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Paramagnetic (1,3-Diborolyl)ruthenium Triple-Decker Complexes and Transformation into Diamagnetic Complexes Having Bridging 1,3-Diborafulvene Ligands

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Dedicated to Professor Helmut Werner

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The paramagnetic triple-decker complexes [(Cp*Ru)$_2${μ-(CMe)$_3$(BCl)(BMe)}] (**3b**) and [(Cp*Ru)$_2${μ-(CMe)$_3$(BCl)$_2$}] (**3c**) are formed by refluxing a mixture of [Cp*RuCl]$_4$ and pentamethyl-2,3-dihydro-1,3-diborole in thf. In CH_2Cl_2 under air complex **3b** slowly looses a hydrogen atom with formation of the diamagnetic triple-decker [(Cp*Ru)$_2${μ-η^5:η^6-(CMe)$_3$-(BCl)(BCH$_2$)}] (**4b**) with the unsymmetrical dihydrodiborafulvene derivative in a bridging position. The analogous complex [(Cp*Ru)$_2${μ-η^5:η^6-(CMe)$_3$(BMe)-(BCH$_2$)}] (**4a**) is obtained by interaction of HCl with the triple-decker [(Cp*Ru)$_2${μ-(CMe)$_3$(BMe)$_2$}] (**3a**). According to calculations, complexes **4a** and **4b** have an almost non-distorted triple-decker arrangement with a strong bending of the B=CH$_2$ group toward one of the Ru atoms. For the formation of **3b** and **3c** the chloro-containing sandwich complexes [Cp*Ru{η^5-(CMe)$_3$-(BCl)(BR^1)}] (**2b**,**c**; R^1 = Me, Cl) are proposed as intermediates. The constitutions of the complexes are derived from NMR, MS and DFT data, and the molecular structure of **3b** is confirmed by an X-ray diffraction analysis.

Introduction

The synthesis of the 34 VE triple-decker cation [Cp$_3$Ni$_2$]$^+$[1] initiated the development of oligodecker sandwich chemistry, which has been enormously expanded by the incorporation of boron-containing ligands in bridging positions.[2] The isomeric carborane ligands $C_2B_3H_5$ with adjacent and separated ring carbon atoms stabilize 30 VE triple-decker complexes [(CpCo)$_2$(μ-$C_2B_3H_5$)]:[3a] A remarkable influence of electron-withdrawing substituents X = Cl, Br, and acetyl of the complexes [Cp*Co{(CEt)$_2$(BH$_2$)$_2$(BX)}] was observed when used for the synthesis of the corresponding tetradecker complexes [Cp*Co{(CEt)$_2$(BH)$_2$(BX)}]$_2$M.[3b] Cyclopentadienyl(pentaalkyl-2,3-dihydro-1,3-diborole)cobalt complexes and their anions [CpCo{1,3-(CR^2)$_3$(BR^1)$_2$}]$^-$ provide versatile building blocks for the construction of dia- and paramagnetic oligodecker sandwich complexes,[4] whereas reactions of the anionic ruthenium complex [Cp*Ru-1,3-(CMe)$_3$(BMe)$_2$]$^-$ [**2a**]$^-$ with transition metal cations M^{2+} did not yield tetradecker complexes. The neutral sandwich **2a**[5] has a strongly folded pentamethyl-2,3-dihydro-1,3-diborolyl ligand[6] which functions as 5e donor in the 18 VE species. The complex is highly reactive toward Lewis bases, oxidative addition as well as stacking and insertion reagents.[7–9] Recently, a new method for the synthesis of **2a** has been reported by treating [Cp*RuCl]$_4$ with pentamethyl-2,3-dihydro-1,3-diborole (**1a**H) in the presence of zinc,[10] which also led to three dinuclear products: the triple-decker complexes [(Cp*Ru)$_2${μ-1,3-(CMe)$_3$(BMe)$_2$}] (**3a**) and [Cp*Ru{μ-1,3-(CMe)$_3$(BMe)$_2$}Ru(H)Cp*] (**3a**H) as well as the slipped triple-decker [(Cp*Ru)$_2$(μ-η^6:η^6-$C_6B_4Me_8H_2$)].

Herein we report on the reaction of [Cp*RuCl]$_4$ with **1a**H in the absence of zinc to give unexpectedly the chloro-containing 29 VE triple-decker complexes [(Cp*Ru)$_2${μ-(CMe)$_3$-(BCl)(BMe)}] (**3b**) and [(Cp*Ru)$_2${μ-(CMe)$_3$-(BCl)$_2$}] (**3c**). The former complex slowly reacts with oxygen, which results in the transformation of **3b** into the diamagnetic μ-dihydro-1-methylenediborafulvene triple-decker [(Cp*Ru)$_2${μ-η^5:η^6-(CMe)$_3$(BCl)(BCH$_2$)}] (**4b**). The paramagnetic triple-decker **3a** looses in the presence of HCl a

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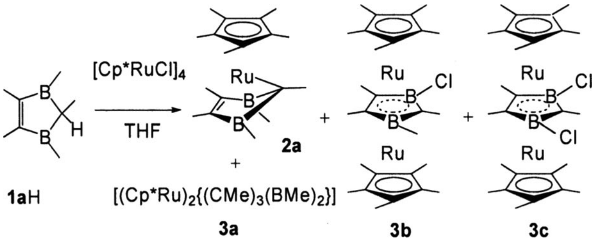
hydrogen atom to give 30 VE complex **4a**. According to DFT calculation compounds **4a** and **4b** hardly exhibit any slip distortion, whereas the known dinuclear complexes with μ-dihydrodiborafulvenes have slipped triple-decker structures.[11,12]

Results and Discussion

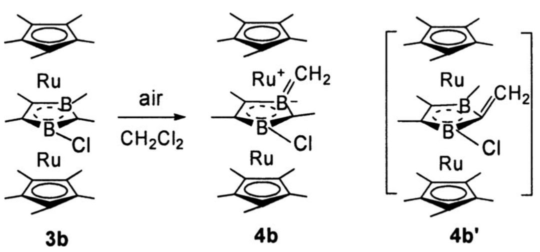
Synthesis and Spectra of the Complexes 2a, 3a–c and 4b

Refluxing of a thf solution of $[Cp^*RuCl]_4$ and **1a**H gave a violet-brown mixture of compounds **2a** and **3a**–**c** (Scheme 1). Column chromatography on silica gel with hexane as eluent allowed to isolate violet **2a**, yellow **3a** and a dark orange mixture of **3b**/**3c** (ca. 2:1), which were separated by TLC.

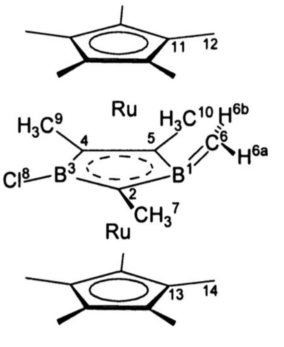


Scheme 1. Reactions of pentamethyl-2,3-dihydro-1,3-diborole (**1a**H) with $[Cp^*RuCl]_4$ in refluxing thf leading to complexes **2a** and the paramagnetic triple-deckers **3a**–**c**.

The compositions of the compounds were deduced by NMR and MS studies. In the ^{11}B NMR spectra rather broad and highly shifted signals for **3b** and **3c** are found that are characteristic for paramagnetic compounds. The solids are air-stable; however, in a CH_2Cl_2 solution under air complex **3b** (29 VE) slowly looses one hydrogen atom as shown by EI-HR MS. Four different methyl groups of the bridging heterocycle could loose a hydrogen atom with formation of the corresponding 1,3-dihydro-1,3-diborafulvene triple-decker. The diamagnetic 1-methylene isomer **4b** (30 VE, Schemes 2 and 3) was identified by NMR spectroscopy. In the ^{11}B NMR spectrum it shows two rather sharp signals at $\delta = 15.1$ and 8.7 ppm (for BCH_2 and BCl, respectively; $\nu_{1/2} \approx 140$ Hz) and in the ^1H NMR spectrum two characteristic doublets at $\delta = 3.53$ and 3.36 ppm ($^2J_{H,H} = 3.5$ Hz) for an AB system of an $X{=}CH_2$ group in an unsymmetrical environment. The Cp* ligands are not equivalent, leading to two ^1H NMR signals ($\delta = 1.49$ and 1.68 ppm). Three singlets (relative intensities 3 H each) originate from three different C–CH_3 groups; the corresponding signals are present in the ^{13}C NMR spectrum. The ^{13}C signals of *B*-bound carbon atoms are obtained at lower temperature (263 K) where a faster relaxation of the ^{11}B nuclei leads to sharper ^{13}C resonances. The ^{13}C signal of the newly formed $B{=}CH_2$ group (B1, C6 atoms; see Scheme 3 and Exp. Sect.) is detected at $\delta = 59.7$ ppm as a broad resonance ($\nu_{1/2} \approx 120$ Hz). In addition, a strong correlation peak in the HSQC spectrum is observed. The ^{13}C resonances of the three non-equivalent carbon atoms of the C_3B_2 ring are observed in the long-range C,H correlation spectrum (HMBC) at $\delta = 81.3$, 81 and 77.8 ppm, respectively. The signal assignment (see Exp. Sect. and Supporting Information) is based on NOE measurements, which are in accordance with the calculated structure of **4b**. Most of the calculated NMR shifts (giao method) are in good agreement with the experimental values; however, the calculated shifts for the carbon atoms near the metal atoms exhibit larger deviations (see Table S1, Supporting Information). The NMR spectroscopic data unambiguously support the constitution of **4b** with a $B{=}CH_2$ unit as depicted in Scheme 3 and Figure 2. Thus, the 2-methylene isomer **4b′** (Scheme 2) and other possible isomers (see Supporting Information) can be ruled out. Complex **4b** has two Ru-d^6 centers, whereas in paramagnetic **3b** different oxidation states for the metal atom (Ru-d^7 and Ru-d^6) are present.



Scheme 2. Abstraction of a hydrogen atom from the triple-decker **3b** (29 VE) by oxygen leading to the diamagnetic complex **4b** (30 VE) with the bridging 3-chloro-1-methylene-1,3-dihydro-1,3-diborafulvene ligand.



Scheme 3. Numbering of atoms in **4b**.

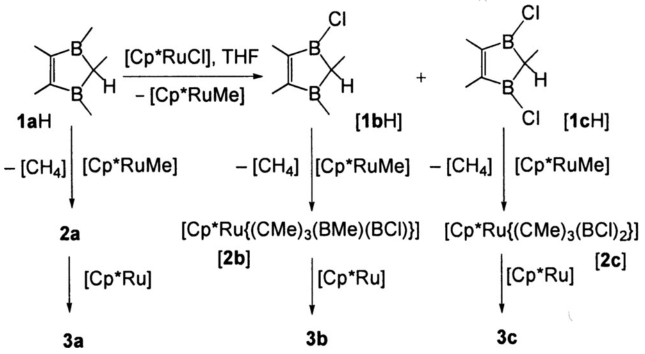
The bonding in 1,3-dihydro-2-methylene-1,3-diborafulvene triple-decker complexes with two $Fe(CO)_3$ and the combination of $Fe(CO)_3$/CoCp complex fragments[12] has been analyzed. These 32 VE compounds are diamagnetic because of their slip distortion, whereas non-distorted 32 VE triple-decker complexes are paramagnetic.[13] In **4b** (Scheme 2) an additional ligand–metal π-bonding occurs between Ru^+ and the $H_2C{=}B^-$ group. At this time all attempts to solve the X-ray diffraction structures of **4a**, **b** (see below) were unsuccessful due to twinning problems of the crystals.

Information on the bonding situation of the B=CH_2 group can be obtained from the observed coupling $^1J_{C,H}$ = 143 Hz. Compared with $^1J_{C,H}$ in the heterocycle **1a**H [$^1J_{C,H}$ ranging from 114 to 123 Hz] this considerably larger value reflects the higher s-character in the C–H bond of the B=CH_2 moiety. The formation of the B=CH_2 group in **4b** occurred serendipidly, when **3b** was crystallized from CH_2Cl_2 under air. This transformation (of **3b** to **4b**) might be possible along the following route. Oxygen may have removed an electron from **3b** to yield the 28 VE cationic complex [**3b**]$^+$, which looses a proton from B–CH_3 and forms the anionic methylene group $^-$B=CH_2 as π-ligand in **4b**. On the other hand, an activation of a C–H bond of the B–CH_3 group via a transient agostic interaction $H_2C\cdots H\cdots Ru$-3c,2e could lead to an oxidative addition linkage B–H_2C–Ru–H. Removal of the weakly bonded Ru–H hydrogen atom by oxygen may lead to **4b** (Ru-d^6,d^6).

Stacking of Postulated Sandwich Complexes 2b,c with [Cp*Ru] Fragments To Give Triple-Decker complexes 3b,c – Formation of Diamagnetic Triple-Decker 4a

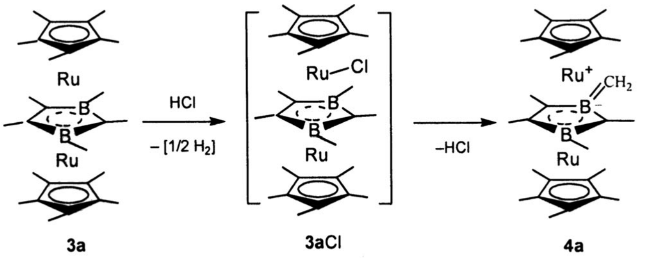
The formation of compounds **2a** and **3a**–**c** (Scheme 1) most likely proceeds via several intermediates. We have assumed[10] that a chloro/methyl exchange between $[Cp^*RuCl]_4$ and **1a**H leads to [Cp*RuMe], the 1-chloro-tetramethyl- (**1b**H) and the 1,3-dichloro-trimethyl-1,3-diborole derivative (**1c**H) (Scheme 4). The latter two react analogously to **1a**H with the [Cp*RuMe] intermediate to give the chloro-containing sandwich complexes **2b** and **2c**. However, **1a**H may also react with [Cp*RuCl] to lead to two possible intermediate complexes depending on the position of the ring hydrogen atom: facing the metal atom or pointing in the opposite direction. In the former intermediate, an H···Cl interaction may lead to an elimination of HCl to yield complex **2a**. Although no spectroscopic evidence for the postulated intermediate complex **2b** is available, it is likely that stacking of **2b** with a [Cp*Ru] fragment gives the chloro-triple-decker complex **3b**. Similarly, the dichloro-triple-decker complex **3c** may form from **2c** and [Cp*Ru]. Alternatively, **2b** and **2c** may also react with the monomer [Cp*RuCl] to yield the intermediates [Cp*Ru(Cl)**2b**] and [Cp*Ru(Cl)**2c**], which by elimination of a Cl atom could result in the formation of the chloro-triple-decker complexes **3b** and **3c**, respectively.

According to Scheme 4 the formation of **2a**–**c** is expected to proceed with elimination of CH_4 and possibly of HCl, the latter of which could cause side reactions. We therefore tested the interaction of HCl with the complexes **2a** and triple-decker **3a** in hexane under nitrogen. As gaseous HCl caused a color change of a solution of **2a** from violet to yellow and finally to dark green, a controlled reaction of $Et_2O\cdot HCl$ with **2a** in pentane was studied. The reaction in a 1:2 molar ratio yielded a yellow solution, which upon addition of a second equivalent of $Et_2O\cdot HCl$ resulted in a dark green solution, and very slowly an orange precipitate was formed. Workup of the reaction products gave paramagnetic **3a** and a mixture of unidentified compounds (showing 5 signals in the ^{11}B NMR spectrum, see Supporting Information).



Scheme 4. Possible formation of complexes **2a**, **3a**, **3b** and **3c** via the postulated ligands [**1b**H] and [**1c**H] as well as the postulated sandwich complexes [**2b**] and [**2c**].

In contrast to **2a** the yellow triple-decker complex **3a** interacted very slowly with HCl gas in a closed vessel to yield a dark orange product. The ^1H and ^{11}B NMR spectra of the crude product indicated the formation of **4a** and the absence of **3a**. After workup in air, the diamagnetic complex was identified by NMR and HR-EI MS as **4a** (**3a** – H). Most likely the interaction of HCl with **3a** yields hydrogen (by reduction of H^+) and an intermediate [**3a**Cl], which looses HCl to yield **4a**. We did not find any evidence for the formation of the isomer **4a′** (compare **4b′**, Scheme 2). The constitution of **4a** is unambiguously confirmed by NMR spectroscopy; the spectra are similar to those of compound **4b**. The ^{11}B NMR spectrum shows two signals at δ = 16.5 and 5 ppm, respectively, of the non-equivalent boron atoms. In the ^1H NMR spectrum an additional singlet (relative intensity 3 H, B-Me) is present at δ = 0.56 ppm. The ^{13}C NMR spectrum shows a broad signal of the B-Me group at δ = –6 ppm. The broad resonances of the *B*-bound ^{13}C atoms are well observable in the ^1H,^{13}C-correlated HSQC spectrum of **4a**, which confirms the assignments of the signals in **4a** (Scheme 5). The calculated ^1H, ^{11}B and ^{13}C NMR shifts are in good agreement with the experimen-



Scheme 5. Interaction of HCl with the paramagnetic triple-decker complex **3a** yields the diamagnetic 1,3-dihydro-1-methylene-1,3-diborafulvene triple-decker complex **4a** via the postulated intermediate **3a**Cl.

tal values; however, the calculated shifts for the carbon atoms near the metal atoms exhibit larger deviations (see Table S1, Supporting Information).

Crystal Structure Analysis of 3b

Single crystals of complex **3b** were obtained from dichloromethane solution. Despite the low *R* values the quality of the structure is hampered by complex disorder of the central ring and a reduced accuracy of the data set due to twinning of the crystals. However, the gross features of the structure are obvious from Figure 1. The complex has the classical triple-decker structure. Inspection of the anisotropic displacement factors of the peripheral groups (Cl and CH_3) on the central ring indicate further disorder, the chlorine atom to some extent being distributed over all five possible positions, with concurrent disorder of the ring due to twofold symmetry, with the crystallographic C_2 axis along the B1–Cl vector. This implies disorder of the second boron atom B2, which shares its position with the carbon atom C2 and other boron and carbon atoms. Unfortunately, the quality of our data was not sufficient to satisfactorily refine such a highly disordered model.

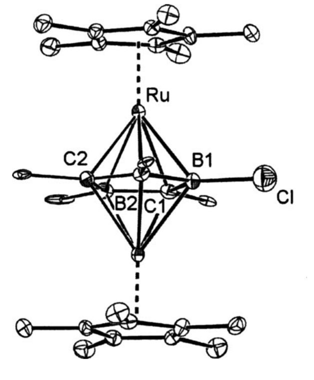


Figure 1. Molecular structure of **3b**. One of the two main disordered orientations of the C_3B_2 ring is shown. Distances [Å]: Ru–C_5Me_5 1.837(2), Ru–C_3B_2 1.738(1); Ru···Ru 3.476(1).

DFT Calculations

The formation of complexes **4a** and **4b**, containing the CH_2 bridge between the Ru and B atoms, is in accordance with DFT calculations. Their optimized structures are shown in Figure 2. These complexes proved to be slightly more stable than other possible isomers, containing the CH_2 bridge between the Ru and diborolyl or cyclopentadienyl C atoms (see Figures S1 and S2 in the Supporting Information).

The five-membered rings are nearly parallel [the dihedral angles C_5(Ru1)/C_3B_2 and C_5(Ru2)/C_3B_2 are equal to 9.5 and 2.6° for **4a** and 9.5 and 1.6° for **4b**, respectively], the C_5(Ru1) ring being more inclined than C_5(Ru2). The Ru1···C_3B_2 distance (1.799 Å for **4a** and 1.804 Å for **4b**) is slightly longer than Ru2···C_3B_2 (1.785 Å in both cases). The Ru1···C_5 distance (1.865 and 1.862 Å) is also longer than Ru2···C_5 (1.811 Å in both cases). This suggests weaker bonding of the Ru1 atom both with the C_3B_2 and C_5 rings, which is apparently caused by its additional coordination with the methylene group.

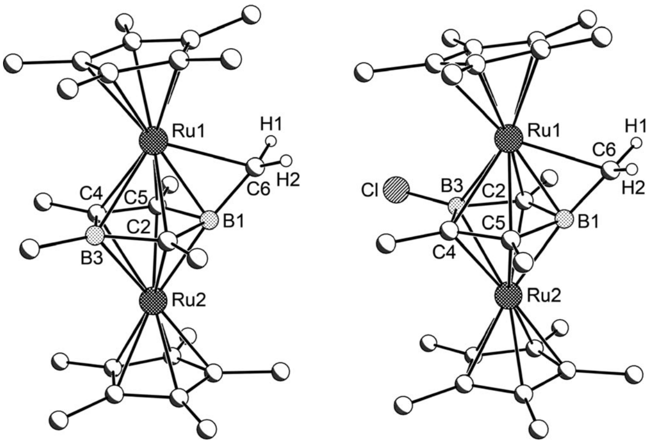


Figure 2. Optimized structures of **4a** (left) and **4b** (right). Hydrogen atoms of the methyl groups are omitted, most of the carbon atoms are not labeled. Selected distances [Å]: **4a**: B1–C6 1.503, B3–CH_3 1.593, Ru1–CH_2 2.265, Ru1···C_3B_2 1.799, Ru2···C_3B_2 1.785, Ru1···C_5 1.865, Ru2···C_5 1.811; **4b**: B1–C6 1.504, Ru1–CH_2 2.266, Ru1···C_3B_2 1.804, Ru2···C_3B_2 1.785, Ru1···C_5 1.862, Ru2···C_5 1.811.

The C_3B_2 ring is slightly folded along the B1···B3 line (2.0° for **4a** and 2.1° for **4b**). The angle between the B1–C6 bond and the best plane of the C_3B_2 ring (49.2° and 49.0°, respectively) is much larger than that in related mononuclear 1,3-dihydro-2-methylene-1,3-diborafulvene complexes.[14] It is also larger than the corresponding angle for the η^6-coordinated fulvene ligand in the ruthenocenylmethylium cations $[(C_5R_5)Ru(C_5R_4CH_2)]^+$ (42.6° for R = H[15] and 40.3° for R = Me[16]).

The B1–C6 bond (1.503 and 1.504 Å) is much shorter than the B3–CH_3 bond (1.593 Å) in **4a**, suggesting its double bond character. As a consequence, the bond alternation in the C_3B_2 ring of **4a**,**b** is larger than in **3a**,**b**. For instance, the bonds B1–C2 (1.623 Å) and B1–C5 (1.647 Å) in **4a** are longer than B3–C4 (1.560 Å) by 0.06–0.09 Å, whereas in **3a** the corresponding elongation is only 0.02 Å. The C6 atom deviates only slightly (by 0.122 Å) from the B1/H1/H2 plane, indicating a classical π-bonding with the metal atom. Indeed, the Ru1–C6 bond length (2.265 and 2.266 Å) is close to other Ru–C π-bond lengths in complexes **4a** (2.185–2.320, av. 2.222 Å) and **4b** (2.182–2.331, av. 2.224 Å).

The predominant π-character of the Ru–CH_2 bond is also confirmed by MO consideration. Figure 3 shows the frontier orbitals of the parent 1-methylene-1,3-diborafulvene dianion $[(CH)_3(BH)B{=}CH_2]^{2-}$. Main contribution to the π-donation $[C_3B_2H_4CH_2]^{2-} \rightarrow [RuCp]^+$ comes from the HOMO and HOMO–1 ligand orbitals, whereas the LUMO is responsible for δ-back donation $[RuCp]^+ \rightarrow [C_3B_2H_4CH_2]^{2-}$. Both HOMO–1 and LUMO have considerable contribution of the p-orbital of the CH_2 carbon atom.

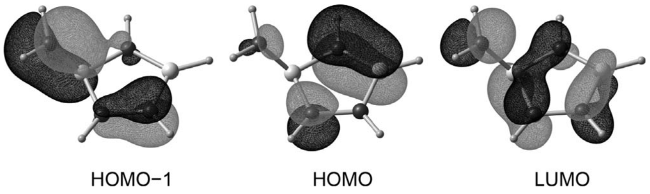


Figure 3. Frontier orbitals of the parent 1-methylene-1,3-diborafulvene dianion $[(CH)_3(BH)B{=}CH_2]^{2-}$ responsible for π-donation (HOMO, HOMO–1) and δ-back donation (LUMO). MO isodensity surface 0.05.

In contrast to the paramagnetic 29 VE complexes **3a**–**c**, triple-decker complexes **4a**,**b** have a closed-shell 30 VE configuration. The additional electron is supplied by the methylene group. Unlike the reported slipped triple-decker complexes with dihydro-diborafulvene ligands in the bridging position,[11,12] complexes **4a**,**b** have an almost undistorted triple-decker structure (the projections of the Ru1 and Ru2 atoms on the C_3B_2 plane are shifted from its centroid toward the B1 atom by only 0.208 and 0.146 Å for **4a** and 0.208 and 0.120 Å for **4b**, respectively).

The non-equivalence of the ruthenium atoms in complexes **4a**,**b** suggests the possibility of a CH_2 bridge inversion. In the case of the parent complex $[(RuCp)_2\{\mu\text{-}\eta^5{:}\eta^6\text{-}(CH)_3(BH)B{=}CH_2\}]$ (**4**) the activation barrier for this transformation was found to be 19.4 kcal mol^{-1} (Figure 4). The transition state has the symmetry plane passing through the diborolyl ring atoms. For complexes **4a** and **4b** the barriers were calculated to 19.1 and 19.2 kcal mol^{-1}, respectively, suggesting that the CH_2 bridge inversion can occur at room temperature.[17] On the NMR time scale, however, this inversion process is slow enough at room temperature in order to see the non-eqivalence of the Cp* rings.

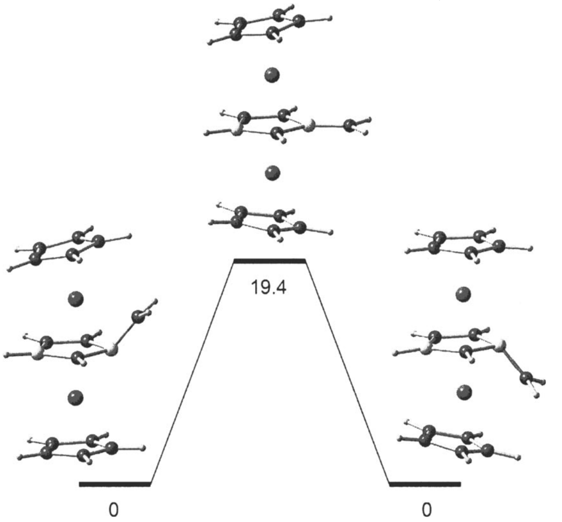


Figure 4. Energy profile for the CH_2 bridge inversion in the parent complex **4**. Relative energies (ZPE-corrected) in kcal mol^{-1}.

Due to the results of the calculation with an activation energy of 19 kcal mol^{-1} a dynamic behaviour in the NMR spectra could be expected at high temperatures. Therefore, variable-temperature measurements in $[D_8]$toluene up to 110 °C were performed. From 20 to 70 °C (at 200 MHz ^1H frequency) no exchange process can be observed. At higher temperatures the signals of the non-equivalent Cp* protons broaden, but no coalescense is reached (Figure 5). Line-shape analysis[18] yielded rate constants for that exchange, and a free activation enthalpy of 18.1 kcal mol^{-1} was obtained.

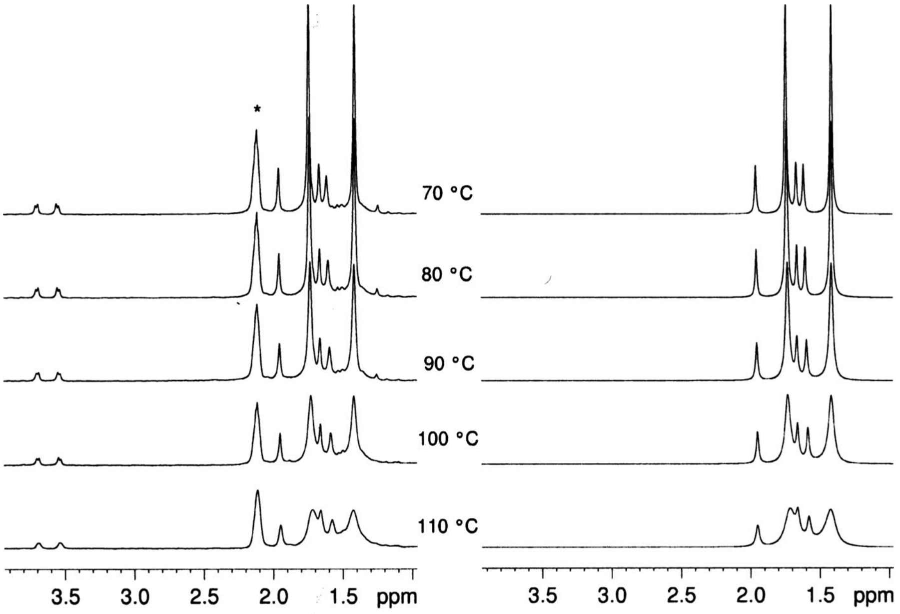


Figure 5. Variable-temperature ^1H NMR spectra of **4b** in $[D_8]$toluene (left, * denotes the methyl group of $[D_8]$toluene) and simulated spectra (right).

Conclusions

The paramagnetic triple-decker complexes $[(\mathrm{Cp^*Ru})_2\{\mu\text{-}(\mathrm{CMe})_3(\mathrm{BCl})(\mathrm{BR}^1)\}]$ (**3b**, R^1 = Me; **3c**, R^1 = Cl) containing B–Cl bonds were obtained by the reaction of pentamethyl-2,3-dihydro-1,3-diborole with $[\mathrm{Cp^*RuCl}]_4$. Most likely the chloro-containing complexes $[\mathrm{Cp^*Ru(CMe)_3\text{-}(BCl)(BMe)}]$ (**2b**) and $[\mathrm{Cp^*Ru(CMe)_3(BCl)_2}]$ (**2c**) are the key intermediates in the formation of the triple-decker complexes **3b** and **3c**. On prolonged standing in CH_2Cl_2 under air the monochloro derivative **3b** unexpectedly lost one hydrogen atom with formation of the diamagnetic triple-decker complex $[(\mathrm{Cp^*Ru})_2\{\mu\text{-}\eta^5\text{:}\eta^6\text{-}(\mathrm{CMe})_3(\mathrm{BCl})(\mathrm{B{=}CH_2})\}]$ (**4b**) having a 1,3-dihydro-1-methylene-1,3-diborafulvene derivative in bridging position. Interaction between HCl and $[(\mathrm{Cp^*Ru})_2\text{-}\{\mu\text{-}(\mathrm{CMe})_3(\mathrm{BMe})_2\}]$ (**3a**) leads with elimination of hydrogen to the analogous 1,3-dihydro-1-methylene-1,3-diborafulvene complex $[(\mathrm{Cp^*Ru})_2\{\mu\text{-}\eta^5\text{:}\eta^6\text{-}(\mathrm{CMe})_3\text{-}(\mathrm{BMe})(\mathrm{B{=}CH_2})\}]$ (**4a**).

Experimental Section

General: All reactions and column chromatography were performed under dry nitrogen by using standard vacuum-line and Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[\mathrm{Cp^*RuCl}]_4$[19] and pentamethyl-2,3-dihydro-1,3-diborole[20] were prepared as described in the literature. TLC was performed on aluminia foils covered with silica gel under air. The NMR spectra were recorded with Bruker DRX200, AV400II and AV600III spectrometers operating at ^{1}H frequencies of 200, 400 and 600 MHz, respectively. MS spectrometer: Jeol JMS-700.

Complexes 2a and 3a,b,c: A mixture of $[\mathrm{Cp^*RuCl}]_4$ (150 mg, 0.14 mmol) and $C_3B_2Me_5H$ (75 mg, 0.56 mmol) in thf (15 mL) was refluxed for 12 h, the solvent evaporated in vacuo, and the dark brown residue was extracted with hexane, filtered and chromatographed on silica gel (1 × 5 cm, 0.04–0.06 mm). The first violet band was eluted with hexane to give **2a** after evaporation of the solvent, yield 10–20 mg (5–10%; all yields are based on $[\mathrm{Cp^*RuCl}]_4$). The second band was eluted with hexane to give yellow **3a**, yield 17 mg (10%), and the third band was eluted with hexane/CH_2Cl_2 (9:1) to give an orange mixture of **3b/3c** in ca. 1:1 ratio according to ^{1}H NMR spectroscopy. The mixture was separated by TLC with hexane as eluent.

2a: ^{1}H NMR (C_6D_6): δ = 2.86 (s, 3 H, Me), 2.25 (s, 6 H, Me), 1.48 (s, 15 H, Cp*), 0.24 (s, 6 H, BMe) ppm. ^{11}B NMR: δ = 20.6 ppm. **3a**: ^{1}H NMR ($CDCl_3$): δ = 194 (v. br., 3 H, B_2CMe) 24.9 (s, 6 H, BMe), 14.5 (s, 30 H, Cp*), –31.8 (s, 6 H, CMe) ppm. ^{11}B NMR: δ = –159 ($\nu_{1/2}$ = 580 Hz) ppm. EI-MS: *m/z* (%) = 605.6 (100) [M^+], 590.5 (43) [M^+ – Me]. **3b**: Yield 49 mg (27%), orange solid. ^{1}H NMR ($CDCl_3$): δ = 174 (v. br., 3 H, Me), 23.7 (s, 3 H, BMe), 14.3 (s, 30 H, Cp*), –31.3 (s, 3 H, CMe), –37.2 (s, 3 H, CMe) ppm. ^{11}B NMR: δ = –134 (br.), –369 (v. br.) ppm. EI-MS: *m/z* (%) = 626.1 (100) [M^+], 610.1 (95) [M^+ – CH_3 – H]. HR-MS: calcd. for $^{12}C_{27}{}^{1}H_{42}{}^{37}Cl^{11}B_2{}^{100}Ru^{101}Ru$ 626.1230, found 626.1208, Δ = –2.2 mmu. **3c**: Yield 23 mg (13%), orange solid. ^{1}H NMR ($CDCl_3$): δ = 157 (v. br., 3 H, Me), 14.3 (s, 30 H, Cp*), –36.7 (s, 6 H, Me) ppm. ^{11}B NMR: δ = –365 (br.) ppm. EI-MS: *m/z* (%) = 646.1 (100) [M^+], 610.0 (50) [M^+ – Cl]. HR-MS: calcd. for $^{12}C_{26}{}^{1}H_{39}{}^{35}Cl_2{}^{11}B_2{}^{101}Ru^{102}Ru$ 646.0720, found 646.0716, Δ = –0.4 mmu.

Formation of Complex 4b: Complex **3b** (30 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was kept at room temperature under air for 3 weeks. The solvent was evaporated in vacuo to give a dark orange residue, which was purified by TLC with hexane as eluent, yield 24 mg (80%). ^{1}H NMR ($CDCl_3$, 600.13 MHz, 295 K; for atom numbering, atoms see Scheme 3): δ = 3.53 (d, *J* = 3.5 Hz, 1 H, H^{6b}), 3.36 (d, *J* = 3.5 Hz, 1 H, H^{6a}), 1.83 (s, 3 H, H_3C^9), 1.68 (s, 15 H, H_3C^{14}), 1.55 (s, 3 H, H_3C^{10}), 1.49 (s, 15 H, H_3C^{12}), 1.34 (s, 3 H, H_3C^7) ppm. ^{11}B NMR ($CDCl_3$, 64.14 MHz, 295 K): δ = 15.1 ($\nu_{1/2}$ = 135 Hz), 8.7 ($\nu_{1/2}$ = 145 Hz) ppm. ^{13}C NMR ($CDCl_3$, 150.9 MHz, 263 K) δ = 89.78 (C_q, C^{11}), 81.3 (br., C_qB, C^2), 81 (br., C_qB, C^5), 80.93 (C_q, C^{13}), 77.8 (br., C_qB, C^4), 59.7 [br., C_qB, CH_2, $J(C^6,H^{6a}/H^{6b})$ = 143 Hz, value obtained from HSQC spectrum], 15.49 (H_3C^7), 15.02 (H_3C^{10}), 12.82 (H_3C^9), 10.58 (H_3C^{14}), 9.22 (H_3C^{12}) ppm. Selected ^{n}J(C,H) correlations in C,H-HMBC spectrum: H^{6b},C^2, H^{6b},C^5, H^{6a},C^5, H^9,C^5, H^9,C^4, H^{10},C^5, H^{10},C^4, H^7,C^2, H^{14},C^{13}, H^{12},C^{11}. Selected NOE intensities for mixing time of 0.6 s (%): H^{6a},H^{6b} (15), H^{6a},H^{12} (1.9), H^{6b},H^{12} (1.8), H^{6b},H^{10} (1.0), H^{6a},H^7 (1.0), H^{10},H^9 (1.5), H^7,H^{12} (2.0), H^7,H^{14} (1.6). EI-MS: *m/z* (%) = 626.1 (100) [M^+], 610.1 [M^+ – CH_3/H]. EI-MS: *m/z* (%) = 624.9 (100) [M^+]. HR-MS: calcd. for $^{12}C_{27}{}^{1}H_{41}{}^{35}Cl^{11}B_2{}^{101}Ru^{102}Ru$ 625.1192, found 625.1179, Δ = –1.3 mmu. $C_{27}H_{41}B_2ClRu_2$ (625.1): calcd. C 51.89, H 6.61; found C 50.89, H 6.49.

Reaction of Complex 2a with $Et_2O\cdot HCl$: To a solution of **2a** (70 mg, 0.19 mmol) in pentane (5 mL) an $Et_2O\cdot HCl$ solution (0.1 mL, 0.095 mmol) was added dropwise. The color of the solution changed from violet to yellow. Upon addition of further $Et_2O\cdot HCl$ solution (0.1 mL, 0.095 mmol), the reaction mixture turned dark green. After stirring for 24 h, an orange residue had formed. The solvents were removed, and the residue was extracted with pentane and chromatographed to give two yellow fractions. The first fraction contained mainly complex **3a** (identified by paramagnetic ^{1}H NMR spectrum), the second fraction contained unidentified boron compounds (5 signals between δ = 80 and 25 ppm).

Formation of Complex 4a: Under dry nitrogen, HCl gas was bubbled through a yellow pentane solution (10 mL) of **3a** (60 mg, 0.1 mmol) for 30 min; no visible change occurred, the ^{11}B NMR showed only signals of **3a**. After 10 d in the closed vessel, the color of the solution had changed to yellow-brown. The solvent was removed to give a dark brown oily product, which was dissolved in hexane and washed with $KHCO_3$/water. The organic phase was dried with Na_2SO_4 and filtered through a short layer of silica gel. The solvent of the orange fraction was removed to give orange microcrystalline **4a** (27 mg, 45%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 3.54 (d, *J* = 3.6 Hz, 1 H, CH_2), 3.32 (d, *J* = 3.6 Hz, 1 H, CH_2), 1.84 (s, 3 H, Me), 1.74 (s, 15 H, Cp*), 1.64 (s, 3 H, Me), 1.53 (s, 15 H, Cp*), 1.37 (s, 3 H, Me) 0.56 (s, 3 H, BMe) ppm. ^{11}B NMR: δ = 16.5 ($\nu_{1/2}$ = 120 Hz), 5 (br., $\nu_{1/2}$ = 320 Hz) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 88.85 ($\mathit{C}_5\mathrm{Me}_5$), 79.99 ($\mathit{C}_5\mathrm{Me}_5$), 59.6 ($\nu_{1/2} \approx$ 100 Hz, B=$\mathit{C}\mathrm{H}_2$), 16.25 ($\mathrm{C}\mathit{Me}$), 14.97 ($\mathrm{C}\mathit{Me}$), 13.61 ($\mathrm{C}\mathit{Me}$), 10.77 ($\mathrm{C}_5\mathit{Me}_5$), 9.42 ($\mathrm{C}_5\mathit{Me}_5$), –6 ($\nu_{1/2} \approx$ 150 Hz, BCH_3) ppm; signals of quaternary carbon atoms of $\mathit{C}_3\mathrm{B}_2$ not found. EI-MS: *m/z* (%) = 605.2 (100) [M^+]. EI-MS: *m/z* (%) = 605.2 [M^+] (100). HR-MS: calcd. for $^{12}C_{28}{}^{1}H_{44}B_2{}^{101}Ru^{102}Ru$ 605.1751, found 605.1750, Δ = +2.2 mmu.

Computational Details: Geometry optimizations were performed by using a PBE exchange-correlation functional,[21] the scalar-relativistic Hamiltonian,[22] atomic basis sets of generally contracted Gaussian functions,[23] and a density-fitting technique[24] as implemented in a recent version of Priroda code.[25] The all-electron double-ζ basis set L1 augmented by one polarization function[26] was used. Frequency calculations were performed to confirm the nature of the stationary points to yield one imaginary frequency for the transition states and none for the minima. The path of the reaction was traced from the transition state to the product and back to the reactant by using the Intrinsic Reaction Coordinate method (IRC).[27] All geometries were optimized without constraints, and the energies were zero-point-corrected. The ChemCraft program[28] was used for molecular modeling and visualization.

X-ray Crystal Structure Determination of 3b: Crystal data: $C_{27}H_{42}B_2ClRu_2$, monoclinic, space group $C2/c$, $a = 14.709(3)$, $b = 14.784(3)$, $c = 12.620(2)$ Å, $\beta = 104.734(3)°$, $V = 2654.2(9)$ Å^3, $Z = 4$, $\mu = 1.252\ \mathrm{mm^{-1}}$, $F(000) = 1276$. $T = 100(2)$ K, $\theta = 2.0$–$32.0°$. Index ranges h,k,l (independent set): –21 to 20, 0 to 21, 0 to18. Reflections measured: 46964, independent: 4960 ($R_{\mathrm{int}} = 0.0420$), observed [$I > 2\sigma(I)$]: 3939. Final R indices [$F_o > 4\sigma(F_o)$]: $R(F) = 0.0445$, $wR(F^2) = 0.1142$, $GooF = 1.289$, residual density 3.183, –2.075 e Å^{-3}. Intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, graphite monochromator, $\lambda = 0.71073$ Å). Inspection of the diffraction pattern revealed the crystal to be twinned, the twin law being a 180° rotation around a face diagonal of the monoclinic unit cell. After de-twinning, the data were corrected for air and detector absorption, Lorentz and polarization effects;[29] absorption by the crystal was treated with a semiempirical multiscan method.[30,31] The structure was solved by the heavy-atom method combined with structure expansion by direct methods applied to difference structure factors[32] and refined by full-matrix least-squares methods based on F^2 against all unique reflections from both crystallites.[33,34] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were input at calculated positions and refined with a riding model. Disorder of C and B atoms across the crystallographic twofold axis was accounted for by placement of two half-atoms at the same position, with anisotropic displacement factor elements constrained to be equal. Apparent additional disorder of the middle ring around the pseudo fivefold axis of the triple-decker (the Ru···Ru vector) could not be modeled in a satisfactory fashion, but is considered to be relatively minor (not more than a few percent). Refinement in the alternative non-centrosymmetric space group Cc did not properly converge and resulted in a chemically unreasonable structure with e.g. non-planar pentamethylcyclopentadienyl rings. CCDC-720835 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Table of experimental and calculated ^{1}H, ^{11}B, and ^{13}C NMR chemical shifts for complexes **4a** and **4b**. Details of DFT calculations for complexes **4a**, **b** and their isomers (atomic coordinates for optimized geometry, energy and frequency data).

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