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Note

Reactions of small boranes with ruthenium phosphine hydrides: Oligomerisation of monoborane-tetrahydrofuran to a nido-hexaruthenaborane

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Abstract

Reaction of $[Ru(PPh_3)_4H_2]$ with $BH_3 \cdot thf$ at room temperature gives borane oligomerisation with the formation of the 6-vertex metallaborane *nido*-2-$[Ru(PPh_3)_2(H)B_5H_{10}]$ (**1**). This cluster is also formed by reaction of $[Ru(PPh_3)_4H_2]$ with *nido*-B_5H_9. Compound (**1**) is readily deprotonated by KH in thf at the unique basal B–H–B bridge to give *nido*-2-$[Ru(PPh_3)_2(H)B_5H_9^-][K^+]$ (**2**). In contrast to $[Ru(PPh_3)_4H_2]$ reaction of [*cis*-$Ru(PMe_3)_4H_2$] with $BH_3 \cdot thf$ gives initially the known borohydride $[Ru(PMe_3)_3(H)(\eta^2\text{-}BH_4)]$ which reacts with excess $BH_3 \cdot thf$ to give the 5-vertex metallaborane *nido*-2-$[Ru(PMe_3)_3B_4H_8]$ (**3**). Reaction of [*cis*-$Ru(PMe_3)_4H_2$] with *nido*-B_5H_9 also gives (**3**) and *nido*-2-$[Ru(PMe_3)_3B_9H_{13}]$ (**4**). [*cis*-$Ru(PMe_3)_4H_2$] is conveniently prepared in high yield in a one-pot synthesis by the sodium amalgam reduction of $RuCl_3 \cdot 3H_2O$ in thf with excess PMe_3 under dinitrogen.

Keywords: Metallaboranes; Ruthenaboranes; Ruthenium; Phosphine hydrides; Boranes

1. Introduction

We are exploring the metal-mediated oligomerisation of boranes. Previously we have reported the synthesis of $[Mo(\eta\text{-}C_5H_5)_2(H)B_2H_5]$, [*arachno*-2-$Mo(\eta\text{-}C_5H_5)(\eta^5{:}\eta^1\text{-}C_5H_4)B_4H_7$] and [*closo*-1-$Mo(\eta\text{-}C_5H_5)(\eta^2{:}\eta^3\text{-}C_3H_3)C_2B_3H_5$] from $[Mo(\eta\text{-}C_5H_5)_2H_2]$ and $BH_3 \cdot thf$ as well as the synthesis of [*arachno*-2-$W(PMe_3)_3(H)_3B_3H_8$] from $[W(PMe_3)_3H_6]$ [1–3]. In the last 12–13 years Fehlner and co-workers have used the reagent $BH_3 \cdot thf$ to systematically produce a range of metallaboranes, often in good yields, using mainly cyclopentadienyl metal chlorides as precursors [4]. Most of these metallaboranes are *closo* and contain two metal atoms. In addition, they have reported the reaction of $BH_3 \cdot thf$ with some Group 8 transition metal hydrides. For example, $[Fe(\eta\text{-}C_5Me_5)H_2]_2$ reacts with $BH_3 \cdot thf$ to give the monometal cluster *arachno*-1-$[Fe(\eta\text{-}C_5Me_5)B_4H_{11}]$ whilst $[Ru(\eta\text{-}C_5Me_5)H_2]_2$ gives initially the dimetalla-cluster *nido*-1,2-$[\{Ru(\eta\text{-}C_5Me_5)H\}_2B_3H_7]$ [5,6]. This cluster reacts further with $BH_3 \cdot thf$ to give first *nido*-1,2-$[\{Ru(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}H)B_4H_9]$ and then larger dimetallaboranes on heating [7,8]. This paper discusses the reaction of two ruthenium phosphine hydrides with $BH_3 \cdot thf$ and pentaborane(9).

2. Results and discussion

Treatment of a toluene solution of $[Ru(PPh_3)_4H_2]$ with 6 equiv. of $BH_3 \cdot thf$ for 48 h at 20 °C gave an approximately 16% yield of the 6-vertex metallaborane *nido*-2-$[Ru(PPh_3)_2(H)B_5H_{10}]$ (**1**) after column chromatography. Large amounts of $BH_3 \cdot PPh_3$ were also formed and no other ruthenium-containing product could be identified. Interestingly, if the reaction is conducted in pure thf, no

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metallaborane products could be isolated. A ^{1}H NMR spectrum of this reaction mixture shows four resonances attributed to butoxy groups [$CDCl_3$, δ (ppm) = 3.76 (t, 2H), 1.52 (m, 2H), 1.34 (m, 2H), 0.93 (t, 3H)], probably from ring-opening of thf. No butoxy product could be isolated pure by crystallisation and decomposition occurred on a silica gel column.

Compound (**1**) is also obtained in 20% yield from the reaction of two equivalents of pentaborane(9) with [$Ru(PPh_3)_4H_2$] in toluene, after column chromatography. The *hypho*-borane $B_5H_9(PPh_3)_2$ and large amounts of $BH_3 \cdot PPh_3$ were also isolated as well as a second red metallaborane in very low yield. NMR spectroscopic analysis of this second metallaborane indicated that it probably contains nine boron atoms but it is not *nido*-6-[$Ru(PPh_3)_3B_9H_{13}$] which would be expected to have a similar ^{11}B NMR spectrum to that of the known metallaborane *nido*-6-[$Ru(PMe_2Ph)_3B_9H_{13}$] [9].

Compound (**1**) has been characterised by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy and is assigned the structure *nido*-2-[$Ru(PPh_3)_2(H)B_5H_{10}$] (**1**) (Fig. 1). Elemental analysis was hampered by the co-crystallisation of $BH_3 \cdot PPh_3$ with (**1**). Further, crystals of (**1**) were twinned making X-ray diffraction analysis poor. However, the NMR data clearly show the pattern of a *nido*-2-metallahexaborane.

The ^{11}B NMR spectrum of (**1**) shows three resonances in a ratio 2:2:1. Terminal B–H coupling could only be resolved for the high field resonance B(1) at $\delta = -49.2$ ppm. That the molecule does not have a plane of symmetry is shown by the $^{11}B\{^1H\}$ NMR spectrum which shows four resonances in a 2:1:1:1 ratio. It was not possible to resolve B(4) from B(5), but the slightly less broad B(3) and B(6) resonances were resolved as separate singlets.

The lack of symmetry in the molecule is further shown in the $^1H\{^{11}B\}$ NMR spectrum. Ten inequivalent resonances (all intensity 1) are sharpened by ^{11}B broad band decoupling and are assigned to the 10 hydrogen atoms of the borane cluster fragment. Interestingly, only one of the equivalent B–H–B bridging protons H(23) and H(26) shows coupling to ^{31}P in the PPh_3 ligands. The metal hydride H(2) is a triplet in the ^{1}H NMR spectrum and does not sharpen with additional ^{11}B decoupling. The complex resonances at $\delta = 7.5$–6.8 ppm are assigned to two inequivalent PPh_3 ligands on the ruthenium centre. This was confirmed in the $^{31}P\{^1H\}$ NMR spectrum which showed two mutually coupled doublets at similar chemical shifts, $\delta = 54.50$ and 57.99 ppm.

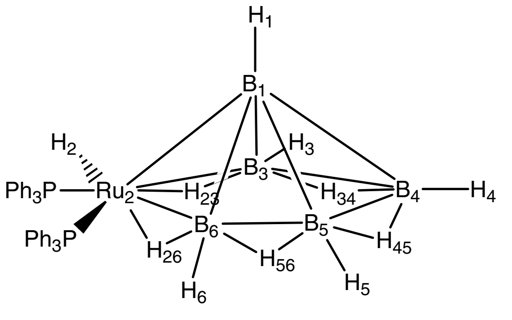

Fig. 1. Proposed structure for *nido*-2-[$Ru(PPh_3)_2(H)B_5H_{10}$] (**1**).

The 10 skeletal protons of the borane fragment in (**1**) were assigned with the aid of selective $^1H\{^{11}B\}$ NMR decoupling experiments. Decoupling B(3) and B(6) sharpened H(3), H(6), H(23) and H(26), decoupling B(4) and B(5) sharpened H(4), H(5), (H45) and H(56), and decoupling B(1) sharpened H(1) only.

Compound (**1**) is isoelectronic with *nido*-2-[(η-C_5Me_5)-RuB_5H_{10}] [10] which unlike (**1**) does not have a plane of symmetry. Compound (**1**) is also isoelectronic with *nido*-2-[(η-C_6Me_6)RuB_5H_9] [26] which does have a plane of symmetry. *nido*-2-Metallahexaboranes are known for a number of transition metals. They contain either a {B_5H_{10}} fragment as in (**1**), or a {B_5H_9} fragment in which the two basal boron atoms furthest from the metal are not bridged by a proton. All of these metallaboranes are made from pentaborane(9) or [$B_5H_8^-$] anion precursor and usually have a plane of symmetry [11–13]. Another ruthenaborane example is *nido*-2-[$Ru(CO)(PPh_3)_2B_5H_9$] which is thermally unstable at room temperature decomposing to *nido*-2-[$Ru(CO)(PPh_3)_2B_4H_8$] [24]. In contrast, compound (**1**) appears to be stable both as a solid and in solution. Solutions of (**1**) are however air-sensitive.

What is remarkable with compound (**1**) is that it is formed from a monoborane precursor, $BH_3 \cdot$ thf. Formation from pentaborane(9) would seem a more rational synthesis, and does work, but for five boron atoms to assemble on a monometallic fragment at ambient temperature is rare. Oligomerisation of $BH_3 \cdot$ thf to 3-boron and 4-boron fragments at room temperature has been observed before. Some examples were given in the introduction. In addition, [(η-C_5H_5)$Fe(PMe_3)_2H$] reacts with 2 equiv. of $BH_3 \cdot$ thf at 0 °C to give a low yield of *arachno*-2-[(η-C_5H_5)$Fe(PMe_3)B_3H_8$] [14]. Fehlner and co-workers have also reported several other reactions of $BH_3 \cdot$ thf with transition metal hydrides. [(η-C_5Me_5)ReH_6] reacts with $BH_3 \cdot$ thf to give *arachno*-2-[$Re(\eta$-$C_5Me_5)H_3B_3H_8$] [15] and [$Ir(\eta$-$C_5Me_5)H_4$] reacts with $BH_3 \cdot$ thf to give *arachno*-1-[$Ir(\eta$-$C_5Me_5)HB_4H_9$] [16]. In addition, Westcott, Marder, Baker, Lin and co-workers have shown that the rhodium phosphine complex [$Rh(\eta$-$H)(DiPPE)]_2$ (DiPPE = 1,2-bis(diisopropylphosphino)ethane] reacts with $BH_3 \cdot Me_2S$ to give a low yield of the dimetallacluster *nido*-[$(RhH(DiPPE))_2$-B_3H_7] [17]. The mechanisms for these metal-mediated borane oligomerisations are not known but the range of structures that can be formed demonstrates that oligomerisation varies from metal to metal and type of ligand environment.

Compound (**1**) readily deprotonates at room temperature on treatment with KH in thf to give *nido*-2-[$Ru(PPh_3)_2(H)B_5H_9^-$][K^+] (**2**) in quantitative yield. The compound which is very air-sensitive was not isolated as a solid as the point of the experiment was simply to demonstrate which hydrogen is lost on deprotonation. The

$^1H\{^{11}B\}$ NMR shows that the molecule is unsymmetrical and that the B–H–B bridging proton furthest from the metal atom has been lost (Fig. 2). The chemical shifts in the ^{11}B NMR spectrum of ionic compound (**2**) [C_6D_6, δ (ppm) = 34.3 (2B), 15.1 (2B), −38.8 (1B)] compare fairly well with that of the isoelectronic metallaborane *nido*-2-[Ru(CO)(PPh_3)$_2$$B_5H_9$] [$CDCl_3$, δ (ppm) = 33.3 (1B), 31.5 (1B), ca. 20 (1B), ca. 19 (1B), −33.4 (1B)] [24].

Having shown that [Ru(PPh_3)$_4$$H_2$] reacts with $BH_3 \cdot$ thf and pentaborane(9) to give the same *nido*-metallahexaborane it was interesting to compare the reactivity of a more electron-rich ruthenium complex such as *cis*-[Ru(PMe_3)$_4$$H_2$] which has more strongly σ-donating phosphines. *cis*-[Ru(PMe_3)$_4$$H_2$] is reported to be formed by hydrogenation in methanol of [Ru(PMe_3)$_3$H(BH_4)] or by reduction of [$Ru_2(O_2CMe)_4Cl$] with sodium amalgam in thf under hydrogen (3 atm) [18,19]. We wondered if a more direct route from $RuCl_3 \cdot 3H_2O$ might give a ruthenium phosphine hydride in one step since it is known that reaction of $FeCl_2$, PMe_3 and sodium amalgam in thf gives a good yield of [Fe(PMe_3)$_4$(η^2-CH_2PMe_2)H] [21]. Further, [Fe(PMe_3)$_4$(η^2-CH_2PMe_2)H] reacts with dihydrogen to give *cis*-[Fe(PMe_3)$_4$$H_2$]. First we tried treatment of $RuCl_3 \cdot 3H_2O$ with 5 equiv. of PMe_3 and excess sodium amalgam in thf under a dinitrogen atmosphere. Surprisingly, we reached the target compound in one step; *cis*-[Ru(PMe_3)$_4$$H_2$] was formed in 80% yield after extraction and crystallisation from pentane. There was no indication of phosphine metallation to form [Ru(PMe_3)$_4$(η^2-CH_2PMe_2)H] [20] by ^1H NMR. This compound can be formed by treating [Ru(PMe_3)$_4$$Cl_2$] with sodium amalgam in the non-polar solvent benzene. The use of thf as a solvent appears to preclude the formation of the metallated compound indicating that the ruthenium hydride ligands in *cis*-[Ru(PMe_3)$_4$$H_2$] are probably derived from the thf solvent.

Treatment of *cis*-[Ru(PMe_3)$_4$$H_2$] with a little over 2 equiv. of $BH_3 \cdot$ thf gave a good yield of the known borohydride [Ru(PMe_3)$_3$H(BH_4)] [18,22] and only a trace of other metal–boron species. Treatment of [Ru(PMe_3)$_3$H(BH_4)] with a further 4 equiv. of $BH_3 \cdot$ thf gave no reaction at room temperature over several days as judged by ^1H NMR spectroscopy. However, after heating this thf solution to 110 °C in a sealed tube for 1 day we were able to isolate a low yield of *nido*-2-[Ru(PMe_3)$_3$$B_4H_8$] (**3**) (Fig. 3) by column chromatography. A second product containing butoxy groups and no trimethylphosphine was also identified but not fully characterised [C_6D_6, δ (ppm) = 3.76 (t, 2H), 1.37 (m, 2H), 1.19 (m, 2H), 0.7 (t, 3H)]. This second product decomposes on a silica gel column. It seems that oligomerisation of borane on the ruthenium atom competes with a process involving complete loss of the PMe_3 ligands and ring-opening of the thf. In contrast, reaction of [Fe(PMe_3)$_3$H(μ^2-CH_2PMe_2)] with excess $BH_3 \cdot$ thf gave complete decomposition and no metallaborane products could be isolated.

Compound (**3**) crystallises from pentane as air-stable, pale brown crystals that decompose in solution on exposure to air. Elemental analysis on (**3**) was 3% high for carbon and correct for hydrogen. Compound (**3**) exhibits ^{11}B, ^1H and ^{31}P NMR spectra very similar to the iron congener *nido*-2-[Fe(PMe_3)$_3$$B_4H_8$] [23] and *nido*-2-[Ru($PPh_3$)$_2(CO)B_4H_8$] [24] and this strongly suggests the proposed structure. For example the chemical shifts in the ^{11}B NMR spectrum of (**3**) [C_6D_6, δ (ppm) = 1.9 (1B), −10.1 (2B), −33.9 (1B)] compare well with that of *nido*-2-[Fe(PMe_3)$_3$$B_4H_8$] [$C_6D_6$, δ (ppm) = 0.3 (1B), −11.4 (2B), −32.6 (1B)]. Assignments were also made using selective $^1H\{^{11}B\}$ NMR decoupling experiments.

The ^{11}B NMR spectrum of (**3**) consists of three doublets in the intensity ratio 1:2:1 assigned to B(4), B(3 and 5) and B(1) showing coupling to terminal hydrogens H(4), H(3 and 5) and H(1) respectively. The broad band $^1H\{^{11}B\}$ NMR spectrum of (**3**) consists of a triplet and doublet due to the PMe_3 ligands and five broader resonances in the ratio 1:2:1:2:2 assigned to the protons of the borane fragment. The greater deshielding effect of the ruthenium fragment compared to that of the iron congener is reflected, for instance, in the higher chemical shifts of the M–H–B bridging protons in the spectrum for (**3**), $\delta = -11.07$ ppm (compare $\delta = -17.39$ ppm for *nido*-2-[Fe(PMe_3)$_3$$B_4H_8$]).

Compound (**3**) was also formed in 10% yield by the reaction of a toluene solution of *cis*-[Ru(PMe_3)$_4$$H_2$] with 2 equiv. of pentaborane(9) followed by column chromatography. A second compound *nido*-2-[Ru(PMe_3)$_3$$B_9H_{13}$] (**4**) was isolated in 40% yield (Fig. 4).

Compound (**4**) crystallises from toluene as red air-stable microcrystals. It has been characterised by elemental analysis and multi-nuclear NMR spectroscopy. The structure is assigned as *nido*-2-[Ru(PMe_3)$_3$$B_9H_{13}$] from selective $^1H\{^{11}B\}$ NMR experiments and on the basis of its very

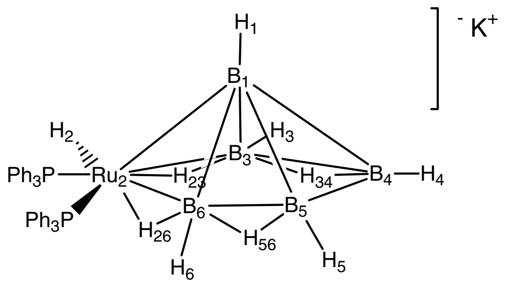

Fig. 2. Deprotonation of (**1**) to form *nido*-2-[Ru(PPh_3)$_2$(H)$B_5H_9^-$][K^+] (**2**).

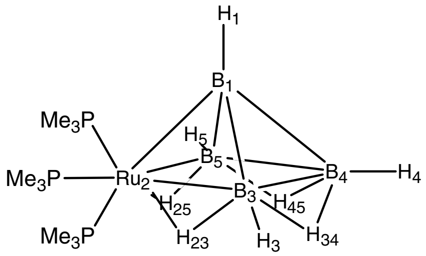

Fig. 3. Proposed structure for *nido*-2-[Ru(PMe_3)$_3$$B_4H_8$] (**3**).

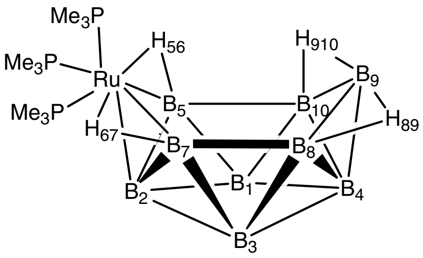

Fig. 4. Proposed structure for *nido*-2-[Ru(PMe$_3$)$_3$B$_9$H$_{13}$] (**4**).

similar NMR spectra to the previously reported isostructural cluster *nido*-2-[Ru(PMe$_2$Ph)$_3$B$_9$H$_{13}$] formed from the reaction of [Ru(PMe$_2$Ph)$_3$Cl$_3$] with [B$_9$H$_{14}^-$] in dichloromethane [9]. Substitution by a metal in all four possible positions in a *nido*-decaborane cluster is known but the 6-position seems to be the most favoured.

The formation of a ruthenadecaborane cluster may occur via deprotonation of pentaborane(9) by [*cis*-Ru(PMe$_3$)$_4$H$_2$] to form [B$_5$H$_8^-$] and [Ru(PMe$_3$)$_4$H$_3^+$] [25] (or the 16e$^-$ species [Ru(PMe$_3$)$_3$H$_3^+$] and PMe$_3$). The borane anion [B$_5$H$_8^-$] is known to decompose above −40 °C to give [B$_9$H$_{14}^-$]. This ion could then react with [Ru(PMe$_3$)$_3$H$_3^+$] with loss of H$_2$ to form compound (**4**).

In contrast to *cis*-[Ru(PMe$_3$)$_4$H$_2$] the reaction of [Fe(PMe$_3$)$_3$H(μ^2-CH$_2$PMe$_2$)] with pentaborane(9) does not give a metalladecaborane but *nido*-2-[Fe(PMe$_3$)$_3$B$_4$H$_8$] and the face-capped *nido* cluster [2,3-{Fe(PMe$_3$)$_2$}$_2$(μ-H)B$_4$H$_9$] [23].

In conclusion we have demonstrated two metal-mediated processes for the oligomerisation of a monoborane reagent, BH$_3$ · thf. Reaction of [Ru(PPh$_3$)$_4$H$_2$] with BH$_3$ · thf at room temperature gives the 6-vertex metallaborane *nido*-2-[Ru(PPh$_3$)$_2$(H)B$_5$H$_{10}$] (**1**) and reaction of [*cis*-Ru(PMe$_3$)$_4$H$_2$] with BH$_3$ · thf gives ultimately the 5-vertex metallaborane *nido*-2-[Ru(PMe$_3$)$_3$B$_4$H$_8$] (**3**). We are continuing to explore metal-mediated oligomerisations of BH$_3$ · thf with other transition metal phosphine precursors.

3. Experimental

3.1. General methods and instrumentation

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 glove-box). Dinitrogen was purified by passage through a column containing BASF catalyst and 4A molecular sieves. Solvents were pre-dried over molecular sieves (4 or 5A), distilled from appropriate drying agents and stored under dinitrogen in Teflon valve ampoules. Deuterated solvents were stored over activated molecular sieves or sodium–potassium alloy. BH$_3$ · thf was used 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 pre-dried but only flushed with dinitrogen before use. Pentaborane(9) was used from stock as a 0.25–0.4 M solution in toluene. Pentaborane(9)-toluene stock solutions were prepared by condensing the pentaborane(9) onto frozen toluene at −196 °C. The solutions were then brought to room temperature, transferred to schlenks and kept at −30 °C under dinitrogen [27]. [Ru(PPh$_3$)$_4$H$_2$] was prepared according to the literature method [28]. The NMR spectra were obtained using Bruker AM-250 or AM-300 or Varian 300 MHz instruments. ^{1}H spectra were referenced internally with respect to the residual protiosolvent (C$_6$D$_6$, δ 7.16); ^{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$_3$PO$_4$–D$_2$O (^{31}P) and BF$_3$–Et$_2$O (^{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.

3.1.1. Preparation of (*1*) using B$_5$H$_9$

[Ru(PPh$_3$)$_4$H$_2$] (4 g, 3.5 mmol) was slurried in toluene (50 ml) and a solution of pentaborane(9) in toluene (26.7 ml, 0.26 M, 7.0 mol) added with stirring. After 1 h there was no solid remaining and the solution had turned orange-brown. After stirring for 16 h, silica gel (10 g) was added and volatiles removed in vacuo. The resulting sand was chromatographed on silica eluting initially with petroleum ether:diethyl ether 4:1. The first colourless fractions were collected and pumped dry to give colourless crystals of BH$_3$ · PPh$_3$ and *hypho*-B$_5$H$_9$(PPh$_3$)$_2$ [29] as shown by ^{11}B NMR spectroscopy. Elution with petroleum ether:diethyl ether 2:1 gave an orange band. Solvent was removed in vacuo and the orange residue dissolved in diethyl ether (50 ml). Cooling for several days at −30 °C gave colourless crystals of BH$_3$ · PPh$_3$, which were filtered off. Concentration and cooling of the mother liquor to −78 °C overnight gave air-sensitive orange-red crystals of (**1**) co-crystallised with some BH$_3$ · PPh$_3$. Yield approx. 0.48 g, 20%. Large red-orange clumps of (**1**) can be obtained by dissolving the compound in dichloromethane and layering with pentane. Some BH$_3$ · PPh$_3$ is still present though by NMR spectroscopy.

NMR data for compound (**1**) (benzene-d_6): ^{11}B [J(^{11}B–^{1}H)] δ 37.7 [overlapping br m, 2B, B(3) and B(6)], 2.8 [br d, 1B, B(4) or B(5)], 5.98 [br d, 1B, B(4) or B(5)], −49.2 [d, 1B, (128), B(1)]. ^{1}H{^{11}B} δ 7.5–6.8 [m, 30H, 2PPh$_3$], 6.80 [s, 1H, H(3) or H(6)], 5.88 [s, 1H, H(6) or H(3)], 4.07 [s, 1H, H(4) or H(5)], 3.99 [s, 1H, H(4) or H(5)], 0.80 [s, 1H, H(34) or H(56)], 0.25 [s, 1H, H(34) or H(56)], −1.12 [s, 1H, H(1)], −1.26 [s, 1H, H(45)], −5.13 [s, 1H, H(23) or H(26)], −9.69 [t, 1H, H(2)], 9.80 [d of d, 1H J(H-P) 34, J(H-P) 3, H(23) or H(26)]. ^{31}P{^{1}H} δ = 54.50 [d, 1P, J(P–P) 31, PPh$_3$], 57.99 [d, 1P, J(P–P) 31, PPh$_3$].

3.1.2. Preparation of (1) using $BH_3 \cdot thf$

$[Ru(PPh_3)_4H_2]$ (2.0 g, 1.71 mmol) was dissolved in toluene (30 ml) and $BH_3 \cdot thf$ (1.0 M, 10.2 ml, 10.2 mmol) added with stirring. The solution immediately turned orange and was left stirring for 48 h at ambient temperature after which time the solution was orange-brown. Volatiles were removed in vacuo and the residue extracted with diethyl ether (4 × 60 ml). The orange extracts were filtered, silica gel (5 g) added and the solvent removed in vacuo. The resulting sand was chromatographed on silica eluting with petroleum ether:diethyl ether 4:1. An orange band was eluted and pumped dry to give a 1:2 mixture of colourless crystals of $BH_3 \cdot PPh_3$ and orange-red crystals of (**1**) as observed by NMR spectroscopy. Total yield of (**1**) ca. 0.19 g, 16%.

3.1.3. Preparation of nido-2-$[Ru(PPh_3)_2(H)B_5H_9^-][K^+]$ (2)

A ca. 30 mg sample of (**1**) was dissolved in thf-d_8 and treated with excess KH. Effervescence occurred and a yellow-orange solution resulted. After 10 min the contents were filtered into an NMR tube, sealed under vacuum and characterised by multi-nuclear NMR spectroscopy as compound (**2**).

NMR data for compound (**2**) (thf-d_8): ^{11}B [$J(^{11}B–^1H)$] δ 34.3 [br m, 2B, B(3) and B(6)], 15.1 [br m, 2B, B(4) and B(5)], −38.8 [d, 1B, (128), B(1)]. $^1H\{^{11}B\}$ δ 7.3–6.9 [m, 30H, $2PPh_3$], 6.29 [s, 1H, H(3) or H(6)], 5.80 [s, 1H, H(6) or H(3)], 3.89 [s, 1H, H(4) or H(5)], 3.87 [s, 1H, H(4) or H(5)], −2.19 [s, 1H, H(1)], −2.38 [s, 1H, H(34) or H(56)], −2.72 [s, 1H, H(34) or H(56)], −7.71 [s, 1H, H(23) or H(26)], −10.58 [br s, 1H, H(2)] −10.69 [s, 1H, H(26) or H(23)].

3.1.4. Preparation of [cis-$Ru(PMe_3)_4H_2$]

$RuCl_3 \cdot 3H_2O$ (1.0 g, ca. 3.8 mmol) and PMe_3 (1.5 g, 20 mmol) were dissolved in thf (30 ml). Excess sodium amalgam (0.4 g Na as a 1% solution in Hg, 18 mmol) was added and the solution vigorously stirred for 3 h. After 1 h the solution was green-brown and a dark precipitate had formed. Solvent was removed in vacuo and the residue extracted with pentane (3 × 40 ml). The orange extracts were filtered through a frit and concentrated to 30 ml. Cooling to −478 °C overnight gave yellow-orange crystals which were filtered off, washed with cold pentane (5 ml) and pumped dry. Yield of [*cis*-$Ru(PMe_3)_4H_2$] 1.25 g, 80%.

3.1.5. Reaction of [cis-$Ru(PMe_3)_4H_2$] with $BH_3 \cdot thf$: preparation of $[Ru(PMe_3)_3H(BH_4)]$ (3)

[*cis*-$Ru(PMe_3)_4H_2$] (0.15 g, 0.37 mmol) was dissolved in thf (5 ml) and treated with $BH_3 \cdot thf$ (0.94 ml, 1.0 M, 0.94 mmol) with stirring. The orange solution immediately lightened to orange-yellow. Stirring was continued for 18 h after which some green-yellow precipitate had formed in the orange-yellow solution. Volatiles were removed in vacuo until all the $BH_3 \cdot PMe_3$ crystals had sublimed out of the flask. The residue was extracted with pentane (10 ml) and concentrated to 2 ml. Yellow crystals began to deposit. The solution was left at −70 °C overnight after which yellow crystals of (**3**) were filtered off, washed with cold pentane and dried. Yield: 0.085 g, 68%.

3.1.6. Reaction of $[Ru(PMe_3)_3H(BH_4)]$ with $BH_3 \cdot thf$

$[Ru(PMe_3)_3H(BH_4)]$ (85 mg, 0.247 mmol), $BH_3 \cdot thf$ (2 ml, 1.0 M, 2 mmol) and thf (5 ml) were heated with stirring at 110 °C for 16 h in a sealed ampoule. Volatiles were removed and the solution extracted with toluene and filtered. Solvent was removed in vacuo to leave a brown solid. The solid was redissolved in diethyl ether and silica gel added. Volatiles were again removed and the sand chromatographed on a silica gel column eluting with petroleum ether:diethyl ether 5:1. A pale brown band was collected. Volatiles were removed in vacuo to leave a pale brown solid (**3**). Yield: 8 mg, 9%.

3.1.7. Reaction of [cis-$Ru(PMe_3)_4H_2$] with pentaborane (9)

[*cis*-$Ru(PMe_3)_4H_2$] (1.0 g, 2.5 mmol) was dissolved in toluene (10 ml) and treated with a solution of pentaborane(9) in toluene (0.25 M, 17 ml, 4.2 mmol) and stirred for 18 h at ambient temperature. The yellow-orange solution darkened to a deep orange-red. Silica gel (3 g) was added and volatiles removed in vacuo. The resulting sand was chromatographed on silica eluting with petroleum ether:diethyl ether 9:1. A pale yellow band eluted followed by orange and red bands. The orange second band was collected and the third red band was eluted with petroleum ether:diethyl ether 2:3 and also collected. The solvent containing the first band was removed in vacuo and the residue recrystallised from petroleum ether at −78 °C to give pale brown crystals of compound (**3**). Yield 90 mg, 10% based on ruthenium. The second band was pumped dry to give only <2 mg of impure solid which we were unable to characterise by multi-nuclear NMR. The third band was pumped dry and recrystallised from toluene at −78 °C to give red crystals of compound (**4**). Yield: 0.43 g, 40% based on ruthenium.

Compound (3). NMR data (benzene-d_6): ^{11}B [$J(^{11}B–^1H)$] δ 1.9 [d, 1B, (143) B(4)], −10.1 [d, 2B, (128) B(3) and B(5)], −33.9 [d, 1B, (134) B(1)]; $^1H\{^{11}B\}$ δ 4.60 [s, 1H, H(4)], 2.95 [s, 2H, H(3) and H(5)], 1.17 [v tr, 18H, $2PMe_3$], 1.09 [d, 9H, J(H–P) 7, PMe_3], 0.89 [s, 1H, H(1)], −1.76 [s, 2H, H(34) and (H(45)], −11.07 [d, 2H, J(H–P) 15H(23) and H(25)]; $^{31}P\{^1H\}$ δ 1.66 [d, 2P, J(P–P) 30, PMe_3], −13.12 [br s, 1P, PMe_3].

Compound (4). Elemental analysis (%): $C_9H_{40}B_9P_3Ru$, Found: C, 25.4; H, 9.4. Calcd.: C, 24.6; H, 9.2.

NMR data (benzene-d_6): ^{11}B [$J(^{11}B–^1H)$] δ 11.6 [br d, 2B, B(5) and B(7)], 10.1 [d, 2B, (126), B(1) and B(3)], 1.6 [br d, 1B, B(9)], −0.40 [d, 2B, (125), B(8) and B(10)], −24.4 [d, 1B, (137) B(2)], −32.8 [d, 1B, (151), B(4)]; $^1H\{^{11}B\}$ δ 4.02 [s, 2H, H(5) and H(7)], 3.42 [s, 2H, H(1) and H(3)], 2.96 [s, 1H, H(9)], 2.81 [s, 2H, H(8) and

H(10)], 1.63 [virt. t, 18H, $2PMe_3$], 1.24 [m, 9H, PMe_3], 0.91 [s, 1H, H(4)], −0.20 [s, 1H, H(2)], −3.39 [s, 2H, H(89) and H(910)], −10.80 [s, 2H, H(56) and H(67)]. $^{31}P\{^1H\}$ δ 1.59 [br s, $3PMe_3$].

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