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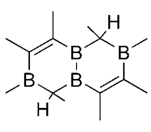
Metallocene Fusion

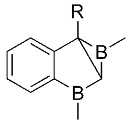
Fusion of a 1,3-Diboraruthenocene to Form a Slipped μ-Hexahydrotetraboranaphthalene Triple-Decker Complex with Two Axial C–H Bonds**

Elena V. Mutseneck, Hubert Wadepohl, Markus Enders, Alexander R. Kudinov, and Walter Siebert**

Numerous complexes with three-center, two-electron C-H-M interactions have been investigated by X-ray and neutron diffraction, and by NMR spectroscopy.[1] Long C–H bonds in complexes such as $[\{Ta(CHCMe_3)(PMe_3)Cl_3\}_2]$,[2] $[\{(MeO)_3P\}_3Fe(\eta^3\text{-}C_8H_{13})]^+$,[3] and $[(\eta^3\text{-}6\text{-}endo\text{-}Me\text{-}C_6H_9)Mn(CO)_3]$[4] indicate agostic bonding. A different kind of 3c,2e bonding involving C–H bonds was found in cobalt 2,3-dihydro-1,3-diborole complexes in which the *endo* hydrogen atom at the pentacoordinate carbon of the MeC*–H group could be in a bridging (C*-H-B) or in an axial (Co-C*-H) position.[5] The X-ray diffraction study of $[CpCo\{\eta^5\text{-}(EtC)_2(EtB)_2C^*HMe\}]$ did not give reliable data for the position of the hydrogen atom; however, evidence for a 3c,2e interaction was derived from the reduced magnitude of the ^{13}C–^1H coupling constant.[6] In contrast, the molecular structures of $[CpCo\{(C_6H_{12})C_2(MeB)_2CHMe\}]$[7a] and of $[(\{(MeC)_2(tBuB)_2(CHMe)\}RhCl)_2]$[7b] have C*-H-B bridges. Herein we report on the formation of the dinuclear complex **4**, which contains the unprecedented hexahydrotetraboranaphthalene ligand **A** with two MeC*–H groups. Of great interest are its generation, the location of the *endo* hydrogen atoms, and their contribution to the stability of **4**. As a multiple Lewis acid, **A** is related to the dihydrodiboranaphthalenes **B**[8] and **C**,[9] and doubly deprotonated **A** is isoelectronic to the unknown isomer **D.**



A



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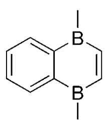

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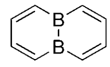
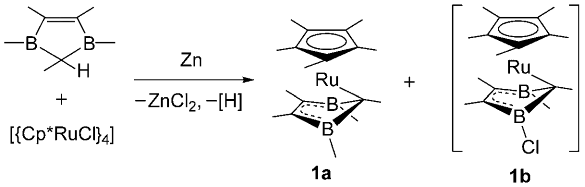
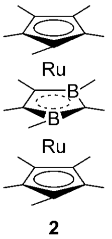


D

The procedure for the preparation of the decamethyl derivative **1a** is based on the reaction of $[\{Cp^*RuCl\}_4]$ with the adduct formed from pentamethyl-2,3-dihydro-1,3-diborole and MeLi.[10] To improve the synthesis, a reaction analogous to $[\{Cp^*RuCl\}_4]$/cyclopentadiene/zinc dust giving pentamethylruthenocene[11] was carried out with $C_3B_2Me_5H$ in THF (Scheme 1). Addition of zinc to the mixture produced a violet solution, and after column chromatography, **1a** was obtained in about the same yield as previously. Furthermore, an orange–yellow solid was isolated and separated by TLC, giving the orange triple-decker complexes **2**[12] and **3**[10] and the yellow compound **4**. The HR-EI mass spectrum of **4** is in agreement with the molecular composition, and the molecular structure, established by X-ray diffraction (Figure 1). Unfortunately, the assignment of non-hydrogen atoms of the bridging ligand to boron and carbon was not conclusive. Based on the evidence from spectroscopy and DFT calculations, a disordered centrosymmetric model with partially occupied carbon and boron atoms in the 2- and 3-positions was refined. The occupancies of carbon and boron refined to



Scheme 1. Formation of complex **1a** and the intermediate side product **1b**.



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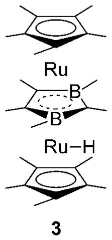

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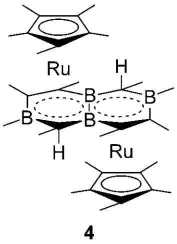

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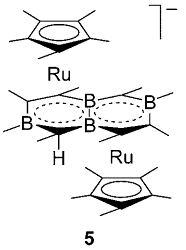

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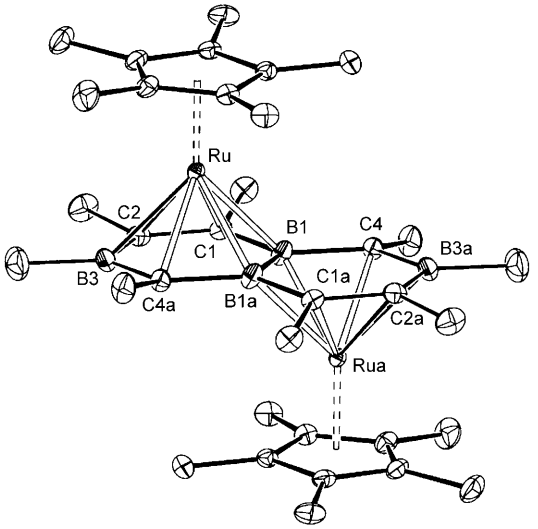

Figure 1. Molecular structure of **4** in the crystal (50% probability ellipsoids, hydrogen atoms are omitted, only one of the two disordered atom sets is shown). Selected bond lengths [Å]: Ru–B1 2.2672(16), Ru–B1a 2.2141(16), Ru–C1 2.2296(13), Ru–B2 2.2552(15), Ru–C3a 2.2478(16), Ru–C4a 2.2050(14), B1–B1a 1.754(3), B1–C1 1.566(2), B1–C4 1.614(2), C1–C2 1.472(2), C2–B3 1.546(2), B3a–C4 1.566(2).

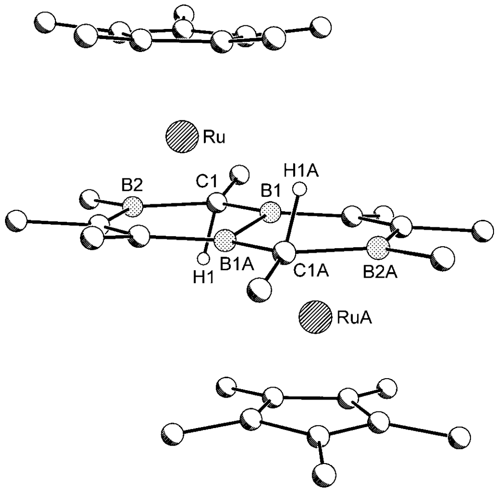

Figure 2. Optimized structure of **4** (hydrogen atoms of the methyl groups are omitted).

0.7 and 0.3, respectively; the methyl groups in positions 1 and 4 are equally bent away from the ring plane toward ruthenium, by 10.4 and 10.8°, respectively. No evidence was found in the difference Fourier map syntheses for the location of the *endo* hydrogen atoms. The ten-membered bicyclic ligand is essentially planar with the two ruthenium atoms that are 1.578 Å above and below the ring plane. The B-B distance (1.754 Å) amounts to a normal B–B bond, and the two symmetry-independent B-Ru distances differ by about 0.05 Å.

The relatively sharp signals in the ^{11}B NMR spectrum ($\delta =$ 31.6 and 22.1 ppm in a 1:1 ratio) suggests two different boron environments. ^{1}H NMR spectra, in particular by homonuclear decoupling and 2D experiments, clearly show the presence of a MeC–H group by an upfield quartet at δ–4.65 ppm. From the ^{13}C satellites, the coupling constant $^1J_{CH} \approx 93$ Hz is obtained; a broad ^{13}C NMR signal at 16 ppm is assigned to the Me*C*H carbon atom and is confirmed by the correlation in the ^{1}H,^{13}C-HSQC spectrum (see the Supporting Information). The reduced magnitude of J_{CH} indicates a weakening of the *endo* C–H bonds, one of which reacts with potassium mirror in THF to yield the anion **5**.

Density functional calculations (BP86/TZ2P) confirmed that the *endo* hydrogen atoms occupy axial positions at the B_2C units. Two conformers that differ by their B···H contacts were found with virtually equivalent energies. In the conformer shown in Figure 2, the axial hydrogen atoms are located closer to the single boron atoms B2,2A (H1-C1 1.132, H1···B1 2.010, H1···B2 1.731 Å), whereas in the other conformer they are closer to the bridgehead boron atoms B1,1A (H1-C1 1.125, H1···B1 1.760, H1···B2 2.024 Å).

We consider that the first step of the process leading to **4** is the formation of the chloro-substituted complex [Cp*Ru($C_3B_2Me_4Cl$)] (**1b**, Scheme 1), possibly by a nonselective Me/Cl exchange between [{Cp*RuCl}$_4$] and $C_3B_2Me_5H$. The formation of **1b** is supported by our recent finding that the two reagents without zinc dust yield the paramagnetic triple-decker complexes [(Cp*Ru)$_2$(μ-$C_3B_2Me_3ClX$)] (X = Me, Cl), apparently by the stacking of **1b** with a {Cp*Ru} or with a {Cp*RuCl} moiety. In the presence of zinc dust, **1b** could undergo a Wurtz-type reaction, which most likely proceeds via intermediate formation of the radical species [Cp*Ru($C_3B_2Me_4$)]$^{\bullet}$. According to DFT calculations, coupling of two radicals results in the fusion of two complexed C_3B_2 rings giving the 32 VE intermediate **E** with a bridging tetracyclic ligand (Figure 3). A similar fusion of complexed C_2B_3 rings yielding the structurally characterized slipped triple-decker complex [{Cp*Co($Et_2C_2B_3H_3$)}$_2$] has been reported as a side reaction in the synthesis of a tetradecker complex.[13] Cleavage of the B–C bonds of the edge-fused C_3B_2 rings in **E** could lead with uptake of two hydrogen atoms to complex **4**. The role of the axial hydrogen atoms in **4** consists of the donation of two additional electrons to reach the stable 34 VE configuration.[14]

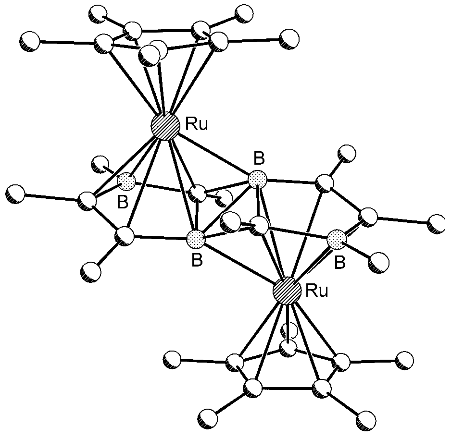

Figure 3. Optimized structure of the intermediate **E** (hydrogen atoms of the methyl groups are omitted).

In conclusion, treatment of the reaction mixture of [{Cp*RuCl}$_4$]/$C_3B_2Me_5H$ with zinc leads to the known complexes **1a**, **2**, **3**, and unexpectedly to the slipped triple-decker complex **4.** A transformation of the chloro-containing intermediate **1b** by reductive coupling is postulated to yield the edge-fused dimer **E**, which has a diamond-like linkage. Its rearrangement with incorporation of two hydrogen atoms may lead to **4**, in which two C_3B_2 rings have merged to form two six-membered rings in a naphthalene-like framework. Calculations support the location of the *endo* hydrogen atoms in axial positions, whereas in metal 2,3-dihydro-1,3-diborole complexes, bridging C*-H—B bonds are present, which have pronounced C*-H acidity. Deprotonation of **4** leads to the anion **5**, which is the expected basis for its high synthetic potential.

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