Synthesis and Crystal Structure of the Triple-decker Complex $[(\eta^5\text{-}C_5Me_5)\text{-}Ru(\mu,\eta^5\text{-}1,3\text{-}C_3B_2Me_5)RhCl\text{-}(Ph_2PCH_2)_2]$

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The dimer $[(\eta^5\text{-}C_5Me_5)Ru(C_3B_2Me_5)RhCl]_2$ (**2**) reacts with 1,2-bis(diphenylphosphino)ethane (dppe) to give the triple-decker complex $[(\eta^5\text{-}C_5Me_5)Ru(C_3B_2Me_5)Rh(dppe)Cl]$ (**3**). Its constitution follows from NMR and MS data, and a single-crystal X-ray diffraction study.

Key words: Diborolyl, Ruthenium, Rhodium, Triple-decker Complexes

Introduction

Since the discovery of the first triple-decker sandwich complex by Werner and Salzer [1, 2], extensive studies on the topic of stacked complexes have been reported. While carba- and phospha-cyclic ligands are able to stabilize triple-decker complexes [3, 4], the electron-poor C_3B_2 and C_2B_3 heterocycles [5 – 9] allow the formation of more highly stacked compounds. These ligands act as electron-donors *and* -acceptors, which favors the bifacial coordination to metal atoms, leading to triple-, tetra- and multidecker complexes.

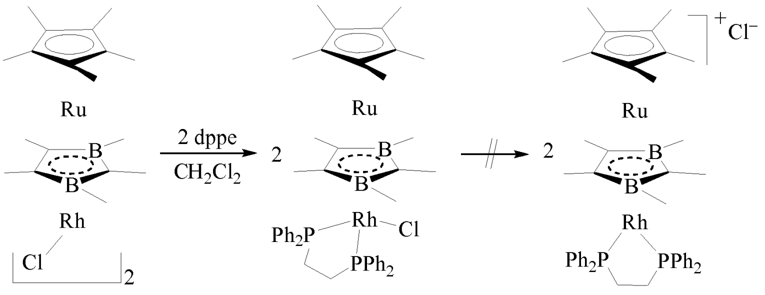
We have been interested in the 2,3-dihydro-1,3-diborole/diborolyl ligands ($C_3B_2HR_5/C_3B_2R_5$), of which the former function as 4e donors, whereas the latter supply 3e or 5e as folded ligands. Specific cases were first detected in the green iron complexes $[(\eta^5\text{-}C_5R_5)Fe\text{-}\{(CR^1)_2(BR^2)_2CR^3\}]$ having the diborolyl ring severely folded along the B···B vector [10 – 12]. The violet ruthenium compounds $[(\eta^5\text{-}C_5Me_5)Ru\{(CR^1)_2(BR^2)_2CR^3\}]$ **1** [13] have a similar folding, as has been shown by an X-ray diffraction analysis (of the derivative with $R^1 = R^3 = Me$, $R^2 = CH_2SiMe_3$, 41°) and by quantum chemical calculations [14]. Accordingly, the ruthenium complexes **1** have a unique reactivity towards various donor molecules [15], *e. g.* terminal acetylenes which insert into the diborolyl heterocycle to produce 4-borataborepine sandwich complexes [16, 17].

The stacking reaction of **1** with $[RhCl(C_2H_4)_2]_2$ yields the brown chloro-bridged tetranuclear complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu,\eta^5\text{-}C_3B_2Me_5)RhCl]_2$ (**2**) [13]. It reacts with polyhedral carborane anions to yield various hybrid diborolyl/carboranyl triple-decker species such as the anion $[(\eta^5\text{-}C_5Me_5)Ru(\mu,\eta^5\text{-}C_3B_2Me_5)\text{-}Rh(\eta^5\text{-}2,3\text{-}Et_2C_2B_4H_5)]^-$ [18]. Treatment of **2** with $AgBF_4$ followed by the addition of cyclic ligands gave new triple-decker cations $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}C_3B_2Me_5)Rh(ring)]^+$ [19]. To extend the reactivity study, we have investigated the reaction of **2** with 1,2-bis(diphenylphosphino)ethane and obtained the dinuclear complex **3**.

Results and Discussion

The reaction of **2** with dppe in CH_2Cl_2 afforded, after column chromatography of the reaction mixture, the neutral complex **3** rather than the cationic complex **4** (Scheme 1). Although **1** is a tetranuclear complex in which each of the two triple-decker moieties has 28 VE, the cation **4** is not formed because complex **3** is favored having a 30 VE closed-shell. The ^{11}B NMR spectrum of **3** shows a signal at δ = 18.2 ppm, which is slightly upfield shifted when compared with that of **2** (21 ppm). Its ^{31}P NMR spectrum exhibits a doublet at δ = 47.2 ppm, and the HR EI-MS confirms the molecular ion of the compound.

The structure of **3** is shown in Fig. 1, selected bond lengths and angles are given in Table 1. One molecule of CH_2Cl_2 and one disordered benzene/toluene molecule were found per unit cell, but attempts of an accurate assignment of the latter have not been successful. However, the main structure was



2 **3** **4**

Scheme 1.

Table 1. Selected bond lengths (Å) and angles (deg) for **3**, with estimated standard deviations in parentheses.

Rh1–P1	2.323(1)	Ru1–C52	2.214(3)
Rh1–P2	2.314(1)	Ru1–C53	2.205(3)
Rh1–Cl1	2.423(1)	Ru1–B54	2.250(4)
Rh1–B51	2.242(3)	Ru1–C55	2.232(3)
Rh1–C52	2.181(3)	B51–C52	1.600(5)
Rh1–C53	2.242(3)	C52–C53	1.467(5)
Rh1–B54	2.297(3)	C53–B54	1.587(5)
Rh1–C55	2.210(3)	B54–C55	1.559(5)
Ru1–Cp*	2.145(4) – 2.159(5)	B51–C55	1.602(5)
Ru1–B51	2.219(3)		
P2–Rh1–P1	82.45(3)	P1–Rh1–Cl1	86.10(3)
P2–Rh1–Cl1	85.08(3)		

solved and refined without a problem. The almost planar 1,3-diborolyl ring in **3** is bifacially coordinated to the Ru and Rh atoms, and is parallel to the Me_5C_5 ring (interplanar angle 1.1°). Moreover, the heterocycle has very similar distances to both metal atoms, and the bond lengths and angles within the C_3B_2 ring are found to be similar to those reported for $[(\eta^5\text{-}C_5Me_5)Ru(\mu,\eta^5\text{-}C_3B_2Me_5)Rh(\eta^5\text{-}2\text{-}Me,2,3,4\text{-}C_3B_7H_9)]$ [18]. This metric similarity indicates that despite of the different coordination environment, the geometry of the $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}C_3B_2Me_5)Rh]$ moiety is largely unchanged. In the Rh(dppe)Cl part, the Rh–Cl bond length is 2.423(1) Å, and the angles in the tripod Rh(P2,P1,Cl1) are similar (83 – 86°).

Experimental Section

The reaction and all manipulations were performed in dry glassware under nitrogen using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. NMR specta were recorded on a Bruker DRX 200 spectrometer (^1H: 200.13 MHz, ^{11}B: 64.21 MHz, ^{13}C: 50.32 MHz, ^{31}P: 80.9 MHz) in CD_2Cl_2. $Et_2O\cdot BF_3$ was used as external standard for ^{11}B NMR, and 85 % H_3PO_4 for ^{31}P NMR. As internal references for ^1H and ^{13}C NMR, the shifts were calculated relative to TMS and given in ppm. MS: ZAB-2F VH Micromass CTD spectrometer, and a JEOL MS Station JMS 700 spectrometer.

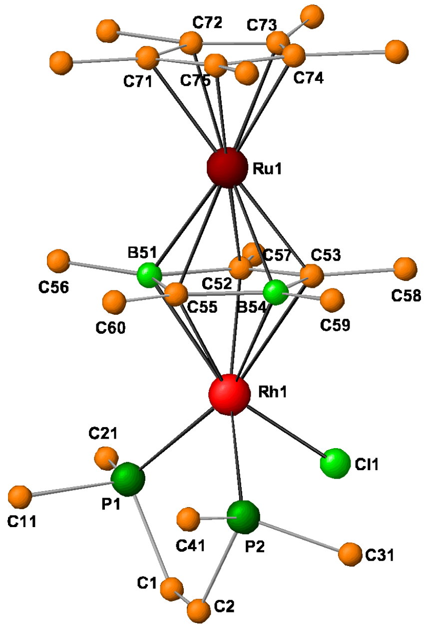


Fig. 1. Molecular structure of **3**. Hydrogen atoms and solvent molecules are omitted, and only the *ipso* carbon atoms of the dppe moiety are shown for clarity.

Synthesis of the triple-decker complex $[(\eta^5\text{-}C_5Me_5)\text{-}Ru(\mu,\eta^5\text{-}1,3\text{-}C_3B_2Me_5)RhCl(Ph_2PCH_2)_2]$ (3)

A portion of dppe (57 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) was added to a solution of **2** (70 mg, 0.07 mmol) in CH_2Cl_2 (2 mL) at −30 °C. The reaction mixture was warmed to r. t. and stirred for 3 d. After concentration of the mixture the resulting red-brown solution was subjected to column chromatography (silica gel). With toluene a first light-yellow band was eluted (a very small amount, not identified), and subsequently CH_2Cl_2 as eluent gave a dark brown band. The elute was concentrated and cooled to −25 °C. Dark brown crystals of **3** (70 mg, 56 %) were grown. M. p. 183 – 185 °C. – ^{1}H NMR: δ = 7.85 – 7.13 (m, 20 H; aryl), 2.8 (m, 2 H; CH_2), 2.2 (m, 2 H; CH_2), 1.88, d, $J_{RhH} \approx 5$ Hz, 6 H; =CCH_3), 1.56 (s, 3 H; =CCH_3), 1.52 (s, 15 H; $C_5(CH_3)_5$), 0.86 (s, 3 H; BCH_3). – ^{11}B NMR: δ = 18 (br). – ^{13}C NMR: δ = 134.8, 134.4, 134.1, 133.6, 130.1, 128.0, 127.7, 127,4 (Ph), 77.6 ($C_5(CH_3)_5$), 29.7 ($BCCH_3$), 28.5 (CH_2), 16.8, 16.1 (=CCH_3), 10.1 ($C_5(CH_3)_5$). The signals for the boron-bound ring carbon atoms were n. o. – ^{31}P NMR: δ = 47.2 ppm, d, J_{RhP} = 126 Hz. – EI-MS: *m/z* (%) = 906 $[M]^+$ (70), 891 $[M–CH_3]^+$ (20), 870 [M–Cl]$^+$ (100). – HR-MS: *m/z* = 906.1714 (calcd. 906.1673 for $^{12}C_{44}{}^1H_{54}{}^{11}B_2{}^{35}Cl^{31}P_2{}^{102}Ru^{103}Rh$; Δ = 4.1 mmu).

X-Ray structure determination of ***3***

Data were collected on a Bruker APEX CCD area-detector diffractometer using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). Intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS [20] based on the Laue symmetry of the reciprocal space (T_{min} = 85.6 %, T_{max} = 87.0 %). The structure was solved by Direct Methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL software package [20]. Hydrogen atoms were treated using appropriate riding models. Dichloromethane was found as solvent inclusion in the crystal structure, with only 25 % occupancy with respect to the host compound. At the same position an additional molecule, assigned as benzene, was found also with an occupancy of 25 %. Additionally, both solvent components were found to be disordered around a crystallographic center of inversion. Due to this incomplete occupancy of the interstitial solvent molecules, these components could not be safely confirmed.

Crystal data for **3**: $C_{44}H_{54}B_2ClP_2RuRh$, M_r = 905.91, black (irregular), 0.18 × 0.16 × 0.16 mm^3, monoclinic space group $P2_1/n$ with a = 12.3480(7), b = 26.9014(15), c = 13.9044(8) Å, β = 103.4530(10)°, V = 4492.0(4) Å^3, Z = 4, ρ_{calc} = 1.400 g cm^{-3}, μ = 0.89 mm^{-1}, $F(000)$ = 1940, T = 296(2) K, $R1$ = 0.045, $wR2$ = 0.120 for $I \geq 2\sigma(I)$, for 8829 observed reflections [$2\theta \leq 56.56°$], and a total of 11130 unique reflections; residual electron density (min/max): −0.54/1.19 e Å^{-3}.

CCDC 698303 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.

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