Synthesis, Structure, and Phosphine-Induced Degradation of a Ruthenapentaborane Cluster with a Sterically Demanding Hexamethylbenzene Ligand

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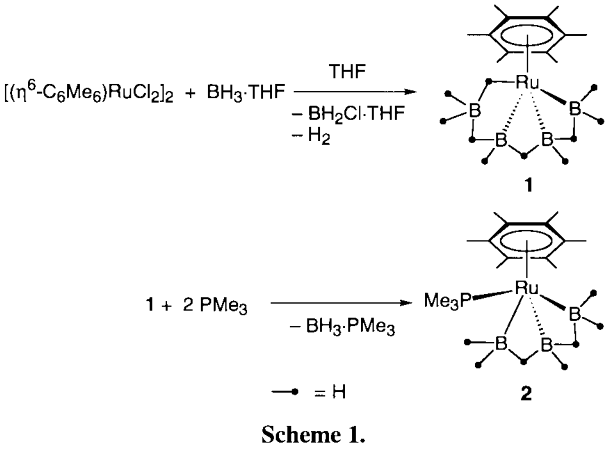
The reaction of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ with excess $BH_3{\cdot}THF$ produced a ruthenaborane cluster, *arachno*-$[(\eta^6\text{-}C_6Me_6)RuB_4H_{10}]$ (**1**). Compound **1** underwent cluster degradation through the action of PMe_3 to afford *arachno*-$[(\eta^6\text{-}C_6Me_6)Ru(PMe_3)B_3H_7]$ (**2**).

Metallaborane chemistry has rapidly developed in the last decade.[1] Use of a pentamethylcyclopentadienyl (Cp*) ligand brought new aspects onto this research area. It allowed high yield syntheses and systematic understanding of metallaborane clusters.[2–5] In many cases, the cluster cores of metallaboranes form through dehydrogenative condensation of B_1 species, $BH_3{\cdot}THF$ or BH_4^-, in the presence of appropriate metal fragments. In contrast to Cp* systems, reports on metallaborane clusters with η^6-arene ligands are rather limited.[6,7] In particular, monoborane condensation has never been applied for the syntheses of such compounds. η^6-Arene ligands are electronically neutral unlike Cp*. Therefore, their incorporation can give the cluster core higher electron density and different reactivity. Moreover, since substituted arene ligands like hexamethylbenzene are sterically more demanding than Cp*, its steric influence on the cluster geometry is of interest. We report herein the syntheses and characterization of new hexamethylbenzene-coordinated ruthenaborane clusters.

When a hexamethylbenzene-coordinated Ru (II) complex, $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ was treated with excess $BH_3{\cdot}THF$, H_2 gas evolved and a dark green solution was produced. Subsequent workup afforded *arachno*-$[(\eta^6\text{-}C_6Me_6)RuB_4H_{10}]$ (**1**) as pale orange crystals in 53% yield (Scheme 1).[8] Compound **1** was described previously by Greenwood and co-workers. In the literature, its synthesis was accomplished by the reaction between $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ and $K[B_4H_9]$, and the structure was deduced spectroscopically.[6] Cluster **1** is an *arachno* ruthenapentaborane derivative of B_5H_{11}, with the apical BH group replaced by the $[(\eta^6\text{-}C_6Me_6)Ru]$ fragment which is isolobal with BH. Similar skeletal structures are found in group 9 metallaboranes, *arachno*-$[Cp^*CoB_4H_{10}]$ and *arachno*-$[Cp^*IrB_4H_{10}]$, whose metal fragments are isoelectronic with $[(\eta^6\text{-}C_6Me_6)Ru]$ in **1**.[4,5]



Scheme 1.

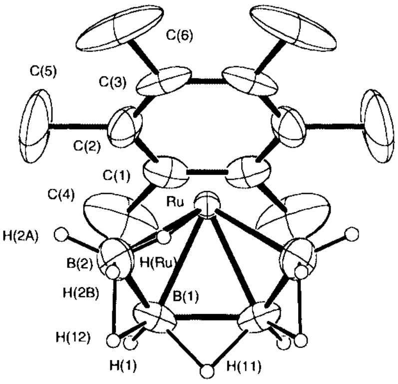
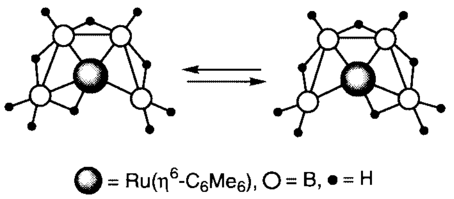


Figure 1. The structure of **1**. Selected interatomic distances (Å) and bond angles (°): Ru–B(1) 2.108(8), Ru–B(2) 2.223(7), B(1)–B(2) 1.768(11), B(1)–B(1)' 1.79(2), B(1)–Ru–B(1)' 50.1(3), B(1)–Ru–B(2) 48.1(3), B(2)–Ru–B(2)' 88.2(3), Ru–B(1)–B(2) 69.3(4), Ru–B(2)–B(1) 62.6(3), Ru–B(1)–B(1)' 65.0(3); dihedral angle between Ru–B(1)–B(2) and Ru–B(1)–B(1)' 127.7°.

An X-ray diffraction study clearly showed the *arachno* skeletal structure of **1** (Figure 1).[9] In the basal plane composed of four boron atoms, no boron–boron bond exists between B(2) and B(2)', giving an open edge. The molecule has a crystallographic mirror plane passing through Ru, H(11), and the center of the six-membered ring of the η^6-C_6Me_6 ligand. The hydrogen atom bridging Ru and B(2), H(Ru), is found with 0.5 occupancy. The Ru–B(1) and Ru–B(2) bond distances (2.108(8) and 2.223(7) Å, respectively) fall within the range of reported Ru–B bond lengths in ruthenaborane clusters (2.02–2.25 Å).[2,3,7]

The ^{11}B NMR spectrum of **1** shows a doublet and a triplet in 1:1 intensity ratio at –0.1 and –8.0 ppm, respectively, despite the fact that the static structure supports four boron atom environments. This indicates rapid migration of the H(Ru) atom between the Ru–B(2) and Ru–B(2)' edges (Scheme 2). On lowering the solution temperature, the two ^{11}B signals collapsed



Scheme 2.

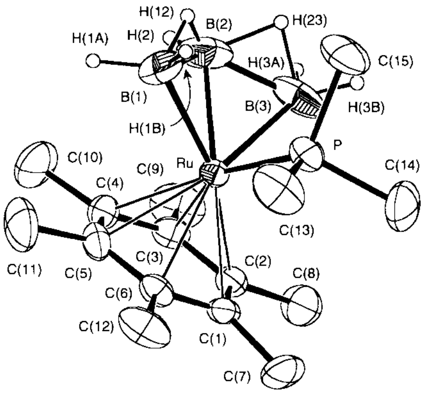


Figure 2. The structure of **2**. Selected interatomic distances (Å) and bond angles (°): Ru–P 2.265(1), Ru–B(1) 2.200(6), Ru–B(2) 2.137(5), Ru–B(3) 2.195(5), B(1)–B(2) 1.833(11), B(2)–B(3) 1.783(11); B(1)–Ru–B(2) 5 0.0(3), B(2)–Ru–B(3) 48.6(3), B(1)–Ru–B(3) 90.8(3), Ru–B(1)–B(2) 63.2 (3), B(1)–B(2)–Ru 66.8(2), Ru–B(3)–B(2), 64.0(2), Ru–B(2)–B(3) 67.4(3); dihedral angle between Ru–B(1)–B(2) and Ru–B(2)–B(3) 139.8°.

into the base line with broadening. The collapse and broadening were more pronounced for the resonance of B(2) and B(2)' atoms, to which the H(Ru) atom is directly bound. It disappeared completely at –60 °C although the decoalesced signals were not observed even at –90 °C. The Ru–H–B proton resonates at –10.62 ppm as a broad signal coupled with boron in ^{1}H NMR.

In the formation of Cp*-coordinated ruthenaboranes from $[Cp^*RuCl]_4$ and $BH_3{\cdot}THF$, clusters containing two metal fragments, *nido*-$[\{Cp^*Ru(\mu\text{-}H)\}_2B_3H_7]$ and *nido*-$[(Cp^*Ru)_2(\mu\text{-}H)\text{-}B_4H_9]$ are produced.[2,3] In the related Co system, the interaction of $[Cp^*CoCl]_2$ with $BH_3{\cdot}THF$ affords *arachno*-$[Cp^*CoB_4H_{10}]$ (isoelectronic with **1**), and a dimetalla derivative *nido*-$[(Cp^*Co)(\mu\text{-}H)\{(\eta^4\text{-}C_5Me_5H)Co\}B_3H_7]$ as well.[4] The exclusive formation of a monometallaborane **1** is attributable to the bulkiness of the η^6-C_6Me_6 ligand. Thus, the use of a sterically demanding hexamethylbenzene ligand could give the formation of metallaborane clusters selectivity.

Because of the Lewis acidic character of metallaboranes, their interaction with Lewis bases is of interest.[10,11] Compound **1** reacted with two equivalents of PMe_3 to result in the degradation of the cluster framework, thereby liberating $BH_3{\cdot}PMe_3$, and the formation of the ruthenatetraborane derivative **2** (see Scheme 1).[12] An ORTEP diagram of **2** is shown in Figure 2.[13] The B_3H_7 "borallyl" ligand coordinates to the ruthenium atom to form a butterfly-like framework, in which ruthenium occupies the hinge position. On the other hand, in Greenwood's cluster $[\{(\eta^6\text{-}C_6Me_6)RuCl\}B_3H_8]$, the ruthenium atom is located at the wing-tip.[9] The η^6-C_6Me_6 ligand is situated at the *exo* position with respect to the butterfly framework of the RuB_3 core.

Phosphine-induced formation of **2** shows a pattern of reaction different to related compounds. The parent borane of **1**, B_5H_{11} is readily cleaved through the action of three equivalents of PMe_3 to give a more open cluster, *hypho*-$B_4H_8{\cdot}2PMe_3$ and $BH_3{\cdot}PMe_3$.[14] Addition of excess PMe_3 to **2** did not lead to further incorporation of PMe_3 into the cluster core. Note that the reaction of *nido*-$[\{Cp^*Ru(\mu\text{-}H)\}_2B_3H_7]$ with PMe_3 affords $[(Cp^*Ru)_2(PMe_3)(\mu\text{-}H)(\mu\text{-}\eta^4\text{-}B_2H_5)]$.[2] This reaction is also different from the cleavage of its parent compound B_5H_9 with PMe_3, which gives $B_3H_5{\cdot}3PMe_3$ and $B_2H_4{\cdot}2PMe_3$ through the 1:2 adduct, *hypho*-$B_5H_9{\cdot}2PMe_3$.[15]

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References and Notes

1 a) L. Barton and D. K. Srivastava, "Comprehensive Organometallic Chemistry II," ed. by E. W. Abel and F. G. A. Stone, Pergamon, Oxford (1995), Vol. 1, p 275. b) T. P. Fehlner, *Organometallics*, **19**, 2643 (2000), and references cited therein.

2 Y. Kawano, H. Matsumoto, and M. Shimoi, *Chem. Lett.*, **1999**, 489.

3 X. Lei, M. Shang, and T. P. Fehlner, *J. Am. Chem. Soc.*, **121**, 1275 (1999).

4 Y. Nishihara, K. J. Deck, M. Shang, T. P. Fehlner, B. S. Haggerty, and A. L. Rheingold, *Organometallics*, **13**, 4510 (1994).

5 X. Lei, M. Shang, and T. P. Fehlner, *Chem. Eur. J.*, **6**, 14 (2000).

6 M. Bown, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, **309**, C67 (1986).

7 For example, a) M. Bown, X. L. R. Fontaine, N. N. Greenwood, P. MacKinnon, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, **1987**, 2781. b) R. L. Thomas and L. Barton, *Inorg. Chim. Acta.*, **289**, 134 (1999). c) X. Lei, M. Shang, and T. P. Fehlner, *Organometallics*, **20**, 1479 (2001).

8 To a THF (30 mL) solution of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (307 mg, 0.448 mmol) was added a THF (10 mL) solution of $BH_3{\cdot}THF$ (10.0 mmol) via a syringe with stirring. The solution was stirred overnight at room temperature and then volatiles were removed under vacuum. The resulting dark green residue was extracted with hexane (65 mL × 3) and filtered. The pale orange extract was concentrated and cooled to –80 °C to provide pale orange crystals of **1** (144 mg, 0.45 mmol, 53%). ^{1}H NMR (C_6D_6, 500 MHz, 20 °C) δ –10.62 (br, 1H, Ru*H*B), –3.86 (br, 3H, B*H*B. At –90 °C, this broad hump splits into two peaks with a 2:1 intensity ratio due to the quadrupole-induced thermal decoupling), 1.73 (s, 18H, C_6Me_6), 2.60 (brq, J_{BH} = 118 Hz, 6H, overlapped signals of terminal BH protons). ^{11}B NMR (160.4 MHz, 20 °C) δ –8.0 (t, J_{BH} = 114 Hz, BH_2), –0.1 (d, J_{BH} = 142 Hz, BH). IR (KBr, cm^{-1}) 2480, 2439 (s, ν_{BH}), 2397 (s, ν_{BHB}), 1918 (m, ν_{RuHB}). MS (EI) *m/z* 314 (100, $M^+ - 3H$), 300 (50, $M^+ - BH_3$), 162 (30, $C_6Me_6{}^+$), 147 (59, $C_6Me_5{}^+$). Anal. Calcd for $C_{12}H_{28}B_4Ru$: C, 45.51; H, 8.91%. Found: C,45.17; H, 8.83%.

9 Crystal data for **1**. pale orange crystals, orthorhombic, space group *Pnmn* (variant of No. 58); $a = 11.160(8)$, $b = 14.536(8)$, $c = 9.811(10)$ Å; $V = 1591.62(4)$ Å^3; $Z = 4$. $R = 0.036$, $wR2 = 0.089$ for 1156 reflections with $|F_o| > 4\sigma(F_o)$, 82 parameters, $GooF = 1.081$.

10 L. N. Pangan, Y. Kawano, and M. Shimoi, *Organometallics*, **19**, 5575 (2000).

11 X. Lei, M. Shang, and T. P. Fehlner, *Organometallics*, **19**, 5272 (2000).

12 To a solution of **1** (102 mg, 0.32 mmol) in hexane (20 mL) was added PMe_3 (104 µL, 73 mmol) with stirring using a micro syringe. This solution was stirred at ambient temperature overnight. Volatiles were then removed under vacuum. The resultant solid residue was recrystallized from hexane at –25 °C to afford pale orange crystals of **2** (73 mg, 0.19 mmol). Concentration and cooling of the mother liquor gave the second crop (10 mg, 0.03 mmol). The total yield of **2** was 68%. ^{1}H NMR (500 MHz, C_6D_6) δ –4.15 (br, 2H, B*H*B), 0.95 (d, $^2J_{PH}$ = 8.0 Hz, 9H, PMe_3), 1.80 (s, 18H, C_6Me_6), 2.60 (brq, J_{BH} = 99 Hz, 5H, overlapped signals of terminal BH protons). ^{11}B NMR (160.4 MHz, C_6D_6) δ –2.7 (t, BH_2), –2.4 (d, BH), the coupling constant values could not be resolved because of partialy overlapped signals. ^{31}P NMR (202 MHz, C_6D_6) δ 9.0. IR (KBr, cm^{-1}) 2457, 2439 (s, vBH), 2399, 2325 (s, ν_{BHB}). MS (EI) *m/z* 378 (100, $M^+ - H$), 366 (38, $M^+ - BH_2$), 352 (75, $[(\eta^6\text{-}C_6Me_6)Ru(PMe_3)BH]^+$). Anal. Calcd for $C_{15}H_{34}B_3PRu$: C, 47.55; H, 9.04%. Found: C, 47.26; H, 8.79%.

13 Crystal data for **2**: pale orange crystals, orthorhombic, space group $P2_12_12_1$ (No. 19); $a = 8.6656(10)$, $b = 12.005(2)$, $c = 18.342(3)$ Å; $V = 1908.1(5)$ Å^3; $Z = 4$. $R = 0.0256$, $wR2 = 0.0509$ for 3444 reflections with $|F_o| > 4\sigma(F_o)$, 218 parameters, $GooF = 0.779$.

14 G. Kodama and M. Kameda, *Inorg. Chem.*, **18**, 3302 (1979).

15 M. Kameda and G. Kodama, *Inorg. Chem.*, **19**, 2288 (1980).