

Phosphine–Boranes as Bidentate Ligands: Formation of
 $[8,8-\eta^2-\{\eta^2-(\text{BH}_3)\cdot\text{dppm}\}-\text{nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ and
 $[9,9-\eta^2-\{\eta^2-(\text{BH}_3)\cdot\text{dppm}\}-\text{nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$ from
 $[8,8-(\eta^2\text{-dppm})-8-(\eta^1\text{-dppm})-\text{nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ and
 $[9,9-(\eta^2\text{-dppm})-9-(\eta^1\text{-dppm})-\text{nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$, Respectively

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The two clusters $[8,8-(\eta^2\text{-dppm})-8-(\eta^1\text{-dppm})-\text{nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**1**) and $[9,9-(\eta^2\text{-dppm})-9-(\eta^1\text{-dppm})-\text{nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$ (**2**) (dppm = $\text{PPh}_2\text{CH}_2\text{PPh}_2$), both of which contain pendant PPh_2 groups, react with $\text{BH}_3\cdot\text{thf}$ to afford the species $[8,8-\eta^2-\{\eta^2-(\text{BH}_3)\cdot\text{dppm}\}-\text{nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**3**) and $[9,9-\eta^2-\{\eta^2-(\text{BH}_3)\cdot\text{dppm}\}-\text{nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$ (**4**), respectively. These two species are very similar in that they both contain the bidentate ligand $[(\text{BH}_3)\cdot\text{dppm}]$, which coordinates to the Rh center via a PPh_2 group and also via a $\eta^2\text{-BH}_3$ group. Thus, the B atom in the BH_3 group is four-coordinate, bonded to Rh by two bridging hydrogen atoms, to a terminal H atom, and to a PPh_2 group. At room temperature, the BH_3 group is fluxional; the two bridging H atoms and the terminal H atom are equivalent on the NMR time scale. The motion is arrested at low temperature with $\Delta G^\ddagger = \text{ca. } 37$ and 42 kJ mol^{-1} , respectively, for **3** and **4**. Both species are characterized completely by NMR and mass spectral measurements as well as by elemental analysis and single-crystal structure determinations.

Introduction

The activation of C–H bonds has attracted interest and has seen much success in recent times, but the idea of the activation of B–H bonds is quite new.¹ Perhaps the best-documented example of the latter is the photolysis of $\text{Cp}^*\text{W}(\text{CO})_3\text{CH}_3$ in the presence of $\text{H}_3\text{B}\cdot\text{PMe}_3$ to afford $\text{Cp}^*\text{W}(\text{CO})_3\text{-BH}_2\cdot\text{PMe}_3$, along with the elimination of CH_4 , presumably via an oxidative addition or a concerted methane elimination process.² Such activation is likely to involve a B–H–metal linkage either as a transition state or as an intermediate. The B–H–metal bridge is ubiquitous in organometallic chemistry involving boranes,³ but interactions of this nature are commonly found when the borane ligands are anionic

species, for example, $\text{Cu}(\text{PPh}_2\text{Me})_3\text{BH}_4$ and $[\text{BH}_4\text{Cr}(\text{CO})_4]^-$ in which a $\text{BH}_3\cdot\text{H}^-$ adduct coordinates to the metal moiety through a single B–H–Cu bond⁴ or two B–H–Cr bonds,⁵ respectively. Compounds in which a neutral borane adduct coordinates to a metal center are less common, although there is a growing list of examples. Thus, following an initial discovery by Kodama et al.,⁶ there are now several examples in which the neutral species $1,2\text{-(PMe}_3)_2\cdot\text{B}_2\text{H}_4$ acts as a bidentate chelating ligand to the moieties ZnCl_2 ,⁶ CuI ,⁶ Cu^+ ,⁷ $\text{Ni}(\text{CO})_2$,⁸ and $\text{M}(\text{CO})_4$,^{9,10} ($\text{M} = \text{Cr, Mo, W}$) (**I**). Another system involves a diborane(4)–bidentate phosphine complex

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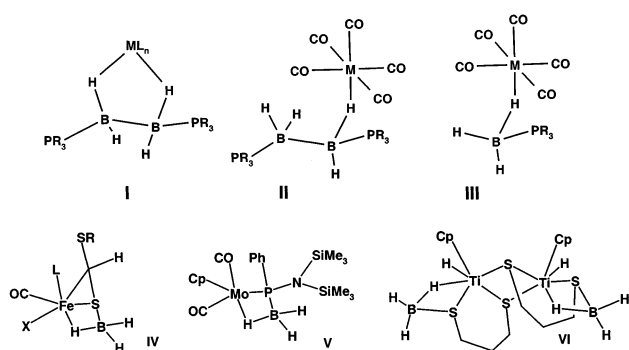
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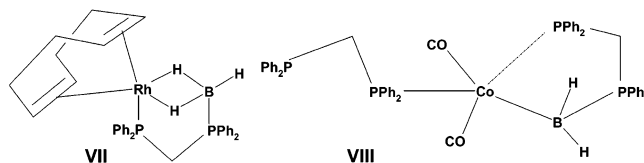
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such that the diborane is part of a cyclic system and utilizes all four H atoms in coordination.¹¹ Related are the chromium and tungsten pentacarbonyl systems wherein $1,2-(\text{PMe}_3)_2 \cdot \text{B}_2\text{H}_4$ ⁹ or $\text{BH}_3 \cdot \text{L}^{11,12}$ ($\text{L} = \text{PMe}_3, \text{PPh}_3, \text{or NMe}_3$) coordinates through a single B–H–metal bond, as seen in structures **II** and **III**, respectively. There is now a gallium analogue of **III** which involves a quinuclidine–GaH₃ moiety coordinating $\text{W}(\text{CO})_5$ through a Ga–H–W linkage.¹³ Additional examples exist in which a ligated metal moiety complexes to a monoborane adduct, via a M–H–B interaction, which is also coordinated to the metal atom through the donor atom bonded to the borane.^{14–18} Examples of these types of compounds are $[\text{Fe}\{\eta^3\text{-HBH}_2\text{SCH}(\text{SR}')(\text{CO})(\text{PR}_3)\}]$,^{14,15} $[\text{CpMo}(\text{CO})_2\text{-}\{\text{P}(\text{BH}_3)(\text{Ph})\{\text{N}-(\text{SiMe}_3)_2\}\}]$,¹⁶ $[\text{CpTiH}(\text{BH}_3\text{SCH}_2\text{CH}_2\text{S})_2]$ ¹⁷ (**IV–VI**, respectively), and $[\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{Ti}(\text{BH}_4)_2]_2$, a *N,N'*-ethylenebis(salicylideneiminato)borane complex in which the ligand coordinates to Ti(II) through N and a BH linkage.¹⁸



Our interest in this area stems from attempts to employ bidentate ligands involving borane–phosphine complexes such as $[\text{dppm} \cdot \text{BH}_3]$ ($\text{dppm} = \text{PPh}_2\text{CH}_2\text{PPh}_2$). One of our approaches has been to prepare metal-ligated dppm species and to coordinate BH_3 to the pendant PPh_2 group in $[\{\text{P}(\text{Ph})_2\}_2(\text{CO})\text{OsB}_4\text{H}_7\}(\text{BH}_2 \cdot \text{dppm})]$.²⁰ Our efforts to convert a metal-ligated $\text{dppm} \cdot \text{BH}_3$ moiety into species in which the ligand served as a bidentate one, involving the PPh_2 and the BH_3 as the donor groups, were

not completely successful, but a recent report of the preparation of $[(\text{COD})\text{Rh}\{\eta^2\text{-}(\text{BH}_3)\text{Ph}_2\text{PCH}_2\text{PPh}_2\}][\text{PF}_6]$ by Weller et al.²¹ (see **VII**) demonstrates that this may be accomplished. Indeed there are other examples of dppm–borane complexes of metals as illustrated in structure **VIII**,²²



but these are not quite analogous to the systems in which we are interested. The approach we describe herein is to use the pendant phosphines in $[8,8-(\eta^2\text{-dppm})\text{-}8-(\eta^1\text{-dppm})\text{-}nido\text{-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**1**)²³ and $[9,9-(\eta^2\text{-dppm})\text{-}9-(\eta^1\text{-dppm})\text{-}nido\text{-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$ (**2**)²⁴ and to see whether $[\text{dppm} \cdot \text{BH}_3]$ can be induced to function as a bidentate ligand on Rh. Herein we describe the formation of two related isoelectronic species in which this goal has been achieved. A preliminary communication describing the formation and structure of **3** has been published.^{23a}

Experimental Section

General Procedures. The solvents used were reagent grade and were dried before use. Some reactions were carried out using a Schlenk line and standard techniques for handling air-sensitive compounds.²⁵ The starting materials $[8,8-(\eta^2\text{-dppm})\text{-}8-(\eta^1\text{-dppm})\text{-}nido\text{-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**1**)²³ and $[9,9-(\eta^2\text{-dppm})\text{-}9-(\eta^1\text{-dppm})\text{-}nido\text{-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$ (**2**)²⁴ were prepared according to literature methods from the reaction of dppm with $[8,8-(\text{PPh}_3)_2\text{-}nido\text{-}8,7\text{-RhSB}_9\text{H}_{10}]$ ²⁶ and $[9,9-(\text{PPh}_3)_2\text{-}nido\text{-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}]$,²⁷ respectively. $\text{BH}_3 \cdot \text{thf}$ was obtained from Aldrich and used without purification as was dppm, obtained from Strem. NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer operating at 500.1 MHz for proton, 160.5 MHz for boron-11, and 202.5 MHz for phosphorus-31, in CD_2Cl_2 at 25 °C, except for low-temperature spectra. Chemical shifts are reported in parts per million for CD_2Cl_2 solutions to low field (high frequency) of $\text{Et}_2\text{O} \cdot \text{BF}_3$ for ¹¹B, SiMe_4 for ¹H, and 85% H_3PO_4 for ³¹P. Elemental analyses were obtained from Atlantic Microlabs Inc., Norcross, GA. NMR spectra were run on all samples sent for mass spectra, and crystal growth was done on NMR samples, after spectral analysis. The samples were evaporated to dryness and then dissolved in the appropriate solvent for subsequent crystallization. The mass spectra of **3** were measured at low resolution on an MS Finnegan TSQ-

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700 (ESI, CHCl₃/TFA), and those for **4** were measured in the FAB mode on a JEOL MStation JMS-700 spectrometer using 3-nitrobenzyl alcohol (3-NBA/CsI).

Preparation of [8,8-η²-{η²-(BH₃)·dppm}-nido-8,7-RhSB₉H₁₀] (3). A 20-fold excess of BH₃·thf (0.34 mmol) was added to a solution of [8,8-(η²-dppm)-8-(η¹-dppm)-nido-8,7-RhSB₉H₁₀] (17 mg, 0.017 mmol) in CH₂Cl₂. The resulting orange solution was stirred at room temperature under a nitrogen atmosphere for 20 h. Then the solvent was removed in a vacuum, and the resulting yellow residue was applied to TLC, using a mixture of CH₂Cl₂/pentane (3:2) as eluent. Two components were isolated, yellow and UV-active bands of R_f 0.4 and 0.5, respectively; slow diffusion of pentane into a CH₂Cl₂ solution of the yellow component yielded air-stable orange crystals, which were characterized as [8,8-η²-{η²-(BH₃)·dppm}-nido-8,7-RhSB₉H₁₀] (**3**) (7.4 mg, 0.012 mmol, 71%). Anal. Calcd for C₂₅H₃₅B₁₀P₂RhS: C, 46.88, H, 5.51. Found: C, 46.65, H, 5.41; LR-MS (ESI, CHCl₃/TFA): *m/z* 644 [*M*⁺ for C₂₅H₃₅B₁₀P₂RhS]. The parent envelope pattern conforms to values calculated from isotopic abundances. ¹H{¹¹B} NMR (−80 °C): δ 7.80–6.52 (m, 20H; C₆H₅), 4.19 (s, 1H; BH), 3.58 (s, 1H; BH), 3.12 (s, 1H; BH), 2.91 (br s, 1H; BH₃), 2.73 (br d, *J* = 17 Hz, 1H; BH), 2.47 (s, 1H; BH), 1.53 (s, 1H; BH), 1.18 (s, 2H; BH), 1.09 (s, 1H; BH), −0.24 (br s, 1H; BH₃), −0.52 (br s, 1H; BH₃), −1.39 (s, 1H; μ-H); ¹H{³¹P} NMR: δ 3.06, 3.36 (each d, ²*J*(H,H) = 15 Hz, 2H; CH₂); ¹¹B{¹H} NMR: δ 17.2 (v br s, 1B; BH), 13.1 (br s, 1H; BH), 10.8 (s, 1B; BH), 5.1 (s, 1B; BH), 1.9 (s, 1B; BH), −14.3 (s, 1B; BH), −19.1 (s, 1B; BH), −19.6 (s, 1B; BH), −24.1 (br d, ¹*J*(B,P) = 17 Hz, 1B; BH₃), −31.2 (br s, 1B; BH); ³¹P NMR (−50 °C): δ 49.3 (dd, ¹*J*(P,Rh) = 151 Hz, ²*J*(P,P) = 6 Hz), 14.43 (v br, 1P; PBH₃).

Preparation of [9,9-η²-{η²-(BH₃)·dppm}-nido-9,7,8-RhC₂B₈H₁₁] (4). A 10-fold excess of BH₃·thf (0.25 mmol) was added to a solution of [9,9-(η²-dppm)-9-(η¹-dppm)-nido-9,7,8-RhC₂B₈H₁₁] (25 mg, 0.025 mmol) in 10 mL of CH₂Cl₂ under nitrogen. The resulting orange solution was stirred overnight. Then the solution was reduced in volume, and the reaction mixture was applied to the Chromatotron (a radial chromatograph obtained from Harrison Research, Palo Alto, CA) using a 25 cm diameter circular plate coated with 0.1 cm of silica gel (EM Science) and a CH₂Cl₂/hexane (2:3) mixture as the mobile phase. An orange component was isolated and after recrystallization in CH₂Cl₂/pentane was identified as [9,9-η²-{η²-(BH₃)·dppm}-nido-9,7,8-RhC₂B₈H₁₁] (12 mg, 0.019 mmol; 76%). Single crystals of this compound precipitated from the CH₂Cl₂/pentane mixture. Anal. Calcd for C₂₇H₃₆B₉P₂Rh: C, 52.08; H, 5.83. Found: C, 52.18; H, 5.94. HR-MS (FAB with 3-NBA/CsI): *m/z* calcd for C₂₇H₃₆B₉CsP₂Rh 756.1294 (*M* + Cs⁺), found 756.1258. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements. ¹H NMR: δ 7.61–7.22 (m, 20 H; C₆H₅), 4.14 (s, 1H; C₂H₂B₈H₆), 3.46 (s, 1H; C₂H₂B₈H₆), 3.17 (m, 1H; Ph₂PCH₂PPh₂), 2.99 (m, 1H; Ph₂PCH₂PPh₂). ¹H{¹¹B} NMR: δ 3.62 (1H, BH), 3.55 (2H, BH), 1.74 (1H, BH), 1.54 (1H, BH), 1.45 (2H, BH), 0.89 (1H, BH), 0.54 (3H, BH₃), 0.12 (1H, μ-H). ¹H{¹¹B} NMR (−80 °C): δ 3.44 (3H, BH), 2.66 (1H, BH₃), 1.63 (1H, BH), 1.34 (1H, BH), 1.19 (2H, BH), 0.71 (1H, BH), 0.13 (1H, BH₃), −0.04 (1H, μ-H), −1.56 (1H, BH₃). ³¹P{¹H} NMR: δ 43.4 (dd, *J*(P,Rh) = 143 Hz, *J*(P,P) = 77 Hz, 1P), 19.0 (v br, 1P). ¹¹B NMR: δ 15.6 (d, *J*(H,B) = 122 Hz, 1B), 13.8 (v br, 1B), 9.4 (d, *J*(H,B) = 120 Hz, 1B), −2.2 (v br, 1B), −16.2 (d, *J*(H,B) = 103 Hz, 1B), −21.4 (v br, 3B), −23.6 (d in ¹¹B{¹H}), *J*(P,B) = 76 Hz, 1B).

Structure Determinations for 3 and 4. Crystals were mounted onto glass fibers in random orientations. Preliminary examination

Table 1. Crystal Data and Structure Refinement for [8,8-η²-{η²-(BH₃)·dppm}-nido-8,7-RhSB₉H₁₀] (**3**) and [9,9-η²-{η²-(BH₃)·dppm}-nido-9,7,8-RhC₂B₈H₁₁] (**4**)

	3	4
empirical formula	C ₂₅ H ₃₅ B ₁₀ P ₂ RhS	C ₂₇ H ₃₆ B ₉ P ₂ Rh
fw	640.54	622.70
temp/K	223(2)	140(2)
wavelength/Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 1
<i>a</i> /Å	13.2721(1)	10.8504(9)
<i>b</i> /Å	11.5727(1)	16.1632(14)
<i>c</i> /Å	19.9181(2)	18.1727(15)
α/deg	90	91.269(6)
β/deg	94.898(1)	91.546(6)
γ/deg	90	106.672(6)
<i>V</i> /Å ³	3048.13(5)	3050.5(4)
<i>Z</i>	4	4
<i>D</i> (calcd)/Mg m ^{−3}	1.396	1.356
abs coeff/mm ^{−1}	0.750	0.682
cryst size/mm	0.36 × 0.28 × 0.20	0.30 × 0.18 × 0.12
<i>F</i> (000)	1304	1272
θ range for data collectn/deg	1.78 to 27.50	1.12 to 29.00
index ranges	−18 ≤ <i>h</i> ≤ 18, −15 ≤ <i>k</i> ≤ 15, −26 ≤ <i>l</i> ≤ 26	−14 ≤ <i>h</i> ≤ 14, −22 ≤ <i>k</i> ≤ 22, −24 ≤ <i>l</i> ≤ 24
no. of reflns collected	61274	45520
no. of independent reflns	6964 [<i>R</i> (int) = 0.07]	16095 [<i>R</i> (int) = 0.081]
max and min transm	0.83 and 0.63	0.9226 and 0.8215
no. of data/restraints/aroms	6943/0/492	16095/0/814
GOF on <i>F</i> ²	1.045	1.051
final <i>R</i> indices		
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0303	0.0633
<i>wR</i> 2 (all data)	0.0661	0.1736
largest diff peak and hole/e Å ^{−3}	0.618 and 0.688	1.696 and 1.411

and data collection were performed using a Bruker SMART CCD detector system diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) equipped with a sealed tube X-ray source at −93 °C. Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.4° in ω) scans. The data set collected consists of 3636 frames with a frame width of 0.3° in ω and typical counting time of 15 s/frame at a crystal to detector distance of 4.930 cm. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. SMART and SAINT software packages^{28a} were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of *xyz* centroids. The collected data were corrected for systematic errors using SADABS^{28b} based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 1. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.^{28c} The structures were solved by a combination of Patterson and direct methods and refined successfully in the space groups *P*1 and *P*2₁/*n*, for **3** and **4**, respectively. Full-matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The cage hydrogens for both compounds and all hydrogen atoms for **3** were located and refined freely. For **4** the remaining hydrogen atoms were treated using AFIX

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Table 2. Selected Bond Distances (Å) and Angles (deg) in [8,8- η^2 - $\{\eta^2$ -(BH₃) \cdot dppm]-*nido*-8,7-RhSB₉H₁₀] (**3**)

distance/angle (Å/deg)	distance/angle (Å/deg)	distance/angle (Å/deg)	distance/angle (Å/deg)
Rh(8)–B(9)	2.174(2)	Rh(8)–B(4)	2.193(2)
Rh(8)–B(3)	2.195(2)	Rh(8)–P(2)	2.2803(5)
Rh(8)–B'	2.323(2)	Rh(8)–S(7)	2.3658(5)
Rh(8)–H'2	1.97(2)	Rh(8)–H'3	1.93(2)
S(7)–B(11)	1.918(3)	S(7)–B(3)	2.082(3)
P(1)–C(1)	1.816(2)	P(1)–B'	1.921(2)
P(2)–C(1)	1.848(2)	B'–H'1	1.09(2)
B'–H'2	1.13(2)	B'–H'3	1.12(2)
B(9)–B(10)	1.848(4)	B(10)–B(11)	1.855(4)
B(9)–H(910)	1.39(3)	B(10)–H(910)	1.18(3)
B(9)–Rh(8)–S(7)	90.42(7)	B(9)–Rh(8)–P(2)	92.40(7)
B'–Rh(8)–S(7)	93.46(6)	B(4)–Rh(8)–B'	169.00(9)
P(2)–Rh(8)–H'2	88.5(6)	P(2)–Rh(8)–B'	88.36(6)
S(7)Rh(8)–H'2	89.7(6)	B(4)–Rh(8)–S(7)	90.16(7)
B(4)–Rh(8)–H'3	161.1(7)	P(2)–Rh(8)–S(7)	172.92(2)
P(2)–Rh(8)–H'3	91.0(7)	B(9)–Rh(8)–H'2	170.7(7)
S(7)–Rh(8)–H'3	93.9(7)	B(9)–Rh(8)–H'3	112.8(7)
C(8)–P(1)–C(2)	110.25(9)	B(3)–Rh(8)–H'3	144.6(7)
C(8)–P(1)–B	112.77(10)	H2–Rh(8)–H'3	57.9(10)
C(1)–P(1)–B	105.19(10)	C(8)–P(1)–C(1)	109.90(10)
C(14)–P(2)–C(1)	102.14(10)	C(2)–P(1)–B'	113.65(10)
C(14)–P(2)–Rh(8)	120.42(7)	C(14)–P(2)–C(20)	107.09(10)
C(1)–P(2)–Rh(8)	108.74(7)	C(20)–P(2)–C(1)	100.38(10)
P(1)–B'–H'1	112.1(12)	C(20)–P(2)–Rh(8)	115.40(8)
P(1)–B'–H'2	103.3(11)	H(10)–B(10)–H(910)	107.6(18)
H'1–B'–H'2	111.4(16)	Rh(8)–B'–H'1	135.5(11)
H'2–B'–H'3	113.8(17)	Rh(8)–B'–H'2	58.1(11)
B(11)–B(10)–H(910)	87.4(12)	P(1)–B'–H'3	104.6(12)
B(10)–B(9)–H(910)	39.7(11)	B(10)–B(9)–Rh(8)	116.3(2)

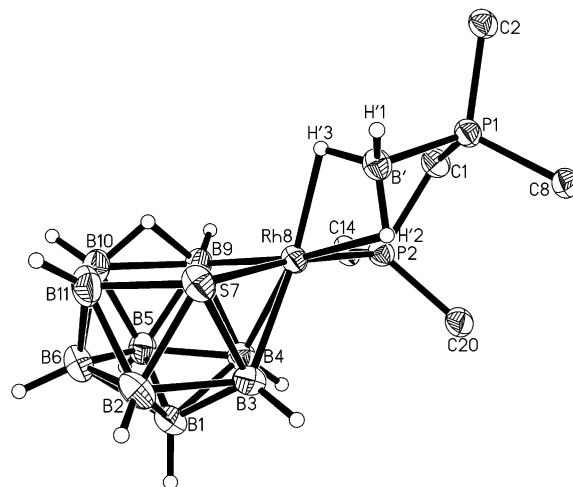
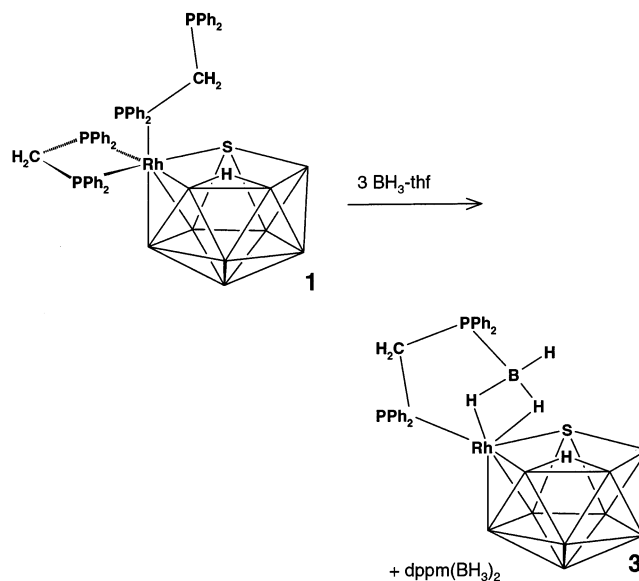
Table 3. Selected Bond Distances (Å) and Angles (deg) in [9,9- η^2 - $\{\eta^2$ -(BH₃) \cdot dppm]-*nido*-9,7,8-RhC₂B₈H₁₁] (**4**)^a

distance/angle (Å/deg)	distance/angle (Å/deg)	distance/angle (Å/deg)	distance/angle (Å/deg)
Rh(9)–B(10)	2.144(7)	Rh(9)–C(8)	2.162(6)
Rh(9)–P(2)	2.2857(15)	Rh(9)–B'	2.323(7)
Rh(9)–H(12B)	1.81(5)	Rh(9)–H(12D)	2.08(6)
P(2)–C(1)	1.844(6)	P(1)–B'	1.918(7)
B'–H(12B)	1.10(5)	B'–H(12D)	1.25(7)
B'–H(12C)	1.01(6)	B(10)–B(11)	1.849(11)
B(10)–H(13)	1.34(6)	B(11)–C(7)	1.668(10)
C(7)–C(8)	1.530(8)	B(11)–H(13)	1.33(6)
B(10)–Rh(9)–P(2)	94.7(2)	B(10)–Rh(9)–C(8)	85.7(3)
B(4/5) ^c –Rh(9)–H(12B)	116.3	C(8)–Rh(9)–P(2)	175.94(16)
B(4/5) ^c –Rh(9)–H(12D)	150.0	B(10)–Rh(9)–H(12D)	115.2(18)
P(2)–Rh(9)–H(12D)	94.9(18)	B(10)–Rh(9)–H(12B)	174.1(18)
C(1A)–P(1)–C(1)	106.9(3)	C(8)–Rh(9)–H(12B)	91.4(17)
C(7A)–P(1)–B'	112.5(3)	P(2)–Rh(9)–H(12B)	88.5(17)
C(1)–P(2)–Rh(9)	110.02(19)	C(8)–Rh(9)–H(12D)	88.6(18)
B(11)–B(10)–H(13)	46(2)	C(1A)–P(1)–B'	115.2(3)
P(1)–B'–H(12B)	107(3)	B(11)–B(10)–Rh(9)	109.0(4)
P(1)–B'–H(12C)	115(3)	Rh(9)–B'–H(12B)	49(3)
H(12B)–B'–H(12C)	113(4)	Rh(9)–B'–H(12C)	133(3)
P(1)–B'–H(12D)	108(3)	H(12B)–B'–H(12D)	112(4)
H(12C)–B'–H(12D)	102(4)	C(7)–C(8)–Rh(9)	118.3(4)

^a B(4/5)^c is the centerpoint of B(4)–B(5). H(13) is the bridging H atom.

m3. Structure refinement parameters are listed in Table 1, and selected bond distances and angles are given in Tables 2 and 3. The structures, with non-hydrogen atoms represented by 50% probability ellipsoids and showing the atom labeling, are given in Figures 1 and 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-XX and -YY. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Rd., GB-Cambridge CB2 1EZ, U.K. (fax +44 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

**Figure 1.** Molecular structure of [8,8- η^2 - $\{\eta^2$ -(BH₃) \cdot dppm]-*nido*-8,7-RhSB₉H₁₀] (**3**). The phenyl rings on phosphorus, *ipso*-carbon atoms excepted, are omitted for clarity, as are all the H atoms on carbon.**Scheme 1****Results and Discussion**

The species [8,8-(η^2 -dppm)-8-(η^1 -dppm)-*nido*-8,7-RhSB₉H₁₀] (**1**) is conveniently prepared as a yellow crystalline solid from the reaction between [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] and dppm. Species **1** contains both a bidentate and a monodentate dppm ligand as indicated in Scheme 1. The existence of the dangling phosphine in **1** suggested that it might be amenable to further chemistry analogous to our work with [(PPh₃)₂-(CO)OsB₄H₈(BH₂·dppp)], [dppp = PPh₂(CH₂)₃PPh₂] in which we were able to observe reactions of the free phosphine with other reagents.²⁰ Accordingly, reaction of a 20-fold excess of BH₃·thf with **1** in CH₂Cl₂ at room temperature affords the new rhodathiaborane [8,8- η^2 - $\{\eta^2$ -(BH₃) \cdot dppm]-*nido*-8,7-RhSB₉H₁₀] (**3**) as an air-stable orange crystalline solid in 71% yield. **3** was characterized by multinuclear NMR spectroscopy, elemental analysis, mass spectrometry, and a crystal structure determination.

The molecular structure of compound **3** is depicted in Figure 1. It is an 11-vertex *nido*-rhodathiaborane with a

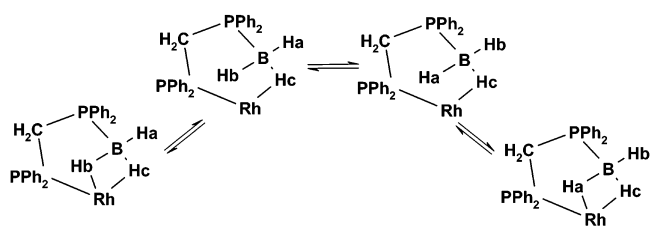
unique *exo*-polyhedral ligand, [dppm·BH₃], that chelates the rhodium atom through a phosphine group and a borane unit. The BH₃ end of this ligand can be considered as a neutral adduct of BH₃ coordinating to the rhodium atom in a *bidentate* fashion via two Rh–H–B three-center two-electron bonds. The distances of the rhodathaborane cage are within the ranges found in **1** and in other related metallathia-boranes.^{23,26,29} The chelate angle P(2)–Rh(8)–B' in **3** is 88.36(6)°, significantly larger than the corresponding chelate angle P(1)–Rh(8)–P(2) of 71.45(98)° in the precursor **1**. The P(1)–B' bond distance of compound **3** is 1.921(2) Å, essentially the same value found in the dangling PPh₂Me–BH₂ group of [(PPh₃)₂(CO)OsB₄H₇](BH₂·PPh₂Me)²⁰ and in the Co–BH₂–PPh₂ interaction of the bridged cobaltaborane [(CO)(*η*¹-dppm)Co(*μ*-dppm)·BH₂] (**VIII**),²² which also contains a dangling phosphine.

The hydrogen atoms were refined successfully and indicate approximately tetrahedral geometry around the BH₃ group. The arrangement of ligands including B(9), S, P(2), H'2, and H'3, and the centroid of the B(3)–B(4) vector, around Rh represents, essentially, octahedral geometry. The H atoms bridging the unique boron B' and Rh are quite asymmetrical with the H atom situated closer to B'.

The course of the reaction in which **3** is formed, illustrated in Scheme 1, is not obvious; however, it is most probable that the large excess of BH₃·thf displaces the dangling dppm ligand in compound **1** as [dppm·(BH₃)₂] (also isolated from the reaction mixture)³⁰ and inserts between the Rh and P atoms in the {Rh(dppm)} chelate, affording the title compound. Conversely, BH₃ may remove the chelating ligand as [dppm·(BH₃)₂] and add to the dangling end of the monodentate dppm, which, in turn, coordinates to the Rh center.

NMR data for compound **3** conform to the molecular structure described above. The ¹¹B NMR spectrum consists of 10 broad resonances in the range from +17.2 to –31.2 ppm. The boron peak at –24.1 ppm shows coupling to a phosphorus atom and is assigned to the BH₃ group (B' in Figure 1). All the terminal hydrogen atoms were related to their corresponding boron atoms by ¹H{¹¹B} experiments. The resonance of the bridging hydrogen atom on the B(9)–B(10) edge appears at –1.37 ppm. The ³¹P{¹H} spectrum shows a sharp doublet of doublets, assigned to the PPh₂ group *trans* to the sulfur atom, and a very broad signal assigned to the phosphorus atom directly bound to the BH₃ unit. At room temperature, the three hydrogen atoms of the BH₃ group are equivalent on the NMR time scale, giving rise to a broad single resonance at 0.85 ppm. As the temperature is lowered, this single peak broadens and finally splits into three different resonances at 2.91, –0.24, and –0.52 ppm, one shifted to lower field and the other two to higher field, probably the H atoms bonded to Rh moving to

Scheme 2



higher field and the B–H moving to lower field. These three resonances average to 0.71 ppm, reasonably close to the value of the coalesced resonance for the three H_μ atoms which is observed at 0.85 ppm. This suggests that the BH₃ group is fluxional in solution, more likely undergoing a rotational motion around the B–P bond, rendering the two bridging and one terminal H atoms on B' equivalent on the NMR time scale ($\Delta G^\ddagger = \text{ca. } 37 \text{ kJ mol}^{-1}$). A suggested mechanism is given in Scheme 2. There are six possible combinations for two bridging H atoms and one terminal H atom on boron for the Rh–(*μ*-H)₂–BH linkage. These can exchange by breaking a Rh–H bond to form an additional terminal H on B and rotation about the B–P bond. This would result in positional exchange of the two terminal H atoms on B and formation of a Rh–H bond such that a different H atom is now the terminal one on B. Six such transformations need to occur to scramble all the H atoms in the BH₃ moiety. One such transformation is illustrated in Scheme 2. Alternatively, the process can proceed by an associative process, and that would involve tridentate Rh–(*μ*-H)₃–B intermediates. Such associative mechanisms have been suggested for the fluxional species [(BH₄)Mn(CO)₄][–] and [(BH₄)Cu(PPh₃)₂], on the basis of ab initio molecular orbital calculations.³¹ Indeed fluxional processes involving tetrahydroborate groups bonded to metals have been known and studied using NMR spectroscopy for many years.³² Such species may involve [BH₄][–] groups bonded to the metal through one, two, or three bridging H atoms, but most of those for which dynamic NMR studies have been carried out involve the bi- or tridentate species. All except one of the estimations of the ΔG^\ddagger values are lower than our value for **3**. The range is from 18 to 42 kJ mol^{–1}.^{33,34} Examples of fluxional processes involving borane moieties bonded to metal centers are much less common, because such species are less common. Dynamic exchange of the bridging and terminal H atoms is observed in the borane complexes illustrated as structures **III**¹² and **VII**,²¹ but only for the former was a ΔG^\ddagger value reported (ca. 30 kJ mol^{–1}).

The ¹¹B NMR data for the BH₃ group compare reasonably well to those of a pure phosphine–borane adduct. Thus, **3** is best described as a metallathiaaborane containing such an adduct that coordinates a rhodium center, donating two electrons through each of two three-center two-electron

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(30) The following are data for [dppm·(BH₃)₂]. ¹H{¹¹B} NMR (299.9 MHz, CDCl₃, 25 °C): δ 7.66–7.34 (m, 20H; C₆H₅), 3.24 (t, ²J(H,P) = 17.0 Hz, 2H; CH₂), 0.92 (d, ²J(H,P) = 15.6 Hz, 6H; BH₃). ¹¹B NMR (96.2 MHz, CDCl₃, 25 °C): δ –37.1. ³¹P NMR (121.4 MHz, CDCl₃, 25 °C): δ 15.2.

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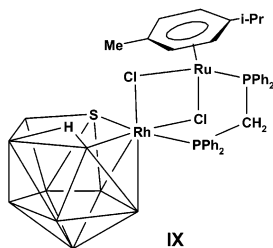
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(33) Bommer, J. C.; Morse, K. W. *Inorg. Chim. Acta* **1983**, 74, 25.

(34) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. W. *J. Am. Chem. Soc.* **1977**, 99, 7154.

B–H–Rh bonds, and another pair from the P atom. According to a metal complex description, **3** could be formally regarded as an 18-electron species, with bonding vectors toward the sulfur atom, the cluster B(3)–B(4) edge, B(9), the phosphine group, and the bridging H atoms of the BH₃ unit, the novel *exo*-polyhedral ligand [(dppm)•BH₃] acting as a six electron donor. This would require six-coordination around Rh, and as described above, this is effectively what is observed. Alternatively, compound **3** can be considered as a saturated rhodathiaborane cluster, conforming to the polyhedral skeletal electron pair theory description for an 11-vertex *nido*-cluster.³⁵ The proposed fluxional process illustrated in Scheme 2 is consistent with electron counting for the metal center. Breaking a Rh–H bond affords a transient 16-electron metal center which, after rotation of the BH₂ group, forms a new B–H–Rh bridge bond, restoring the 18-electron metal center.

The species [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] is iso-electronic with [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀], and we recently have prepared and characterized fully the analogue of **1**, [9,9-(η²-dppm)-9-(η¹-dppm)-*nido*-9,7,8-RhC₂B₈H₁₁] (**2**).²⁴ Species **1** and **2** are also isoelectronic, so it was appropriate to see whether **2** would undergo the same reaction chemistry as **1**. Indeed we had discovered this in the reactions of **1** and **2** with organometallic reagents when we were able to prepare derivatives containing the bridging ligand [(μ-Cl)₂Ru(η⁶-*p*-cym)(dppm)].^{24,36} The pair of species formed, [8,8-η²-{(μ-Cl)₂Ru(η⁶-*p*-cym)(dppm)}]-*nido*-8,7-RhSB₉H₁₀] (**6**) and [9,9-η²-{(μ-Cl)₂Ru(η⁶-*p*-cym)(dppm)}]-*nido*-9,7,8-RhC₂B₈H₁₁] (**7**), both have the same structure. That for **6** is illustrated as structure **IX**. In fact these species



are quite similar to **3** in that they contain ligands which bond to the Rh through a donor P atom and also via two bridging atoms such that the ligand supplies six electrons to the cluster. In **3**, the two BH moieties contribute a pair of electrons each to the Rh atom, whereas in **6** and **7** the two Ru–Cl moieties do the same. The difference is that in **6** and **7** the interaction involves two two-center, two-electron bonds whereas in **3** there are two three-center, two-electron bonds.

Reaction of BH₃•thf with [9,9-(η²-dppm)-9-(η¹-dppm)-*nido*-9,7,8-RhC₂B₈H₁₁] (**2**) in CH₂Cl₂ under nitrogen affords an orange solution which after workup including chromatographic separation gives an orange solid, which we identified

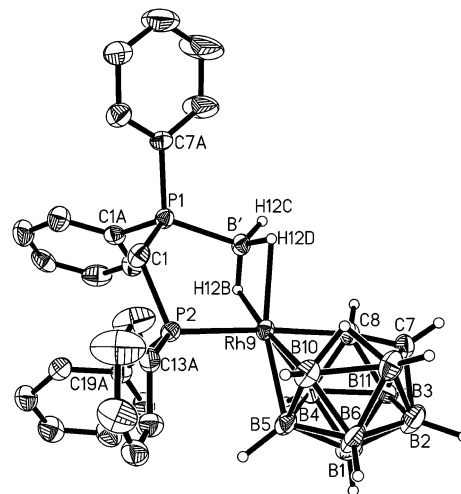


Figure 2. Molecular structure of [9,9-η²-{η²-(BH₃)•dppm}-*nido*-9,7,8-RhC₂B₈H₁₁] (**4**). The hydrogen atoms on carbon are omitted for clarity.

as [9,9-η²-{η²-(BH₃)•dppm}-*nido*-9,7,8-RhC₂B₈H₁₁] (**4**), in 76% yield. NMR spectra were very similar to those for **3**, and elemental analysis and also high-resolution mass spectra were supportive of our identification. Crystals suitable for X-ray analysis were grown, and the structure obtained is given in Figure 2. Again hydrogen atoms were located. The structure is quite similar to that of **3**. The [(dppm)•BH₃] ligand coordinates to the Rh via two Rh–H–B bridge bonds and also via a Rh–P bond. The latter P atom, P(2), is *trans* to C(8), the angle P(2)–Rh–C(8) is 175.9(2) Å, and the orientation of the atoms around Rh, including P(2), H12(B), H12(D), B(10), C(8), and the centroid of B(4)–B(5), is essentially octahedral. The bond distances and the geometries of **3** and **4** are very similar.

The behavior of the BH₃ group mirrors that in **3**. The ¹¹B NMR chemical shift values compare very well; that for **3** is –24.1 ppm, and that for **4** is –23.6 ppm. The BH₃ protons are also fluxional, with Δ*G*[‡] = ca. 42 kJ mol^{–1}. Thus, it appears that these two isoelectronic species, **3** and **4**, are very similar in their chemistry. An interesting feature is that the orientations of the dppm•BH₃ ligands in **3** and **4** are essentially the same in each species although the relative positions of the two dppm ligands in **1** and **2** are not. In **1**, the bidentate dppm ligand lies in the same plane as the open face of the RhSB₉H₁₀ cluster and the monodentate one is located perpendicular to the plane. However, in **2**, the bidentate ligand spans sites on the Rh atom both perpendicular to and in the plane of the open face and the monodentate ligand lies essentially in the plane.²⁴ Attempts to deprotonate and isolate the products for either **3** or **4** have thus far been unsuccessful, but this work continues.

Summary

In conclusion, compounds **3** and **4** represent a unique pair. They are the first known examples of a polyhedral borane derivative in which a BH₃ adduct coordinates a metal center in a bidentate fashion through the hydrogen atoms. This is novel chemistry involving a borane–phosphine adduct, the paradigm of boron chemistry, and polyhedral borane cluster

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chemistry. The good yield and clean chemistry affording **3** and **4** may provide an opportunity to study the reactivity of this and related species involving a BH₃ adduct coordinated to a metal center. These aspects are currently being investigated in our laboratory.

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and MS facilities. We also thank Prof. R. E. K. Winter and Mr. J. Kramer for the MS data.

Note Added after ASAP: A bond is missing from the structure of compound **III** in the version of this article posted ASAP on October 5, 2002. It is included in the version posted on October 10, 2002.

Supporting Information Available: Crystallographic data, positional parameters, anisotropic displacement parameters, and bond lengths and angles for **3** and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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