Syntheses of Diruthenaborane Clusters, $[\{Cp^*Ru(\mu\text{-}H)\}_2B_3H_7]$, $[\{(Cp^*Ru)_2(\mu\text{-}H)\}B_4H_9]$, and $[(Cp^*Ru)_2(\mu\text{-}H)(PMe_3)(\mu\text{-}\eta^4\text{-}B_2H_5)]$

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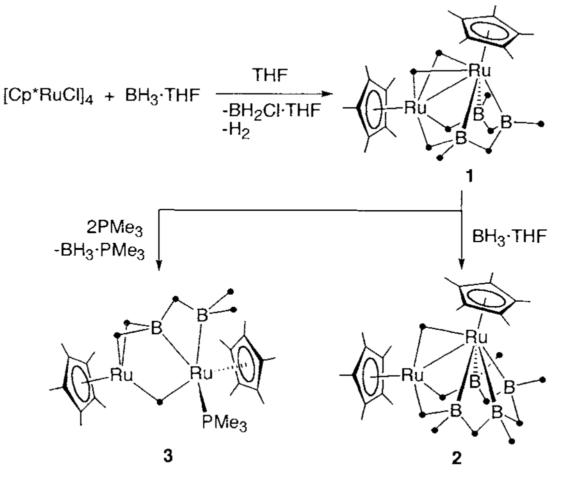
A diruthenapentaborane cluster $[\{Cp^*Ru(\mu\text{-}H)\}_2B_3H_7]$ (**1**) was synthesized by the reaction of $[Cp^*RuCl]_4$ with BH_3·THF. Compound **1** undergoes cluster expansion by further interaction with BH_3·THF to give $[\{(Cp^*Ru)_2(\mu\text{-}H)\}B_4H_9]$ (**2**). Reaction of **1** with PMe_3 leads to degradation of the cluster framework to give $[\{(Cp^*Ru)_2(\mu\text{-}H)\}(PMe_3)(\mu\text{-}\eta^4\text{-}B_2H_5)]$ (**3**).

Metallaboranes have attracted much interest because of their structures and bonding.[1-3] A number of metallaboranes with Cp* ligands were recently reported.[2] During the course of study on activation of borane-Lewis base adducts by metal complexes, we recently found that the reaction of $[Cp^*RuCl]_4$ with BH_3·PMe_3 results in unexpected bond rearrangement to afford $[Cp^*Ru(PMe_3)(\eta^2\text{-}BH_3Cl)]$.[4] Although the mechanism of this reaction is currently not clear, it is quite probable that the very strong coordinating ability of PMe_3 toward ruthenium is one of the driving forces. This suggests that interaction of $[Cp^*RuCl]_4$ with BH_3–weaker donor adducts gives entirely different products. We report here the reaction of $[Cp^*RuCl]_4$ with BH_3·THF, which produces novel ruthenaborane clusters. Degradation reaction of the cluster by PMe_3 is also discussed.

A THF solution of $[Cp^*RuCl]_4$[5] was treated with excess amount of BH_3·THF at room temperature for 40 min, to give an orange-red solution with evolution of H_2. Removal of volatiles and following recrystallization of the residue from hexane provided yellow-orange crystals of $[\{Cp^*Ru(\mu\text{-}H)\}_2B_3H_7]$ (**1**) in 23% yield (Scheme 1).[6] Monitoring of the reaction using NMR spectroscopy showed that the chlorine atom on Ru was removed as BH_2Cl·THF. Compound **1** is a diruthenapentaborane cluster, with the apical BH and one of the basal BH groups in square pyramidal pentaborane(9) replaced by the Cp*RuH fragments, which are isolobal with BH. The number of the skeletal electrons of **1** is 14, which is consistent with the *nido* structure. We note that **1** and **2**, which is discussed below, were independently synthesized by Fehlner group with the use of $[Cp^*RuCl_2]_2$.[7]

In the ^1H NMR spectrum of **1**, the two Cp* signals were observed at inequivalent positions. In the high field, three signals are observed with the integral intensities of 2H, respectively, at -4.06, -11.30, and -13.60 ppm. The first signal is broad, and assigned to the B–*H*–B protons. The second is a broad quartet coupled with ^{11}B, and is attributed to Ru–*H*–B protons. The third sharp signal is assignable to the Ru–*H*–Ru protons. Terminal BH protons resonate at 2.65 and 3.23 ppm as partially overlapped broad quartets. The ^{11}B NMR spectrum exhibits two peaks at 0.0 and -1.7 ppm in the 1 : 2 ratio of intensity. The crystal structure of **1** is shown in Figure 1.[9] The molecule of **1** is disordered over the crystallographic C_2 axis through the midpoint of the Ru–Ru' bond and that between B(1) and B(1)' (One of the possible positions for B(2) is drawn in the Figure). Hydrogen atoms except for H(B1), H(B2) and H(3) were not located. Owing to the fact that the Ru–Ru' bond (2.812(2) Å) is much longer than the B(1)–B(2) and Ru–B bonds (1.77(3), 2.25(2) Å), **1** adopts a highly distorted square pyramidal geometry.



Scheme 1. —• = H

The square pyramidal Ru_3B_2 framework, related to **1**, has been described with $[\{Ru(CO)_3\}_3(\mu\text{-}H)B_2H_5]$ and its phosphine derivatives by Housecroft et al.[10] Fehlner and co-workers reported several *nido*-dimetallapentaborane clusters, e.g. $[\{Fe(CO)_3\}_2B_3H_7]$ (**A**),[3b] $[(Cp^*Co)\{Fe(CO)_3\}B_3H_7]$ (**B**),[2f] $[(CoCp^*)\{Co(\eta^4\text{-}C_5Me_5H)\}(\mu\text{-}H)B_3H_7]$ (**C**),[2a] $[(CoCp^*)_2\text{-}B_3H_7]$ (**D**),[2a] and $[(RhCp^*)_2B_3H_7]$ (**E**).[7] In **A**–**C**, the metal atoms occupy positions 1 and 2 in the cluster core as found in **1**, whereas they occupy positions 2 and 4 in **D**, positions 2 and 3 in **E**. In a heterodimetallapentaborane $[(Cp^*Ir)\{Os(CO)(PPh_3)_2\}\text{-}(\mu\text{-}H)B_3H_6]$, positions 2 and 3 are occupied by Ir and Os.[3a]

The prolonged reaction of $[Cp^*RuCl]_4$ with BH_3·THF (r.t., 50 h) afforded another diruthenaborane cluster $[\{(Cp^*Ru)_2(\mu\text{-}H)\}B_4H_9]$ (**2**) in 83% yield.[11,12] Reaction of **1** with BH_3·THF also gave **2** almost quantitatively (Scheme 1). Thus, the cluster

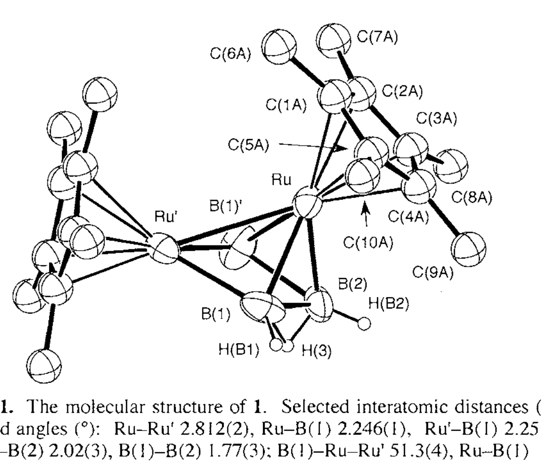


Figure 1. The molecular structure of **1**. Selected interatomic distances (Å) and bond angles (°): Ru–Ru' 2.812(2), Ru–B(1) 2.246(1), Ru'–B(1) 2.25(2), Ru–B(2) 2.02(3), B(1)–B(2) 1.77(3); B(1)–Ru–Ru' 51.3(4), Ru–B(1)–Ru' 77.5(5), B(1)–Ru–B(1)' 73.3(6), B(1)–Ru–B(2) 48.6(8), Ru–B(2)–B(1) 72.3(8), Ru–B(1)–B(2) 59.0(10), B(1)–B(2)–B(1)' 88(1).

framework of **1** is expanded by the capture of a BH fragment during the formation of **2**. Complex **2** is regarded as a 1,2-disublogated hexaborane(10) cluster with a pentagonal pyramidal framework. The ^{1}H NMR spectrum of **2** exhibits two signals of B–*H*–B protons at -3.94 and -3.62 ppm in the 2 : 1 ratio. The signal of the Ru–*H*–B protons was observed at -13.41 ppm as a broad quartet with the integral intensity of 2H, and the Ru–*H*–Ru proton was found at -13.49 ppm as a sharp singlet. If **2** is divided to $[Cp^*{}_2Ru_2(\mu\text{-}H)]^+$ and $(B_4H_9)^-$ fragments, the $(B_4H_9)^-$ ligand is isoelectronic with butadiene and its frontier orbitals are the *p* orbitals perpendicular to the B_4 plane. In this respect, **2** can be described as a dinuclear complex with a B_4 ligand which coordinates to one ruthenium atom in an η^4 fashion and to the other one through two agostic BH atoms. In this model, each Ru atom completes the 18 electron rule.

Complex **1** undergoes cleavage of the cluster-framework by Lewis bases. Treatment of **1** with 2 equivalents of PMe_3 at -64 °C gives a dinuclear complex, $[\{(Cp^*Ru)_2(\mu\text{-}H)\}(PMe_3)(\mu\text{-}\eta^4\text{-}B_2H_5)]$ (**3**) in 54% yield along with $BH_3{\cdot}PMe_3$ (Scheme 1).[13] The molecular structure of **3** is illustrated in Figure 2.[14] Ru(2) bears a PMe_3 ligand, and Ru(1) and Ru(2) are bridged by a hydrido ligand. The B_2H_5 group coordinates to the diruthenium moiety in an unprecedented, μ-η^4-mode: it is bound to Ru(2) by a closed BBRu 3c2e bond, while the two hydrogen atoms on B(1) coordinate to Ru(1). An asymmetrically bridging μ-η^3-B_2H_5 ligand is found in $[Cp_2Co_2(\mu\text{-}PPh_2)(\mu\text{-}\eta^3\text{-}B_2H_5)]$[15] and $[(B_6H_9)Pt_2(PMe_2Ph)_2(\mu\text{-}\eta^3\text{-}B_2H_5)]$.[16] The bond length between Ru(2) and the boron atom at the bridging position (B(1)) (2.136(6) Å) is substantially shorter than that between Ru(2) and the other boron atom (B(2)) (2.241(6) Å). Similar phenomena have been observed in the above-mentioned cobalt and platinum complexes. The interatomic distance between Ru(1) and Ru(2) (3.008(1) Å) is substantially longer than those of general Ru–Ru single bonds. Further reaction of **3** with PMe_3 affords $[Cp^*Ru(PMe_3)_2H]$.[8]

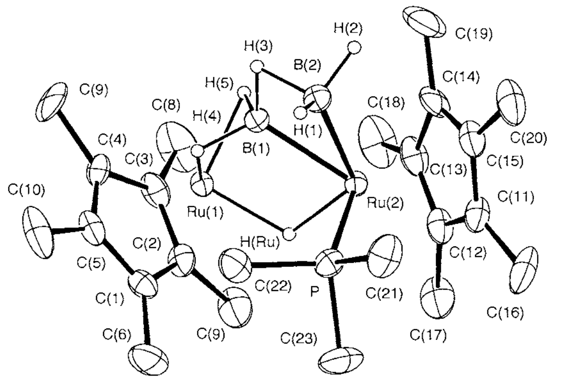


Figure 2. The structure of **3**. Selected interatomic distances (Å) and bond angles (°): Ru(1)···Ru(2) 3.008(1), Ru(1)··B(1) 2.304(6), Ru(2)–B(1) 2.136 (6), Ru(2)–B(2) 2.241(6), Ru(2)–P 2.258(2), Ru(1)–H(4) 1.83(5), Ru(1)–H(5) 1.66(5), B(1)–H(4) 1.36(5), B(1)–H(5) 1.23(5), B(2)–H(1) 1.15(5), B(2)–H(2), 1.13(6), B(1)–H(3) 1.24(5), B(2)–H(3) 1.34(5), B(1)···B(2) 1.7 33(9), Ru(1)–H(Ru) 1.851(7), Ru(2)–H(Ru) 1.715(7); Ru(1)–B(1)–Ru(2) 92.3(2), B(1)–Ru(2)–B(2) 46.6(2), Ru(1)–Ru(2)–P 95.35(4).

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References and Notes

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6 Data for **1**: ^{1}H NMR (500 MHz, C_6D_6) δ -13.60 (s, 2H, Ru*H*Ru), -11.30 (q, J_{BH} = 62.3 Hz, 2H, Ru*H*B), -4.06 (s, br, 2H, B*H*B), 1.92, 1.79 (s, 15H × 2, Cp*), 2.65 (q, J_{BH} = 131 Hz, 2H, BH), 3.23 (q, J_{BH} = 130 Hz, 1H, BH). ^{13}C NMR (125.7 Hz, C_6D_6) δ 11.5, 12.1 (C_5Me_5), 84.6, 96.6 (C_5Me_5). IR (hexane, cm^{-1}) 2498, 2450 (m, ν(BH)), 2423 (m, ν(BHB)), 1957 (m, ν(RuHB)), 1867 (m, ν(RuHRu)). MS (EI) *m* / *z* 510 (100, M^+ – 4H), 498 (48, $[Cp^*{}_2Ru_2B_2H_4]^+$), 486 (23, $[Cp^*{}_2Ru_2BH_3]^+$). Anal. Found C, 46.38; H, 7.31%. Calcd for $C_{20}H_{39}B_3Ru_2$: C, 46.70; H, 7.60.

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9 Crystal data for **1**: Yellow–orange crystals, monoclinic, space group *A*2/*a* (variant of No.15); a = 15.290(2), b = 14.070(2), c = 11.380(1) Å, β = 102.07(3)°; V = 2383.8(7) Å^3; Z = 4. The positions of Ru and B were refined anisotropically. The pentamethylcyclopentadienyl group was disordered over two sites. Refinement of the positions of the carbon atoms was accomplished isotropically by the use of a rigid model with a regular pentagon. R = 0.066 for 1497 reflections with $|F_o| > 6\sigma(F_o)$.

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11 Data for **2**: ^{1}H NMR (500 MHz, C_6D_6) δ -13.49 (s, 1H, Ru*H*Ru), -13.41(q, J_{BH} = 94 Hz, 2H, B*H*Ru), -3.94 (br, 2H, B*H*B), -3.62 (br, 1H, B*H*B), 1.81, 1.85 (s, 15H × 2, Cp*), 2.67 (q, J_{BH} = 130 Hz, 2H, BH), 3.35 (q, J_{BH} = 135 Hz, 2H, BH). ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6) δ 4.2, 17.7. ^{13}C NMR (125.7 Hz, C_6D_6) δ 6.1, 7.6 (C_5Me_5), 84.5, 92.3 (C_5Me_5). IR (KBr, cm^{-1}) 2482, 2428, 2360 (m, ν(BH)), 2338 (m, ν(BHB)), 1910 (m, ν(RuHB)), 1847 (m, ν(RuHRu)). MS (EI) *m* / *z* 526 (79, M^+), 514 (100, M^+ – BH). Anal. Found C, 45.87; H, 7.61%. Calcd for $C_{20}H_{40}B_4Ru_2$: C, 45.67; H, 7.67.

12 The crystal structure of **2** was reported by Fehlner et al. in ref 7.

13 Data for **3**: ^{1}H NMR (500 MHz, C_6D_6) δ -14.74 (d, J_{PH} = 21 Hz, 1H, Ru*H*Ru), -10.93 (q, J_{BH} = 82 Hz, 1H, Ru*H*B), -8.45 (q, J_{BH} = 93 Hz, 1H, Ru*H*B), -2.82(br, 1H, B*H*B), 1.02 (d, $^{2}J_{PH}$ = 8.5 Hz, 9H, PMe_3), 1.83 (d, J_{PH} = 1.5 Hz, 15H, C_5Me_5), 1.88 (s, 15H, C_5Me_5), 1.99 (br, 1H; BH), 3.15 (q, J_{BH} = 85 Hz, 1H, BH). ^{11}B{^{1}H} NMR (160.4 MHz, C_6D_6) δ -4.8, 41.5. ^{13}C NMR (125.7 Hz, C_6D_6) δ 11.4, 12.6 (C_5Me_5), 19.7 (d, J_{PC} = 29.0 Hz, PMe_3), 82.6 (C_5Me_5), 92.2 (d, J_{PC} = 2 Hz, C_5Me_5). ^{31}P{^{1}H} NMR (202 Hz, C_6D_6) δ 18.9. IR (KBr, cm^{-1}): 2453 (s), 2386 (s) (ν(BH)), 2294 (m, ν(BHB)), 1991 (w), 1913 (m) ν(BHRu), 1810 (m, ν(RuHRu)). MS (EI) *m* / *z* 574 (100, M^+ – 2H), 486 (40, M^+ – PMe_3 – BH_3). Anal. Found C, 48.20; H, 7.65%. Calcd for $C_{23}H_{45}B_2PRu_2$: C, 47.92; H, 7.87.

14 Crystal data for **3**: Orange crystals, monoclinic, space group $P2_1/n$ (variant of No.14); a = 13.850(2), b = 17.849(1), c = 10.7815(8) Å, β = 94.392(7)°; V = 2657.5(4) Å^3; Z = 4. R = 0.042 for 4244 reflections having $|F_o| > 3\sigma(F_o)$.

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