is assigned to the CH group in the two-position. In the ^{13}C-NMR spectrum the signal for the olefinic carbon atoms is shifted by about 75 ppm to high-field relative to that of **1b**. For the carbon atom in the two-position the resonance appears as a doublet at $\delta = 41.8$ ($^{1}J_{RhC} = 23$ Hz), and coupling experiments provide $^{1}J_{CH} = 85$ Hz. Thus, the high-field signal for the C(2)–H atom in the ^{1}H-NMR spectrum as well as the low coupling constant $^{1}J_{CH}$ for the C(2) atom in the ^{13}C-NMR spectrum indicate the presence of a C–H⇀B 3c/2e bond [7–9], which is also confirmed in the solid state.



1b **2b**

The crystal structure determination of **2b** reveals that the axial H atom is located on the opposite side of the heterocycle than the rhodium center. The hydrogen atoms H2 and H22 bridge C2–B1 and C22–B21, respectively, and the B–C distances are elongated by 0.168 and 0.164 Å compared to C2–B3 and C22–B23. Thus, **2b** is the first complex in which the bridging hydrogen atom has clearly been located. The other known structures of 1,3-diborole complexes show an ambiguity for the position of this hydrogen atom. For the $(C_5H_5)Co[(CEt)_2(BEt)_2(CMe)H]$ sandwich complex, it was not possible to determine whether the hydrogen atom lies on the mirror plane or whether it is disordered [8a,b]. The sandwich $(C_5H_5)Co\{[C(CH_2)_3]_2(BMe)_2(CMe)H\}$ exhibits a disordered axial hydrogen atom [10]. At the terminal 1,3-diborole ligand of the triple-decker sandwich complex $(C_5H_5)Co[(CEt)_2(BMe)_2(CH)]Co[(CEt)_2(BMe)_2(CH)H]$ the axial hydrogen atom was found directly above the carbon atom, probably resulting from disorder of the hydrogen atom [11]. For the iron sandwich $(MeC_6H_5)Fe[(CEt)_2(BEt)_2(CMe)H]$, the disordered hydrogen atom was located in two positions [8b]. Our NMR results and the X-ray structure analysis of **2b** confirm the presence of a 3c/2e interaction C–H⇀B.

The diborole–rhodium distances are 1.676(1) [Rh–(B1–C2–B3–C4–C5)] and 1.675(1) Å [Rh–(B21–C22–B23–C24–C25)]. The diborole rings are more tightly bonded to the metal center than in (η^5-2,3-dihydro-1,3-diborolyl)arenerhodium complexes **3** [1]. The (η^5-diborole)Rh–Cl units differ slightly, probably as a result of crystal packing effects. Because of the folding of 33.7° along the Cl1–Cl2 vector the 2,3-dihydro-1,3-diborole rings (**1b**) are tilted towards each other. Such foldings along the Cl–Cl vectors are well known for complexes with acceptor ligands [12] (Fig. 1).

2.3. Cleavage of 2b to yield 3b, 4b, 6b, and 7b, and formation of 3a

Yellow **3b** is obtained upon treatment of **2b** with MeLi in toluene followed by chromatography. The alternative synthesis from the pentamethyldiborole with *t*-BuLi, $[(C_2H_4)_2RhCl]_2$, and toluene proceeds to **3b** in only 6% yield. The ^{11}B-NMR spectrum of **3b** shows, as for **3a**, a signal at 32.3 ppm, which is typical for monofacially coordinated 2,3-dihydro-1,3-diborolyl

rings with B–*t*-Bu groups. In the ^{1}H-NMR spectrum, characteristic multiplets are found for the aromatic protons of the coordinated toluene at 5.32 and 5.10 ppm. The protons of the methyl groups show singlets with the corresponding intensities. In the ^{13}C-NMR spectrum, the carbon ring atoms of the coordinated toluene each exhibit a doublet, caused by coupling with the rhodium center ($^1J_{RhC} = 3.39–4.52$ Hz) [13]. Four sharp signals for the methyl C atoms and two broad signals for the carbon atoms next to boron are observed, whereas a signal for the carbon atom between the boron atoms was not detected. The EI mass spectrum, the elemental analysis, and the single crystal structure analysis confirm the formation of **3b** (see below).

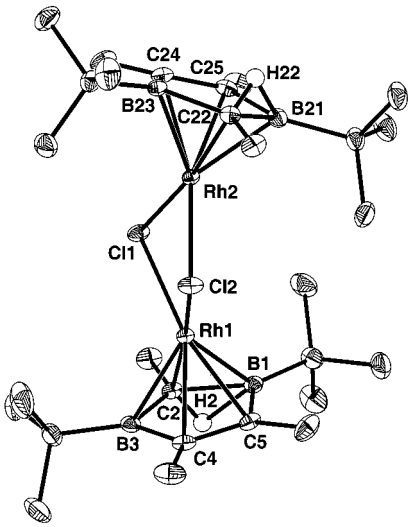


Fig. 1. Molecular structure of **2b**. Selected distances (Å): Rh1–B1 2.104(2), Rh1–C2 2.128(2), Rh1–B3 2.186(2), Rh1–C4 2.175(2), Rh1–C5 2.148(2), B1–C2 1.746(3), C2–B3 1.578(3), B3–C4 1.570(3), C4–C5 1.422(3), C5–B1 1.550(3), B1–H2 1.49(2), C2–H2 0.92(2), Rh2–B21 2.095(2), Rh2–C22 2.128(2), Rh2–B23 2.218(2), Rh2–C24 2.154(2), Rh2–C25 2.148(2), B21–C22 1.750(3), C22–B23 1.586(3), B23–C24 1.563(3), C24–C25 1.423(3), C25–B21 1.559(3), B21–H22 1.49(2), C22–H22 0.93(2).

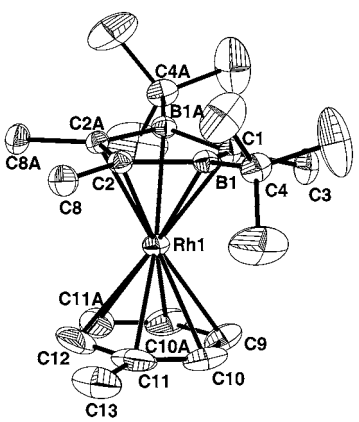
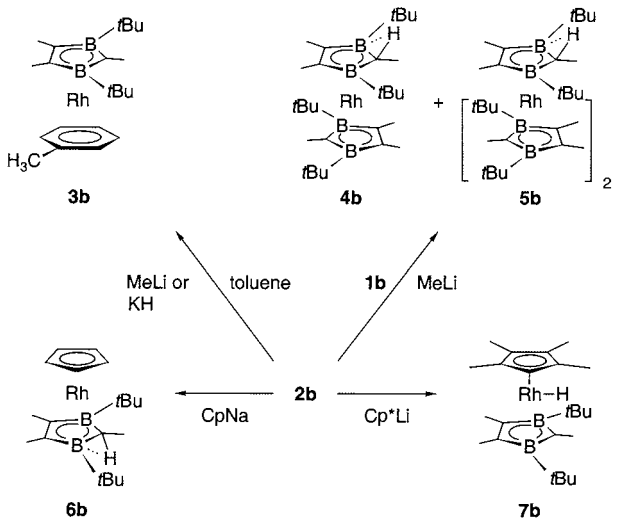


Fig. 2. Molecular structure of **3b**. Selected distances (Å): Rh1–B1 2.320(3), Rh1–C1 2.180(4), Rh1–C2 2.164(3), Rh1–C9 2.297(6), Rh1–C10 2.290(5), Rh1–C11 2.272(5), Rh1–C12 2.274(9), B1–C1 1.549(4), B1–C2 1.544(5), C2–C2A 1.438(6).

As mentioned in the introduction, formation of the ligand **1a**(-H$^\bullet$) was observed in the (η^5-2,3-dihydro-1,3-diborolyl)(η^6-toluene)rhodium sandwich **3a**, which was obtained by adding a THF solution of the 1,3,4,5-tetramethyl-2,3-dihydro-1,3-diborole and *t*-BuLi to a suspension of $[(C_2H_4)_2RhCl]_2$ in toluene [1a,c]. Complex **3a** is also formed from the reaction of **1a** and MeLi or KH with $[(C_2H_4)_2RhCl]_2$ in toluene. However, reactions of the 1,3,4,5-tetramethyldiborole with MeLi or *n*BuLi and then $[(C_2H_4)_2RhCl]_2$ in toluene did not lead to the corresponding sandwich complexes **3**. The stability of **3a** shows that the bulky *t*-butyl groups at the boron atoms of the heterocycle protect the equatorial H atom in the C(2)-position and prevent decomposition.



In **3b** the 2,3-dihydro-1,3-diborolyl ring **1b**(-H$^\bullet$) is folded along the B–B vector by 15.1° [**1a**(-H$^\bullet$) in **3a**: 9.9°]. The diborolyl–Rh and toluene–Rh distances are similar [1.816(2), 1.810(2) Å], and the toluene ligand is disordered; the methyl group is at C11 or C11A. In **3a** the methyl group of complexed toluene lies below the C(2)–H hydrogen atom of the diborolyl ring, thus minimizing the steric interactions [1a,c] (Fig. 2).

(η^5-2,3-Dihydro-1,3-diborole)-Rh-(η^5-2,3-dihydro-1,3-diborolyl) complexes **4** are formed by the reaction of **2** with MeLi and the corresponding 1,3-diborole **1** [7]. The 16 VE complex **4b** is obtained as an orange–red solid from **2b**, **1b**, and MeLi; its chromatographic work-up on Al_2O_3 with hexane yields two fractions. The first fraction contains **4b** and a by-product, which could not be removed by further chromatography. In spite of the presence of different ligands the sandwich **4b** exhibits only one ^{11}B-NMR shift at $\delta = 36.6$. The ^{1}H-NMR signals are assigned as follows: In the case of the 1,3-diborole ring **1b** there are two singlets at 1.71 ppm for the protons of the two C-methyl groups, one

singlet at 1.28 ppm for the *t*-butyl groups, one doublet at 1.19 ppm ($^3J_{HH} = 4.84$ Hz) for the C(2)-methyl protons, and one *pseudo*-quintet at −3.80 ppm ($^3J_{HH} = {}^2J_{RhH} = 4.84$ Hz) for the proton at the carbon atom in the two-position. The protons of the diborolyl ring **1b**(-H•) show singlet resonances at $\delta = 2.01$, 2.00, and 0.99. They were identified by comparing the intensities of the signals for the methyl protons at C(2), at the olefinic C atoms, and of the *t*-butyl groups. The signals in the ^{13}C-NMR spectrum cannot fully be accounted for. For the quaternary carbon atoms of the *t*-butyl groups two broad peaks at 26 and 23 ppm are obtained; the olefinic methyl carbon atoms give two sharp peaks at 19.2 and 16.9 ppm. Signals for carbon ring atoms next to boron atoms are not detected. The methyl groups of the *t*-butyl substituents appear at $\delta = 31.8$ [**1b**(-H•)] and 29.5 (**1b**). A larger difference of $\Delta\delta = 6.9$ ppm is observed for the methyl groups at C(2): 20.0 ppm for **1b**(-H•) and 13.1 ppm for **1b** in **4b**.

Because of its low yield the dark-green triple-decker **5b**, which was isolated in the second fraction, was characterized only by mass spectrometry and high-resolution FAB mass spectroscopy.

Cleavage of the chlorine bridges in the dimer **2b** with CpNa and Cp*Li results in the formation of complexes **6b** and **7b**, respectively. A sample of **2b** obtained in situ is filtered and added to a solution of CpNa in THF or to solid Cp*Li at −18°C. The reaction of **2b** with CpNa results in the formation of the yellow–brown sandwich **6b** in 51% yield. This complex shows a resonance in the ^{11}B-NMR spectrum at 26.5 ppm. In the ^{1}H-NMR spectrum a doublet for the C(2)–Me protons ($\delta = 1.14$) and a doublet of quartets at $\delta = -6.68$ for the proton at C(2) ($^3J_{HH} = 4.5$, $^2J_{RhH} = 7.3$ Hz) are observed. In addition there are three singlets for the protons of the cyclopentadienyl ring, the olefinic methyl groups, and the *t*-Bu substituents at 4.72, 1.79, and 1.42 ppm. Apart from signals for the cyclopentadienyl C atoms and the methyl groups of the *t*-butyl substituents at 85.0 and 33.4 ppm, the other signals in the ^{13}C-NMR spectrum could not unambiguously be assigned due to the presence of by-products. A high-resolution EI mass spectrum verifies the formation of **6b**.

The reaction of **2b** with Cp*Li does not lead to the expected sandwich (C_5Me_5)Rh(**1b**) (**6b***), which should show a 'doublet of quartets' with $^2J_{RhH} = 4.5$–7.5 Hz in the region of −6 to −8 ppm as well as a doublet for the C(2)-methyl protons in the ^{1}H-NMR spectrum. Instead a doublet is found at $\delta = -11.90$ (1H) with a coupling constant of 23 Hz along with a singlet (3H) at 1.57 ppm. The high-field shift ($\Delta\delta = 4$–6 ppm) as well as the strong Rh–H coupling is typical for a hydridic hydrogen atom bonded directly to the rhodium center, as in **7b** [13]. The absence of coupling with the protons of the C(2)-methyl group supports this assignment. The ^{11}B-NMR signal at $\delta = 23.0$ is in the expected region. The ^{13}C-NMR spectrum shows four singlets for the chemically unique methyl carbon atoms, one broad signal for the quaternary carbon atoms of the *t*-butyl groups, and two doublets for the carbon ring atoms of Cp* and the olefinic C atoms of the 2,3-dihydro-1,3-diborolyl ring **1b**(-H•). The signal for the C(2) atom was not found.

3. Conclusions

With the 1,3-di*t*-butyl-2,3-dihydro-1,3-diboroles (**1a**,**b**) we were able to generate new diborole- and diborolyl-rhodium complexes. In particular, it was possible to stabilize the reactive C(2)–H unit in **3a**, through incorporation of bulky substituents at the boron atoms. The crystal structure determination of **2b** unequivocally shows the position of the C(2)–H atom, which forms a 3c/2e C–H⇀B bond on the opposite side of the heterocycle than the rhodium center. The formation of **7** with the π-ligand Cp* exhibits the stabilization of the Rh(+III) oxidation state, in comparison to the Rh(+I) center obtained in compound **6**, which contains the less strongly donating ligand Cp.

4. Experimental

The reactions were carried out under purified argon or nitrogen. The solvents were dried and freed of oxygen before use. NMR: Bruker AC 200, Bruker DRX 200, and Bruker AC 500. MS: Varian MAT CH-7, ZAB-2F VH Micromass CTD, JEOL MS Station JMS 700. C and H analysis was performed by the Organisch-Chemisches Institut der Universität Heidelberg. The starting compounds 1,3-diethoxy-4,5-dimethyl-2,3-dihydro-1,3-diborole [14], 1,3-diiodo-2,4,5-trimethyl-2,3-dihydro-1,3-diborole [14], 1,2,3,4,5-pentamethyl-2,3-dihydro-1,3-diborole [15], $[(C_2H_4)_2RhCl]_2$ [16], and Cp*Li [17] were prepared according to literature methods.

*4.1. 1,3-Dit-butyl-4,5-dimethyl-2,3-dihydro-1,3-diborole (**1a**)*

A total of 12.0 ml (18.0 mmol) of *t*-butyllithium (1.5 M in pentane) in 30 ml of pentane was added to a solution of 1.57 g (8.7 mmol) of 1,3-diethoxy-4,5-dimethyl-2,3-dihydro-1,3-diborole in 20 ml of pentane at 0°C and refluxed for 1 h. After removal of the solvent colorless **1a** was distilled at 90°C/10 mbar. Yield: 830 mg (47%) of **1a**. ^{1}H-NMR (C_6D_6): $\delta = 1.91$ (s, 6H, $=CCH_3$), 1.57 (s, 2H, $C2H_2$), 1.09 (s, 18H, $C(CH_3)_3$). ^{13}C-NMR (C_6D_6): $\delta = 176$ (br, $=CCH_3$), 35 (br, C2), 28.1 ($C(CH_3)_3$), 24 (br, $C(CH_3)_3$), 16.4 ($=CCH_3$). ^{11}B-NMR (C_6D_6): $\delta = 68.8$. MS EI: *m*/*z*

(%) = 204 (M^+, 42), 147 ($M^+ - t$-Bu, 70), 131 ($M^+ - t$-Bu, –H, $-CH_3$, 51), 105 ($M^+ - t$-Bu, $-C_3H_7$, 43), 91 ($M^+ - t$-Bu, $-C_4H_8$, 24), 41 ($C_2H_6B^+$, 100).

4.2. 1,3-Diethoxy-2,4,5-trimethyl-2,3-dihydro-1,3-diborole

A total of 11.36 g (153.2 mmol) of diethyl ether was added at room temperature (r.t.) to a solution of 26.33 g (76.6 mmol) of 1,3-diiodo-2,4,5-trimethyl-2,3-dihydro-1,3-diborole in 30 ml of pentane, and the resulting mixture was stirred for 0.5 h. The solvent was removed, and colorless 1,3-diethoxy-2,4,5-trimethyl-2,3-dihydro-1,3-diborole distilled at 70°C/7 mbar. Yield: 9.69 g (65%) of 1,3-diethoxy-2,4,5-trimethyl-2,3-dihydro-1,3-diborole. ^{1}H-NMR (C_6D_6): $\delta = 3.97$ (*pseudo*-qui, 4H, $^3J_{HH} = 7.07$ Hz, OCH_2), 1.95 (s, 6H, $=CCH_3$), 1.17 (t, 6H, $^3J_{HH} = 7.07$ Hz, OCH_2CH_3), 1.01 (d, 3H, $^3J_{HH} = 7.79$ Hz, C2–CH_3), 0.32 (q, 1H, $^3J_{HH} = 7.79$ Hz, C2–H). ^{13}C-NMR (C_6D_6): $\delta = 167$ (br, $=CCH_3$), 62.8 (OCH_2), 18.0 ($=CCH_3$), 13.7 (OCH_2CH_3), 10.0 (C2–CH_3), C2 n.d. ^{11}B-NMR (C_6D_6): $\delta = 50.1$. MS EI: m/z (%) = 194 (M^+, 3), 166 ($M^+ - CHCH_3$, 3), 131 ($M^+ - C_4H_4B$, 22), 117 ($M^+ - C_5H_6B$, 27), 101 ($M^+ - C_5H_6BO$, 43), 73 ($M^+ - C_7H_{10}BO$, 54), 45 (OEt^+, 98), 28 ($CHCH_3^+$, 100).

4.3. 1,3-Dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborole (**1b**)

A total of 58.8 ml (100.0 mmol) of *t*-butyllithium (1,7 M in pentane) in 10 ml of pentane was added to a solution of 9.69 g (50.0 mmol) of 1,3-diethoxy-2,4,5-trimethyl-2,3-dihydro-1,3-diborole in 10 ml of pentane at 0°C, and the resulting mixture was refluxed for 1 h. After removal of the solvent, colorless **1b** was distilled at 65°C/5 mbar. Yield: 6.29 g (58%) of **1b**. ^{1}H-NMR (C_6D_6): $\delta = 2.05$ (q, 1H, $^3J_{HH} = 6.89$ Hz, C2–H), 1.94 (s, 6H, $=CCH_3$), 1.22 (d, 3H, $^3J_{HH} = 6.89$ Hz, C2–CH_3), 1.09 (s, 18H, $C(CH_3)_3$). ^{13}C-NMR (C_6D_6): $\delta = 177$ (br, $=CCH_3$), 38 (br, C2), 28.1 ($C(CH_3)_3$), 25 (br, $C(CH_3)_3$), 19.0 (C2–CH_3), 16.9 ($=CCH_3$). ^{11}B-NMR (C_6D_6): $\delta =$ 69.9. MS EI: m/z (%) = 218 (M^+, 7), 161 ($M^+ - t$-Bu, 17), 145 ($M^+ - t$-Bu, –H, $-CH_3$, 16), 119 ($M^+ - t$-Bu, –H, $-C_3H_5$, 15), 81 ($M^+ - t$-Bu, $-C_5H_8B$, 20), 57 (t-Bu^+, 76), 41 ($C_3H_5^+$, 100).

4.4. Bis-[(η^5-1,3-dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborole)rhodiumchloride] (**2b**)

A total of 119 mg (0.55 mmol) of **1b** was added at r.t. to a suspension of 106 mg (0.27 mmol) of $[(C_2H_4)_2RhCl]_2$ in 15 ml of THF, and the mixture was stirred for 18 h. After filtration (G4 frit) the solvent was removed, and yellow–brown solid **2b** was purified by chromatography on silica gel with hexane. Yield: 178 mg (91%) of **2b**. ^{1}H-NMR (C_6D_6): $\delta = 1.53$ (s, 36H, $C(CH_3)_3$), 1.46 (s, 12H, $=CCH_3$), 1.17 (d, 6H, $^3J_{HH} =$ 4.19 Hz, C2–CH_3), -7.87 (dq, 2H, $^3J_{HH} = 4.19$ Hz, $^2J_{RhH} = 7.2$ Hz, C2–H). ^{13}C-NMR (C_6D_6): $\delta = 102$ (br, $=CCH_3$), 41.8 (dd, $^1J_{RhC} = 23$ Hz, $^1J_{CH} = 85$ Hz, C2), 31.1 ($C(CH_3)_3$), 20 (br, $C(CH_3)_3$) 16.1 ($=CCH_3$), 14.8 (C2–CH_3). ^{11}B-NMR (C_6D_6): $\delta = 30.6$. MS EI: m/z (%) = 712 (M^+, 9), 653 ($M^+ - t$-Bu, $-2 \times$ H, 12), 57 (t-Bu^+, 65), 41 ($C_3H_7^+$, 100).

4.5. (η^5-1,3-Dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborolyl)(η^6-toluene)rhodium (**3b**)

A total of 0.43 ml (0.64 mmol) of methyllithium (1.5 M in diethyl ether) was added dropwise at -30°C to a solution of 228 mg (0.32 mmol) of **2b** in 10 ml of toluene. After the mixture was allowed to warm to r.t. overnight, the solution was filtered (G4 frit) and the solvent removed. Yellow, crystalline **3b** was purified by chromatography on Al_2O_3 with hexane. Yield: 104 mg (79%) of **3b**; m.p. = 95°C (decomp.). ^{1}H-NMR (C_6D_6): $\delta = 5.32$ (m, 4H, CH_{ar}), 5.10 (m, 1H, p-CH_{ar}), 1.88 (s, 3H, C2–CH_3), 1.77 (s, 6H, $=CCH_3$), 1.54 (s, 3H, $C_{ar}CH_3$), 1.46 (s, 18H, $C(CH_3)_3$). ^{13}C-NMR (C_6D_6): $\delta = 110$ (br, $=CCH_3$), 109.6 (d, $^1J_{RhC} = 3.39$ Hz, $C_{ar}CH_3$), 98.1 (d, $^1J_{RhC} = 3.95$ Hz, o- or m-C_{ar}), 97.1 (d, $^1J_{RhC} = 3.95$ Hz, o- or m-C_{ar}), 94.0 (d, $^1J_{RhC} = 4.52$ Hz, p-C_{ar}), 33.2 ($C(CH_3)_3$), 23.2 (C2–CH_3), 20 (br, $C(CH_3)_3$), 18.6 ($C_{ar}CH_3$), 17.2 ($=CCH_3$), C2 n.d. ^{11}B-NMR (C_6D_6): $\delta = 32.3$. MS EI: m/z (%) = 412 (M^+, 100), 355 ($M^+ - t$-Bu, 18), 300 ($M^+ - 2 \times C_4H_8$, 13). $C_{21}H_{35}B_2Rh$ (412,0) Anal. Calc.: C, 61.21; H, 8.56; B, 5.24; Rh, 24.97. Found: C, 60.79; H, 8.80%.

A total of 0.93 ml (1.39 mmol) of *t*-butyllithium (1,5 M in pentane) was added at -60°C to 186 mg (1.39 mmol) of 1,2,3,4,5-pentamethyl-2,3-dihydro-1,3-diborole in 10 ml of THF, and the mixture was stirred for 0.5 h. The solution was transferred dropwise to a suspension of 270 mg (0.69 mmol) of $[(C_2H_4)_2RhCl]_2$ in 10 ml of toluene at -30°C. After the mixture was allowed to warm to r.t. overnight and the solvent removed, **3b** was purified by chromatography on Al_2O_3 with hexane. Yield: 34 mg (6%) of **3b**.

4.6. (η^5-1,3-Dit-butyl-4,5-dimethyl-2,3-dihydro-1,3-diborolyl)-(η^6-toluene)rhodium (**3a**) from **1a** with MeLi and KH

4.6.1. MeLi

A total of 0.33 ml (0.53 mmol) of methyllithium (1.6 M in diethyl ether) was added at -60°C to a solution of 109 mg (0.53 mmol) of **1a** in 10 ml of THF, and the mixture was stirred for 0.5 h. This solution was transferred dropwise to a suspension of 104 mg (0.27 mmol) of $[(C_2H_4)_2RhCl]_2$ in 10 ml of toluene at -30°C. After the mixture was allowed to warm to r.t. overnight the

solvent was removed, and **3a** was sublimed at 90°C/5 × 10^{-2} mbar or purified by chromatography on Al_2O_3 with hexane. Yield: 85 mg (40%) of **3a**.

4.6.2. KH

A total of 386 mg (1.89 mmol) of **1a** was added to 117 mg (2.90 mmol) of KH in 10 ml of THF at −60°C. After 0.5 h the mixture was filtered (G4 frit), and the filtrate was added to 368 mg (0.95 mmol) of $[(C_2H_4)_2RhCl]_2$ in 10 ml of toluene at −30°C. After the mixture was allowed to warm to r.t. overnight the solvent was removed, and **3a** was sublimed at 90°C/5 × 10^{-2} mbar or purified by chromatography on Al_2O_3 with hexane. Yield: 150 mg (20%) of **3a**.

4.7. (η^5-1,3-Dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborole)-(η^5-1,3-dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborolyl)rhodium (**4b**) and triple-decker **5b**

A total of 243 mg (1.12 mmol) of **1b** was added at r.t. to a suspension of 217 mg (0.56 mmol) of $[(C_2H_4)_2RhCl]_2$ in 10 ml of THF, and the mixture was stirred for 18 h. A total of 0.70 ml (1.12 mmol) of methyllithium (1.6 M in diethyl ether) was added at −60°C to another 243 mg (1.12 mmol) of **1b** in 10 ml of THF, and the mixture was filtered (G4 frit) and after 0.5 h transferred at −30°C to the solution of the diborole–Rh–Cl dimer. After removal of the solvent orange–red **4b** was obtained by chromatography on Al_2O_3 with hexane. Yield: 406 mg (67%) of **4b**; m.p. = 153°C (decomp.). ^{1}H-NMR (C_6D_6): $\delta = 2.01$ (s, 3H, C2–CH_3^a)^a = **1b**(-H$^\bullet$), 2.00 (s, 6H, =CCH_3^a), 1.71 (s, 6H, =CCH_3^b)^b = **1b**, 1.28 (s, 18H, C(CH_3)$_3^b$), 1.19 (d, 3H, $^3J_{HH} = 4.84$ Hz, C2–CH_3^b), 0.99 (s, 18H, C(CH_3)$_3^a$), −3.80 (*pseudo*-qui, 1H, $^3J_{HH} = {}^2J_{RhH} = 4.84$ Hz, C2–H^b). ^{13}C-NMR (C_6D_6): $\delta = 31.8$ (C(CH_3)$_3^a$), 29.5 (C(CH_3)$_3^b$), 26 + 23 (br, $C(CH_3)_3^{a+b}$), 20.0 (C2–CH_3^a), 19.2 + 16.9 (=CCH_3^{a+b}), 13.1 (C2–CH_3^b), =CCH_3^{a+b} and $C2^{a+b}$ n.d. ^{11}B-NMR (C_6D_6): $\delta = 36.6$. MS EI: m/z (%) = 538 (M^+, 54), 481 ($M^+ - t$-Bu, 100), 424 ($M^+ - 2 \times t$-Bu, 26), 368 ($M^+ - C_4H_8$, $-2 \times t$-Bu, 45). MS HR-EI: Calc. for $C_{28}H_{55}B_4Rh$: 538.3731; found: 538.3727, $\Delta = 0.4$ mmu. Yield: 23 mg (2%) of dark-green **5b**. MS FAB: m/z (%) = 856 ($M^+ - 2 \times$ H, 50), 640 (M^+–1h, 35), 537 ($4b^+$–H, 100), 481 ($4b^+ - t$-Bu, 86). MS HR-FAB: Calc. for $C_{42}H_{82}B_6Rh_2$: 858.5619; found: 858.4952, $\Delta = 4.8$ mmu.

4.8. (η^5-Cyclopentadienyl)-(η^5-1,3-dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborole)rhodium (**6b**)

A total of 228 mg (1.04 mmol) of **1b** was added at r.t. to a suspension of 203 mg (0.52 mmol) of $[(C_2H_4)_2RhCl]_2$ in 10 ml of THF, and the mixture was stirred for 18 h. After filtration (G4 frit) the filtrate was added at −18°C to CpNa, which was synthesized from 151 mg (6.29 mmol) of NaH in 10 ml of THF and 69 mg (1.04 mmol) of CpH at r.t. After the mixture had warmed to r.t., the solvent was removed. Yellow–brown **6b** was obtained by chromatography on Al_2O_3 with hexane. Yield: 204 mg (51%) of **6b**. ^{1}H-NMR (C_6D_6): $\delta = 4.72$ (s, 5H, C_5H_5), 1.79 (s, 6H, =CCH_3), 1.42 (s, 18H, C(CH_3)$_3$), 1.14 (d, 3H, $^3J_{HH} = 4.5$ Hz, C2–CH_3), −6.68 (dq, 1H, $^3J_{HH} = 4.5$ Hz, $^2J_{RhH} = 7.3$ Hz, C2–H). ^{13}C-NMR (C_6D_6): $\delta = 85.0$ (d, $^1J_{RhC} = 5.5$ Hz, C_5H_5), 33.4 (C(CH_3)$_3$), C2, C2–CH_3, $C(CH_3)_3$, =CCH_3, and =CCH_3 not assigned. ^{11}B-NMR (C_6D_6): $\delta = 26.5$. MS HR-EI: m/z (%) = 386 (M^+, 100), 327 ($M^+ - t$-Bu, $-2 \times$ H, 60), 313 ($M^+ - t$-Bu, $-CH_3$, –H, 60), 299 ($M^+ - t$-Bu, $-2 \times CH_3$, 22), 285 ($M^+ - C_4H_8$, $-3 \times CH_3$, 46), 271 (M^+–H, $-2 \times t$-Bu, 46), 233 (Cp_2Rh^+, 27), 168 ($CpRh^+$, 34). Calc. for $C_{19}H_{33}B_2Rh$: 386.1824; found: 386.1848, $\Delta = 2.4$ mmu.

4.9. (η^5-Pentamethylcyclopentadienyl)-(η^5-1,3-dit-butyl-2,4,5-trimethyl-2,3-dihydro-1,3-diborolyl)-rhodiumhydride (**7b**)

A total of 419 mg (1.15 mmol) of **1b** were added at r.t. to a suspension of 374 mg (0.57 mmol) of $[(C_2H_4)_2RhCl]_2$ in 8 ml of THF, and the mixture was stirred for 18 h. After filtration (G4 frit) the filtrate was added to 273 mg (1.17 mmol) of Cp*Li at −18°C and the solvent removed. Orange–brown, crystalline **7b** was obtained by chromatography on Al_2O_3 with hexane. Yield: 636 mg (73%) of **7b**; m.p. = 83–88°C (decomp.). ^{1}H-NMR (C_6D_6): $\delta = 1.59$ (s, 6H, =CCH_3), 1.57 (s, 3H, C2–CH_3), 1.55 (s, 15H, $C_5(CH_3)_5$), 1.43 (s, 18H, C(CH_3)$_3$), −11.90 (d, 1H, $^1J_{RhH} = 23$ Hz, Rh–H). ^{13}C-NMR (C_6D_6): $\delta = 98.2$ (d, $^1J_{RhC} = 5.45$ Hz, $C_5(CH_3)_5$), 97.7 (d, $^1J_{RhC} = 5.45$ Hz, =CCH_3), 33.4 (C(CH_3)$_3$), 21.5 (C2–CH_3), 20 (br, $C(CH_3)_3$), 15.6 (=CCH_3), 10.0 ($C_5(CH_3)_5$), C2 n.d. ^{11}B-NMR (C_6D_6): $\delta = 23.0$. MS EI: m/z (%) = 456 (M^+, 21), 398 ($M^+ - t$-Bu, –H, 39), 383 ($M^+ - t$-Bu, $-CH_3$, –H, 12), 355 ($M^+ - t$-Bu, $-C_3H_8$, 14), 342 ($M^+ - 2 \times C_4H_8$, 35), 238 (Cp^*Rh^+, 39), 43 ($C_3H_7^+$, 100). MS HR-FAB: Calc. for $C_{24}H_{43}B_2Rh$: 456.2606; found: 456.2678, $\Delta = 7.2$ mmu.

4.10. Crystal structure determinations of **2b** and **3b** (see Section 5)

Crystal data and details of the structure determinations are listed in Table 1. Intensity data were collected at −100°C (**2b**) and r.t. (**3b**) with a Bruker AXS SMART 1619 diffractometer with CCD area collector (Mo–K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω-scan). Empirical absorption corrections (multi-scan) were applied. The structures were solved

Table 1
Crystal data and structure refinement of **2b** and **3b**

	2b	**3b**
Empirical formula	$C_{28}H_{56}B_4Cl_2Rh_2 \cdot 0.5C_6H_{14}$	$C_{21}H_{35}B_2Rh$
Formula weight	755.8	412.0
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pnma*
Unit cell dimensions		
a (Å)	16.6351(3)	12.9250(2)
b (Å)	11.6179(2)	17.6758(2)
c (Å)	19.3161(3)	9.5081(1)
β (°)	94.273(1)	
V (Å^3)	3722.75(11)	2172.22(5)
Z	4	4
D_{calc} (g cm^{-3})	1.35	1.26
μ (Mo–K$_\alpha$) (cm^{-1})	10.5	7.9
Crystal size (mm)	$0.17 \times 0.20 \times 0.32$	$0.18 \times 0.48 \times 0.54$
Transmission	0.780–0.862	0.610–0.862
2θ max (°)	56.6	56.5
Unique reflections	9153	2778
Observed ($I > 2\sigma I$)	7732	1950
Parameters	600	132
R_1	0.024	0.042
wR_2	0.062	0.125
Max. residual electron density (e Å^{-3})	$-0.3/+1.0$	$-0.6/+0.8$

by direct methods (SHELXS-86) [18] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97) [18]. Non-hydrogen atoms were refined anisotropically. For **2b**, hydrogen atoms were located and refined isotropically and for **3b** they were included in calculated positions or as part of a rigid group.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 142818 for compound **2b** and CCDC no. 142819 for compound **3b.** 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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References

[1] (a) S. Huck, A. Ginsberg, H. Pritzkow, W. Siebert, J. Organomet. Chem. 571 (1998) 107. (b) S. Huck, Dissertation Universität Heidelberg, 1997. (c) A. Ginsberg, Dissertation, Universität Heidelberg, 213.
[2] T. Müller, W. Siebert, unpublished results.
[3] (a) G.F. Hennion, P.A. McCusker, E.C. Ashby, A.J. Rutkowski, J. Am. Chem. Soc. 79 (1957) 5190. (b) G.F. Hennion, P.A. McCusker, A.J. Rutkowski, J. Am. Chem. Soc. 80 (1958) 617. (c) P.A. McCusker, J.V. Marra, G.F. Hennion, J. Am. Chem. Soc. 83 (1961) 1924.
[4] (a) G.W. Kramer, H.C. Brown, J. Organomet. Chem. 73 (1974) 1. (b) E. Negishi, H.C. Brown, J. Am. Chem. Soc. 95 (1973) 6757.
[5] A. Maderna, H. Pritzkow, W. Siebert, Angew. Chem. 108 (1996) 1664; Angew. Chem. Int. Ed. Engl. 35 (1996) 1501.
[6] C. Ester, A. Maderna, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. (2000) 1177.
[7] (a) K. Geilich, W. Siebert, Z. Naturforsch. 41b (1986) 671. (b) K. Geilich, Dissertation, Universität Heidelberg, 1986.
[8] (a) J. Edwin, M.C. Böhm, N. Chester, D.M. Hoffman, R. Hoffmann, H. Pritzkow, W. Siebert, K. Stumpf, H. Wadepohl, Organometallics 2 (1983) 1666. (b) W. Siebert, Angew. Chem. 97 (1985) 924; Angew. Chem. Int. Ed. Engl. 24 (1985) 943. (c) K. Geilich, K. Stumpf, H. Pritzkow, W. Siebert, Chem. Ber. 120 (1987) 911. (d) G.E. Herberich, in: E. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comp. Organomet. Chem. II, Vol. 1, Pergamon Press, Oxford, 1995, p. 197.
[9] C. Elschenbroich, A. Salzer, Organometallchemie, 3rd ed., Teubner-Verlag, Stuttgart, 1993, p. 320.
[10] U. Fenner, H. Pritzkow, W. Siebert, Z. Naturforsch. 49b (1994) 315.
[11] T. Grell, Dissertation, Universität Heidelberg, 1986.
[12] P. Binger, J. Haas, G. Glaser, R. Goddard, C. Krüger, Chem. Ber. 127 (1994) 1927.
[13] J. Mason, Multinuclear NMR, Plenum Press, New York, London, 1987, p. 521 and references cited therein.
[14] W. Siebert, U. Ender, W. Herter, Z. Naturforsch. B 40 (1985) 326.
[15] G. Knörzer, W. Siebert, Z. Naturforsch. B 45 (1990) 15.
[16] (a) R. Cramer, Inorg. Chem. 1 (1962) 722. (b) R. Cramer, Inorg. Synth. 15 (1974) 14.
[17] U. Kölle, B. Fuss, Chem. Ber. 117 (1984) 743.
[18] (a) G.M. Sheldrick, SHELXS-86 Program for Crystal Structure Solution, University of Göttingen, Germany, 1986. (b) G.M. Sheldrick, SHELXL-97 Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.