Metallocenes

Ruthenocene Analogues with a Novel C_5B_2 Ligand: (η^7-4-Borataborepine)(η^5-pentamethylcyclopentadienyl)ruthenium Complexes**

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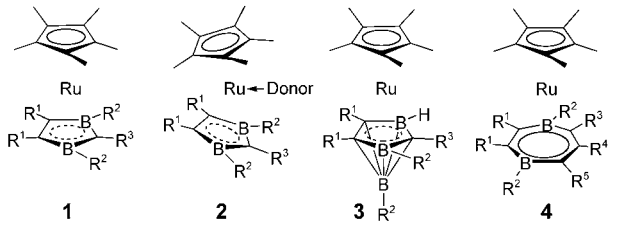
Dedicated to Professor Michael Veith on the occasion of his 60th birthday

The violet, formally 16 valence electron (VE) sandwich complexes **1**[1] are folded along the B···B vector of the heterocycle, as are the corresponding green iron complexes (folding angle $\alpha = 41.3°$).[2] This effect causes a unique reactivity leading to classic 18 VE complexes. Coordination of the donor ligands :CO and :CN-R at the ruthenium center yields yellow **2** with decreased folding angles ($< 20°$).[1a] The



incorporation of boranediyl ([:BH] from BH_3·THF) results in the formation of ruthenacarboranes **3** and likewise the incorporation of sulfur (from H_2S) gives ruthenathiacarboranes.

With phosphines, **1** forms donor–acceptor complexes **1**-PH_2R (R = H, Ph), however, the triorganylphosphine adducts **1**-PR_3 (R = Me, Ph) are unstable. With *tert*-butylphosphaalkyne :P≡C-CMe_3, no adduct but its incorporation into **1** is observed, however, it is not yet known which of the possible isomers of the resulting ruthenaphosphacarborane is formed.[1b]

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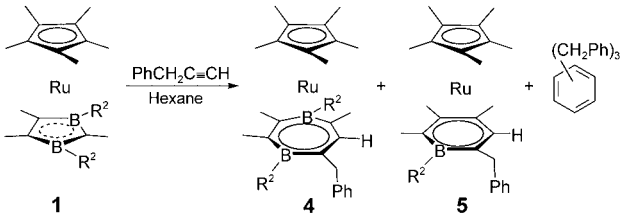
Herein we report the insertion of terminal alkynes into the heterocycle of **1**, which leads to the 18 VE complexes **4** with the novel η^7-4-borataborepine as a six-electron (6e) ligand, whereas with diorganylacetylenes the formation of boratabenzene complexes **5** occurs.

Treatment of **1a** with 3-phenyl-1-propyne (Scheme 1) in hexane yields the yellow, relatively air-stable solid **4a**, which exhibits one broad signal at $\delta = 29$ ppm in the ^{11}B NMR



Scheme 1. Insertion of a terminal alkyne into **1** to give the 4-borataborepine complexes **4**; $R^2 = CH_2SiMe_3$ (**4a**), $R^2 = Me$ (**4b**).

spectrum (downfield compared to that of **1a**, $\delta = 21.7$ ppm). The absence of a second ^{11}B NMR signal in the upfield region indicates that the uptake of the alkyne did not give a ruthenacarborane with an apical boron atom, such as **3**. In the EI-MS spectra, a cutoff peak at *m*/*z* 630 [M^+] shows that the 1:1 product does not lose the alkyne (which would occur an adduct of **2**). A weak signal at *m*/*z* 532 [**4a**−BCH_2SiMe_3]$^+$ was tentatively assigned to the complex [Cp*Ru(boratabenzene)] (**5a**; Cp* = C_5Me_5). In addition, tribenzylbenzene was identified by MS as a side product. The structure of **4a** (Figure 1), established by a single-crystal X-ray diffraction,[3] demonstrates the formation of a novel sandwich complex with the 4-borataborepine ligand, as a result of the insertion of the C≡C unit of the alkyne into a B–C bond of **1a**.[5] As the B1–C2 and B3–C2 bonds in **1a** are equivalent, both bonds react with the alkyne yielding enantiomers, which are found in the crystal structure.[3]

The seven-membered ring in **4a** is less folded along the B···B vector ($\alpha = 26°$), and the Ru–B separations (2.527 and 2.542 Å) are significantly elongated compared to those in **1a**.[5] The Ru–C bond lengths of the C_5B_2 ring vary between 2.203 (Ru–C4) and 2.345 Å (Ru–C2). Because of the bonding between the ruthenium center and the larger ring, the bonds to the exocyclic α-atoms are tilted towards the ruthenium, with the exception of those to C16 and C20, which are bound to the boron atoms, which tilt in the opposite direction.

The influence of the bulky silyl groups in **4a** is evident when compared with **4b**, obtained from the reaction of violet **1b** and 3-phenyl-1-propyne in hexane (Scheme 1). The yellow product was identified as a mixture of the expected 4-borataborepine complex **4b** and the boratabenzene compound **5b** by MS. While most of the bond lengths and angles are similar to those in **4a**, some differences arise in **4b** (Figure 1)[3] owing to the absence of the silyl groups: the Ru–B bond lengths of 2.429 and 2.443 Å are significantly shorter than those in **4a**, and the folding along the B···B vector ($\alpha = 12.5°$) is only half the value of that in **4a**. The seven-

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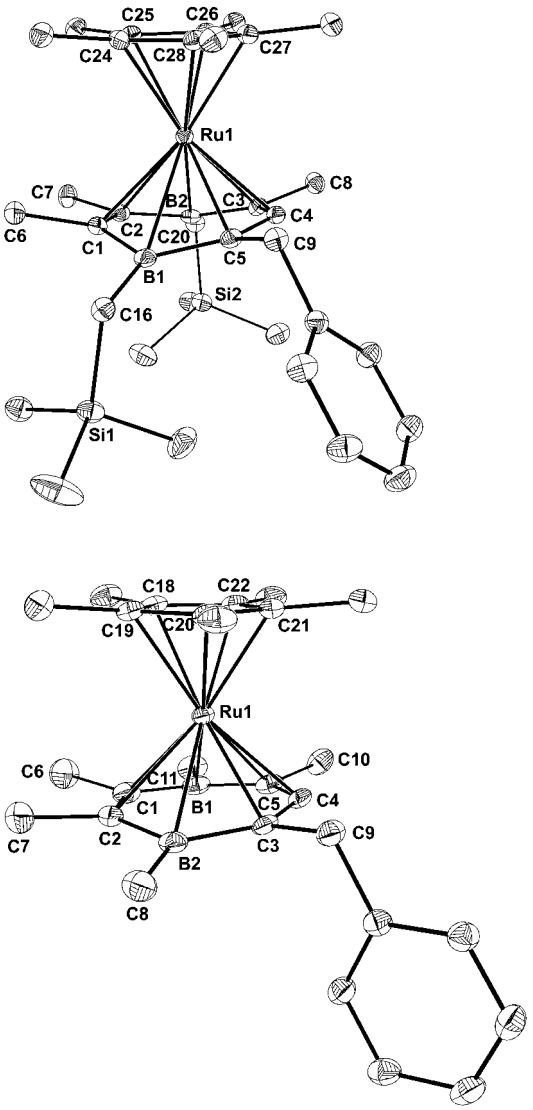
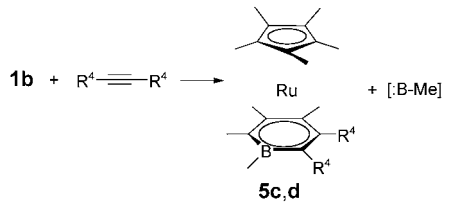


Figure 1. Molecular structures of **4a** (top) and **4b** (bottom). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: **4a**: Ru-C_{Cp^*} 2.172(3)–2.205(3), Ru-C1 2.287(3), Ru-C2 2.345(3), Ru-B2 2.542(3), Ru-C3 2.311(3), Ru-C4 2.203(3), Ru-C5 2.303(3), Ru-B1 2.527(3), B1-C5 1.531(4), C5–C4 1.409(4), C4-C3 1.412(4), C3-B2 1.524(4), B2-C2 1.540(4), C2-C1 1.413(4), C1-B1 1.545(4). **4b**: R–C_{Cp^*} 2.178(3)-2.201(3), Ru-C2 2.332(3), Ru-B2 2.443(3), Ru-C3 2.299(3), Ru-C4 2.234(3), Ru-C5 2.315(3), Ru-B1 2.429(4), Ru-C1 2.330(3), B2-C3 1.520(5), C3-C4 1.415(4), C4-C5 1.400(4), C5-B1 1.528(5), B1-C1 1.531(5), C1-C2 1.415(5), C2-B2 1.542(5).

membered C_5B_2 ring is almost parallel to the Cp* ring, the dihedral angle between the two best planes is 6.6°.

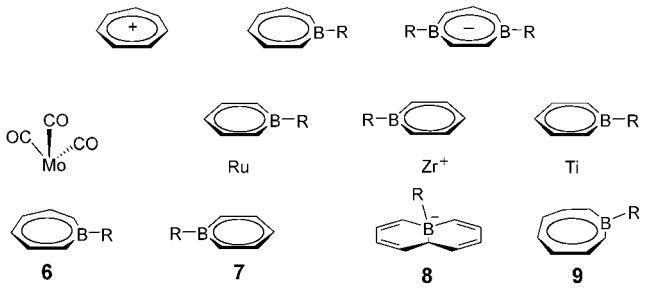
To elucidate the unexpected formation of boratabenzene complexes **5a**,**b**, the stability of **4a** in solution was monitored by ^{11}B NMR spectroscopy. Over several weeks a weak signal at $\delta = 16$ ppm increased, which indicates that the boratabenzene complex **5a** was formed from **4a**. In addition, the reactions of **1b** and 3-hexyne and di-*p*-tolylacetylene, respectively, were carried out (Scheme 2), which led to the boratabenzene complexes **5c**,**d**, identified by MS and confirmed by an X-ray crystallographic study of **5c**.[6] Clearly steric requirements in the anticipated peralkylated complexes



Scheme 2. Insertion of disubstituted alkynes into **1b** to give the boratabenzene complexes **5**; R^4 = Et (**5c**), R^4 = *p*-tolyl (**5d**).

4c,**d** cause the complete elimination of one methylboranediyl moiety [:B-Me] to give **5c**,**d** directly, whereas **4a**,**b** eliminate [:B-R^2] only slowly in solution (Scheme 2).

As with boratabenzenes,[7a] the 4-borataborepines in **4** function as 6e ligands, their 2e ene and the 4e allylic groups are separated by two boron atoms, but are electronically connected by their p_z orbitals, as indicated by the short boron–carbon bond lengths. The 4-borataborepine is formally derived from the tropylium ion $[C_7H_7]^+$ and the neutral borepine C_6H_6BR[8a] (a 6e ligand in **6** with R = Cl[8b]) by replacing two CH in $[C_7H_7]^+$ by two BR^- units and one CH in C_6H_6BR by one BR^- unit. Thus **4** is an isomer of **7**[7b] and a structural analogue of (η^5-cyclopentadienyl)(η^7-cycloheptatrienyl)chromium.[9]



The driving force for the alkyne insertion into the electron-poor complex **1** is the formation of the 6π-electron ligand 4-borataborepine in the 18 VE complexes **4**. The first insertion reactions of ethyne into one of the boratabenzene rings of bis(boratabenzene)-zirconium and -titanium complexes were reported by Ashe et al.[10] and Bazan et al.,[11] who obtained complexes **8** and **9** containing 8a*H*-4-boratanaphthalene (R = Ph)[10] and boratacyclooctatetraene (R = Me)[11] ligands, respectively.

In conclusion, we have demonstrated that the insertion of terminal alkynes into the C_3B_2 heterocycle of the complexes **1** results in 18 VE boron-containing ruthenocene analogues **4**, which contain 4-borataborepine as a 6e ligand with classical π bonding,[12] as the main products, together with the formation (from **4**) of boratabenzene complexes **5**, which are formed as the only products in the reactions of **1** with disubstituted alkynes.

Experimental Section

4a: 3-Phenyl-1-propyne (82 mg, 0.7 mmol) in hexane (5 mL) was added to a violet solution of **1a**[1a] (244 mg, 0.47 mmol) in hexane

(10 mL) at −45 °C. After 30 min the cooling bath was removed and the reaction mixture warmed to room temperature, during which the solution turned yellow. After filtration, the filtrate was dried in vacuo, and the resultant oily residue purified by column chromatography on silica gel. Eluting with hexane and then with hexane/CH_2Cl_2 (4:1) gave a yellow elute, which was dried in vacuo and gave **4a** as a yellow solid (100 mg, 34 %). Crystals suitable for X-ray analysis were grown from a CH_2Cl_2 solution of **4a** at room temperature, m.p. 175 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.39$–7.17 (m, 5H; Ph), 5.41 (s, 1H; CH), 3.86 (d, 1H; ^2J(H,H) = 14.3 Hz, CH_2Ph), 3.07 (d, 1H; ^2J(H,H) = 14.3 Hz, CH_2Ph), 1.94 (s, 3H; BCCH_3CH), 1.85 (s, 3H; =CCH_3), 1.80 (s, 3H; =CCH_3), 1.57 (s, 15H; C_5(CH_3)$_5$), 0.15 (s, 18H; $SiMe_3$), −0.28 (s, 2H; BCH_2), −0.51 ppm (s, 2H; BCH_2); ^{11}B NMR (64 MHz, $CDCl_3$): $\delta = 34$ ppm (br.); ^{11}B NMR (64 MHz, CD_2Cl_2): $\delta = 29$ ppm (br.); ^{13}C NMR (53 MHz, $CDCl_3$): $\delta = 143.3$, 128.8, 128.0, 125.4 (Ph), 117.4 (allyl moiety, central carbon), 86.1 (C_5(CH$_3$)$_5$), 47.7 (CH$_2$Ph), 28.7 (BCCH$_3$CH), 19.8, 18.3 (BC=CCH$_3$), 9.7 (C_5(CH$_3$)$_5$), 1.02 ppm ($SiMe_3$). The signals for the boron-bound carbon atoms of the allyl moiety, for BCH$_2$SiMe$_3$, and for the two =CMe moieties were not observed; EI-MS: m/z (%) = 630 [M^+] (57), 615 [M^+−CH$_3$] (11), 557 [M^+−SiMe$_3$] (32), 532 [M^+−SiMe$_3$−BCH$_2$] (66), 446 [M^+−2 SiMe$_3$−BCH$_2$−CH] (100). HR-MS: m/z calcd for $^{12}C_{33}{}^1H_{54}{}^{28}Si_2{}^{11}B_2{}^{102}Ru$: 630.2993, found: 630.2996, $\Delta = 0.3$ mmu.

4b: obtained analogously to **4a**. 3-phenyl-1-propyne (58 mg, 0.5 mmol) in hexane, **1b**[1a] (140 mg, 0.38 mmol) in hexane (20 mL) gave a yellow reaction mixture. After filtration a yellow residue was obtained (40 mg), which is a mixture of **4b**, **5b** and tribenzylbenzene (detected by MS). The filtrate resulted in a yellow solid (150 mg), a mixture of **4b** and **5b** (detected by MS), which was recrystallized in CH_2Cl_2 at room temperature to give **4b** (81 %), m.p. 203–205 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.09$–7.36 (m, 5H; Ph), 5.54 (s, 1H; CH), 3.97 (d, 1H; ^2J(H,H) = 14.7 Hz, CH_2Ph), 3.02 (d, 1H; ^2J(H,H) = 14.7 Hz, CH_2Ph), 1.97 (s, 3H; BCCH_3CH), 1.92 (s, 3H; =CCH_3), 1.88 (s, 3H; =CCH_3),1.57 (s, 15H; C_5(CH$_3$)$_5$), 0.68 (s, 3H; BCH$_3$), 0.61 ppm (s, 3H; BCH$_3$); ^{11}B NMR (64 MHz, $CDCl_3$): $\delta = 26$ ppm (br.); ^{13}C NMR (53 MHz, $CDCl_3$): $\delta = 142.9$, 128.7, 127.9, 125.3 (Ph), 118.5, (allyl moiety, central carbon), 86.3 (C_5(CH$_3$)$_5$), 46.5 (CH$_2$Ph), 27.9 (BCCH$_3$CH), 22.2, 22.1 (BC=CCH$_3$), 9.5 ppm (C_5(CH$_3$)$_5$). The signals for the boron-bound carbon atoms of the allyl moiety, for BCH$_3$, and for the two =CMe moieties were not observed. EI-MS: m/z (%) = 486 [M^+] (54), 444 [M^+−BCH$_3$−CH$_4$] (41), [M^+−CH$_2$Ph] (100). HR-MS: m/z calcd. for $^{12}C_{27}{}^1H_{38}{}^{11}B_2{}^{102}Ru$: 486.2203, found: 486.2218, $\Delta = 1.5$ mmu.

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[3] Crystal structure analyses for **1a**, **4a**, and **4b**: intensity data for **1a** were collected on a Bruker AXS SMART CCD diffractometer at $T = 103$ (2) K, for **4a** and **4b** on a Bruker Apex CCD diffractometer at $T = 120(2)$ K. $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω-scans. The structures were solved by direct methods and refined by least-squares methods based on F^2 with all measured reflections, all non-hydrogen atoms are refined anisotropically.[4] **1a**: Monoclinic, space group $P2_1/c$, $C_{24}H_{46}B_2RuSi_2$, $a = 18.7559(8)$, $b = 8.9859(4)$, $c = 18.0098(8)$ Å, $\beta = 114.131(1)°$, $V = 2770.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.231$ g cm^{-3}; 38020 reflections ($\theta_{max} = 32°$) collected, 9545 independent reflections [R(int) = 0.0539]. $R1 = 0.0338$ ($I > 2\sigma$(I)), $wR2 = 0.0823$ (all data). **4a**: Monoclinic, space group $P2_1/n$, $C_{33}H_{54}B_2RuSi_2$, $a = 11.2417(7)$, $b = 19.6225(13)$, $c = 15.6347(10)$ Å, $\beta = 102.466(3)°$, $V = 3367.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.242$ g cm^{-3}; 53110 reflections ($\theta_{max} = 28.4°$) collected, 8451 unique reflections [R(int) = 0.0820]. $R1 = 0.0477$ ($I > 2\sigma$(I)), $wR2 = 0.0956$ (all data). **4b**: Triclinic, space group $P\bar{1}$, $C_{27}H_{38}B_2Ru$, $a = 7.5443(6)$, $b = 8.8867(7)$, $c = 18.6554(15)$ Å, $\alpha = 87.062(4)$, $\beta = 88.683(4)$, $\gamma = 69.228(4)°$, $V = 1167.88(16)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.380$ g cm^{-3}; 18121 reflections ($\theta_{max} = 28.3°$) collected, 5778 unique reflections [R(int) = 0.0391]. $R1 = 0.0401$ ($I > 2\sigma$(I)), $wR2 = 0.0926$ (all data). CCDC-244072 (**1a**), CCDC-244073 (**4a**), CCDC-244074 (**4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[5] **1a**,[1a] a dark violet oil, on cooling in hexane finally yielded suitable crystals for an X-ray structural analysis,[3] which confirms that the 1,3-diborolyl ring C_3B_2 is folded by 40.7° along the B···B vector, very similar to its green iron analogue.[2] The Ru–C2 bond length [2.029, cf. Fe-C 1.899 Å] is markedly shorter than the other Ru–C bond lengths of the heterocycle.

[6] Crystal data for **5c**: data were collected on a Bruker Apex CCD diffractometer at 200 K, triclinic, space group $P\bar{1}$, $C_{23}H_{37}BRu$, $a = 7.6562(9)$, $b = 8.928(1)$, $c = 16.051(2)$ Å, $\alpha = 92.905(2)$, $\beta = 93.060(2)$, $\gamma = 104.370(2)°$, $V = 1061.6(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.33$ g cm^{-3}; 6546 reflections ($\theta_{max} = 26.4°$) collected, 4077 independent reflections [R(int) = 0.0193]. $R1 = 0.031$ ($I > 2\sigma$(I)), $wR2 = 0.0823$. CCDC number: CCDC-256654. **5c**: HR-MS: m/z calcd. for $^{12}C_{23}{}^1H_{37}{}^{11}B^{102}Ru$: 426.2031, found: 426.2023, $\Delta = -0.8$ mmu. **5d**: HR-MS: m/z calcd. for $^{12}C_{33}{}^1H_{41}{}^{11}B^{102}Ru$: 550.2344, found: 550.2338, $\Delta = -0.7$ mmu.

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[12] MO calculations for **1** and **4** are in progress (Dr. I. Hyla-Kryspin, University of Münster, Germany).

