

Reactivity of electron-poor decamethyl-1,3-diboraruthenocene with sulfur and phosphorus compounds

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Received 13 August 2003; accepted 15 September 2003

Dedicated to Professor Bernt Krebs on the occasion of his 65th birthday

Abstract

Decamethyl-1,3-diboraruthenocene $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\eta^5\text{-(CMe)}_3\text{(BMe)}_2\}]$ (**1**) reacts with *cyclo*-octasulfur in hexane to give $[(\eta^5\text{-C}_5\text{Me}_5)\{\eta^5\text{-(CMe)}_3\text{(BMe)}_2\}\text{Ru}=\text{S}]$ (**3**), which may also be obtained from **1** and propylene sulfide. **1** reacts with H_2S to form the ruthenathiacarboranyl complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\eta^4\text{-(CMe)}_3\text{(BMe)}_2\text{S}\}]$ (**6**), for which a *nido*-structure is proposed. The isomeric compounds **3** and **6** have different stabilities: **3** loses sulfur and unexpectedly the *closo*-cluster $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2\text{H(CMe)}_3\text{(BMe)}_2]$ (**4**) is formed with hydrogen bridging the basal and apical Ru centers. Reaction of **1** with carbonylsulfide (COS) yields the dinuclear ruthenium compound $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\eta^5\text{-(CMe)}_3\text{(BMe)}_2\text{(S)(COBMe)}\}]_2$ (**7**) in which two B–O groups bridge two ruthenium complexes. Its formation results from a complex reaction sequence: sulfur inserts into the diborolyl ring and the ligand CO forms an oxygen–boron bridge to a second molecule, followed by insertion of the carbonyl carbon into the double bond of the diboraheterocycle. Carbon disulfide reacts with **1** to give the dinuclear complex **8** with two CS_2 molecules connecting the ruthenium centers. When **1** and P_4 are heated in toluene, the sandwich **9** is obtained by formal insertion of a P–H group into the diborolyl ring of **1** and the triple-decker $\{[\eta^5\text{-(C}_5\text{Me}_5)\text{Ru}]_2\{\mu\text{-(MeC)}_3\text{P(MeB)}_2\}$ (**10**) is detected in the mass spectrum. The phosphalkyne $\text{P}\equiv\text{C}t\text{Bu}$ inserts into **1** to give the ruthenaphosphacarborane $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{(CMe)_2\text{(BMe)(PC}t\text{Bu)(CMe)(BMe)}\}]$ (**11**) in high yield. Phosphanes react with **1** to give weak donor–acceptor complexes $\mathbf{1} \cdot \text{PH}_2\text{R}$ (**12**) ($\text{R} = \text{Ph, H}$). The compositions of the compounds are deduced from spectroscopic and analytical data and are confirmed for **4** and **7** by X-ray structural analyses.

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Keywords: Ruthenium; Sandwich complexes; Diboroles; Sulfur; Phosphorus

1. Introduction

Organometallic complexes of the iron triad having fewer than 18 valence electrons (VE) are of particular interest for catalytic and preparative studies. Recently we reported the synthesis and some reactions of the title compound **1**, obtained from 1,2,3,4,5-pentamethyl-2,3-dihydro-1,3-diborole, methyl lithium, and $[(\text{C}_5\text{Me}_5)\text{RuCl}]_4$ [1]. The electron-poor sandwich compound **1**, which is presumed to be folded along the $\text{B} \cdots \text{B}$ vector like the corresponding iron compound (ca. 41°), forms donor–acceptor compounds with CO [2] and isonitrile [1], and a classic dihydride complex with H_2 . A complex reaction

between $\text{BH}_3 \cdot \text{thf}$ and **1** leads to (1,2,3,5,6-pentamethyl-4-hydro-2,3,5-tricarbahexaboranyl)(η^5 -pentamethylcyclopentadienyl)ruthenium [1] (**2**), which is formed by oxidative addition of BH_3 to **1**, followed by $\text{HB-H} \cdots \text{BMe}$ interaction and migration of this BMe group to the *apical* position and BH to the *basal* position of the pyramidal ligand (Scheme 1). In this paper we describe reactions of sulfur and phosphorus compounds with **1**.

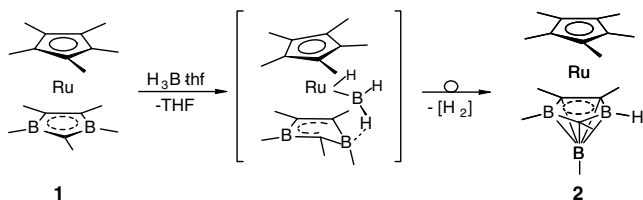
2. Results and discussion

2.1. Formation of the sulfur complexes **3**, **6** and the diruthenacarborane **4**

Reaction of violet **1** with *cyclo*-octasulfur leads to the yellow decamethyl-1,3-diboraruthenocene-sulfide **3**,

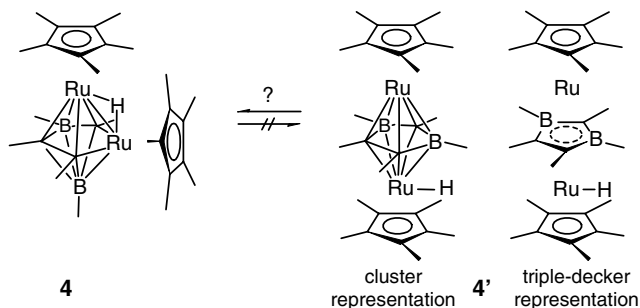
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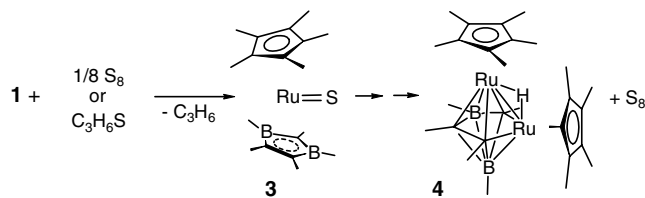
Scheme 1. Formation of the ruthenacarboranyl complex **2**.

which is also obtained from **1** and propylene sulfide, even at -50°C , in higher yield (Scheme 2). Its mass spectrometric and NMR data support the proposed composition. In the ^1H -NMR spectrum of **3**, five signals for CMe and BMe groups of the 1,3-diboroly ring appear and in the ^{11}B -NMR spectrum two signals in a 1:1 ratio ($\delta = 21.5, 15.1$ ppm) indicate that the sulfur atom is unsymmetrically bound with respect to the heterocycle.

Surprisingly, after some weeks crystals of the diruthenacarborane **4** and *cyclo*-octasulfur separated from a hexane solution of **3** at -20°C . In addition, unidentified products were also present in the solution. The composition of the *closo*-cluster **4** was deduced from spectroscopic data and an X-ray structure analysis (see below). Attempts to synthesize **4** by various routes [3] led instead to the isomeric *closo*-cluster/triple-decker **4'**, which had been obtained initially by reacting $[(\text{C}_5\text{Me}_5)\text{RuCl}]_4$ with an excess of NaH in the presence of the 1,2,3,4,5-pentamethyl-2,3-dihydro-1,3-diborole heterocycle [2].

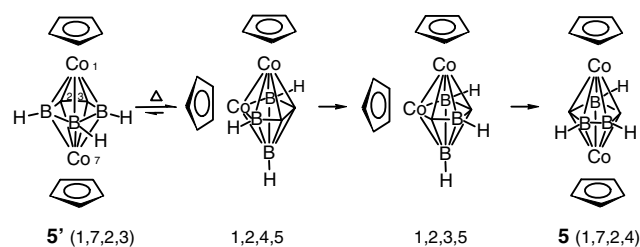
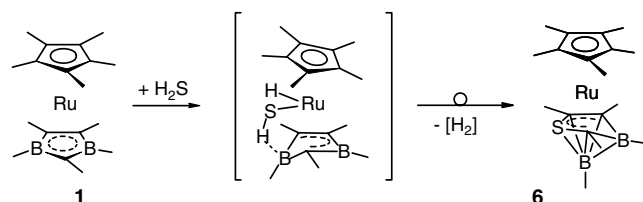


As **4** might undergo rearrangement to form the triple-decker **4'** we monitored the thermal reaction by ^1H - and ^{11}B -NMR spectra. However, in toluene above 80°C

Scheme 2. Formation of the diboraruthenocene-sulfide **3** and further reaction to the diruthenacarborane **4**.

decomposition of **4** takes place and presently it is not known if the reverse reaction proceeds. The possible rearrangements of **4/4'** are related to that of the isomeric triple-deckers **5'**, **5** and their isomeric *closo*-clusters reported by Grimes et al. [4] (Scheme 3). In the red **5'** and the green triple-decker complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}]_2(\mu, \eta^5\text{-C}_2\text{B}_3\text{H}_5)$ (**5**) the carbon atoms of the bridging ligands are adjacent and separated, respectively. Heating the red species **5'** with the cluster atoms Co_2C_2 in 1,7,2,3-position to $200\text{--}250^\circ\text{C}$ leads to green **5** via the isolable 1,2,4,5- and 1,2,3,5-intermediates. In the latter compounds the $(\text{C}_5\text{H}_5)\text{Co}$ moieties occupy both *apical* and *basal* positions. It has been suggested that this rearrangement proceeds via cooperative movements of the atoms on the surface of the seven-vertex polydeltahedral clusters. Scheme 3 indicates, that the $1,7,2,3 \rightarrow 1,2,4,5$ conversion is reversible.

As described in Scheme 1, the reaction between **1** and $\text{BH}_3 \cdot \text{thf}$ gives the tricarbahexaboranyl–ruthenium complex **2** with elimination of dihydrogen. Analogously, H_2S reacts with **1** in pentane to give the tricarbathiahexaboranyl–ruthenium complex **6**. Two ^{11}B -NMR signals of equal intensity indicate the presence of a thiacarboranyl ligand with one boron ($\delta = -12.2$ ppm) in the *apical* position. From the broad signal at $\delta = 43$ ppm a decreased coordination number of the other boron atom is deduced compared to that of **1**. The formation of **6** may occur according to Scheme 4: After oxidative addition of H_2S to the ruthenium center the S–H bond interacts with one B–Me group, and results in its migration into the *apical* position. Simultaneously, the S–H group moves into the empty ring position to yield, with elimination of hydrogen, the ruthenathi-

Scheme 3. Rearrangement of isomeric $\text{Co}_2\text{C}_2\text{B}_3$ compounds.Scheme 4. Formation of the ruthenathi-carborane **6**.

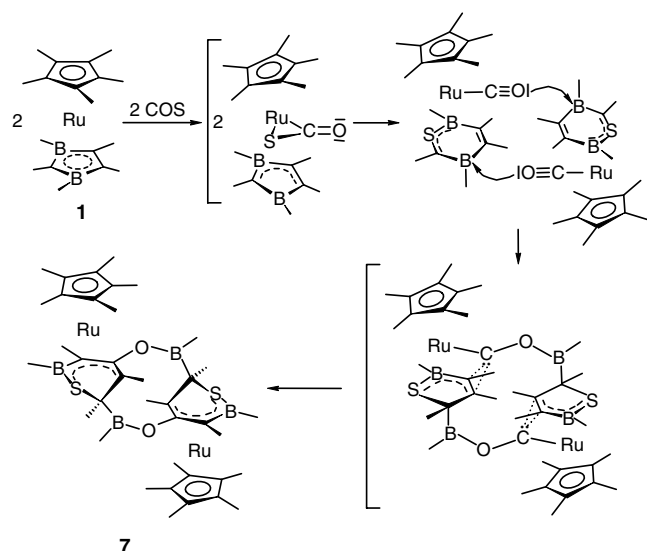
carborane **6**. According to the cluster electron counting rules, the seven vertex cluster **6** with 18 skeletal electrons (SE) is expected to form a *nido*-structure with one non-triangular face (RuC_2B).

Alternatively, **6** may be described as an 18 VE complex, in which the η^4 -ligand 4-thia-2,3,5-tricarbahexaboranyl supplies 5e for bonding to the metal. As the anionic thiacarboranyl ligand has an *arachno*-structure ($2n+6=18$ SE), it donates as a neutral species 5e (each carbon 1e and 2e from the sulfur). The *apical* boron of an *arachno* ligand [5] does not contribute any electrons to the bonding between ruthenium and thiacarboranyl ligand (see Scheme 4).

2.2. Reactions of **1** with COS and CS_2 to give the dinuclear complexes **7** and **8**

A complex reaction of carbonylsulfide [6,7] with **1** in hexane produces a brown solution from which the yellow dinuclear complex **7** can be isolated in 63% yield. The X-ray structure analysis (see Scheme 5) reveals that **7** is composed of two doubly bridged 18 VE complexes. Its formation may occur according to the following sequence of reactions:

In the first step, COS is coordinated via its CS π -bond to the ruthenium atom of electron-poor **1** to give an intermediate 18 VE complex. This is followed by cleavage of the CS bond and insertion of sulfur into the B1–C2 bond of the 1,3-diborolyl ligand. The resulting η^3 - $\text{C}_2\text{B}_2\text{CS}$ six-membered heterocycle forms with the CO ligand of a second sandwich intermediate an intermolecular acceptor–donor interaction to give a dimeric complex which is stabilized by insertion of two carbene centers of the CO ligands into the double bond of the



Scheme 5. Mechanism of the formation of **7**.

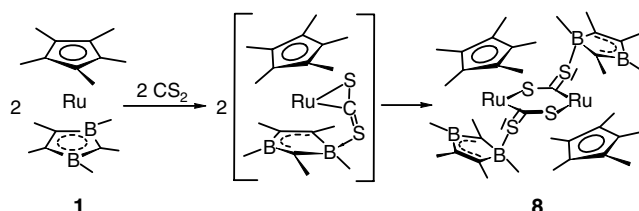
$\text{C}_2\text{B}_2\text{CS}$ rings. This is accompanied by the formation of an exocyclic boryl group from an *endo*-cyclic boron atom and the new C_3BSC cycle is now η^5 -bonded to the ruthenium center. As a result, the two B–O bridges build a 10-membered ring by connecting two 18 VE complexes.

The ^1H -NMR spectrum shows the expected five singlets for the methyl groups of the heterocycle and one for the C_5Me_5 protons. In the ^{11}B -NMR spectrum, the signal of the oxygen-bonded boron atom is observed at $\delta = 60.9$ ppm, whereas the signal for the boron interacting with ruthenium is observed at $\delta = 20.4$ ppm (similar to that of **1**). The high-resolution FAB mass spectrum of **7** provides further evidence for its composition; its molecular structure is shown in Fig. 2.

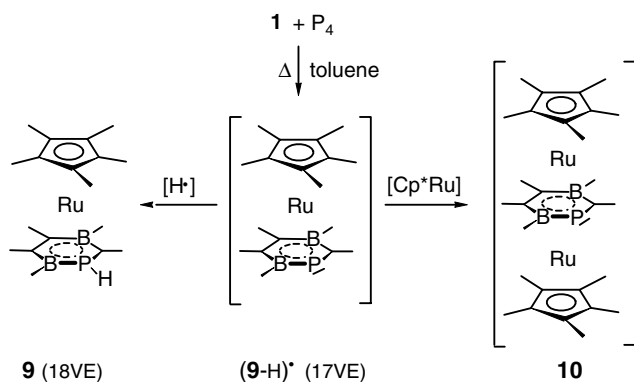
A similar reaction of **1** with carbon disulfide [8,9] in hexane at low temperature leads to the coordination of CS_2 to **1**, followed by dimerisation to give **8**. According to NMR and mass spectrometric data, two CS_2 molecules bridge two ruthenium centers giving a dimeric complex. One of the two ^{11}B -NMR signals indicates an interaction of the C=S sulfur atom with one of the boron atoms (at $\delta = 11.4$ ppm). This should cause a tilting of the 1,3-diborolyl and a change from η^5 to η^4 -bonding of the 1,3-diborolyl ring to the metal. The signal of the other boron is at $\delta = 31.1$. Contrary to the reaction with COS, neither cleavage of the CS bond in CS_2 nor insertion into the diborolyl ring is observed (see Scheme 6).

2.3. Reactions of phosphorus, phosphacetylene and phosphanes with **1**

As described above, sulfur and sulfur compounds exhibit a unique reactivity towards **1**. In the following we report on the reaction of **1** with phosphorus. Heating a toluene solution of **1** and P_4 results in formation of a yellow–orange reaction mixture from which the sandwich **9** was isolated. However, mass spectroscopic data of the crude product also indicates the presence of the triple-decker **10**, which could not be separated. It is likely that insertion of phosphorus into **1** leads to the paramagnetic 17 VE sandwich (**9-H**) which picks up a hydrogen atom from toluene to give the diamagnetic sandwich **9** with an incorporated P–H group as proven



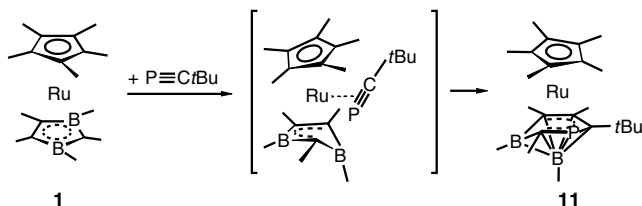
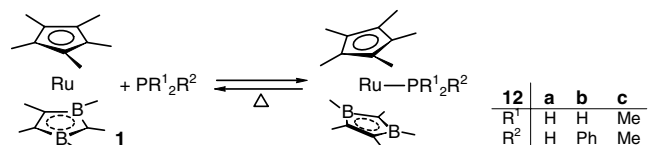
Scheme 6. Reaction of **1** with CS_2 .

Scheme 7. Reaction of **1** with P_4 .

by ^{31}P - and ^1H -NMR spectroscopy. The diamagnetic triple-decker sandwich **10** may be formed when the Cp^*Ru group of **1** stacks with the sandwich $(9\text{-H})^*$ (see Scheme 7).

When $\text{P}\equiv\text{C}t\text{Bu}$ [10–13] is added to **1** in hexane, the color of the solution immediately changes from violet to orange and the tetracarba-phosphaheptaboranyl complex **11** is formed. Its composition follows from mass spectrometric and NMR data. The ^{11}B -NMR spectrum exhibits two signals in a 1:1 ratio ($\delta = -0.3, 32.1$ ppm), which indicate that one boron is in the *apical* position ($\delta = -0.3$ ppm) and the other has a weak interaction with the metal. The exact structure cannot be deduced from the spectroscopic data. We propose that phosphacetylene is pre-coordinated side-on to the ruthenium center which is followed by migration of one BMe group into the *apical* position. In the next step, insertion of the coordinated $\text{P}\equiv\text{C}t\text{Bu}$ into the heterocycle occurs via C–C and C–P coupling to give the ruthenaphosphacarborane **11** with a BCCCPC face of the phosphacarborane. It was pointed out by a referee that “in principle an isomer of **11** is possible in which $\text{P}\equiv\text{C}$ has inserted the other way round, to give a species with a BCCPCC six atom face”.

According to the Wade–Mingos rules [14,15], **11** with eight cluster atoms and 20 skeletal electrons is expected to have a *nido*-structure. Alternatively, **11** may be described as an 18 VE complex, in which the *arachno*-

Scheme 8. Formation of the ruthenaphosphacarborane **11**.Scheme 9. Formation of the phosphane adducts **12**.

3,4,6,7-tetracarba-5-phosphaheptaboranyl ligand supplies **5e** for bonding to the metal [5] (see Scheme 8).

As indicated in Section 1 the ruthenium sandwich **1** shows excellent to good coordination properties towards CO and isonitrile. Coordination of the small phosphanes PH_3 , PH_2Ph and PMe_3 results in the formation of yellow, classic 18 VE complexes **12a**, **b** and **c**, whereas no interaction between **1** and PPh_3 is observed (see Scheme 9).

The reaction of PH_3 and PH_2Ph with **1** give the adducts **12a**, **b** almost quantitatively. Their identification follows from spectroscopic data. In the ^{11}B -NMR spectrum, the adducts **12a** and **12b** exhibit only one broad signal at $\delta = 32$ ppm for **12a** and $\delta = 29$ ppm for **12b**, whereas the ^1H -NMR spectrum shows two signals for BMe and three signals for CMe of the 1,3-diboroly ring. Furthermore, phosphorus–hydrogen couplings were only observed for one of the BMe groups and the methyl group on C2 of **12a** and **12b** and additionally for one of the methyl groups connected to the C=C double bond of **12b**. This indicates that the phosphane ligand is not symmetrically bonded with respect to the boron heterocycle; a similar situation was observed for the sulfur ligand in **3**. One single doublet for the five methyl groups of the cyclopentadienyl ring at $\delta = 1.45$ ppm ($^5J_{\text{PH}} = 4.0$ Hz) for **12a** and $\delta = 1.38$ ppm ($^5J_{\text{PH}} = 2.8$ Hz) for **12b** indicates, that free rotation of the carbocycle occurs. Due to coupling with the directly bonded hydrogen atoms, the ^{31}P -NMR spectrum of **12a** shows a quartet at $\delta = -81.5$ ppm ($^1J_{\text{PH}} = 335.0$ Hz) and for **12b** a triplet at $\delta = 11.1$ ppm ($^1J_{\text{PH}} = 341.7$ Hz), respectively. Compared with non-coordinated phosphanes, the signals are clearly shifted to higher frequencies ($\Delta = 173$ ppm for **12a** and 133 ppm for **12b**). Above 85°C decomposition of **12a** occurs; the phosphane ligand dissociates and **1** is reformed. **12b** is thermally even less stable and begins to decompose at 60°C .

Addition of PMe_3 to **1** in toluene at 0°C leads to the labile complex **12c** which could not be isolated. It decomposes when warming to room temperature and the weakly bonded trimethylphosphane may be easily removed in vacuum. The solution of the complex **12c** has been studied by ^{11}B - and ^{31}P -NMR measurements. In the ^{11}B -NMR spectrum the complex exhibits one signal at $\delta = 27$ ppm and the ^{31}P -NMR shows a singlet at $\delta = -48.8$ ppm which is shifted to low field (13 ppm) compared with free PMe_3 .

2.4. X-ray structure analyses of 4 and 7

2.4.1. Crystal structure of 4

In agreement with the cluster electron count, the diruthenacarborane **4** adopts a *closo* structure. The molecular structure is shown in Fig. 1. Ru1 and B7 occupy the apical positions of a pentagonal bipyramid. The ruthenium atom Ru2 is part of the pentagon and the Ru1–Ru2 edge (2.747 Å) is bridged by H1 connecting the two ruthenium centers via a 3c, 2e bond. Because of the Ru1–H1–Ru2 interaction, the planes through

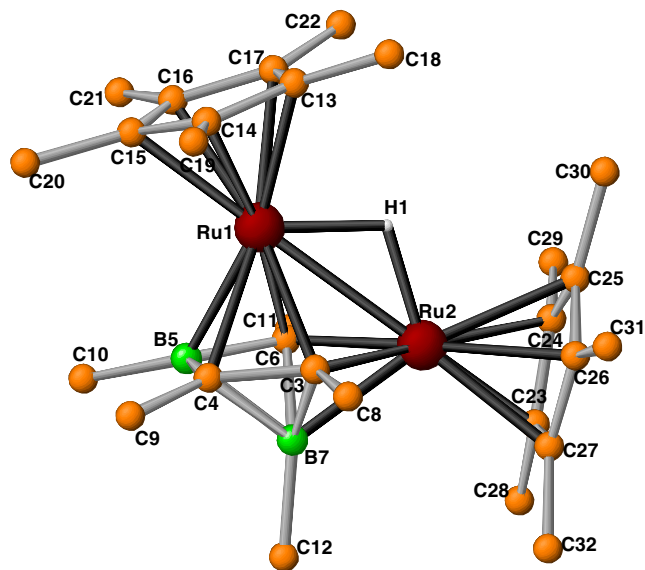


Fig. 1. Molecular structure of **4**.

$C_5Me_5(Ru1)$ and C_3BRu2 form an angle of 13.6° . The boron atom B7 is located in a five coordinate cluster position having a distance of 1.124 Å to the plane of the C_3BRu heterocycle (see Table 1).

2.4.2. Crystal structure of 7

The crystal structure analysis shows **7** to have an inversion center (Fig. 2). A non-planar 10-membered ring connects two ruthenium complexes to form a dimeric structure. Each ruthenium atom is 1.851 Å above/below the center of the η^5 -bonded C_5Me_5 ligand and the best plane through the S1B1C1C2C3 ligand atoms has a distance of 1.662 Å to the metal. The planes S1B1C1C2C3/C3C4S1 form an angle of 52.4° . The distance between Ru1 and C4 is about 0.75 Å longer than the distances to the coordinated carbon atoms of the heterocycle (see Table 2).

Table 1
Selected distances (Å) and angles ($^\circ$) in **4**

| | | | |
|-------------|----------------|------------|----------|
| Ru1–Ru2 | 2.7470(2) | B7–C3 | 1.770(4) |
| Ru1–H1 | 1.74(3) | B7–C4 | 1.796(4) |
| Ru2–H1 | 1.69(2) | B5–B7 | 1.827(3) |
| Ru1–C (Cp*) | 2.167–2.194(2) | | |
| Ru2–C (Cp*) | 2.173–2.243(2) | Ru1–H–Ru2 | 106.8(8) |
| Ru1–B5 | 2.207(2) | Ru2–C3–C4 | 121.2(2) |
| Ru2–B7 | 2.150(2) | C3–C4–B5 | 113.4(2) |
| Ru1–C6 | 2.223(2) | C4–B5–C6 | 107.0(2) |
| Ru2–C6 | 2.099(2) | B5–C6–Ru2 | 122.3(1) |
| Ru2–C3 | 2.079(2) | C6–Ru2–C3 | 75.98(8) |
| C3–C4 | 1.475(3) | Ru1–Ru2–B7 | 72.23(7) |
| C4–B5 | 1.540(4) | Ru1–B5–B7 | 92.5(1) |
| B5–C6 | 1.523(3) | Ru1–C3–Ru2 | 79.11(6) |
| B7–C6 | 1.702(3) | Ru1–C6–Ru2 | 78.87(6) |

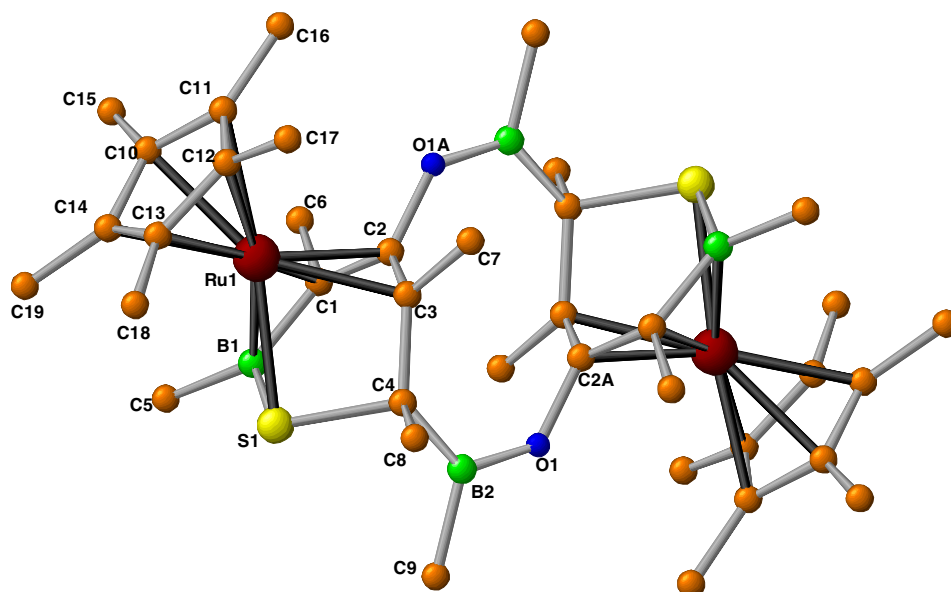


Fig. 2. Molecular structure of **7**.

Table 2
Selected distances (Å) and angles (°) in **7**

| | | | |
|------------|----------------|-----------|-----------|
| Ru1–C(Cp*) | 2.191–2.234(2) | C4–B2 | 1.602(3) |
| Ru1–S1 | 2.3852(5) | B2–O1 | 1.358(2) |
| Ru1–B1 | 2.274(2) | O1–C2A | 1.396(2) |
| Ru1–C1 | 2.238(2) | S1–B1–C1 | 115.5(1) |
| Ru1–C2 | 2.194(2) | B1–C1–C2 | 122.0(2) |
| Ru1–C3 | 2.205(2) | C1–C2–C3 | 124.5(2) |
| S1–B1 | 1.859(2) | C2–C3–C4 | 118.2(1) |
| B1–C1 | 1.516(3) | C3–C4–S1 | 101.4(1) |
| C1–C2 | 1.429(2) | B1–S1–C4 | 104.87(8) |
| C2–C3 | 1.433(2) | B2–C4–C3 | 121.6(1) |
| C3–C4 | 1.532(2) | O1–B2–C4 | 127.6(2) |
| C4–S1 | 1.870(2) | B2–O1–C2A | 130.9(1) |

3. Conclusion

The electron-poor sandwich complex **1** reacts with sulfur or sulfur-donating agents to yield the classic 18 VE complex **3** which slowly decomposes to give the diruthenacarborane **4**. With H₂S, formation of the ruthenathiacarborane complex **6** occurs. Reactions of **1** with the heterocumulenes COS and CS₂ give the dinuclear complexes **7** and **8**, respectively. The crystal structure analysis of **7** reveals two B–O bridges of a 10-membered ring connecting the two ruthenium complexes. By formal insertion of P–H into **1**, sandwich **9** is formed and the triple-decker **10** is observed in the mass spectrum. Insertion of P≡CtBu into **1** leads to the ruthenaphosphacarborane complex **11**. With PR₃ ligands, **1** forms donor–acceptor compounds **12** of different stabilities: PH₃ > PH₂Ph ≫ PMe₃.

4. Experimental

General: Experiments were carried out under argon, which had been dried and purified before use. Solvents were dried by conventional methods and saturated with argon. NMR spectra were recorded on a Bruker DRX-200 spectrometer (¹H: 200.13 MHz, ¹³C: 50.32 MHz, ¹¹B: 64.21 MHz) in C₆D₆ as solvent. Chemical shifts are relative to TMS and BF₃·OEt₂. The mass spectra were recorded on Varian MAT CH7 and Jeol JMS 700 spectrometers (reference for HRMS is perfluorated kerosine). GC mass spectra were recorded on a HP-5890 II gas chromatograph with HP-5971 MSD (column HP-3, 12.5 m × 0.25 mm × 0.25 μm).

4.1. (η⁵-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η⁵-pentamethylcyclopentadienyl)-rutheniumsulfide (**3**)

(a) To a suspension of sulfur (50 mg, 1.56 mmol) in pentane (50 ml), a solution of **1** (240 mg, 0.65 mmol) dissolved in pentane (5 ml) was added. After stirring for

2 h, the reaction mixture was filtered and the solvent removed in vacuum. The brown residue was purified by chromatography (silica gel, hexane) to give **3** as a yellow solid. Yield: 140 mg (53%). (b) 42 mg (0.11 mmol) of **1** was dissolved in 10 ml of hexane and cooled to –50 °C. 207 mg (0.56 mmol) of methylthiirane was slowly added. After warming to room temp. the solvent was removed in vacuum and the brown residue was dissolved in 2 ml of hexane and purified by chromatography on silica gel using hexane as eluent to give **3**. Yield: 30 mg (67%). M.p. 87 °C (dec.). ¹H-NMR: δ = 0.85 (s, 3H, BCH₃), 0.91 (s, 3H, BCH₃), 1.39 (s, 15H, C₅(CH₃)₅), 1.81 (s, 3H, =CCH₃), 1.83 (s, 3H, =CCH₃), 1.91 (s, 3H, B₂CCH₃). ¹³C-NMR: δ = –3.51 (BCH₃, br), 9.87 (C₅(CH₃)₅), 10.67 (BCH₃), 17.31 (=CCH₃), 18.04 (=CCH₃), 24.29 (B₂CCH₃), 88.34 (C₅(CH₃)₅). ¹¹B-NMR: δ = 21.5, 15.1. MS (EI): *m/z* (%) = 402 (M⁺, 100), 387 (M⁺–CH₃, 41), 370 (M⁺–S, 87), 325 (M⁺–S–3CH₃, 54), 233 (Cp*⁺Ru⁺–4H, 63), 41 (C₃H₅⁺, 96).

4.2. 1,2-Bis(η⁵-pentamethylcyclopentadienyl)-(1,2-μ-hydrido-1,2-diruthenium-3,4,5,6,7-pentamethyl)-3,4,6-tricarbaheptaborane (**4**)

After several weeks at –20 °C, yellow **4** and *cyclo*-octasulfur crystallized from a solution of **3** in hexane. The residue of the hexane solution contained unidentified products. M.p. (**4**) 120 °C (dec.). ¹H-NMR: δ = –10.2 (s, 1H, Ru₂H), –0.1 (s, 3H, BCH₃), 0.68 (s, 3H, BCH₃), 1.46 (s (br), 30H, C₅(CH₃)₅), 1.65 (s, 3H, CCH₃), 1.68 (s, 3H, CCH₃), 1.75 (s, 15H, C₅(CH₃)₅), 1.88 (s, 3H, CCH₃). ¹³C-NMR: δ = 10.8 (C₅(CH₃)₅), 11.3 (C₅(CH₃)₅), 14.4 (CCH₃), 23.1 (CCH₃), 32.0 (CCH₃), 83.0 (C₅(CH₃)₅), BCH₃, CCH₃ not observed. ¹¹B-NMR: δ = 12 (br). MS (EI): *m/z* (%) = 606 (M⁺, 13), 591 (M⁺–CH₃, 19), 235 (Cp*⁺Ru⁺–H, 19), 57 (C₄H₉⁺, 100).

4.3. (η⁴-1,2,3,5,6-Pentamethyl-2,3,5-tricarba-4-thiahexaboranyl)(η⁵-pentamethyl-cyclopentadienyl)ruthenium (**6**)

Complex **1** (50 mg, 0.14 mmol) was dissolved in 20 ml of pentane, and H₂S was bubbled through the solution for 5 min at a flow rate of 10 ml min^{–1}. The solvent was removed in vacuum and the violet residue was dissolved in 2 ml of hexane and purified by chromatography on silica gel at room temp. using hexane as eluent. **6** was isolated as a violet solid. Yield: 44 mg (78%). M.p. 130 °C. ¹H-NMR: δ = –0.38 (s, 3H, BCH₃), 0.63 (s, 3H, BCH₃), 1.49 (s, 3H, CCH₃), 1.51 (s, 15H, C₅(CH₃)₅), 1.88 (s, 3H, CCH₃), 1.93 (s, 3H, CCH₃). ¹³C-NMR: δ = 0.8 (BCH₃), 10.1 (C₅(CH₃)₅), 13.3 (CCH₃), 14.1 (CCH₃), 19.8 (CCH₃), 84.4 (C₅(CH₃)₅), BCH₃, (BS)CCH₃ and CCH₃ not observed. ¹¹B-NMR: δ = –12.2, 43 (br), MS (CI): *m/z* (%) = 402 (M⁺, 60), 387 (M⁺–CH₃, 100), 375 (M⁺–CCH₃, 97).

4.4. Dinuclear ruthenium complex **7**

Complex **1** (147 mg, 0.40 mmol) was dissolved in 20 ml of hexane and gaseous COS bubbled through the solution at room temperature. The colour changed within a few minutes from violet to yellow. Dark yellow **7** crystallized from a solution in hexane. Yield: 108 mg (63%). M.p. 80 °C (dec.). ¹H-NMR: δ = 0.74 (s, 3H, BCH₃), 1.29 (s, 3H, BCH₃), 1.43 (s, 15 H, C₅(CH₃)₅), 1.57 (s, 3H, CCH₃) 1.59 (s, 3H, CCH₃), 1.75 (s, 3H, CCH₃), ¹³C-NMR: δ = 9.0 (CCH₃), 9.7 (C₅(CH₃)₅), 10.3 (CC H₃), 17.6 (CCH₃), 88.2 (C₅(CH₃)₅), 95.2 (CO). ¹¹B-NMR: δ = 20 (br), 60 (br), MS (FAB): m/z (%) = 858 (M⁺, 5), 773 (M⁺-SBCMe₂, 8), 537 (M⁺-Cp*⁺Ru, -SBCMe₂, 45), 402 ([Cp*⁺Ru(C₃B₂Me₅)S]⁺, 100), 233 ([Cp*⁺Ru-H]⁺, 97).

4.5. Bis[(η^5 -pentamethyl-2,3-dihydro-1,3-diboroly)]-(η^5 -pentamethylcyclopentadienyl)ruthenium-carbondisulfide (**8**)

40 mg (0.53 mmol) of CS₂ was condensed into a solution of 185 mg (0.50 mmol) **1** in toluene (20 ml) at room temperature. The colour of the reaction mixture immediately changed to brown. After stirring for 15 min the solvent was removed in vacuum and dark yellow **8** was isolated from the brown residue by recrystallization from hexane. Yield: 71 mg (32%). M.p. 75 °C (dec.). ¹H-NMR: δ = 0.59 (s, 3H, BCH₃), 1.03 (s, 3H, BCH₃), 1.40 (s, 15 H, C₅(CH₃)₅), 1.47 (s, 3H, B₂CCH₃), 1.53 (s, 6H, =CCH₃), ¹³C-NMR: δ = 9.0 (C₅(CH₃)₅), 10.0 (CCH₃), 14.1 (CCH₃), 88.1 (C₅(CH₃)₅), ¹¹B-NMR: δ = 11.4, 33.1, MS (FAB): m/z (%) = 891 (M⁺, 2), 537 (M⁺-Cp*⁺Ru(CS₂BMe), 33), 421 (1/2 M⁺-BMe, 22), 388 (1/2 M⁺-SBMe, 40).

4.6. (1,2,3,5,6-Pentamethyl-1,3-dibora-4-phospha-cyclohexa-2,5-dienyl)(η^5 -pentamethylcyclopentadienyl)ruthenium (**9**)

A toluene solution (10 ml) containing P₄ (13 mg, 0.10 mmol) was added dropwise to a solution of **1** (150 mg, 0.41 mmol) in toluene (20 ml). The reaction mixture was heated for 4 h under reflux. The colour slowly changed from violet to brown. After removing the solvent in vacuum **9** was isolated as an orange solid, contaminated with the triple-decker **10**. Yield: 87 mg (53%). M.p. 160 °C. ¹H-NMR: δ = 0.21 (s, 3H, BCH₃), 0.91 (s, 3H, BCH₃), 1.40 (s, 3H, B₂CCH₃), 1.43 (C₅(CH₃)₅), 1.56 (s, 3H, =CCH₃), 1.62 (s, 3H, =CCH₃), ¹³C-NMR: δ = 10.0 (C₅(CH₃)₅), 83.5 (C₅(CH₃)₅), BCH₃, CCH₃, not observed. ¹¹B-NMR: δ = 26 (br), ³¹P-NMR (C₆D₆, 80.9 MHz): δ = -85.3 (d, PH, ¹J_{PH} = 263 Hz), MS (FAB): m/z (%) = 636 (10⁺, 8), 605 (10⁺-P, 20), 401 (M⁺, 100).

4.7. (η^5 -Pentamethyl-2,3-dihydro-1,3-diboroly)](η^5 -pentamethylcyclopentadienyl)-ruthenium-phosphaacetylene (**11**)

Complex **1** (150 mg, 0.41 mmol) was dissolved in hexane (10 ml) and a solution of PCC(CH₃)₃ (46 mg, 0.46 mmol) in hexane (5 ml) was slowly added. After stirring for 30 min, the solvent was removed in vacuum and **11** was obtained as a dark yellow solid. Yield: 153 mg (79%). ¹H-NMR: δ = 0.31 (s, 3H, BCH₃), 0.41 (s, 3H, BCH₃), 1.27 (d, 3H, J_{PH} = 1.5 Hz, CCH₃), 1.37 (d, 9H, ⁴J_{PH} = 1.8 Hz, C(CH₃)₃), 1.55 (s, 3H, CCH₃), 1.66 (s, 15 H, C₅(CH₃)₅), 1.70 (s, 3H, CCH₃). ¹³C-NMR: δ = 10.4 (CCH₃), 10.5 (CCH₃), 10.9 (C₅(CH₃)₅), 23.0 (CC H₃), 33.5 (d, C(C H₃)₃), ³J_{CP} = 12.1 Hz, 91.9 (C₅(CH₃)₅), BCH₃, CCH₃ and C(CH₃)₃ not observed. ¹¹B-NMR: δ = -0.3, 32 (br). ³¹P-NMR (C₆D₆, 80.9 MHz): δ = 51.1. MS(FAB): m/z (%) = 470 [M⁺] (20). HR MS for C₂₃H₃₉B₂PRu: Calc. 470.2019; found: 470.1999; Δm = 2.0 mmu.

4.8. (η^5 -Pentamethyl-2,3-dihydro-1,3-diboroly)](η^5 -pentamethylcyclopentadienyl)-ruthenium phosphane (**12a**)

Complex **1** (0.54 g, 1.46 mmol) was dissolved in 100 ml of hexane, and PH₃ gas bubbled through the solution for 5 min at a flow rate of 10 ml min⁻¹. After removing the solvent in vacuum, **12a** was obtained as a yellow solid. Yield: 588 mg (100%). M.p. 85 °C (diss. to starting materials). ¹H-NMR: δ = 0.65 (d, 3H, ⁴J_{PH} = 12 Hz, BCH₃), 0.93 (s, 3H, BCH₃), 1.45 (d, 15H, ⁴J_{PH} = 4 Hz, C₅(CH₃)₅), 1.49 (s, 3H, =CCH₃), 1.50 (s, 3H, =CCH₃), 1.79 (d, 3H, ⁴J_{PH} = 2 Hz, B₂CCH₃), 4.96 (d, 3H, ¹J_{PH} = 335 Hz, PH₃). ¹³C-NMR: δ = 8.9 [C₅(CH₃)₅], 10.7 (B₂CCH₃), 13.9 (=CCH₃), 14.7 (=CCH₃), 88.9 [C₅(CH₃)₅], BC H₃, B₂CCH₃, =CCH₃ not observed. ¹¹B-NMR: δ = 30 (br). ³¹P-NMR (C₆D₆, 80.9 MHz): δ = -81.5 (q, ¹J_{PH} = 335 Hz, PH₃).

4.9. (η^5 -Pentamethyl-2,3-dihydro-1,3-diboroly)](η^5 -pentamethylcyclopentadienyl)-ruthenium-phenylphosphane (**12b**)

Phenylphosphane (81 mg, 0.74 mmol) was added dropwise to a solution of **1** (275 mg, 0.74 mmol) in 20 ml of toluene. After stirring for 30 min, the solvent was removed in vacuum. **12b** was obtained as a yellow solid. Yield: 300 mg (85%). M.p. 60 °C (diss. to starting materials). ¹H-NMR: δ = 0.56 (d, 3H, ⁴J_{PH} = 9.6 Hz, BCH₃), 0.96 (s, 3H, BCH₃), 1.38 (d, 15H, ⁴J_{PH} = 2.8 Hz, C₅(CH₃)₅), 1.48 (d, 3H, ⁴J_{PH} = 3.1 Hz, =CCH₃), 1.53 (s, 3H, =CCH₃), 1.75 (d, 3H, ⁴J_{PH} = 1.8 Hz, B₂CCH₃), 5.88 (dd, 2H, ¹J_{PHa} = 335.1 Hz, ¹J_{PHb} = 346.7 Hz, ²J_{HaHb} = 6.1 Hz, PH₂), 7.10–7.13 (m, 2H, PPh), 7.38–7.49 (m, 3H, PPh). ¹³C-NMR: δ = 10.3 (B₂CCH₃), 10.7 [C₅(CH₃)₅], 13.5 (=CCH₃), 14.5 (=CCH₃), 89.4

Table 3
Crystal and collection parameters for compound **4** and **7**

| Identification code | 4 | 7 |
|--|--|---|
| Empirical formula | C ₂₈ H ₄₆ B ₂ Ru ₂ | C ₃₈ H ₆₀ B ₄ O ₂ S ₂ Ru ₂ · C ₆ H ₁₄ |
| Formula weight | 606.41 | 944.53 |
| Temperature | 190(2) K | 103(2) K |
| Crystal system | monoclinic | monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> |
| Unit cell (Å, °) | | |
| <i>a</i> | 9.0783(4) | 8.7270(6) |
| <i>b</i> | 15.6274(8) | 11.2703(7) |
| <i>c</i> | 19.901 (1) | 23.247(2) |
| α | 90 | 90 |
| β | 98.866 (1) | 98.393(1) |
| γ | 90 | 90 |
| <i>V</i> (Å ³) | 2789.6(2) | 2262.0(3) |
| <i>Z</i> | 4 | 2 |
| Calculated density (g/cm ³) | 1.444 | 1.387 |
| Absorption coefficient (mm ⁻¹) | 1.096 | 0.795 |
| <i>F</i> (000) | 1248 | 988 |
| Crystal size (mm ³) | 0.33 × 0.22 × 0.17 | 0.30 × 0.30 × 0.20 |
| Maximum (°) | 32.04 | 32.04 |
| Index ranges | –13/13, 0/23, 0/29 | –12/12, 0/16, 0/34 |
| Number of measured reflections | 49056 | 26251 |
| Unique | 9451 | 7778 |
| Final <i>R</i> indices | | |
| <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] | 0.0263 | 0.0315 |
| <i>WR</i> ₂ (all reflections) | 0.0689 | 0.0759 |
| Largest difference peak/hole (e/Å ³) | +0.74/–0.56 | 1.01/–1.41 |

[C₅(CH₃)₅], BCH₃, B₂C CH₃, =CCH₃ not observed. ¹¹B-NMR: δ = 29 (br). ³¹P-NMR (C₆D₆, 80.9 MHz): δ = 11.1 (t, ¹J_{PH} = 341.7 Hz, PH₂).

4.10. (η⁵-Pentamethyl-2,3-dihydro-1,3-diborolyl)(η⁵-pentamethylcyclopentadienyl)-ruthenium-trimethylphosphane (**12c**)

Trimethylphosphane (20 mg, 0.26 mmol) was added dropwise to a solution of **1** (90 mg, 0.24 mmol) in 5 ml of toluene at 0 °C. The colour changed reversibly from violet to orange. The product could not be isolated. NMR studies of the yellow solution: ¹¹B-NMR: δ = 27. ³¹P-NMR (C₆D₆, 80.9 MHz): δ = –48.8.

4.11. Crystal structure determination for **4** and **7**

Diffraction data were collected on a Bruker-AXS SMART 1000 (Mo Kα radiation, graphite monochromator) in the ω-scan mode. Crystal data and details of the measurements are summarized in Table 3. The structures were solved by direct methods (SHELXS86) and refined by full-matrix least-squares methods (SHELXL93) based on *F*² with all reflections. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in difference Fourier syntheses and refined isotropically. **7** crystallizes with one hexane molecule.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219133 for compound **4** and CCDC No. 219134 for compound **7**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 247), the Land Baden-Württemberg, and the Fonds der Chemischen Industrie for support of this work and Prof. U. Zenneck (Erlangen) for supplying P≡CtBu.

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