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Synthesis and Interconversion of Some Small Ruthenaboranes: Reaction of a Ruthenium Borohydride with Pentaborane(9) to Form Larger Ruthenaboranes

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A number of ruthenaborane clusters have been prepared containing the {(η-C_5Me_5)Ru(PMe_3)} fragment. Reaction of [(η-C_5Me_5)Ru(PMe_3)H_3] with 1 equiv of BH_3·thf gives [(η-C_5Me_5)Ru(PMe_3)BH_4] (**1**), which reacts further with another equivalent of BH_3·thf to give [(η-C_5Me_5)Ru(PMe_3)B_2H_7] (**2**) in nearly quantitative yield. Thermolysis of **2** in solution at 60 °C gives a mixture of **1**, *arachno*-2-[(η-C_5Me_5)Ru(PMe_3)B_3H_8] (**3**), and *arachno*-1-[(η-C_5Me_5)Ru(PMe_3)B_3H_8] (**4**). Thermolysis of the wing isomer **3** in solution at 100 °C gives 100% conversion to the hinge isomer **4**. Thermolysis in a solution of *arachno*-3-[(η-C_5Me_5)Ru(PMe_3)B_4H_9] also gives **4** and **1**. The borohydride **1** reacts with pentaborane(9) to give four ruthenaborane clusters, compound **3**, *nido*-2-[(η-C_5Me_5)RuB_5H_{10}] (**5**), *arachno*-2-[(η-C_5Me_5)Ru(PMe_3)B_5H_8] (**6**), and *arachno*-3-[(η-C_5Me_5)Ru(PMe_3)B_4H_9] (**7**). Thermolysis of **5** in solution gives *nido*-1-[(η-C_5Me_5)RuB_5H_{10}] (**8**) in good yield. Compound **5** deprotonates cleanly at the unique basal B−H−B bridge on reaction with KH in thf to form *nido*-2-[(η-C_5Me_5)Ru$B_5H_9^-$][K^+] (**9**). Compound **8** deprotonates cleanly at a B−H−B bridge on reaction with KH in thf to form fluxional *nido*-1-[(η-C_5Me_5)Ru$B_5H_9^-$]-[K^+] (**10**). The X-ray crystal structure of **3** is reported.

Introduction

Metallaboranes of ruthenium (ruthenaboranes) have a rich and diverse chemistry.[1−3] Most early work on ruthenaboranes concentrated on using ruthenium fragments that are isolobal with {BH^t} such as {(η-C_6R_6)Ru}[4] or {(L_3)Ru} (L = carbonyl or phosphine).[5,6] For example, Greenwood, Kennedy, and co-workers have shown that [(η-C_6Me_6)RuCl_2]$_2$ reacts with a variety of borane anions to give ruthenaboranes containing 3−17 boron atoms.[7−10] More recently, Shimoi and co-workers synthesized *arachno*-1-[(η-C_6Me_6)RuB_4H_{10}] by the reaction of [(η-C_6Me_6)RuCl_2]$_2$ with excess BH_3·thf.[11]

Some years ago we decided to explore the chemistry of ruthenaboranes containing the 1 and 3 electron fragments {(η-C_5Me_5)Ru} and {(η-C_5Me_5)(PMe_3)Ru}. We reported the reaction of [(η-C_5Me_5)Ru(PMe_3)Cl_2] with $NaBH_4$, which gave a mixture of [(η-C_5Me_5)Ru(PMe_3)BH_4] (**1**) and [(η-C_5Me_5)Ru(PMe_3)B_2H_7] (**2**), the latter molecule in low yield.[12] Compound **2** is still the only example of an η^2-B_2H_7 bonding geometry in a three-vertex metallaborane. We also synthesized the first *arachno*-3-metallapentaborane *arachno*-3-[(η-C_5Me_5)Ru(PMe_3)B_4H_9] along with other metallaboranes from the reaction of [(η-C_5Me_5)Ru(PMe_3)H_3] with pentaborane(9).[13]

In the last 10 years, the groups of Fehlner and Shimoi have synthesized a range of mostly diruthenaboranes containing the fragment {(η-C_5Me_5)Ru}. For example, reaction of BH_3·thf with [(η-C_5Me_5)RuCl_2]$_2$ or [(η-C_5Me_5)RuH_2]$_2$ gives initially the dimetalla cluster *nido*-1,2-[{Ru(η-C_5Me_5)H}$_2B_3H_7$].[14−16] This

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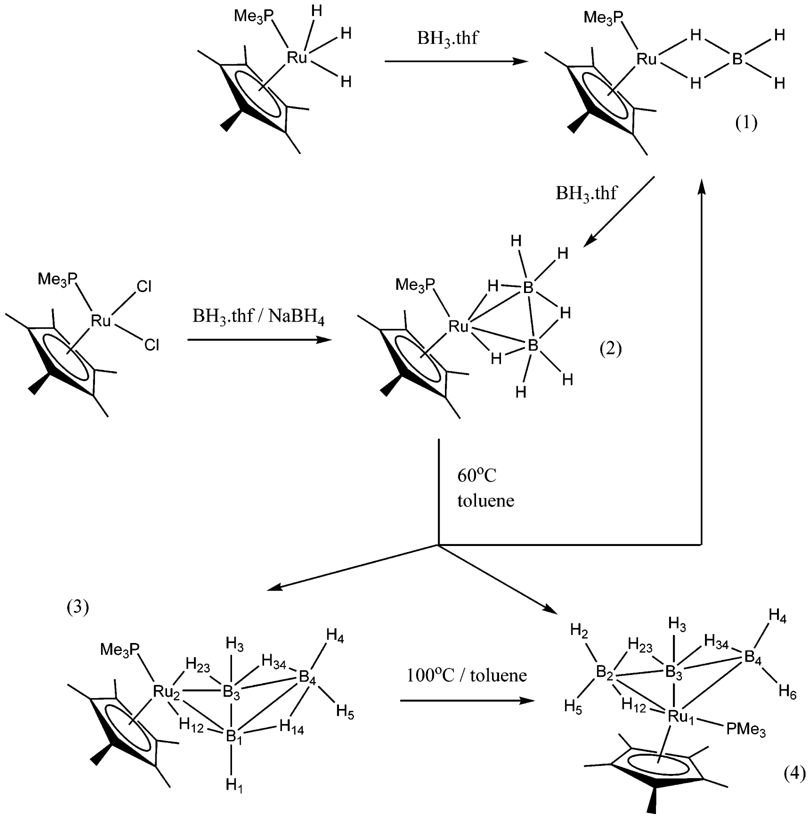
Scheme 1



cluster reacts further with BH$_3$·thf to give first *nido*-1,2-[{Ru(η-C$_5$Me$_5$)}$_2$(μ-H)B$_4$H$_9$] and then larger dimetallaboranes on heating in further equivalents of BH$_3$·thf.[17,18] Shimoi has further shown that *nido*-1,2-[{Ru(η-C$_5$Me$_5$)H}$_2$B$_3$H$_7$] reacts with tertiary phosphines to give the electron-deficient metallaborane [1,2-{Ru(η-C$_5$Me$_5$)}$_2$(μ-H)(||-μ-η^4-B$_2$H$_5$)(PMe$_2$Ph)] containing the fragment {(η-C$_5$Me$_5$)Ru(PMe$_2$Ph)}. The unusual properties of metallaboranes containing the {(η-C$_5$Me$_5$)Ru(PR$_3$)} fragment, as shown by us and Shimoi, led us to probe its chemistry further.[19]

Results and Discussion

We wished to synthesize **2** in high yield, and it seemed reasonable to try using a ruthenium hydride precursor to make the metallaborane, on the basis of earlier success in using other transition metal hydrides. For example, we have shown that photolysis of [(η-C$_5$H$_5$)$_2$MoH$_2$] with BH$_3$·thf gives [(η-C$_5$H$_5$)$_2$MoHB$_2$H$_5$],[12] while treatment of [W(PMe$_3$)$_3$H$_6$] with BH$_3$·thf gives *arachno*-2-[W(PMe$_3$)$_3$H$_3$B$_3$H$_8$].[20] More recently, Fehlner and co-workers have reported reactions of BH$_3$·thf with transition metal hydrides. Reaction of BH$_3$·thf with [Fe(η-C$_5$Me$_5$)H$_2$]$_2$ gives the monometal cluster *arachno*-1-[Fe(η-C$_5$Me$_5$)B$_4$H$_{11}$],[15] while [(η-C$_5$Me$_5$)ReH$_6$ reacts with BH$_3$·thf to give *arachno*-2-[(η-C$_5$Me$_5$)ReH$_3$B$_3$H$_8$].[21]

We found that treatment of [(η-C$_5$Me$_5$)Ru(PMe$_3$)H$_3$][22] with 1 equiv of BH$_3$·thf gives [(η-C$_5$Me$_5$)Ru(PMe$_3$)BH$_4$] (**1**) in an isolated yield of 90%. Further, [(η-C$_5$Me$_5$)Ru(PMe$_3$)H$_3$] reacts with 2 equiv of BH$_3$·thf to give [(η-C$_5$Me$_5$)Ru(PMe$_3$)B$_2$H$_7$] (**2**) in 80% isolated yield (Scheme 1). Compound **2** does not react further with excess BH$_3$·thf at room temperature. The above reactions represent easy, high-yielding routes to these small ruthenaboranes. It seems clear that **2** is formed from **1** by the addition of a second {BH$_3$} fragment to the original η^2-borohydride. This was confirmed by reacting **1** with 1 equiv of BH$_3$·thf, giving **2** in an isolated yield of 90%. Cage expansion from a borohydride to a {MB$_2$} cluster is an unprecedented reaction for a metal borohydride and underlines the unusual nature of the {(η-C$_5$Me$_5$)Ru(PMe$_3$)} fragment. We also found that compound **2** could be synthesized directly in high yield by the reaction of [(η-C$_5$Me$_5$)Ru(PMe$_3$)Cl$_2$] with a mixture of BH$_3$·thf and NaBH$_4$ at room temperature, thereby eliminating the step of making [(η-C$_5$Me$_5$)Ru(PMe$_3$)H$_3$] from [(η-C$_5$Me$_5$)Ru(PMe$_3$)Cl$_2$].

The only homologation of a 3-vertex metallaborane to have been reported is the thermolysis of [(η-C$_5$H$_5$)$_2$MoHB$_2$H$_5$] to give *arachno*-2-[Mo(η-C$_5$H$_5$)(η^5:η^1-C$_5$H$_4$)B$_4$H$_7$].[23] Therefore we were interested to see if compound **2** would also homologate. Thermolysis in toluene of orange **2** at 60 °C for 3 days gave a deep red solution containing a mixture of products as determined by ^{11}B NMR spectroscopy. The major, pale yellow product **4** was separated by fractional crystallization in 39% yield (based on ruthenium) and characterized as *arachno*-1-[(η-C$_5$Me$_5$)Ru(PMe$_3$)B$_3$H$_8$] by multinuclear NMR and elemental analysis (Scheme 1). Compound **4** was also formed in 40% yield by the

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thermolysis of *arachno*-3-[(η-C_5Me_5)Ru(PMe_3)B_4H_9] (**7**)[13] at 80 °C. The ^{11}B NMR spectrum of **4** shows partial overlap of the B(3) and B(4) resonances such that coupling to B(4) cannot be resolved. The B(3) resonance resolves as a doublet of doublets of doublets using resonance enhancement techniques. The main splitting is due to terminal coupling to H(3) and the minor splittings due to bridging coupling to H(23) and H(34). This was confirmed by selective $^{11}B\{^1H\}$ NMR experiments. The B(2) resonance is a triplet due to terminal coupling to H(2) and H(5). Broad-band ^{11}B decoupling of the ^1H NMR spectrum sharpens eight resonances of equal intensity, and selective $^1H\{^{11}B\}$ NMR experiments were carried out to assign the protons. In particular, decoupling of the B(3) and B(4) atoms sharpens three proton resonances that have chemical shifts typical of terminal B−H protons. Only one of these protons is bonded to B(3); the other two protons are assigned as terminal B−H protons on B(4).

In comparison to *arachno*-2-metallatetraboranes, few $\{MB_3\}$ clusters with the metal at the hinge position have been reported. They include several platinum and palladium clusters of general formulas [M(L_2)B_3H_7] (M = Pt, Pd) and [Ir(CO)(PPh_3)-HB_3H_7].[24−26] The $\{B_3H_7\}$ fragment is formally $\{B_3H_7^{2-}\}$ and can be described as a π-borallyl ligand, an analogue of a π-allyl moiety.[27] Shimoi has recently reported the formation of *arachno*-1-[(η-C_6Me_6)(PMe_3)RuB_3H_7] from the reaction of *arachno*-1-[(η-C_6Me_6)RuB_4H_{10}] with PMe_3.[11] In addition, *arachno*-1-Ir[(η-C_5Me_5)$H_2B_3H_7$] has been reported to be formed via thermal rearrangement of the 2-isomer *arachno*-2-Ir[(η-C_5Me_5)HB_3H_8].[28,29] The 2-isomer is formed together with *arachno*-2-Ir[(η-C_5Me_5)-ClB_3H_8] from the reaction of [Ir(η-C_5Me_5)Cl_2]$_2$ with TlB_3H_8. Interestingly, the chloro complex does not undergo the same thermal rearrangement to the hinge isomer.

The mother liquor from the thermolysis of **2** was shown to be a mixture of **1** and *arachno*-2-[(η-C_5Me_5)Ru(PMe_3)B_3H_8] (**3**). The identity of compound **3** was confirmed by comparison of the NMR spectra with a sample of pure orange **3** made by the reaction of pentaborane(9) with [(η-C_5Me_5)Ru(PMe_3)H_3].[5] Crystals of compound **3** suitable for X-ray diffraction were grown from light petroleum at −30 °C. The molecular structure is shown in Figure 1. Selected bond lengths and bond angles are given in Tables 1 and 2.

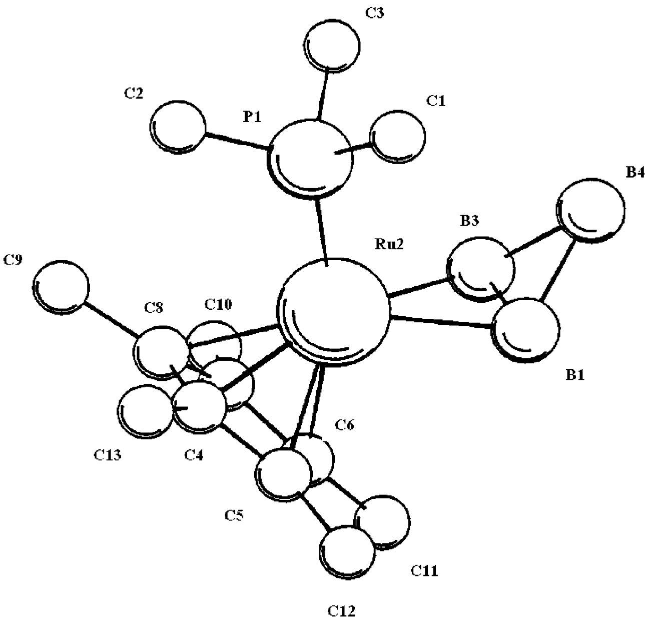

Figure 1. Molecular structure of *arachno*-2-[(η-C_5Me_5)Ru(PMe_3)-B_3H_8] (**3**). Hydrogen atoms are omitted for clarity.

Table 1. Crystal Data, Data Collection, and Structure Refinement for *arachno*-2-[(η-C_5Me_5)Ru(PMe_3)B_3H_8] (3)

empirical formula	$C_{13}H_{32}B_3PRu$
molecular weight	352.87
cryst size/mm	0.7 × 0.8 × 1.25
cryst syst	orthorhombic
space group	*Pcab*
a/Å	12.922(1)
b/Å	15.320(2)
c/Å	18.542(4)
β/deg	90
volume/Å^3	3670.5
Z	4
D_c/g cm^{-3}	1.277
μ/cm^{-1}	9.07
F(000)	1472
T (K)	293 (10)
radiation (λ/μ)	Mo Kα (0.71069)
2θ limits/deg	0−27
scan mode	ω/θ
total data collected	5289
no. of observations	2695
no. of variables	164
obsrvns/variables	16.43
weighting scheme	unit weights
R	0.023
R_w	0.026

The structure of **3** consists of an *arachno*-tetraborane “butterfly” cluster in which a {(η-C_5Me_5)Ru(PMe_3)} fragment substitutes in the 2-position (wing-tip) for a $\{BH_2\}$ fragment. The bond lengths compare well with other *arachno*-2-metallatetraboranes.[1−3] There is a noncrystallographic mirror plane through Ru(2), B(4), and (P1). The dihedral angle between the planes Ru(2)−B(1)−B(3) and B(1)−B(3)−B(4) is 117°, typical of all known *arachno*-2-metallatetraboranes except *arachno*-2-[Mn(CO)$_4$$B_3H_7$-*exo*-Br].[30] The pentamethylcyclopentadienyl ligand occupies the *exo* position and the PMe_3 ligand the *endo* position. The molecule *arachno*-2-[(η-C_5Me_5)-$ReH_3B_3H_8$][21] has been crystallographically characterized, and the pentamethylcyclopentadienyl ligand is also shown to be in the *exo* position. However, the X-ray crystal structure of *arachno*-2-[Ru(η-C_6H_5Me)ClB_3H_8] shows the toluene ligand in the *exo* position and the Cl ligand *endo*.[31]

The ^{11}B NMR of compound **3** consists of a doublet and triplet in an integral ratio of 2:1, the chemical shifts being typical of a wing-tip-substituted *arachno*-2-metallatetraborane. The $^{11}B\{^1H\}$ NMR shows eight protons associated with the boron cage in an integral ratio of 1:1:2:2:2, together with resonances for a PMe_3 ligand and η-C_5Me_5 ligand. Further data from ^1H and ^{11}B decoupling experiments were used to assign the skeletal protons. Compound **3** is the ruthenium congener of the iron metallatetraborane *arachno*-2-[(η-C_5Me_5)Fe(PMe_3)B_3H_8], formed as one of the products from the reaction of pentaborane(9) with [(η-C_5Me_5)Fe(PMe_3)$_2$H], which shows similar chemical shifts in the ^{11}B and $^1H\{^{11}B\}$ NMR spectra.[32] The five resonances for the $\{B_3H_8\}$ fragment in **3** at 20 °C in the ^1H NMR spectrum

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Table 2. Selected Bond Distances and Angles for Compound 3

Bond Distances (Å)	
Ru(2)−B(1)	2.38(1)
Ru(2)−B(3)	2.31(1)
B(1)−B(4)	1.82(2)
B(1)−B(3)	1.83(2)
B(4)−B(3)	1.88(2)
Ru(2)−P(1)	2.311(2)
Ru(2)−C(4)	2.190(8)
Ru(2)−C(5)	2.216(8)
Ru(2)−C(6)	2.217(9)
Ru(2)−C(7)	2.206(8)
Ru(2)−C(8)	2.209(8)
Angles (deg)	
B(1)−Ru(2)−P(1)	99.3(3)
B(3)−Ru(2)−P(1)	99.7(3)
B(3)−Ru(2)−P(1)	45.9(4)
B(4)−B(1)−Ru(2)	109.0(7)
B(3)−B(1)−Ru(2)	65.1(5)
B(3)−B(1)−B(4)	62.0(7)
B(3)−B(4)−B(1)	59.2(6)
B(1)−B(3)−Ru(2)	69.0(5)
B(4)−B(3)−Ru(2)	109.7(7)

suggest a static structure for the molecule. A variety of exchange processes have been observed for the protons of {B_3H_8} fragments in other molecules such as [$Mo(CO)_4B_3H_8^-$], [$Cu(PPh_3)_2B_3H_8$], and [$Be(B_3H_8)_2$].[2]

We were not able to ascertain from our studies whether compound **4** is formed directly from the thermolysis of compound **2** or whether it is formed only via compound **3** because we always obtained a mixture of the two butterfly clusters at various thermolysis temperatures below 70 °C. However, compound **3** clearly rearranges to compound **4** in quantitative yield by raising the thermolysis temperature of a toluene solution to 100 °C for 4 days, as judged by multinuclear NMR. Therefore we assume that compound **3** is the first-formed kinetic product, which rearranges to the thermodynamic product **4** on further heating.

The unique ability of the borohydride **1** to cluster expand to form **2** on reaction with BH_3·thf prompted us to investigate its reaction with larger boranes. Indeed, treatment of a toluene solution of **1** with pentaborane(9) gave four metallaboranes after column chromatography on silica gel (Scheme 2). Two of the products isolated were compound **3** and the previously reported *arachno*-3-[(η-C_5Me_5)Ru(PMe_3)B_4H_9] (**7**).[13] The first orange band off the column was identified as *nido*-2-[(η-C_5Me_5)-RuB_5H_{10}] (**5**) by multinuclear NMR and EI mass spectrometry. Due to its extreme solubility in many solvents, we were not able to prepare crystals suitable for X-ray diffraction. The ^{11}B NMR of **5** consists of three doublets in an integral ratio of 2:2:1 assigned to B(3, 6), B(4, 5), and B(1), each with a single terminal B−H coupling. It was possible to observe bridged-H coupling using line-narrowing techniques. For example, B(3, 6) appears as a doublet of triplets due to coupling to H(23, 34) and H(36, 56). Atoms B(4, 5) also appear as a doublet of triplets, the triplet structure now arising from coupling to H(34, 45) and H(45, 56). The ^{1}H{^{11}B} NMR spectrum of (**5**) consists of six resonances in an integral ratio of 2:2:1:1:2:2 assigned to the 10 cage protons and a sharper resonance due to the η-C_5Me_5 ligand. Assignments were made using selective ^{1}H{^{11}B} NMR experiments. There is a close similarity of the chemical shifts of the boron atoms and cage protons of compound **5** with the iron congeners *nido*-2-[(η-C_5H_5)FeB_5H_{10}][33,34] and *nido*-2-[(η-C_5Me_5)FeB_5H_{10}].[32]

The fourth metallaborane isolated from column chromatography was recrystallized to give a very low yield of an orange metallaborane. It has been characterized only by multinuclear NMR. However, the proposed structure, *arachno*-2-[(η-C_5Me_5)-Ru(PMe_3)B_5H_8] (**6**), seems very plausible on the basis of the NMR data and assuming the cluster obeys the electron-counting rules (Scheme 2).[35−37] The ^{11}B NMR spectrum consists of four resonances in an integral ratio of 1:1:2:1. At $\delta = -22.6$ ppm there is a well-resolved doublet assigned to the apical boron atom B(1) coupled to proton H(1). As we believe the molecule has no plane of symmetry, accidental overlap of the resonances due to B(4) and B(5) must be occurring at $\delta =$ 22.4 ppm. Evidence that it is accidental is based on the fact that decoupling B(4, 5) sharpens the two protons H(4) and H(5) at different chemical shifts ($\delta = 5.90$ and 5.63 ppm, respectively) in the ^{1}H NMR spectrum. The chemicals shifts are typical of terminal B−H protons. The rest of the ^{11}B NMR spectrum consists of two doublets at $\delta = 46.8$ ppm for B(3) and 65.8 ppm for B(6), typical of boron atoms bonded to a metal center. Broad-band ^{11}B decoupling of the ^{1}H NMR spectrum sharpens eight protons associated with the borane fragment, five terminal B−H protons, two B−H−B protons, and one Ru−H−B proton. Selective decoupling experiments were in agreement with the proposed structure and were used to assign the protons.

Assuming compound **6** obeys the electron-counting rules, it has the same *nido*-metallahexaborane structure as compound **5**. Thus **6** can be thought of as being derived from **5** by removing two of the basal bridging protons and coordinating a PMe_3 ligand to the ruthenium atom, thereby keeping the same electron count. Compound **6** is thus the sixth metallaborane with a {(η-C_5Me_5)Ru(PMe_3)} fragment, the others being compounds **1**, **2**, **3**, **4**, and **7**. Three-electron fragments in small *nido* clusters are fairly rare, the most notable example being *nido*-2-[Ir(CO)-(PPh_3)$_2$$B_5H_8$], for which the X-ray crystal structure has been reported.[38] It contains a basal three-electron {Ir(CO)(PPh_3)$_2$} fragment as well as three basal B−H−B bridging protons in an analogous arrangement to compound **6**. Other three-electron fragments in small *nido* clusters have been reported.[39−42]

The formation of small metallaboranes by reaction of an organometallic borohydride complex with neutral pentaborane(9) appears to be unique. Thus, the borohydride ligand in compound **1** is clearly fairly labile. Compound **1** has been determined to be a η^2-borohydride from X-ray crystallography.[43] We propose that one of the Ru−H−B bridges in the η^2-borohydride ligand is broken to form a 16-electron η^1-borohydride intermediate. This then reacts with BH_3·thf to cluster expand to form compound **2** or with pentaborane to form several metallaboranes, the same metallaboranes formed by reaction of [(η-C_5Me_5)Ru-(PMe_3)H_3] with pentaborane(9).[13] Interestingly, we did not observe the formation of any {RuB_6} clusters from the reaction of **1** with pentaborane(9). We have recently shown that

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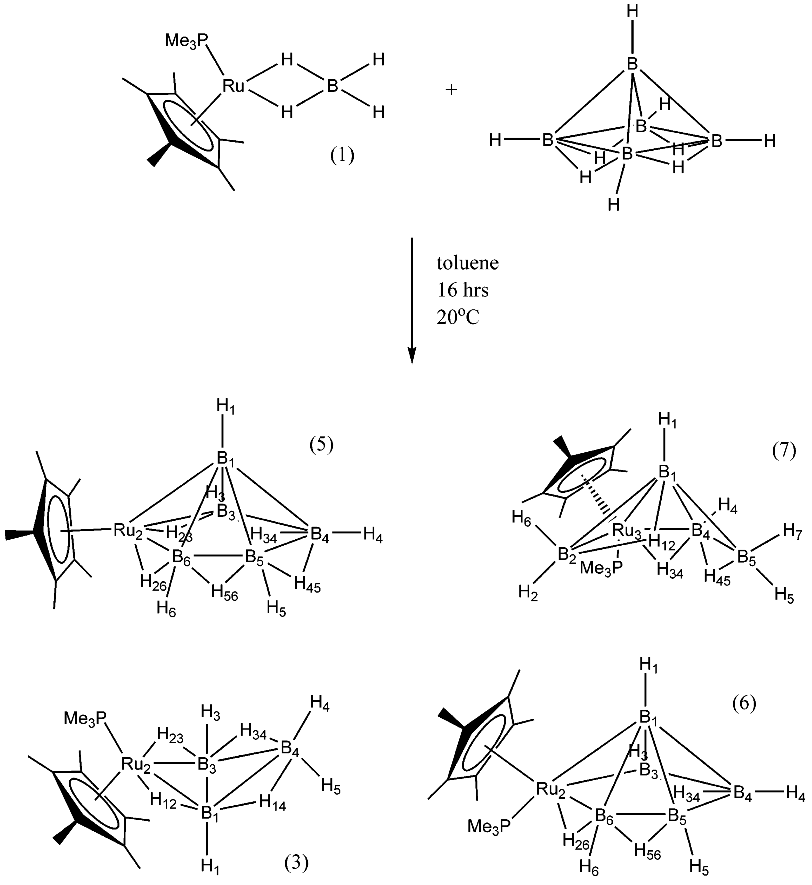
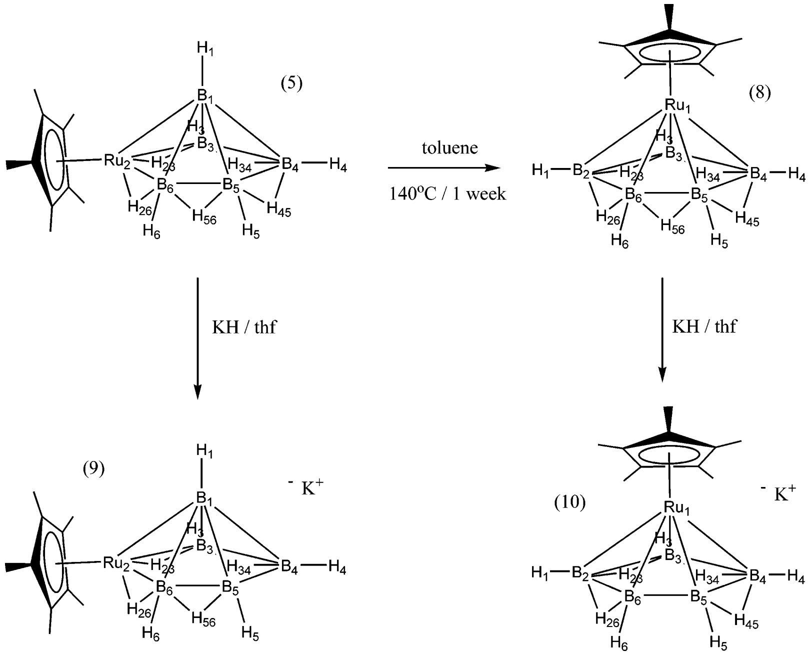
Scheme 2



Scheme 3



the borohydride $[Ru(PMe_3)_3HBH_4]$ reacts with BH_3·thf at 110 °C to give a low yield of *nido*-2-$[Ru(PMe_3)_3B_4H_8]$.[44] This product may also be formed via a 16-electron η^1-borohydride intermediate.

Two reactions of compound **5** are also herein reported. Compound **5** deprotonates cleanly using KH in thf at room temperature to give the ionic product *nido*-2-$[(\eta\text{-}C_5Me_5)RuB_5H_9^-][K^+]$ (**9**) (Scheme 3). From multinuclear NMR spectroscopy it is clear that the unique bridging B−H−B proton furthest from the ruthenium atom has been removed. The cluster now has the same arrangement of skeletal electrons as the previously reported metallaboranes *nido*-2-$[(\eta\text{-}C_6Me_6)RuB_5H_9]$[45] and $[Ru(CO)(PPh_3)_2B_5H_9]$.[5]

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We also investigated the thermolysis of compound **5**. Heating a toluene solution of **5** at 140 °C for 1 week gave a mixture of two compounds, which were separable by fractional crystallization. The first product was isolated in 70% yield and identified as *nido*-1-[(η-C_5Me_5)RuB_5H_{10}] (**8**) by comparison of NMR data first reported by Fehlner's group.[46] They synthesized compound **8** in very low yield by thermolysis of [(η-C_5Me_5)$_2$-$Ru_2B_3H_9$] with 10 equiv of BH_3·thf. The NMR data for **8** also compare well with those of the iron congeners *nido*-1-[(η-C_5R_5)-FeB_5H_{10}] (R = H, Me) (Scheme 3).[32−34] The iron metallaboranes were isolated in low yields by the thermolysis of *nido*-2-[(η-C_5R_5)FeB_5H_{10}]. Thus, switching to ruthenium leads to less decomposition and gives a much higher yield of the apical *nido*-1-metallahexaborane isomer, which is isoelectronic with decamethylruthenocene. Compound **8** deprotonates cleanly at a B−H−B bridge on reaction with KH in thf to form *nido*-1-[(η-C_5Me_5)$RuB_5H_9^-$][K^+] (**10**). The ^{11}B and $^1H\{^{11}B\}$ NMR spectra are consistent with a fluxional molecule in which the four B−H−B bridging protons undergo rapid exchange on the NMR time scale. The neutral molecule *nido*-1-[(η-C_5H_5)-CoB_5H_9] shows a similar fluxional process at room temperature.[47] The ^{11}B NMR spectrum of **10** consists of a doublet at δ = 0.9 ppm. This is very close to the chemical shift of the neutral molecule **8**, indicating that the negative charge is delocalized.

The second product isolated from the thermolysis of **5** has not been fully characterized, but multinuclear NMR spectroscopy data including $^{11}B-^{11}B\{^1H\}$ and $^1H-^1H\{1^1B\}$ COSY studies suggest that the molecule has the empirical formula [(η-C_5Me_5)$_2$$Ru_2B_{10}H_{16}$]. An isomer with this formula has been prepared by Fehlner's group, but the NMR data do not match that of our compound.[48] We have not managed to grow crystals suitable for X-ray diffraction, and we are unable to propose a structure from the NMR data.

Conclusion

We have prepared a number of small monometallic ruthenaboranes containing the {(η-C_5Me_5)Ru} or {(η-C_5Me_5)Ru-(PMe_3)} fragments using small borane precursors. In particular, the borohydride **1** has been shown to undergo cage expansion on reaction with BH_3·thf and to form {RuB_3}, {RuB_4}, and {RuB_5} clusters on reaction with pentaborane(9). We are currently investigating whether other transition metal borohydrides cluster expand on reaction with BH_3·thf.

Experimental Section

All preparations, manipulations, and reactions were carried out under an inert atmosphere of dinitrogen using standard techniques for handling air-sensitive materials (Schlenk line and glovebox). Dinitrogen was purified by passage through a column containing BASF catalyst and 4 Å molecular sieves. Solvents were predried over molecular sieves (4 or 5 Å), distilled from appropriate drying agents, and stored under dinitrogen in Teflon valve ampules. Deuterated solvents were stored over activated molecular sieves or sodium-potassium alloy. BH_3·thf was used as a 1 M solution in thf as supplied by Aldrich Chemical Co. Ltd. Chromatography was carried out on silica gel G (Fluka, type GF 254) under dinitrogen. Reaction mixtures were generally deposited as a "sand" on silica gel and admitted to the top of the column via a tipper tube under a gentle stream of dinitrogen. Solvents used for chromatography (petroleum ether and diethyl ether) were not predried but only flushed with dinitrogen before use. Pentaborane(9) was used from stock as a 0.25−0.4 M solution in toluene. The NMR spectra were obtained using Bruker AM-250 or AM-300 or Varian 300 MHz instruments. ^1H spectra were referenced internally with respect to the residual protiosolvent (C_6D_6, δ 7.10); ^{11}B and ^{31}P spectra were referenced internally relative to the deuterium lock signal using the SR command of standard Bruker software, with respect to the standards 85% $H_3PO_4-D_2O$ (^{31}P) and BF_3-Et_2O (^{11}B). All chemical shifts are quoted in δ (ppm) and coupling constants in hertz (Hz). Elemental analysis was carried out by the analysis department of the Inorganic Chemistry Laboratory, Oxford University.

X-ray Structure Determinations. Data were collected on an Enraf-Nonius CAD4 diffractometer (3° > 2θ < 50°). The structure was solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms were included in calculated positions (C−H 0.96 Å) and refined riding on their attached atom. Hydrogen atoms bonded to boron atoms were located from a difference synthesis and their coordinates and isotropic thermal parameters refined. Crystallographic calculations were carried out using the Oxford "Crystals" package.[49]

Preparation of [(η-C_5Me_5)Ru(PMe_3)BH_4] (1). [(η-C_5Me_5)Ru-(PMe_3)H_3][22] (0.8 g, 2.5 mmol) was dissolved in pentane (10 mL), and BH_3·thf (1.0 M in thf, 2.5 mL, 2.5 mmol) was added dropwise with stirring. The yellow solution immediately became a deep orange-red color. After stirring for 10 min solvent was removed *in vacuo*, and the residue was extracted with pentane (10 mL) and filtered. Cooling to −78 °C overnight gave red crystals of **1**, which were filtered off and dried *in vacuo*. Concentration and cooling of the mother liquor gave two further crops. Total yield: 0.75 g, 90%.

Preparation of [(η-C_5Me_5)Ru(PMe_3)B_2H_7] (2) from [(η-C_5Me_5)Ru(PMe_3)H_3]. [(η-C_5Me_5)Ru(PMe_3)H_3] (0.8 g, 2.5 mmol) was dissolved in pentane (10 mL), and BH_3·thf (1.0 M in thf, 5.0 mL, 5.0 mmol) was added dropwise with stirring. The yellow solution rapidly became deep orange-red. After 1 h the solution had become a less intense orange color. Solvent was removed *in vacuo*, and the residue was extracted with light petroleum (2 × 10 mL) and filtered. The solution was concentrated to about half volume and cooled overnight at −30 °C. Orange crystals of **2** were filtered off and dried in vacuo. Yield: 0.69 g, 80%. Alternatively, addition of 1 equiv of BH_3·thf to **1**, followed by an identical workup, gave **2** in 90% yield.

Preparation of [(η-C_5Me_5)Ru(PMe_3)B_2H_7] (2) from [(η-C_5Me_5)Ru(PMe_3)Cl_2]. $NaBH_4$ (0.6 g, 16.8 mmol) and BH_3·thf (1.0 M in thf, 8.4 mL, 8.4 mmol) slurried in thf (10 mL) was added to a solution of [(η-C_5Me_5)Ru(PMe_3)Cl_2] (1.0 g, 2.6 mmol) in thf (10 mL) and stirred for 4 h at ambient temperature to give an orange solution. Solvent was removed *in vacuo* and the residue extracted with light petroleum (2 × 20 mL). Cooling to −30 °C overnight gave orange crystals of **2**, which were filtered off and dried *in vacuo*. Yield: 0.69 g, 78%.

Thermolysis of [(η-C_5Me_5)Ru(PMe_3)B_2H_7] (2): Preparation of *arachno*-1-[(η-C_5Me_5)Ru(PMe_3)B_3H_8] (4). [(η-C_5Me_5)Ru-(PMe_3)B_2H_7] (0.42 g, 12.3 mmol) was dissolved in toluene (10 mL) and heated in a sealed ampule at 60 °C for 3 days. The original orange solution had by this time become deep red. Volatiles were removed *in vacuo*, and the solid residue was extracted with pentane (10 mL) and filtered. Cooling to −70 °C for several days gave clumps of red crystals, containing compounds **1**, **3**, and **4**. The red crystals were filtered off and washed repeatedly with cold pentane

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(5 × 5 mL) at −70 °C until the washings were pale orange. The mother liquor and washings were combined and shown to be a roughly 2:1 mixture of **1** and **3** by ^{11}B NMR spectroscopy. The remaining red crystals were dissolved in diethyl ether (5 mL), filtered from a little yellow solid, and cooled to −70 °C for 3 days. Pale yellow crystals of *arachno*-1-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_3H_8]$ (**4**) were filtered off, washed with cold diethyl ether, and dried *in vacuo*. Yield: 0.17 g (39% based on ruthenium).

Compound 4: Anal. Calcd (%) for $C_{13}H_{32}B_3Pru$: C, 44.3; H, 9.1. Found: C, 44.6; H 9,7. NMR data, solventbenzene-d_6; ^1H NMR at 300 MHz, ^{31}P NMR at 121.49 MHz, and ^{11}B NMR at 96.25 MHz: ^{11}B −1.9 [M, 2B, B(3,4)], −7.8 [t, 1B, B(2)]; $^{31}P\{^1H\}$ 9.6 [s, PMe_3]; $^1H\{^{11}B\}$ 2.84 8s, 1H, H(3)9, 2.45 [s, 1H, H(2 or 5)], 2.40 [s, 1H, H(5 or 2)], 2.33 [s, 1H, H(4 or 6)], 2.30 [s, 1H, H(6 or 4)], 1.59 [s, 15H, C_5Me_5)], 0.98 [d, 9H, *J*(H−P) 9, PMe_3], −3.34 [s, 1H, H(23)], −4.27 [s, 1H, H(34)], −13.43 [m, 1H, H(12)].

Thermolysis of *arachno*-2-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_3H_8]$ (3). A 10 mg sample of **3** in benzene-d_6 in a sealed NMR tube was heated at 100 °C. The contents were analyzed daily by multinuclear NMR spectroscopy. After 4 days the orange solution had changed to pale yellow, giving 100% conversion to *arachno*-1-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_3H_8]$ (**4**).

Reaction of $[(\eta\text{-}C_5Me_5)Ru(PMe_3)BH_4]$ with B_5H_9. $[(\eta\text{-}C_5Me_5)Ru(PMe_3)BH_4]$ (0.9 g, 2.8 mmol) was stirred with a solution of B_5H_9 in toluene (11 mL, 0.26 M, 2.8 mmol) at room temperature for 16 h. The solution changed color from deep orange-red to yellow-orange. Silica gel (3 g) was added and volatiles were removed *in vacuo*. The sand was chromatographed on silica gel eluting with light petroleum/diethyl ether, 30:1. Three orange bands were collected and recrystallized from pentane at −30 °C to afford orange crystals of *nido*-1-$[(\eta\text{-}C_5Me_5)RuB_5H_{10}]$ (**5**) (15%), *arachno*-1-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_3H_8]$ (**3**) (10%), and *arachno*-3-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_4H_9]$[13] (**7**) (0%). A small fourth band was collected and identified as *arachno*-3-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_5H_8]$ (**6**) (<1%) by multinuclear NMR.

Single crystals of compound **3** suitable for X-ray diffraction were grown from light petroleum at −30 °C.

Compound 3. NMR data, solvent benzene-d_6; ^1H NMR at 300 MHz, ^{31}P NMR at 121.49 MHz, and ^{11}B NMR at 96.25 MHz: ^{11}B −1.9 [t, 1B, *J*(B−H$_t$) 121, B(4)], −34.6 [d, 2B, *J*(B−H$_t$) 133, B(1,3)]; $^{31}P\{^1H\}$ −6.51 [s, PMe_3]; $^1H\{^{11}B\}$ 4.85 [s, 1H, H(4 or 5)], 3.01 [s, 1H, H(5 or 4)], 1.56 [s, 15H, C_5Me_5)], 1.37, [s, 2H, H(1,3)], 0,97 [d, 9H, *J*(H−P) 10, PMe_3)], −0.34 [s, 2H, H(14, 34)], −12.01 [d, 2H, H(12, 23)].

Compound 5. NMR data, solvent benzene-d_6; ^1H NMR at 300 MHz and ^{11}B NMR at 96.25 MHz: ^{11}B 43.5 [t of d, 2B, *J*(B−H$_\mu$) 53, *J*(B−H$_t$) 148, B(4, 5], 5.4 [t of d, 2B, *J*(B−H$_\mu$) 43, *J*(B−H$_t$) 153, B(3,6], −46.7 [d, 1B, *J*(B−H$_t$) 143, B(1)]; $^1H\{^{11}B\}$ 6.49 [s, 2H, H(3,6)], 4.34 [s, 2H, H(4,5)], 1.63 [s, 15H, C_5Me_5], −0.03 [s, 1H, H(1)], −0.63 [s, 2H, H(34,56)], −1.32 [s, 1H, H(45)], −10.75 [s, 2H, H23, 26]. EI mass spectrum: $[M^+] = 301$.

Compound 6. NMR data, solvent benzene-d_6; ^1H NMR at 300 MHz, ^{31}P NMR at 121.49 MHz, and ^{11}B NMR at 96.25 MHz: ^{11}B 65.8 [d, 1B, *J*(B−H$_t$) 137, B(3)], 46.8 [m, 1B, B(6)], 24.4 [m, 2B, B(4,5)], −22.6 [d, 1B, *J*(B−H$_t$) 128, B(1)]; $^{31}P\{^1H\}$ −5.39 [s, PMe_3]; $^1H\{^{11}B\}$ 7.4 [s, 1H, H(3)], 6.55 [s, 1H, H(6)], 5.90 [s, 1H, H(4 or 5)], 5.63 [s, 1H, H(4 or 5)], 1.50 [d, 15H, *J*(H−P) 1.5, C_5Me_5], 0.65 [s, 9H, *J*(H−P) 9, PMe_3], −0.34 [s, 1H, H(1)], −2.15 [s, 2H, H(34, 56)], −12.57 [s, 1H, H(26)].

Thermolysis of *arachno*-3-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_4H_9]$ (7). A solution of *arachno*-3-$[(\eta\text{-}C_5Me_5)Ru(PMe_3)B_4H_9]$[13] in benzene-$d_6$ in a sealed NMR tube was heated at 80 °C overnight, and the contents were analyzed by multinuclear NMR.

Thermolysis of *nido*-2-$[(\eta\text{-}C_5Me_5)RuB_5H_{10}]$ (5). Compound **5** (0.1 g, 0.3 mmol) was dissolved in toluene (10 mL) and heated to 140 °C in a sealed tube for 1 week. The bright orange solution gradually turned yellow-brown. Volatiles were removed *in vacuo*, and the residue was extracted with pentane (3 × 10 mL). The pale orange extracts were filtered, concentrated to 20 mL, and cooled to −78 °C overnight. Pale yellow crystals were filtered off, washed with cold pentane (2 mL), and pumped dry. Yield of *nido*-1-$[(\eta\text{-}C_5Me_5)RuB_5H_{10}]$ (**8**): 0.70 g, 70%. The residue left after pentane extraction was chromatographed on silica eluting with light petroleum ether/diethyl ether, 40:1. Four bands were collected, the first one of which was orange and contained boron by ^{11}B NMR. The band was recrystallized from pentane (5 mL) at −78 °C to give 20 mg of orange crystals of **11**.

Compound 8. NMR data, solvent benzene-d_6; ^1H NMR at 300 MHz and ^{11}B NMR at 96.25 MHz: ^{11}B 0.27 8d, *J*(B−H$_t$) 130, B(2−6)]; $^1H\{^{11}B\}$ 2.63 [s, 5H, H(2−6)], 1.90 [s, 15H, C_5Me_5], −4.01 [s, 5H, H(23−26)].

Deprotonation Experiments. Deprotonations were carried out in benzene-d_6 using KH with added 18-crown-6 or in thf-d_8 with KH. Twenty-milligram samples of **3**, **5**, **7**, and **8** were dissolved in the deuterated solvent, and excess KH was added. Effervescence was observed in all cases except with **3**. The reaction mixtures were filtered into 5 mm NMR tubes and sealed. The samples were examined by multinuclear NMR spectroscopy. Compound **5** deprotonated cleanly to give *nido*-2-$[(\eta\text{-}C_5Me_5)RuB_5H_9^-][K^+]$ (**9**), and compound **6** deprotonated cleanly to give *nido*-1-$[(\eta\text{-}C_5Me_5)RuB_5H_9^-][K^+]$ (**10**). No reaction was observed with compound **3**, and compound **7** gave a mixture of products.

Compound 9. NMR data, solvent thf-d_8; ^1H NMR at 300 MHz and ^{11}B NMR at 96.25 MHz: ^{11}B 45.7 [m, 2B, B(3,6)], 10.9 [m, 2B, B(4,5)], −37.2 [d, 1B *J*(B−H$_t$) 155, B(1)]; $^1H\{^{11}B\}$ 7.18 [s, 2H, H(3,6)], 4.26 [s, 2H, H(4,5)], 2.20 [s, 15H, C_5Me_5], −1.02 [s, 1H, H(1)], −2.17 [s, 2H, H(34, 56), −11.63 [s, 2H, H(23, 26)].

Compound 10. NMR data, solvent thf-d_8; ^1H NMR at 300 MHz and ^{11}B NMR at 96.25 MHz: ^{11}B 0.9 [d, *J*(B−H) 129, B(2−6)]; $^1H\{^{11}B\}$ 2.89 [s, 5H, H(2−6)], 2.37 [s, 15H, C_5Me_5], −4.78 [s, 4H, H23−56 except 26)].

CCDC no. 290786 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +(44) 1223−336-033; or email: deposit@ccdc.cam.ac.uk).

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