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Insertion of alkynes into the heterocycle of (η^5-pentaalkyl-2,3-dihydro-1,3-diborlyl)(η^5-pentamethylcyclopentadienyl)ruthenium: Formation and characterization of 4-borataborepine ruthenium complexes

Yong Nie [a,b], Hubert Wadepohl [a], Chunhua Hu [c], Thomas Oeser [d], Walter Siebert [a,*]

[a] Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
[b] School of Chemistry and Chemical Engineering, University of Jinan, 106 Jiwei Road, 250022 Jinan, PR China
[c] Institut für Anorganische Chemie, RWTH Aachen, Professor Pirlet Strasse 1, 5205Aachen, Germany
[d] Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

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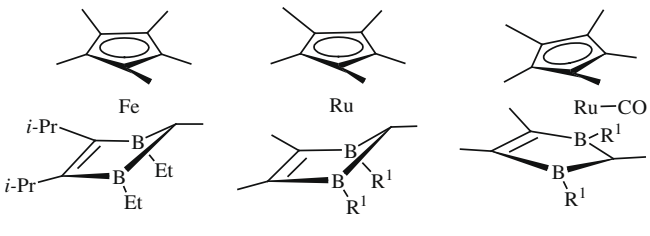
ABSTRACT

The violet ruthenium complex [(η^5-C_5Me_5)Ru(η^5-$C_3B_2Me_4R^1$)] (**2a**, R^1 = Me) reacts with terminal alkynes $R^2C{\equiv}CH$ to give yellow 4-borataborepine compounds [(η^5-C_5Me_5)Ru{η^7-$(MeC)_3(R^1B)_2(R^2C_2H)$}] (**4c**, R^1 = Me, R^2 = Ph; **4d**, R^1 = Me, R^2 = $SiMe_3$; **4e**, R^1 = Me, R^2 = H). The insertion of alkynes into the folded C_3B_2 heterocycle of **2a** causes some steric hindrance, which yields with elimination of the distant boranediyl group the corresponding boratabenzene complexes **5** as byproducts. The analogous reactions with internal alkynes $R^2C{\equiv}CR^2$ proceed slowly and afford predominantly the boratabenzene complexes [(η^5-C_5Me_5)Ru{η^6-$(MeC)_3(MeB)(R^2C)_2$}] (**5f**, R^2 = Et, **5g**, R^2 = *p*-tolyl), respectively. In the latter case, three byproducts are formed: methylboronic acid and 1,2,3,4-tetra-*p*-tolyl-1,3-butadiene (**9**) due to hydrolysis of the postulated 2,3,4,5-tetra-*p*-tolyl-1-methylborole (**10**) and unexpectedly, the cationic triple-decker complex [{(η^5-C_5Me_5)Ru}$_2${μ,η^7-$(MeC)_3(MeB)_2(CH)_2$}]Cl (**11**) having two separated CH groups. The new compounds were characterized by NMR, MS, and single-crystal X-ray studies of **4c**, **5f**, **9** and **11**.

1. Introduction

There has been considerable interest in electron-poor organometallic compounds of the iron triad having fewer than 18 valence electrons (VE). We have reported on formally 16 VE (η^5-pentaalkyl-2,3-dihydro-1,3-diborolyl)(η^5-pentamethylcyclopentadienyl)iron complexes **1** [1,2] and its violet ruthenium analogs **2** [3,4] (e.g. **2a**: R^1 = Me). The unusual structural feature of the green iron complex **1** is the severe folding along the B···B vector of the heterocycle (folding angle α = 41.3°) causing a very short Fe–C2 bonding (1.899 Å), as a result of the interaction of the combination of high-lying σ(B–C) orbitals and the d_{xz} orbital of iron. This bonding is markedly different from other known 1,3-diborolyl sandwich structures. By spectroscopy, the violet ruthenium analogs **2** were assumed to have a similar bonding situation [5–7], which was recently confirmed by an X-ray diffraction study of **2b** (R^1 = CH_2SiMe_3; folding along the B···B vector: α = 40.7°) [8–10] and by the detailed electronic structure of **2** (DFT with the B3LYP functional and extended triple-zeta basis sets) [10].

The ruthenium center of **2** reacts with donor ligands to yield yellow complexes (e.g. **3**) having reduced folding in the heterocycle (angle < 20°) [3–4]. Phosphanes also form donor–acceptor complexes **2** · PH_2R (R = H, Ph), whereas *t*-butylphosphaalkyne P≡C-CMe_3 is incorporated into **2a** yielding a ruthenaphosphacarborane, however, it is not known which of the isomers was formed [4]. Here we report on the reactivity of **2a** toward terminal acetylenes leading with insertion into the heterocycle to yield derivatives of (η^7-4-borata-borepine)(η^5-pentamethylcyclopentadienyl)ruthenium complexes **4**, while with internal acetylenes boratabenzene complexes are obtained. A preliminary account on the formation of **4** [8] as well as the investigation of its stacking with cationic metal complex fragments to triple-decker complexes [11] have been published.



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* Corresponding author. Tel.: +49 6221 548485; fax: +49 6221 545609.
E-mail address: walter.siebert@urz.uni-heidelberg.de (W. Siebert).

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2. Results and discussion

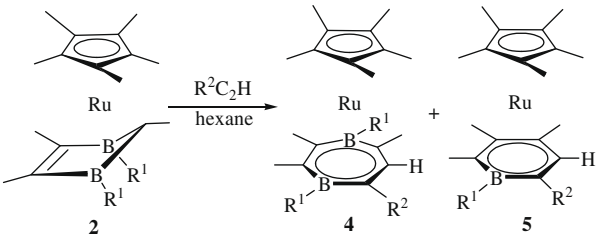
2.1. Formation of 4-borataborepineruthenium complexes *4c–e*

Reactions of 18 VE decamethyl-1,3-diboraruthenocene (**2a**) with terminal alkynes (Scheme 1) in hexane lead to the yellow complexes **4**, which are characterized by NMR and MS data. (Section 4) The ^{11}B NMR spectra show broad signals at lower field (δ = 26–29 ppm, while that for **2a** is at 21.7 ppm. In the EI mass spectra the molecular ions at $m/z = M^+$ exhibits a high stability regarding a loss of the alkyne. However, signals at $m/z = [M-BMe]^+$ indicate that the elimination of boranediyl leads to Cp*Ru(borata-benzene) complexes **5**. As byproducts the trimers of alkynes are identified by MS. The molecular structures of **4a**,**b** [8], and **4c** have been studied by single-crystal X-ray diffraction analyses which confirm the presence of the sandwich complexes with 4-borata-borepine ligands. The insertion of the alkyne into one of the equivalent boron–carbon bonds of **2** yields enantiomers found in the crystal structures.

The seven-membered rings in **4a–c** exhibit a reduced folding along the B···B vector (α = 12, 26 and 15°, respectively), they are almost parallel to the Cp* rings. The bonding between Ru center and the large C_5B_2 ring causes the α-atoms of its substituents more or less to tilt toward the metal atom with the exception of α-carbon at the boron atoms tilting in the opposite direction. Within the seven-membered ring, the B–C bond lengths are between 1.513 and 1.545 Å, which indicates short B–C bonds. The C–C bonds are very similar (1.409–1.417 Å). In **4b** the Ru–B distances of 2.527 and 2.542 Å are significantly elongated compared to those in **4a** (2.429 and 2.443 Å) and **4c**, showing the influence of the bulky Me_3SiCH_2 groups in **4b**. The Ru–C bond distances in **4b** vary within a range of 2.203–2.345 Å, with Ru–C4 being the shortest to the C_5B_2 ring (see Fig. 1).

The reactions of **2a** with trimethylsilylacetylene and ethyne (Scheme 1) give the yellow 4-borataborepine complexes **4d** and **4e**, respectively, and by MS studies the corresponding boratabenzene complexes **5d** and **5e** as well as tris(trimethylsilyl)benzene are detected as byproducts. The ^{1}H NMR spectrum of compound **4e** exhibits two doublets at δ = 5.54, 4.56 ppm, which indicates the two CH moieties remained adjacent in the 4-borataborepine complex. An X-ray diffraction study of **4e** confirms the incorporation of ethyne, however, the seven-membered ring is found to be disordered. In an unexpected triple-decker complex cation the bridging 4-borataborepine ligand contains two separate methylidyne groups (see below).

In general, the yellow 4-borataborepine-ruthenium complexes **4** presented here are relatively stable in the solid state at ambient temperatures. In solution they decompose slowly to give the corresponding boratabenzene complexes **5**, which is found to be faster



2	a	b	c	d	e	4, 5
R^1	Me	CH_2SiMe_3	Me	Me	Me	R^1
	Bn	Bn	Ph	$SiMe_3$	H	R^2

Scheme 1. Formation of borataborepine- and boratabenzene-ruthenium complexes.

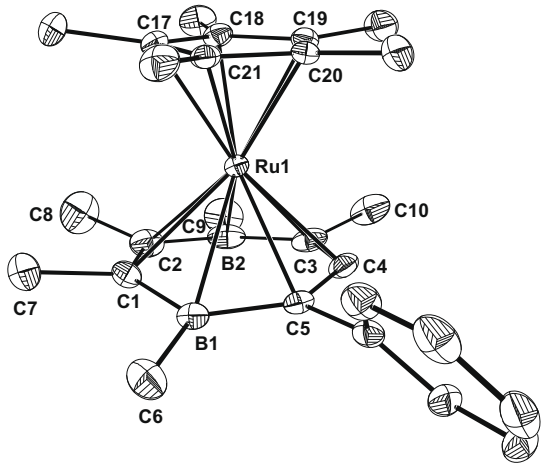
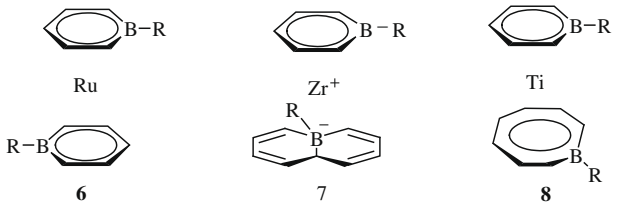


Fig. 1. Molecular structure of **4c**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–Cp* 2.184(2)–2.196(2), Ru–B1 2.446(3), Ru–C1 2.310(2), Ru–C2 2.333(2), Ru–B2 2.456(3), Ru–C3 2.311(2), Ru–C4 2.244(2), Ru–C5 2.319(2), B1–C1 1.524(3), C1–C2 1.412(3), B2–C2 1.525(4), B2–C3 1.513(4), C3–C4 1.413(3), C4–C5 1.417(3), B1–C5 1.519(3); C5–B1–C1 124.2(2), C2–C1–B1 129.4(2), C1–C2–B2 128.9(2), C3–B2–C2 124.5(2), C4–C3–B2 129.7(2), C3–C4–C5 130.1(2), C4–C5–B1 129.6(2).

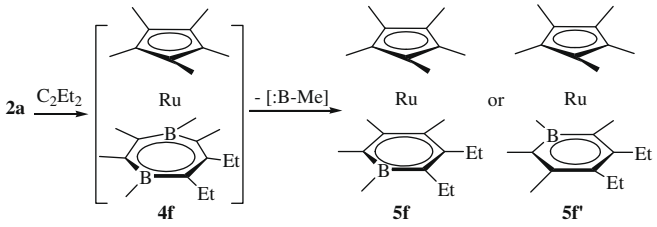
when in contact with air. The donor function of the 4-borataborepines may be conveniently divided into ene (2e) and allyl anion (4e), separated by two boron atoms. The short boron–carbon bond lengths in **4** indicate that the π^2 and π^4 systems are electronically connected via the p_z orbitals of boron atoms. Thus the 4-borata-borepine ligand is electronically related to the tropylium ion $C_7H_7^+$ and the neutral borepine [12,13], respectively. Complexes **4** are isomers of the bis(6-boratabenzene)ruthenium complexes **6** [14] and structural analogs of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)chromium [15].

The driving force for the fast alkyne insertion into the folded heterocycle of complexes **2** is the formation of the 6π electron 4-borataborepine ligand in the 18 VE complexes **4**. It is assumed that the alkyne coordinates weakly to the Ru atom, the substituent of the alkyne being located near one of the boron atoms. Insertion reactions of ethyne into one of the boratabenzene rings of bis(boratabenzene)zirconium [16] and -titanium [17] complexes yield compounds **7** and **8** having an 8a-H-4-boratanaphthalene and a boratacyclooctatetraene as ligand, respectively.



2.2. Boratabenzene ruthenium complex *5f*

To study the formation of boratabenzene complexes **5a**,**b**, the stability of **4b** in solution was monitored by ^{11}B NMR. During a period of several weeks a weak signal at δ = 16 ppm increased, indicating the formation of the boratabenzene complex **5b**. The steric influence of the substituents of R_2C_2 was tested in the reaction of **2a** with bulky acetylenes. With 3-hexyne (Scheme 2) the boratabenzene complex **5f** is obtained and identified by ^{11}B NMR (δ = 16.8 ppm), HR-MS, and by an X-ray diffraction study. Steric



Scheme 2. Formation of the boratabenzene complex **5f**.

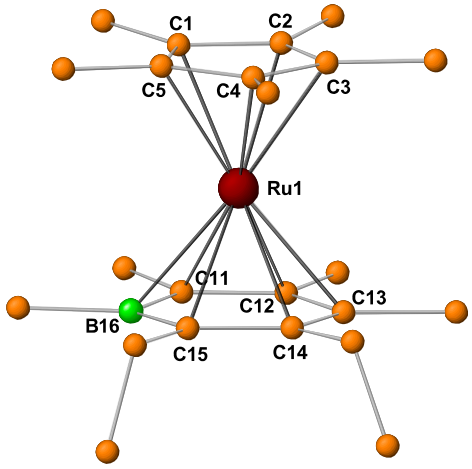
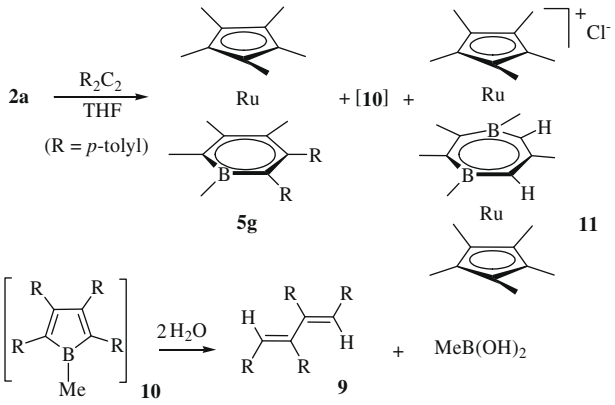


Fig. 2. Molecular structure of **5f**, hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Ru1–Cp* 2.171(3)–2.181(3), Ru1–C11 2.256(3), Ru1–C12 2.262(3), Ru1–C13 2.262(3), Ru1–C14 2.220(3), Ru1–C15 2.232(3), Ru1–B16 2.257(3), C11–C12 1.436(4), C12–C13 1.468(4), C13–C14 1.469(4), C14–C15 1.436(4), C15–B16 1.458(4), C11–B16 1.470(4).

requirements in the anticipated peralkylated complex **4f** cause a fast elimination of one methylboranediyl moiety [:B–Me], whereas **4a,b** eliminate the [:B–R^1] unit slowly in solution. Of the possible isomers only **5f** with the boron atom adjacent to the inserted C_2Et_2 is isolated. The boratabenzene ring is essentially planar (torsion angle C13–C14–C15–B16: −1.3°) as in reported boratabenzene complexes [18]. The bond lengths of C11–B16/C15–B16 [1.470(4) and 1.458(4) Å, respectively] and C12–C13/C13–C14 [1.468(4) and 1.469(4) Å, respectively] are slightly longer that those of C11–C12/C14–C15 [1.436(4) and 1.436(4) Å, respectively] and the Ru–C13/Ru–B16 bond distances [2.262(3) and 2.257(3) Å, respectively] are comparable with those of the other Ru–C distances within the boratabenzene ring [2.220(3)–2.262(3) Å]. This indicates that the boratabenzene ring in **5f** is disordered at the B16/C13 symmetrically equivalent positions (see Fig. 2).

*2.3. Unexpected formation of the triple-decker **11** with a bridging C_5B_2 ligand*

To further investigate the influence of the steric requirements on the formation of the boratabenzene complexes the reaction of **2a** and di-*p*-tolylacetylene (Scheme 3, 1:1 molar ratio) was carried out. The insertion of the bulky acetylene proceeds slowly, yielding a red THF solution. After removal of the solvent the red-brown residue is extracted with toluene leaving a yellow residue (ca. 10 mg). The oily extract was found to be a mixture of the boratabenzene complex **5g** (identified by ^{11}B NMR and HR EI-MS) and 1,2,3,4-tetra-*p*-tolyl-1,3-butadiene (**9**) (identified by an X-ray diffraction analysis). Its formation may have occurred as a result of the elimination of [:BMe] from the expected **4g** and its reaction with di-*p*-tolylacetylene leading to 2,3,4,5-tetra-*p*-tolyl-1-methyl-borole **10** via the



Scheme 3. Reaction of **2a** with di-*p*-tolylacetylene yields boratabenzene complex **5g**, the triple-decker **11** and the intermediate borole **10**, which hydrolyzed to give the butadiene derivative **9** and $MeB(OH)_2$.

corresponding boracyclopropene. During the reaction or work-up (extraction/crystallization in CH_2Cl_2) hydrolysis [19] of **10** with adventitious water resulted in the formation of **9** and methylboronic acid. The HR-MS data of the yellow crystals indicated the novel triple-decker cationic species **11** which was confirmed by an X-ray structure analysis. The bridging seven-membered ligand unexpectedly contained two CH groups separated by a CMe moiety (Fig. 3). At this point attempts to illuminate its formation were not successful.

The crystal structure is comprised of layers of triple-decker cations on the one hand, and hydrogen bonded dimers of methylboronic acid and chloride anions, respectively, on the other. The cation **11** has crystallographic mirror symmetry with the mirror plane bisecting the borataborepine and pentamethylcyclopentadienyl ligands. In contrast to the seven-membered rings in **4**, the borataborepine ligand in **11** is planar, with the largest deviation being 0.01 Å. The three ring ligands are essentially coplanar (interplane angle ~ 1°), and the Ru···Ru distance is 3.34 Å, which is similar to the recently characterized cationic triple-decker complexes with a bridging

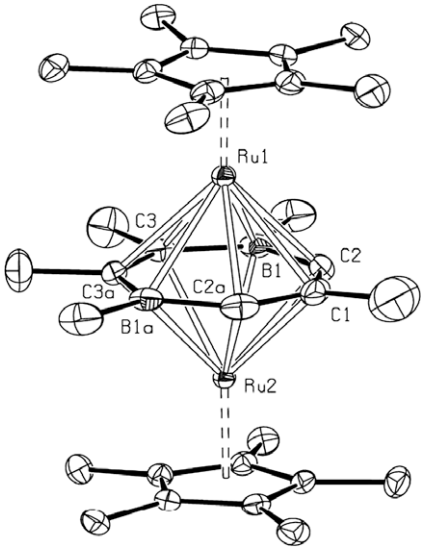


Fig. 3. Molecular structure of the triple-decker cation **11**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2, 1.408(4); B1–C2, 1.527(5); B1–C3, 1.530(5); C3–C3a, 1.417(6); Ru1/Ru2–C1, 2.363(5)/2.382(5); Ru1/Ru2–C2, 2.340(3)/2.329(3); Ru1/Ru2–B1, 2.405(3)/2.413(3); Ru1/Ru2–C3, 2.418(3)/2.423(3), Ru1–C(Cp*), 2.150(4)···2.162(3); Ru2–C(Cp*), 2.156(3)···2.158(4); C2–C1–C2a, 125.8(4); C1–C2–B1, 133.5(3); C2–B1–C3, 124.1(3); B1–C3–C3a, 129.6(2).

borataborepine ligand [11] obtained by stacking experiments of the sandwich $[(\eta^5\text{-}C_5Me_5)Ru\{\eta^7\text{-}(MeC)_4(MeB)_2(CH)\}]$ with cationic Cp^*M complex fragments. Interestingly, the anion Cl^- bridges two dimeric $MeB(OH)_2$ molecules, forming an infinite chain by hydrogen bonding (O–H···O, O–H···Cl).

Compound **11** is the first structurally characterized triple-decker complex having the borataborepine ring as bridging ligand [9]. An early example of an analogous triple-decker from the reaction of $CpCo(C_2H_4)_2$ with 1,4-dimethyl-2,3-diethyl-1,4-diboracyclohepta-2-ene [20] was identified by MS data as [bis(cyclopentadienylcobalt)C_5B_2] triple-decker complex [21].

3. Conclusion

The unique bonding properties of the decamethyl-1,3-diboraruthenocene (**2a**) allow the insertion of alkynes into its folded C_3B_2 ligand to yield 18 VE 4-borataborepine ruthenium complexes **4**. The anion of the C_5B_2 heterocycle functions as 6e donor. Steric crowding of the inserted alkynes causes elimination of one boranediyl group with the formation of boratabenzene complexes **5**, which are directly obtained in the reaction with disubstituted acetylenes. The insertion of ethyne occurs into one of the two equivalent boron–carbon bonds of the B–C–B group is confirmed by an X-ray structure analysis of **4e**, however, its seven-membered ring is distorted. The slow reaction of di-*p*-tolylacetylene with **2a** leads to the expected boratabencene complex and a yellow product in minute amount. Its X-ray diffraction data indicates the formation of the cationic triple-decker **11** which surprisingly contains two separated CH groups. Hydrolysis of the postulated tetra-*p*-tolyl-1-methyl-borole (**10**) leads to the tetra-*p*-tolyl-butadiene **9** and methylboronic acid, identified by X-ray structure analyses; the latter formed with the chloride anion of the triple-decker cation **11** an infinite chain.

4. Experimental

General. All reactions and manipulations were performed in dry glassware under argon or nitrogen using standard Schlenk techniques. Unless otherwise stated, solvents were dried, distilled, and saturated with nitrogen. NMR spectra were recorded on a Bruker DRX 200 spectrometer (^{1}H: 200.13 MHz, ^{11}B: 64.21 MHz, ^{13}C: 50.32 MHz) in $CDCl_3$ and CD_2Cl_2 as solvents. $Et_2O \cdot BF_3$ was used as external standard for ^{11}B NMR. As internal references for ^{1}H and ^{13}C NMR, the signals of the deuterated solvents were used, the shifts were calculated relative to TMS and given in ppm. MS: ZAB-2F VH Micromass CTD and JEOL MS Station JMS 700 spectrometers.

4.1. (η^5-Pentamethylcyclopentadienyl)(η^7-1,2,3,4,5-pentamethyl-7-phenyl-4-borata-borepine)ruthenium (**4c**)

A solution of phenylacetylene (65 mg, 0.64 mmol) in hexane (5 mL) was added to a violet solution of **2a** (180 mg, 0.49 mmol) in hexane (10 mL) at −60 °C. Within 10 min. the reaction mixture turned to an orange red solution. It was warmed to r.t. and filtered to give a yellow precipitate and a yellow filtrate. The filtrate was dried *in vacuo* to yield a yellow solid, and recrystallization in CH_2Cl_2 at r.t. gave yellow crystals of **4c** (164 mg, 71%). The yellow precipitate (ca. 15 mg) was identified by EI-MS to be the boratabenzene complex **5c**. ^{1}H NMR ($CDCl_3$): δ = 7.19–7.42 (m, 5H; Ph), 5.80 (s, 1H; allyl), 2.04 (s, 3H; =CCH_3), 2.02 (s, 3H; =CCH_3), 1.97 (s, 3H; BCCH_3CH), 1.53 (s, 15H; $C_5(CH_3)_5$), 0.68 (s, 3H; BCH_3), 0.62(s, 3H; BCH_3) ppm. ^{11}B NMR ($CDCl_3$): δ = 26 (br.) ppm. ^{13}C NMR ($CDCl_3$): δ = 130.8, 129.7, 126.9, 124.8 (Ph), 114.9, (allyl moiety, center carbon), 86.5 ($C_5(CH_3)_5$), 21.7 (BCCH_3CH), 9.7 ($C_5(CH_3)_5$) ppm. Signals for boron-bound carbon atoms of the allyl, BCH_3 and two =C*C*Me moieties n.o. EI-MS: *m*/*z* (%) = 471 [M^+] (30), 446 [M^+−BCH_3 + 1] (100). HR-MS: *m*/*z* calcd. for $^{12}C_{26}{}^1H_{36}{}^{11}B_2{}^{102}Ru$: 472.2048, found: 472.2049, Δ = 0.1 mmu. EI-MS for **5c**: *m*/*z* (%) = 446 [M^+] (100). HR-MS: *m*/*z* calcd for $^{12}C_{25}{}^1H_{33}{}^{11}B^{102}Ru$: 446.1719, found: 446.1739, Δ = 2.0 mmu.

4.2. (η^5-Pentamethylcyclopentadienyl)(η^7-1,2,3,4,5-pentamethyl-7-trimethylsilyl-4-borataborepine)ruthenium (**4d**)

A solution of trimethylsilylacetylene (43 mg, 0.44 mmol) in hexane (10 mL) was added to a solution of **2a** (140 mg, 0.38 mmol) in hexane (10 mL) at −60 °C. No immediate color change was observed, and the mixture was warmed to r.t., during which time the solution turned from violet to brown and finally yellow and a small amount of precipitate appeared. After filtration, the yellow filtrate was dried *in vacuo* to give a yellow solid, identified to be a mixture of **4d** and **5d** (byproduct), recrystallization in CH_2Cl_2 at r.t. gave crystalline **4d,** mp 110–120 °C (160 mg, 89%). The EI-MS of the yellow precipitate (ca. 10 mg) did not provide clear information. ^{1}H NMR (CD_2Cl_2): δ = 5.82 (s, 1H; allyl), 1.97 (s, 3H; BCCH_3CH), 1.89 (s, 6H; =CCH_3), 1.54 (s, 15H; $C_5(CH_3)_5$), 0.74 (s, 3H; BCH_3), 0.60 (s, 3H; BCH_3), 0.11 (s, 18H; $SiMe_3$) ppm; ^{11}B NMR (CD_2Cl_2): δ = 28.1 (br.) ppm; ^{13}C NMR (CD_2Cl_2): δ = 115.7 (allyl moiety, center carbon), 86.5 ($C_5(CH_3)_5$), 27.9 (BCCH_3CH), 21.7, 21.3 (=CCH_3), 9.8 ($C_5(CH_3)_5$), 0.7 ($SiMe_3$) ppm. Signals for boron-bound carbon atoms of the allyl moiety n.o.; ^{29}Si NMR (CD_2Cl_2, 39.7 MHz): δ = −21.7. EI-MS: *m*/*z* (%) = 467 [**4d**$^+$] (42), 394 [**4d**$^+$−$SiMe_3$] (100), 379 [**4d**$^+$−$SiMe_3$−Me] (39); 442 [**5d**$^+$] (100), 427 [**5d**$^+$−CH_3] (22), 369 [**5d**$^+$−$SiMe_3$] (39). HR-MS: *m*/*z* calcd for $^{12}C_{23}{}^1H_{40}{}^{28}Si^{11}B_2{}^{102}Ru$: 468.2129, found: 468.2133, Δ = 0.4 mmu; *m*/*z* calcd. for $^{12}C_{22}{}^1H_{37}{}^{11}B^{28}Si$ ^{102}Ru: 442.1801, found: 442.1802, Δ = 0.1 mmu. For **5d**: in a CH_2Cl_2 solution at r.t. **4d** slowly transformed into **5d**. ^{1}H NMR (CD_2Cl_2): δ = 4.90 (s, 1H; aromatic), 1.95 (s, 3H; BCCH_3), 1.64 (s, 15H; $C_5(CH_3)_5$), 1.58 (s, 6H; BCCH_3), 0.42 (s, 3H; BCH_3), 0.08 (s, 18H; $SiMe_3$) ppm; ^{11}B NMR (CD_2Cl_2): δ = 17.5 (br.) ppm; ^{13}C NMR (CD_2Cl_2): δ = 109.4, 101.5, 95.3, 87.7 (boratabenzene ring carbon atoms), 85.9 ($C_5(CH_3)_5$), 19.6 (BCCH_3), 16.2 (BCCCH_3), 10.1 ($C_5(CH_3)_5$), 0.7 ($SiMe_3$) ppm. Signals for the other carbon atoms n.o.

4.3. (η^5-Pentamethylcyclopentadienyl)(η^7-1,2,3,4,5-pentamethyl-4-borataborepine)ruthenium (**4e**)

Acetylene was bubbled into a solution of **2a** (143 mg, 0.39 mmol) in hexane (10 mL) at −60 °C. In a few seconds the solution turned from violet to yellow with the formation of a small amount of precipitate. It was stirred at that temperature for 15 min. and then warmed to r.t. and filtered. The yellow filtrate was dried *in vacuo* to give a yellow solid, which was identified to be a mixture of **4e** and **5e** (byproduct). Recrystallization in CH_2Cl_2 at r.t. gave yellow crystals of **4e**, mp 136–138 °C (130 mg, 86%). The yellow residue (ca. 15 mg) was dissolved in minimum CH_2Cl_2 at r.t., and yellow crystals were grown and identified by EI-MS to be the boratabenzene complex **5e**. The cell parameter determination indicated that it was different from **4e**, however, the quality of the crystal was not good enough for further determination. ^{1}H NMR (CD_2Cl_2): δ = 5.54 (d, ^2J(H,H) = 10.4 Hz, 1H; CH), 4.56 (d, ^{2}J(H,H) = 10.6 Hz, 1H; CH), 1.97 (s, 3H; BCCH_3), 1.90 (s, 3H, =CCH_3), 1.89 (s, 3H, =CCH_3), 1.58 (s, 15H; $C_5(CH_3)_5$), 0.71 (s, 3H; BCH_3), 0.68(s, 3H; BCH_3) ppm. ^{11}B NMR (CD_2Cl_2): δ = 26.0 (br.) ppm. ^{13}C NMR (CD_2Cl_2): δ = 115.1 (CH, allyl moiety), 86.8 ($C_5(CH_3)_5$), 26.9 (BCCH_3CH), 22.0, 20.8 (BC=CCH_3), 9.2 ($C_5(CH_3)_5$) ppm. Signals for boron-bound ring carbon atoms n.o. EI-MS: *m*/*z* (%) = 395 [M^+] (100), 355 [M^+−BCH_3−CH_2] (74). HR-MS: *m*/*z* calcd. for $^{12}C_{20}{}^1H_{32}{}^{11}B_2{}^{102}Ru$: 396.1733, found: 396.1747, Δ = 1.4 mmu. HR-MS of **5e**: *m*/*z* calcd. for $^{12}C_{19}{}^1H_{29}{}^{11}B^{102}Ru$: 370.1406, found: 370.1428, Δ = 2.2 mmu.

Table 1
X-ray data and refinement details for **4c**, **5f**, **9** and **11**.

	4c	**5f**	**9**	**11**
Empirical formula	$C_{26}H_{36}B_2Ru$	$C_{23}H_{37}BRu$	$C_{32}H_{30}$	$C_{32}H_{57}B_4ClO_4Ru_2$
Formula weight	471.24	425.41	414.56	786.61
T (K)	120(2)	200(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/m$
a (Å)	10.145(2)	7.6752(9)	20.8374(16)	10.2105(5)
b (Å)	14.508(3)	8.928(1)	5.7266(5)	16.7306(8)
c (Å)	16.007(3)	16.051(2)	20.2349(16)	10.9882(6)
α (°)	90	92.905(2)	90	90
β (°)	102.198(3)	93.060(2)	101.081(2)	106.754(1)
γ (°)	90	104.370(2)	90	90
V (Å^3)	2302.9(7)	1061.6(2)	2369.6(3)	1797.4(2)
Z	4	2	4	2
μ(Mo Kα) (mm^{-1})	0.690	0.74	0.065	0.948
Crystal size (mm)	0.44 × 0.24 × 0.18	0.28 × 0.11 × 0.05	0.15 × 0.15 × 0.10	0.20 × 0.13 × 0.05
Θ_{max} (°)	28.3	26.4	30.5	32.0
Index ranges h, k, l	−13/13, −16/19, −21/21	−9/8, −11/11, −20/20	−29/28, 0/8, 0/28	−15/14, 0/24, 0/16
Reflections collected	22869	6546	10445	31708
Reflections unique [$R_{(int)}$]	5744 (0.0388)	4077 (0.0193)	3612 (0.0410)	6348 (0.0599)
No. of parameters	272	237	176	217
GOF	1.04	1.09	1.02	1.03
$R(F)$ [$F_o > 4\sigma(F_o)$]	0.0311	0.031	0.0542	0.040
$wR(F^2)$ (all reflections)	0.0805	0.0823	0.1567	0.1039
Residual electron density (e Å^{-3})	0.86/−0.33	0.48/−0.31	0.40/−0.31	1.94/−2.24

*4.4. (η^5-Pentamethylcyclopentadienyl)(η^6-1,2,3,4-tetramethyl-5,6-diethylboratabenzene) ruthenium (**5f**)*

A solution of 3-hexyne (75 mg, 0.91 mmol) in hexane (10 mL) was added to a solution of **2a** (179 mg, 0.49 mmol) in hexane (6 mL) at −60 °C. The mixture was warmed to r.t. and stirred for additional 2 h, no clear color change was observed. The solution was cooled to −50 °C and another portion of 3-hexyne (80 mg, 0.98 mmol) was added, warmed up and stirred overnight, during which time it became a light red solution. The solution was dried *in vacuo* to give a yellow brown oily residue, and recrystallization in CH_2Cl_2 at r.t. gave crystalline **5f** (180 mg, 87%). ^{1}H NMR (C_6D_6): δ = 2.25 (m, 4H; CH_2), 1.9 (m, 4H; CH_2), 1.75 (s, 6H, $BCCH_3$), 1.65 (s, 3H, CCH_3), 1.45 (s, 15H; $C_5(CH_3)_5$), 0.80 (s, 3H; BCH_3) ppm; ^{11}B NMR (C_6D_6): δ = 16.4 (br.) ppm. ^{13}C NMR (C_6D_6): δ = 86.3 ($C_5(CH_3)_5$), 25.0 ($BCCH_3$), 17.4, 16.4, 15.4, 15.0, 14.8 (Et and $EtCCH_3$), 9.5 ($C_5(CH_3)_5$) ppm. Signals for the boratabenzene ring carbon n.o. EI-MS: m/z (%) = 425 [M^+] (100), 410 [M^+-CH_3] (12), 395 [M^+-2CH_3] (15). HR-MS: m/z calcd for $^{12}C_{23}{}^1H_{37}{}^{11}B_2{}^{102}Ru$: 426.2031, found: 426.2023, Δ = −0.8 mmu.

*4.5. Reaction of **2a** with di-p-tolylacetylene*

A solution of di-*p*-tolylacetylene (78 mg, 0.38 mmol) in THF (5 mL) was added to a solution of **2a** (140 mg, 0.38 mmol) in hexane/THF (4 + 3 mL) at −50 °C. The mixture was warmed to r.t. and stirred overnight (no color change could be observed, ^{11}B NMR: δ = 31.5 ppm), and then for additional 2 d. The resulting deep red solution was dried, and the dark oily residue was extracted with dry toluene and filtered. The yellow residue isolated (ca. 10 mg) was recrystallized from CH_2Cl_2 at r.t. to give crystalline **11**.

11: HR-MS (EI): m/z (%) = 633.1968 [M^+] (100). Calcd. for $^{12}C_{30}{}^1H_{47}{}^{11}B_2{}^{102}Ru_2$: 633.1952. Replacement of the ring CH groups by either two oxygen atoms or one CH by one oxygen atom has the following formulae (calcd. formula weight): $^{12}C_{28}{}^1H_{45}{}^{11}B_2{}^{16}O_2{}^{102}Ru_2$ (639.1693); $^{12}C_{29}{}^1H_{46}{}^{11}B_2{}^{16}O^{102}Ru_2$ (636.1822). This comparison has helped the X-ray crystallographic analysis to assign the two CH groups, since the alternative assignments did not find suitable HR-MS peaks within experimental error.

The yellow filtrate was dried to give a yellow oil (160 mg, the signal in the ^{11}B NMR spectrum at δ = 31.5 ppm gradually disappeared and new peaks appeared at δ = 14.6 (**5g**) and ca. −0.1 ppm). In addition, 1,2,3,4-tetra-*p*-tolyl-1,3-butadiene (**9**) was identified by an X-ray diffraction analysis after recrystallization from CH_2Cl_2 at r.t.. **5g**: ^{11}B NMR (δ = 14.6 ppm); EI-MS: m/z (%) = 549 [M^+] (100). HR-MS: m/z calcd. for $^{12}C_{33}{}^1H_{41}{}^{11}B^{102}Ru$: 550.2345, found: 550.2338, Δ = −0.7 mmu.

4.6. X-ray crystallography

Intensity data were collected at low temperature on Bruker Apex (**4c, 5f**) and Bruker AXS Smart 1000 CCD diffractometers (**9**, **11**) (Mo Kα radiation, λ = 0.71073 Å, graphite monochromator). Data were corrected for air and detector absorption, Lorentz and polarization effects, [22] absorption by the crystal was treated with a semiempirical multiscan method [23,24]. The structures were solved by conventional direct methods [25,26] and refined by full-matrix least squares methods based on F^2 against all unique reflections.[26,27] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. Most hydrogen atoms in **9** (except those of the methyl groups) were taken from difference Fourier syntheses and refined (see Table 1).

5. Supplementary material

CCDC 704900, 256654, 704901 and 704902 contain the supplementary crystallographic data for **4c**, **5f**, **9** and **11**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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