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Syntheses, structures and reactivity of η^6-arene-η^5-2,3-dihydro-diborolyl-rhodium complexes[1]

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Abstract

The reactions between dirhodium-μ-dichloro-tetraethylene and the 2,3-dihydro-1,3-diborole derivatives **1a**,**b** in toluene and benzene yield the sandwich complexes **3a**–**c** and **4a**,**b**. Their compositions have been derived from spectroscopic and analytical data and were confirmed by single crystal structure analyses for **3a**, **b**, **c** and for **4b**. On heating, these compounds lose the arene ligand and the remaining complex fragments undergo stacking with formation of triple-decker complexes (**6a**,**b**) and a tetradecker complex (**7b**). Thermogravimetric analyses of **3** and **4** indicate that the decomposition occurs in two steps: the first represents the elimination of the arene and the second the thermal decomposition of the residue. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: η^6-Arene-η^5-(2,3-dihydro-1,3-diborolyl)rhodium; Sandwich compounds; Triple-decker complexes

1. Introduction

Metal-containing polymers are long known and are of high interest with respect to their electrical properties [1]. One may divide them into several classes, depending on the connectivities of the monomeric building units: In Krogmann's salt the polymer is formed through direct Pt–Pt bonds, whereas in polymetallaphthalocyanines the metal complexes are connected via chalcogen bridges between the metal atoms.

In polyvinylferrocene the iron atoms of the ferrocenyl groups bonded to the polyethene chain have no electronic contact. A special arrangement is found in oligo- and polydecker sandwich complexes **I** and **II**, in which the 2,3-dihydro-1,3-diborolyl ligands are bifacially bonded to two metals. Five-membered organoboron heterocycles with one, two, or three boron atoms are well-suited as bridging ligands because they act as both electron-donors and -acceptors. A large number of triple- and tetradecker complexes has been reported [2] and designed syntheses has led to structurally characterized [3] penta- and hexadecker complexes. The first polydecker sandwich complexes composed of the metals nickel (**I**) and rhodium (**II**) and the 2,3-dihydro-1,3-diborolyl ligands have been obtained via polycondensation reactions [4,5] of the triple-deckers **III** and of **IV**.

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[1] Dedicated to Professor Alberto Ceccon, on the occasion of his 65th birthday.

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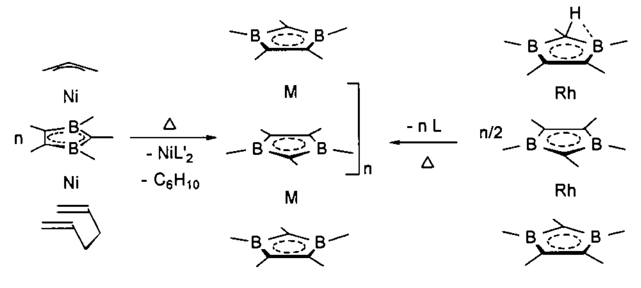


III I M = Ni IV

II M = Rh

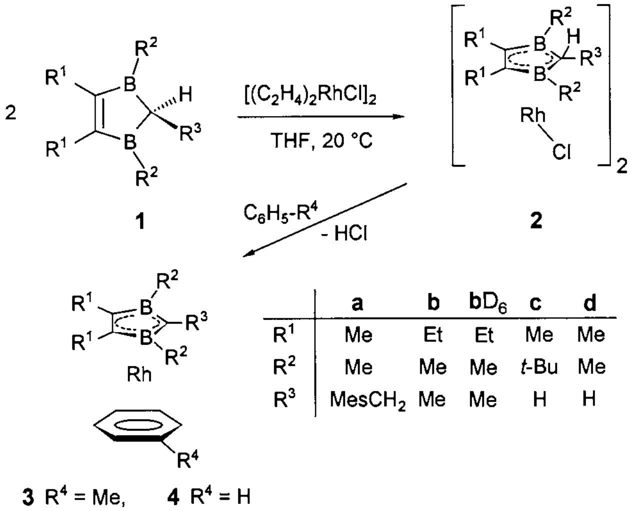
On heating **III** and slowly increasing the vacuum to 10^{-2} Torr, the elimination of bis(η^3-allyl)nickel and 1,5-hexadiene and formation of the polydecker **I**, M = Ni, is observed. The black polymeric material is a semiconductor (10^{-2} S cm^{-1}, four-point measurements) and according to EXAFS-studies has a Peierls-distorted structure with short Ni–C(B) (2.17) and long Ni–C(B) distances (2.56 Å) in a ratio 1:1 and a Ni···Ni distance of 3.35 Å [4]. Quantum mechanical calculations for the one-dimensional solid on the basis of an INDO-Hamiltonian support the proposed structure [6]. The rhodium triple-decker **IV** reacts at 150°C in vacuum with elimination of the 1,3-diborole ligand to form the polydecker **II** which according to conductivity measurements is an insulator.

Stacking reactions to generate oligo- and polydecker compounds should be feasible also with sandwich or halfsandwich compounds, which in addition to the boron heterocycle have a weakly bonded ligand. Heating should result in the elimination of a neutral ligand and the formed reactive complex fragment may stabilize itself by docking at a Lewis-acidic site of a neighboring molecule or a stacking fragment. We report here the formation and reactivity of arene–rhodium-2,3-dihydro-1,3-diborolyl complexes **3** und **4**.

2. Results and discussion

2.1. Syntheses and spectra of sandwiches 3 and 4

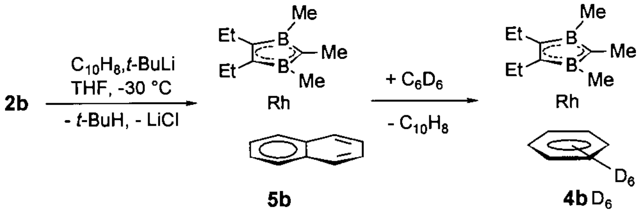
On reaction of the 2,3-dihydro-1,3-diborole derivatives **1a** [7] and **1b** [8] with dirhodium-μ-dichloro-tetraethylene in THF at room temperature (r.t.), the orange compounds **2a**,**b** are formed. The tetraethylmethyl derivative of **2** ($R^1 = R^2 = Et$, $R^3 = Me$) [9] and **2a** exhibit unique high-field 1H-NMR signals for the axial H atom ($\delta = -7.9$; -7.3). The syntheses of the arene-2,3-dihydro-1,3-diborolyl complexes **3a**,**b** and **4a**,**b** are achieved by dehydrochlorination of the dinuclear complexes **2a**,**b** in the desired arene as solvent at r.t. Potassium hydride and *t*-butyllithium are used as bases. Serendipitously, **3b** was first formed without addition of a base during chromatographic workup of **2b** on silica gel with toluene as solvent. Derivatives of the sandwiches **3** and **4** are yellow to brown needles after crystallization in hexane. On heating, the compounds change colors before melting.



	a	b	bD$_6$	c	d
R^1	Me	Et	Et	Me	Me
R^2	Me	Me	Me	*t*-Bu	Me
R^3	MesCH$_2$	Me	Me	H	H

The sandwich complex **3c** cannot be obtained via this route because 2,3-dihydro-1,3,4,5-tetraalkyl-1,3-diboroles with two hydrogens at the C2 atom do not yield **2** upon reaction with dirhodium-μ-dichloro-tetraethylene [9,10]. Therefore, **1d** [11] is reacted with *t*-BuLi in THF at −60°C and the resulting solution is added to a suspension of dirhodium-μ-dichloro-tetraethylene in toluene at −30°C. The complex **3c** is isolated from the hexane-soluble fraction by sublimation in a 29% yield. Its formation occurs by a twofold exchange of Me for *t*-Bu groups via quaternization of the boron atoms [12]. Elimination of methane and LiCl leads to **3c**, the first rhodium-1,3-diborolyl sandwich complex with a hydrogen atom at C2 and *t*-Bu substituents at the boron atoms.

$$\mathbf{1d} \xrightarrow[\text{2. [(C}_2\text{H}_4)_2\text{RhCl]}_2\text{,toluene}]{\text{1. }t\text{-BuLi,THF, -30 °C}} \mathbf{3c} + \text{LiCl} + t\text{-BuH} + \text{ethene}$$



The method of dehydrohalogenation of **2** in the presence of arenes as a preparative route to arene–rhodium-2,3-dihydro-1,3-diborolyl complexes **3** and **4** can be used for the preparation of other compounds. Naphthalene was added to a solution of **2b** in THF at − 30°C, which was then reacted with a stoichiometric amount of *t*-butyllithium. An immediate reaction occurred as indicated by darkening of the solution. After removal of THF in vacuum, hexane was added, the formed lithium chloride separated by filtration and the excess of naphthalene was sublimed at 40°C 10^{-3} Torr. The EI MS of the product indicated the presence of **5b**. As ^{1}H- and ^{13}C-NMR spectra prove that the naphthalene in **5b** is rapidly exchanged for C_6D_6 to give **4b**D_6 in a 58% yield.

The compositions of the compounds **3a**–**c** and **4a**,**b** follow from NMR, MS and analytical data. In the ^{11}B-NMR spectra the complexes exhibit typical shifts [13] for monofacially coordinated boron atoms: $\delta = 27.7$ (**3a**), 27.9 (**3b**), 31.9 (**3c**), 28.6 (**4a**), and 28.4 (**4b**). The ^{1}H-NMR chemical shifts of the compounds are in the expected region. The toluene and benzene complexes show very little differences in their shifts and the coordinated arenes exhibit shifts to higher fields relative to those of the free arenes ($\Delta\delta$ (CHtol) ca. 2.0, $\Delta\delta$ (CH_3tol) ca. 0.7, $\Delta\delta$ (C_6H_6) ca. 2.2).

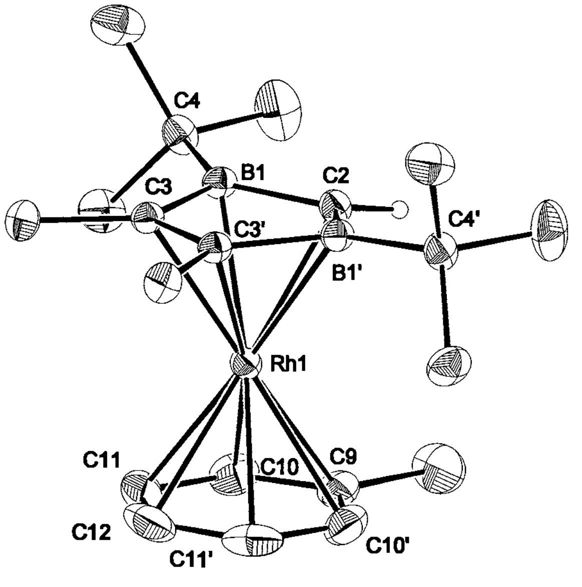
The ^{13}C-NMR shifts are observed in the expected region. The signals for the boron methyl groups are shifted ca. 8 ppm to a higher field relative to that of the free diborole. The resonances of the complexed arenes are about 30 ppm upfield relative to those of the free arenes.

The assignment of the signal $\delta = 23.1$ of the methylene group in **3b** was possible by DEPT spectrum, whereas the assignment of the signals $\delta = 18.6$ and 18.7 for the methyl carbon at C2 and that of complexed toluene was not possible. The signals of the carbon atoms adjacent to boron could not always be detected.

2.2. Crystal structures analyses of *3a*–*c* and *4b*

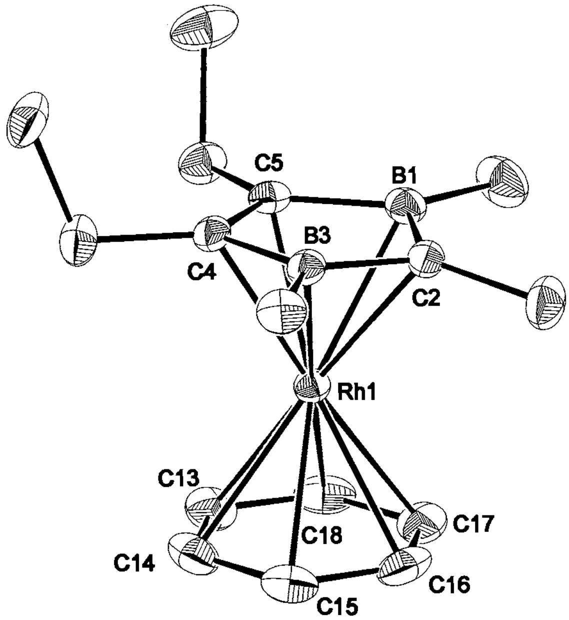
The molecular structures of the four sandwich compounds **3a**–**c**, and **4b** are very similar. The best planes through the heterocycle and arene ligand are almost coplanar (angles between the planes 1–3°). The distances from the Rh atom to the arene plane (1.788–1.796(3) Å) and to the heterocycle plane (1.790–1.815(3) Å) differ only slightly. The diborolyl ring is folded along a line through the boron atoms (7–10°) (Figs. 1 and 2).

Significant elongation of the C–C bond lengths of the arenes by complexation does not occur. According to the Dewar–Chatt–Duncanson model there is a connection between the change of ligand geometry by complexation and the bond strength. Our results indicate that the 1,3-diborolyl ligand in **3a**, **b**, **c** and **4b** is more tightly bonded to the rhodium atom than benzene or toluene. This is an important prerequisite for the thermal polycondensation of these complexes to yield 1,3-diborolyl-rhodium stacked oligomers, which is in agreement with the thermogravimetric studies (see below).



3c

Fig. 1. Molecular structure of **3c**. Selected distances (Å): Rh1–B1 2.299(5), Rh1–C2 2.185(6), Rh1–C3 2.181(4), Rh1–C9 2.287(7), Rh1–C10 2.287(5), Rh1–C11 2.265(5), Rh1–C12 2.253(8), B1–C2 1.538(6), B1–C3 1.559(6), C3–C3′ 1.446(8).



4b

Fig. 2. Molecular structure of **4b**. Selected distances (Å): Rh1–B1 2.253(6), Rh1–C2 2.206(2), Rh1–B3 2.286(3), Rh1–C4 2.167(6), Rh1–C5 2.159(2), Rh1–C13 2.281(3), Rh1–C14 2.284(3), Rh1–C15 2.287(3), Rh1–C16 2.238(3), Rh1–C17 2.256(3), Rh1–C18 2.284(3), B1–C2 1.537(4), C2–B3 1.544(4), B3–C4 1.558(4), C4–C5 1.444(4), B1–C5 1.545(4).

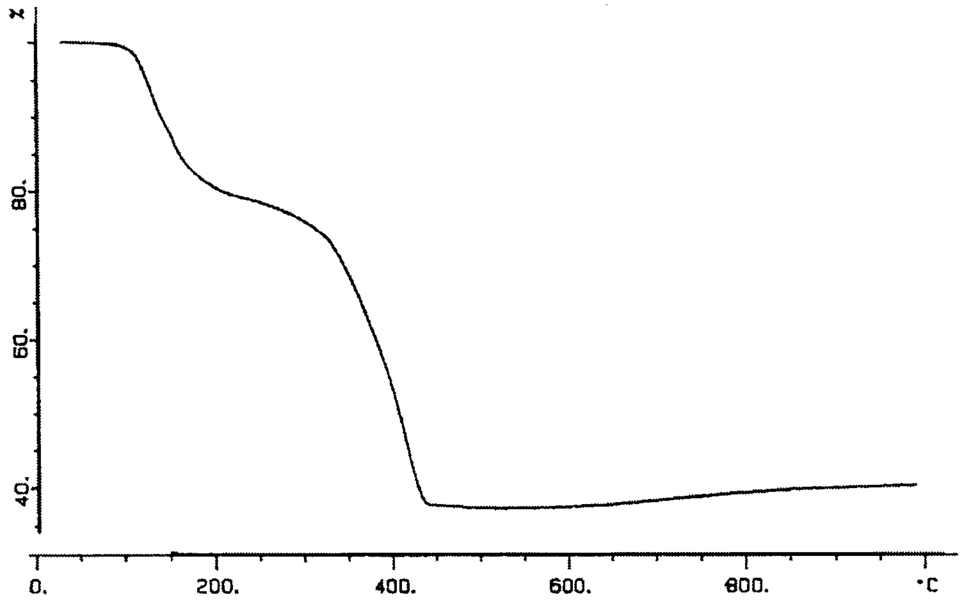
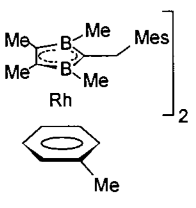


Fig. 3. TG curve of **3a**. Start temperature 25°C, final temperature 1000°C, heating rate 10 K min^{-1}, flowgas N_2.

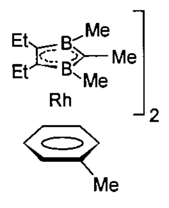
2.3. Thermogravimetric analyses and condensation reactions

The thermal decomposition of the sandwich compounds **3a**,**b** and **4b** occurs in two steps (s. Fig. 3 and Fig. 4). The mass decrease of 20% in the first step (onset at $T = 100-130$°C) represents the expected loss of the arene and occurs for **4b** in a temperature range of only 6 K. The final decomposition takes place at temperatures > 240°C (Table 1, Figs. 3 and 4).

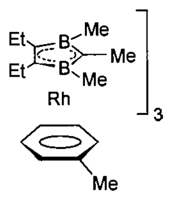
For the detection of the condensation products, 25 mg of **3a** were heated under a constant flow of inert gas to 145°C and left for 15 min at this temperature. At 110°C a color change from yellow–brown to black occurs. The FAB mass spectra of the residue exhibits besides the masses of **3a** also those of the triple-decker **6a**. Heating of **3b** to 130°C leads to the formation of the triple- and tetradecker **6b** and **7b** identified by FAB mass spectrometry.



6a



6b



7b

3. Experimental

The reactions were carried out under purified argon or nitrogen. The solvents were dried and oxygen was removed. NMR: Bruker AC 300, Bruker AC 200 and Jeol FX-90. MS: Varian MAT CH7 and Finnigan MAT 8230. Thermogravimetry: Mettler TG 50, TC11-Processor. C,H Analyses: Organisch-Chemisches Institut der Universität Heidelberg. The starting compounds dirhodium-μ-dichloro-tetraethylene [14], **1a** [7], **1b** [7,8] and **1d** [11] were prepared according to the literature.

3.1. *Bis[η⁵-(1,3,4,5-tetramethyl-2-(2,4,6-trimethylbenzyl)-2,3-dihydro-1,3-diborole)rhodiumchlorid]* (**2a**)

In total 390 mg (1.55 mmol) of **1a** was added at r.t. to a solution of 292 mg (0.75 mmol) of dirhodium-μ-dichloro-tetraethylene in 15 ml of THF. The orange solution darkened and ethene was evolved. After stirring for 18 h the solution was filtered (G3-frit) and the solvent removed in vacuum. The orange oily residue was subjected to high vacuum for 6 h. Yield: 540 mg (92%) of **2a**. ^{1}H-NMR (C_6D_6): $\delta = 6.72$ (s, 2H, *mes*), 3.04 (d, 2H, CH–CH_2, $^3J = 3.9$ Hz), 2.23 (s, 6H, *mes*), 2.13 (s, 3H, *mes*), 1.49 (s, 6H, CMe), 0.97 (s, 6H, BMe), -7.21 (1H, m, CH–CH_2). ^{11}B-NMR (C_6D_6): $\delta = 30$. MS FAB: m/z (%) = 355 [M^+/2-Cl] (100).

3.2. *Bis[η⁵-(4,5-diethyl-1,2,3-trimethyl-2,3-dihydro-1,3-diborole)rhodiumchlorid]* (**2b**)

In total 167 mg (1.03 mmol) of **1b** was added at r.t. to a solution of 171 mg (0.44 mmol) of dirhodium-μ-dichloro-tetraethylene in 10 ml of THF. The orange solution darkened and ethene was evolved. After stirring for 18 h the solution was filtered (G3-frit) and the solvent removed in vacuum. The orange oily residue was subjected to high vacuum for 6 h. Yield: 250 mg

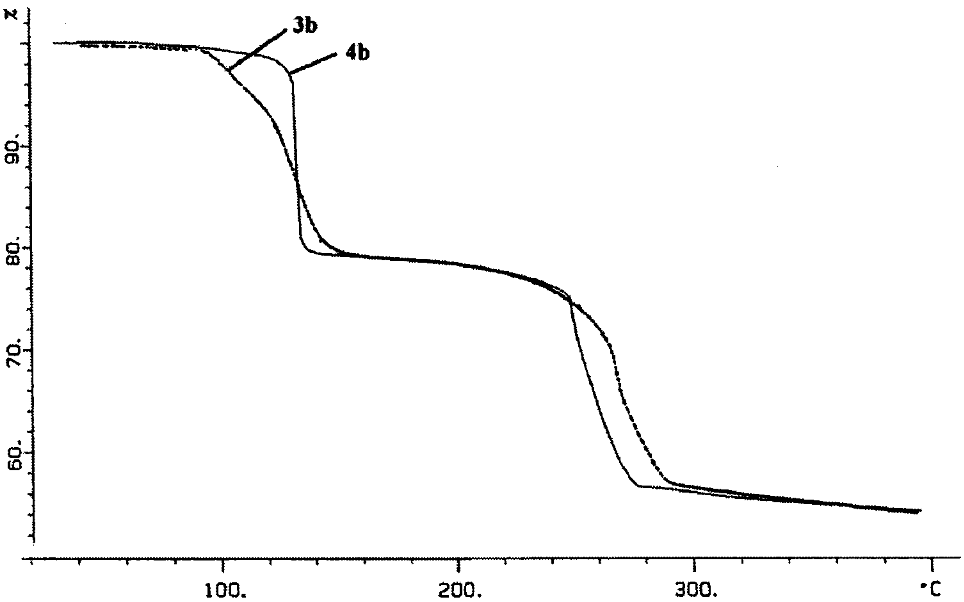


Fig. 4. TG curves of **3b** and **4b**. Start temperature 25°C, final temperature 400°C, heating rate 5 K min^{-1}, flowgas N_2.

(95%) of **2b**. ^{1}H-NMR (C_6D_6): $\delta = 2.24$ (m, 4H, =C–CH$_2$, $^3J = 7.6$ Hz), 2.01 (m, 4H, =C–CH$_2$, $^3J = 7.6$ Hz), 1.05 (t, 12H, =C–CH$_2$–C*H*$_3$, $^3J = 7.6$ Hz), 1.00 (d, 6H, C2–CH$_3$, $^3J = 3.5$ Hz), 0.94 (s, 12H, B–CH$_3$), −7.98 (m, 2H, C2–H, $^3J = 3.5$ Hz). ^{13}C-NMR (C_6D_6): $\delta =$ 103.5 (br, =C), 45.7 (br, C2), 22.2 (=C–*C*H$_2$–), 14.3 (=C–CH$_2$–*C*H$_3$), 11.1 (C2–*C*H$_3$), −2.5 (br, B–CH$_3$). ^{11}B-NMR (C_6D_6): $\delta = 29.5$. MS EI: *m*/*z* (%) = 600 [M$^+$] (49).

3.3. η^5-(1,3,4,5-Tetramethyl-2-(2,4,6-trimethylbenzyl)-2,3-dihydro-1,3-diborolyl)(η^6-toluene)rhodium (*3a*)

In total 290 mg (48 mmol) of **2a** was dissolved in 5 ml of toluene and chromatographed on silica gel with toluene. A brown fraction contained **3a**, which was recrystallized from hexane to give yellow–brown needles. Yield: 199 mg (45%). ^{1}H-NMR (C_6D_6): $\delta =$ 6.88 (s, 2H, *mes*), 5.3–5.0 (5H, tol), 3.38 (s, 2H, CH$_2$), 2.45 (s, 6H, *mes*), 2.23 (s, 3H, *mes*), 1.70 (s, 6H, tol), 1.65 (s, 3H, CCH$_3$), 0.70 (s, 6H, BCH$_3$). ^{13}C-NMR (C_6D_6): $\delta = 139.7$, 136.1, 133.7, 129.0, 114.5, 98.1, 96.6, 95.8, 33.0, 21.5, 21.1, 18.5, 15.1, −3 (br, BCH$_3$). ^{11}B-NMR (C_6D_6): $\delta = 27.9$. MS EI: *m*/*z* (%) = 446 [M$^+$] (33), 354 [M$^+$–C_7H_8)] (100), 92 [$C_7H_8^+$] (36), 91 [$C_7H_7^+$], (42). $C_{24}H_{33}B_2Rh$ (446.1) Anal. calc.: C 64.63, H 7.46; found: C 64.75, H 7.68.

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

In total 222 mg (0.37 mmol) of **2b** obtained in situ from **1b** and [RhCl(C_2H_4)]$_2$, were dissolved in 20 ml of toluene and at −30°C, 25 mg (0.62 mmol) of potassium hydride was added. After stirring for 1 h without cooling the reaction mixture was filtered and the solvent was removed in vacuum. The complex **3b** was obtained from hexane as yellow–brown needles. Yield: 180 mg (69%). ^{1}H-NMR (C_6D_6): $\delta = 5.2$–5.0 (5H, tol), 2.08 (m, 4H, C*H*$_2$CH$_3$), 1.70 (s, 3H), 1.65 (s, 3H), 1.21 (t, 6H, CH$_2$CH$_3$), 0.79 (s, 6H, BCH$_3$). ^{13}C-NMR (C_6D_6): $\delta = 119.0$ (br, =*C*CH$_3$), 109.2, 98.0, 96.1, 95.4, 23.1, 18.7, 18.6, 16.7, −4.3 (br, BCH$_3$). ^{11}B-NMR (C_6D_6): $\delta = 27.7$. MS EI: *m*/*z* (%) = 356 [M$^+$] (100), 327 [M$^+$–C_2H_5)] (33), 262 [M$^+$–C_7H_8] (22). $C_{17}H_{27}B_2Rh$ (355.9) Anal. calc.: C 57.37, H 7.65; found: C 56.63, H 7.59.

3.5. η^5-(1,3-Di-*t*-butyl-2,3-dihydro-4,5-dimethyl-1,3-diborolyl)(η^6-toluene)rhodium (*3c*)

To a solution of 0.21 g (1.75 mmol) of **1d** in 30 ml of THF at −60°C 1.2 ml (1.75 mmol) of *t*-butyllithium in pentane was added and stirred for 0.5 h at −60°C. The reaction mixture was dropped at −30°C to a suspension of toluene and 0.34 g (0.87 mmol) of dirhodium-μ-dichloro-tetraethylene. After warm-up over night the solvent mixture was removed and **3c** sublimed at 90°C 5×10^{-2} mbar. Yield: 100 mg (29%). ^{1}H-NMR (C_6D_6): $\delta = 5.41$–5.11 (5H, tol), 3.81 (s, 1H, B$_2$CH), 1.80 (s, 6H, CCH$_3$), 1.56 (s, 3H, CH$_3$), 1.36 (s, 18H, C(CH$_3$)$_3$). ^{13}C-NMR (C_6D_6): $\delta = 113.4$ (br, =*C*CH$_3$), 109.6, 98.1, 96.3, 92.4, 77.4 (br, B$_2$CH), 32.4, 19.3 (br, BC(*C*H$_3$)$_3$), 16.5. ^{11}B-NMR (C_6D_6): $\delta = 31.9$. MS EI: *m*/*z* (%) = 398 [M$^+$] (100), 341 [M$^+$–C_4H_9] (16), 286 [M$^+$–2x C_4H_8] (13). $C_{20}H_{33}B_2Rh$ (398.0) Anal. calc.: C 60.36, H 8.36; found: C 60.39, H 8.07.

Table 1
TG data of the compounds **3a**, **b** and **4b**

Compound	Heating[a]	Onset[b]	*m* (%)	End[b]	*m* (%)	Onsetc	*m* (%)	End[c]	*m* (%)
3a	10	113	100	176	82	329	77	435	38
3b	5	94	100	143	79.6	254	77.2	283	56.5
4b	5	129	100	135	79.7	243	77.5	272	57

[a] Rate (K $\min^{-1}$); [b] (°C) first step; [c] (°C) second step.

3.6. *η^5-(1,3,4,5-Tetramethyl-2-(2,4,6-trimethylbenzyl)-2,3-dihydro-1,3-diborolyl)(η^6-benzene)rhodium **(4a)***

To a solution of 250 mg (0.32 mmol) of **2a** in 10 ml of benzene at −30°C 0.43 ml (0.65 mmol) of *t*-butyllithium in pentane was added. After stirring for 1 h at r.t. the reaction mixture was filtered and **4a** chromatographed on silica gel with toluene. The complex **4a** was obtained as a light brown solid. Yield: 109 mg (39 %); m.p. 150°C. ^{1}H-NMR (C_6D_6): $\delta = 6.88$ (s, 2H, *mes*), 5.16 (6H, C_6H_6), 3.41 (s, 2H, CH_2), 2.43 (s, 6H, CCH_3), 2.23 (s, 3H, CCH_3), 1.74 (s, 6H, CCH_3), 0.73 (s, 6H, BCH_3). ^{13}C-NMR (C_6D_6): $\delta = 139.7$, 136.0, 133.8, 129.0, 116 (br, =*C*CH3), 96.7 (d, $^2J(^{103}\text{Rh}, {}^{13}\text{C}) = 3.9$ Hz, C_6H_6), 43.1 (br, B_2C), 33.2, 21.4, 21.1, 15.4, −3.6 (br, BCH_3). ^{11}B-NMR (C_6D_6): $\delta = 28.6$. MS EI: *m*/*z* (%) = 432 [M^+] (10), 354 [$M^+ - C_6H_6$] (24), 133 [*mes*-CH_2^+] (39), 78 [$C_6H_6^+$] (100).

3.7. *η^5-(4,5-Diethyl-1,2,3-trimethyl-2,3-dihydro-1,3-diborolyl)(η^6-benzene)rhodium **(4b)***

Analogous to the synthesis of **3b** the sandwich **4b** was obtained by the reaction of 250 mg (0.42 mmol) of **2b** with 33 mg (0.82 mmol) of potassium hydrid in benzene. Recrystallization from hexane gave yellow crystals. Yield: 180 mg (69%); m.p. 123°C. ^{1}H-NMR: (C_6D_6) $\delta = 5.15$ (6H, C_6H_6), 2.10 (m, 4H), 1.77 (s, 3H, B_2CCH_3), 1.20 (t, 6H, CCH_3), 0.84 (s, 6H, BCH_3). ^{13}C-NMR (C_6D_6): $\delta = 120.0$ (br, =*C*CH_3), 96.5 (d, $^2J(^{103}\text{Rh}, {}^{13}\text{C}) = 3.5$ Hz, C_6H_6), 23.3, 19.1, 16.7, −4.3 (br, BCH_3). ^{11}B-NMR (C_6D_6): $\delta = 28.4$. MS EI: *m*/*z* (%) = 342 [M^+] (100), 313 [$M^+ - C_2H_5$)] (38), 262 [$M^+ - C_7H_8$] (24). $C_{16}H_{25}B_2Rh$ (341.9) Anal. calc.: C 56.21, H 7.37; found: C 55.73, H 7.69.

3.8. *η^5-(4,5-Diethyl-1,2,3-trimethyl-2,3-dihydro-1,3-diborolyl)(η6-naphthalene)rhodium **(5b)** and η^5-(4,5-diethyl-1,2,3-trimethyl-2,3-dihydro-1,3-diborolyl)(η^6-deuterobenzene)rhodium **(4b**D_6)*

To 1 g of naphthalene was added at r.t. 180 mg (0.30 mmol) of **2b** in 15 ml of THF. After cooling to −30°C 0.38 ml (0.57 mmol) of a solution of *t*-butyllithium in pentane was added. The reaction mixture turned black. After 5 h stirring the reaction mixture was filtered, the solvent was removed and excess of naphthalene was sublimed at 10^{-2} mbar. The complex **5b** was identified by EI MS: *m*/*z* (%) = 392 [M^+] (18), 363 [$M^+ - C_2H_5$] (16), 128 [$C_{10}H_8^+$] (100). The reaction product was dissolved in C_6D_6, and after 12 h the solvent and excess of naphthalene removed at r.t. 10^{-2} mbar. Yield: 120 mg (58%) of **4b**D_6. ^{1}H-NMR (C_6D_6): $\delta = 2.08$ (m, 4H), 1.77 (s, 3H), 1.21 (t, 6H), 0.85 (s, 6H). ^{13}C-NMR (C_6D_6): $\delta = 120.0$ (br, =*C*CH_3), 96.3 (C_6H_6), 96.2 (t, C_6D_6), 23.3, 19.1, 16.7, −4.3 (br, BCH_3). ^{11}B-NMR (C_6D_6): $\delta = 28.3$. MS EI: *m*/*z* (%) = 348 [M^+] (100), 319 [$M^+ - C_2H_5$] (36), 84 [$C_6D_6^+$] (95).

3.9. *Formation of the triple-decker **6a***

In total 25 mg (0.06 mmol) of **3a** was slowly heated at 10^{-2} mbar above the m.p. (135°C) to 145°C and kept at this temperature for 15 min. At 110°C the light-brown crystals turned black. After cooling of the residue, the product was studied by MS FAB: *m*/*z* (%) = 800 [M^+(**6a**)] (16), 708 [M^+(**6a**)-tol] (17), 446 [M^+(**3a**)] (55), 354 [M^+(**3a**)-tol] (100).

3.10. *Triple-decker **6b** and tetra-decker **7b***

In total 20 mg (0.06 mmol) of **3b** was slowly heated at 10^{-2} mbar to 125–130°C and kept for ca. 15 min at this temperature. The blackening of the crystals already occurred at 90°C. After cooling the residue was studied by FAB MS: MS FAB: *m*/*z* (%) = 883 [M^+(**7b**)] (20), 620 [M^+(**6b**)] (92), 356 [M^+(**3b**)] (100).

3.11. *Crystal structure determinations of **3a–c** and **4b** [15]*

Crystal data and details of the structure determinations are listed in Table 2. Unique sets of intensity data were collected at −70°C with a four-circle diffractometer (Mo–K_α radiation $\lambda = 0.7107$ Å, graphite monochromator, ω-scan). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods [SHELXS86] [16] and refined by least-squares methods based on F^2 with all measured reflections [SHELXL97] [16]. All non-hydrogen atoms were refined anisotropically. For **3a**,**b**, and **4b** hydrogen

Table 2
Crystal data and structure refinement for **3a**, **b**, **c** and **4b**

	3a	**3b**	**3c**	**4b**
Empirical formula	$C_{24}H_{33}B_2Rh$	$C_{17}H_{27}B_2Rh$	$C_{20}H_{33}B_2Rh$	$C_{16}H_{25}B_2Rh$
Formula weight	446.1	355.9	398.0	341.9
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	*Pbnm*	$P2_12_12_1$
Unit cell dimensions				
a (Å)	8.656(4)	10.148(6)	9.838(7)	8.306(1)
b (Å)	18.864(9)	14.394(6)	12.149(11)	12.305(2)
c (Å)	14.250(7)	23.984(15)	17.069(12)	16.306(2)
β (°)	105.58(4)	93.41(5)		
V (Å^3)	2241(2)	3497(3)	2040(2)	1666.6(4)
Z	4	8	4	4
$D_{calc.}$ (g cm^{-3})	1.32	1.35	1.30	1.36
μ(Mo–K$_\alpha$) (cm^{-1})	7.7	9.6	8.3	10.1
Crystal size (mm)	0.5 × 0.6 × 0.6	0.3 × 0.5 × 0.7	0.3 × 0.35 × 0.65	0.3 × 0.3 × 0.5
Transmission	0.76–1.00	0.84–1.00	0.70–1.00	0.88–1.00
2θmax (°)	58	54	54	50
Reflections unique	5972	5598	2291	2934
Observed ($I > 2\sigma$I)	4287	4764	1641	2831
Parameters	258	383	171	181
R_1	0.041	0.050	0.038	0.018
wR_2	0.096	0.120	0.080	0.043
Max. residue of electron density (e Å^{-3})	−0.5/+1.3	−2.1/+2.8	−1.0/+1.8	−0.3/+0.2−

atoms were included in calculated positions or as part of a rigid group (methyl). In **3c** all hydrogen atoms (besides those of one methyl group) were located in a difference Fourier map and refined.

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