Chemistry of a Metallathiaborane Cluster. 5.[†] Reaction of [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] and Its Derivatives with Organotransition-Metal Reagents

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The phosphine ligands on [8,8-(PPh$_3$)$_2$-*nido*-8,7-RhSB$_9$H$_{10}$] (**2**) may be replaced by the bidentate phosphine dppm {dppm = [(CH$_2$)(PPh$_2$)$_2$]} to form the species [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] (**3**). The latter reacts with [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$ to afford [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (**4**), which contains the group [(μ-Cl)$_2$Ru-(η^6-*p*-cym)(dppm)] that coordinates in a multidentate mode to Rh, in 77% yield. Similar chemistry using [Cp*Ir(μ-Cl)$_2$]$_2$ {Cp* = [η^5-C$_5$(CH$_3$)$_5$]} affords the related species [8,8-η^2-{(μ-Cl)$_2$Cp*Ir(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (**5**), and [8,8-η^2-{(μ-Cl)$_2$Cp*Rh(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (**6**) is obtained from the reaction between **2** and [Cp*RhCl$_2$(η^1-dppm)]. Reactions of **3** with [IrCl(CO)(PPh$_3$)$_2$] or [RhCl(PPh$_3$)$_3$] result in removal of dppm. [RhCl(PPh$_3$)$_3$] reacts with **3** to afford [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$] (**7**), but on reaction for extended periods [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (**8**) is also formed. Reaction between **7** and dppe {dppe = [(CH$_2$)$_2$(PPh$_2$)$_2$]} gives [1,1-(η^2-dppe)-3-(η^1-dppm)-*closo*-1,2-RhSB$_9$H$_8$] (**9**), which when treated with [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$, affords [1,1-(η^2-dppe)-3-η^1-{(dppm)Ru(η^6-*p*-cym)Cl$_2$)}-*closo*-1,2-RhSB$_9$H$_8$] (**10**), in which the rhodathiaborane cage has a pendent metal-ligated dppm group at the 3-position. A rationale for the formation of **7** and **8** in the reaction of **3** with [RhCl(PPh$_3$)$_3$] is presented, and it provides evidence for the pathways for reactions of the other metal-containing moieties with **3**. The existence of **8** provides support for some earlier proposals concerning the chemistry of **3**. The new species **4**, **5**, **6**, **8**, and **10** are characterized by NMR spectroscopy, elemental analysis, mass spectrometry, and in the case of **4**, **8**, and **10**, crystal structure determinations.

Introduction

The idea of carrying out organometallic chemistry[1] or even catalysis[2] on metallaborane clusters is certainly not new. The chemistry can involve ligand exchange,[3] ligand addition,[4] or metal(s) incorporation either into the cage[5] or as *exo*-polyhedral moieties.[6] Ligands can also react with each other at the metal site in a metallaborane.[7] For example, two acetylene groups have been coupled to form a metallacyclopenta-2,4-dienyl moiety[7a] or a noncyclic butadienyl moiety.[7b] Other reactions of alkynes and alkenes with metallaboranes which appear to take place at the metal center include aromatization of norbornadiene at a Rh center[7c] and

reactions involving metal-promoted alkyne[7d] and norbornadiene[7e] insertion into BH bonds. Approaches to catalysis have typically involved interconversion of *closo*/*exo-nido* metallacarborane complexes so as to open up potential coordination sites.[2] Extensions of the chemistry of these *exo-nido* metallacarboranes involved the formation of metal complexes of boranes or metallacarboranes with a transition metal auxiliary not part of the cage. This has led to a series of bimetallacarboranes and some interesting organometallic chemistry associated with these species. The examples of metallaboranes containing *exo*-polyhedral transition metal auxiliaries are limited to a few systems, especially those involving a second metal-containing moiety connected to the cage with at least two connecting bonds. Species based on 11- or 12-vertex *closo*-clusters involving bridging H, O, or halogen atoms between cage borons and the *exo*-polyhedral metal moiety have been described.[8−14] Examples from the *nido* class of polyhedral metallaboranes are much less common. Structures **A** and **B**,[10] shown in Chart 1, are examples of *nido*-carboranes with *exo*-polyhedral metal auxiliaries, and they have been known for quite some time. These species are precursors to structures of the type **C** and **D**,[2c,d,10,14] also shown in Chart 1.

Our contributions to this area are twofold. We have used the redox flexibility of some iridanonaboranes to

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Chart 1
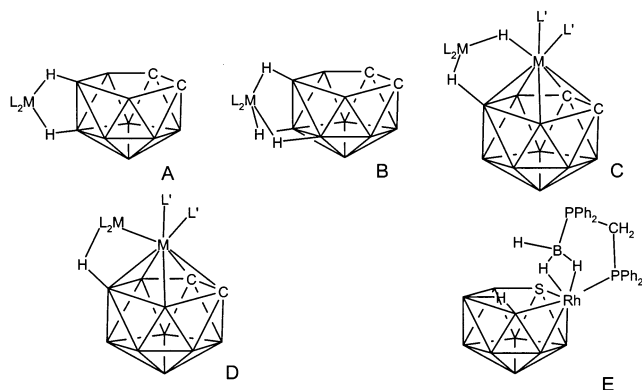
effect incorporation of heteroatoms into the clusters. This led to the incorporation of alkenes, alkynes, enynes, sulfur-containing moieties, and nitrogen.[15] Our other approach has involved the reaction of some bidentate

phosphine ligands with unsaturated metallahetero-boranes.[16,17] The isoelectronic pair of metallahetero-boranes, $[9,9-(PPh_3)_2-nido-9,7,8-RhC_2B_8H_{11}]$ (**1**)[18] and $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$ (**2**),[19] are two electrons short of the number notionally required to satisfy the polyhedral skeletal electron pair theory (PSEPT).[20] The

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Scheme 1
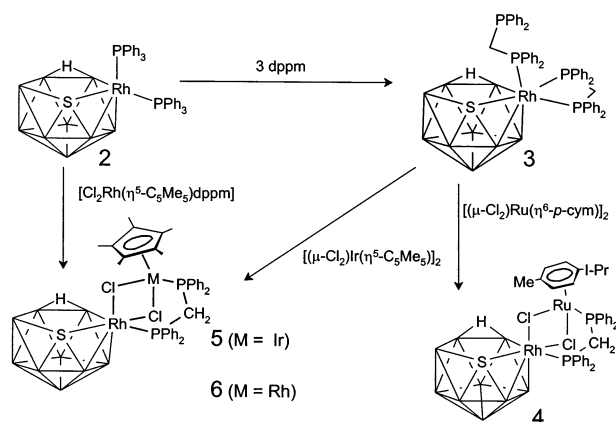
chemistry of the rhodathiaborane cluster **2**, whose structure is illustrated in Scheme 1, has received more attention than the metallacarborane cluster **1**. The latter is identical to **2** except that the C(H)C(H) atom string replaces the isoelectronic SB(H) atom string in the open face of the cluster. The molecules **1** and **2** have a formal skeletal electron count that conforms to a *closo*-cluster, but the open cage structure is clearly that of a *nido*-cluster.[21] The apparent electronic unsaturation in **2**, and in related species with square planar 16-electron metal centers, has been the subject of much discussion in the literature.[21-23] We will not repeat that herein but simply note that a consequence of this unsaturation is a rich chemistry.[16-19,22-25] Species **2** is stable, easily prepared, and reactive toward both electrophiles and nucleophiles. In particular, the reactions of **2** with Lewis bases, L (where L = CO, PMe$_2$Ph, or CH$_3$CN),[19] or L$_2$ {where L$_2$ = dppm, dppe, or dppp which is [C$_3$H$_6$-(PPh$_2$)$_2$]},[16b] result in either addition of the ligand, L or L$_2$, to the metal center or addition and substitution, or in terminal hydrogen substitution on the RhSB$_9$ cage. Reaction of **2** with [RhCl(PPh$_3$)$_3$] is reported to form *closo* 12-vertex bimetallic species.[19b] Of particular pertinence to the present work is the formation of [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] (**3**) from the reaction between dppm and **2**. Herein we report the results of a study of the reactions of **3** with additional metal reagents in efforts to form heterobimetallathiaboranes and also to probe the reaction pathways exhibited by this fascinating system. A minor aspect of this work has appeared in a preliminary communication.[16c]

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Experimental Section

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.[26] **2**, **3**, [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$] (**7**), and [1,1-(η^2-dppe)-3-(η^1-dppm)-*closo*-1,2-RhSB$_9$H$_8$] (**9**) were prepared according to literature methods: **2**[19b] from the reaction between Cs[SB$_9$H$_{12}$][27] and [RhCl(PPh$_3$)$_3$],[28] **3** from **2** and dppm,[16b] **7** from **2** and **3**,[16d] and **9** from **7** and dppe.[16d] The organotransition-metal reagents [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$,[29] [Cp*Ir(μ-Cl)$_2$]$_2$,[30] and [Cp*Rh(μ-Cl)$_2$]$_2$[31] were prepared using literature methods. PPh$_3$ and dppe were obtained from Aldrich, dppm was obtained from Strem, and [Cp*RhCl$_2$(η^1-dppm)] was prepared from the reaction between [Cp*Rh(μ-Cl)$_2$]$_2$ and dppm as described in the literature.[32] 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. Chemical shifts are reported at 25 °C in ppm for CD$_2$Cl$_2$ solutions to low field (high frequency) of Et$_2$O·BF$_3$ for ^{11}B, of SiMe$_4$ for ^{1}H, and of 85% H$_3$PO$_4$ for ^{31}P. 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 generated from NMR samples, after spectral analysis. The samples were evaporated to dryness and then dissolved in the appropriate solvent for subsequent crystallization. The mass spectra were measured in the FAB mode on a JEOL MStation JMS-70 spectrometer using 3-nitrobenzyl alcohol (3-NBA, or 3-NBA/CsI).

Preparation of [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (4). A sample of [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$ (20 mg, 0.033 mmol) was added under nitrogen to a solution of [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] (**3**) (30 mg, 0.030 mmol) in CH$_2$Cl$_2$ (ca. 10 mL) and stirred overnight at room temperature. Then the solution was filtered over SiO$_2$ to remove chromatographically immobile components and reduced in volume. Addition of pentane gave a red precipitate, isolated as 23 mg of a species which was characterized as [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$]·0.5CH$_2$Cl$_2$ (**4**: 0.023 mmol, 77% yield). Single crystals of this compound precipitated from CH$_3$CN/Et$_2$O. Anal. Calcd for C$_{35}$H$_{46}$B$_9$Cl$_2$P$_2$RhRuS(CH$_2$Cl$_2$)$_{0.5}$: C, 43.71; H, 4.86. Found: C, 44.21; H, 4.57. ^{11}B NMR: δ 14.9 (v br, 1B), 10.2 (d, J(H,B) = 103 Hz, 1B), 7.8 (v br, 1B), 1.7 (d, J(H,B) = 115 Hz, 1B), −0.8 (v br, 1B), −18.2 (d, J(H,B) = 137 Hz, 1B), −20.6 (d, J(H,B) = 103 Hz, 1B), −22.3 (d, J(H,B) = 140 Hz, 1B), −31.8 (v br, 1B). ^{31}P{^{1}H} NMR: δ 31.8 (br d, J(P,Rh) = 153 Hz, 1P), 26.6(d, J(P,P) = 4 Hz, 1P). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): δ 7.76−6.94 (m, 20H; C$_6$H$_5$), 5.80 (d, J(H,H) = 6 Hz, 1H; Me*C$_6$H$_4$*CHMe$_2$), 5.37 (d, J(H,H) = 6 Hz, 1H; Me*C$_6$H$_4$*CHMe$_2$), 4.99 (d, J(H,H) = 6 Hz, 1H; Me*C$_6$H$_4$*CHMe$_2$), 4.71 (d, J(H,H) = 6 Hz, 1H; Me*C$_6$H$_4$*CHMe$_2$), 4.37 and 3.06 (each td, J(H,H) = 13 Hz, J(H,P) = 14 Hz, 2H; Ph$_2$P*CH$_2$*PPh$_2$), 2.44 (sept, J(H,H) = 7 Hz, 1H; MeC$_6$H$_4$*CH*Me$_2$), 1.78 (s, 3H; *Me*C$_6$H$_4$CHMe$_2$), 1.23 (d, J(H,H) = 7 Hz, 3H; MeC$_6$H$_4$CH*Me$_2$*), 1.01 (d, J(H,H) =7 Hz, 3H; MeC$_6$H$_4$CH*Me$_2$*). Additional ^{1}H{^{11}B} NMR: δ 3.74 (1H, BH), 3.49 (1H, BH), 2.90 (2H, BH), 2.50 (1H, BH), 1.73 (1H, BH), 1.29 (1H,BH), 1.09 (1H, BH), 0.94 (1H, BH), −2.08 (1H, μ-H). HR-MS (FAB with 3-NBA/CsI) m/z calcd for C$_{35}$H$_{46}$B$_9$Cl$_2$CsP$_2$RhRuS: 1066.0229 (M + Cs$^+$), found 1066.0233. The

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mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements.

Preparation of [8,8-η^2-{(μ-Cl)$_2$Cp*Ir(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (5). To a solution of **3** (30 mg, 0.030 mmol) in CH$_2$Cl$_2$ (ca. 20 mL) was added [Cp*Ir(μ-Cl)$_2$]$_2$ (24 mg, 0.030 mmol) under N$_2$, and the reaction mixture was stirred at room temperature overnight. Then the solution was filtered over SiO$_2$, and a yellow component was collected. Addition of pentane gave 14 mg of a yellow product, which was characterized as [8,8-η^2-{(μ-Cl)$_2$Cp*Ir(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$]·1.5CH$_2$-Cl$_2$ (**5**: 0.014 mmol, 40%). Anal. Calcd for C$_{35}$H$_{47}$B$_9$Cl$_2$IrP$_2$-RhS(CH$_2$Cl$_2$)$_{1.5}$: C, 38.04; H, 4.37. Found: C, 38.11; H, 4.47. ^{11}B NMR: δ 15.6 (v br, 1B), 10.3 (d, J(H,B) = 130 Hz, 1B), 8.8 (v br, 1B), 1.7 (v br, 1B), −0.8 (v br, 1B), −18.3 (d, J(H,B) = 137 Hz, 1B), −20.6 (d, J(H,B) = 145 Hz, 1B), −22.2 (d, J(H,B) = 158 Hz, 1B), −32.2 (v br, 1B). ^{31}P{^{1}H} NMR (202.5 MHz, CD$_2$Cl$_2$, 25 °C): δ 32.9 (d, J(P,Rh) = 153 Hz, 1P), 3.7 (s, 1P). ^{1}H{^{31}P} NMR: δ 7.69−6.99 (m, 20H; C$_6$H$_5$), 4.36 and 3.47 (each d, J(H,H) = 14 Hz, 2H; Ph$_2$PCH$_2$PPh$_2$), 1.32 (s, 15H; C$_5$-(CH$_3$)$_5$). Additional ^{1}H{^{11}B} NMR: δ 3.65 (1H, BH), 3.50 (1H, BH), 2.89 (2H, BH), 2.59 (1H, BH), 2.56 (1H, BH), 1.65 (1H, BH), 1.10 (1H, BH), 0.98 (1H, BH), −2.01 (1H, μ-H). HR-MS (FAB with 3-NBA/CsI) m/z calcd for C$_{35}$H$_{47}$B$_9$Cl$_2$CsIrP$_2$RhS: 1158.0879 (M + Cs$^+$), found 1158.0858. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements.

Preparation of [8,8-η^2-{(μ-Cl)$_2$Cp*Rh(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (6). [Cp*RhCl$_2$(η^1-dppm)] (37 mg, 0.053 mmol) was added to a solution of **2** (20 mg, 0.026 mmol) in CH$_2$Cl$_2$ (ca. 10 mL) under N$_2$. The reaction mixture was stirred at room temperature for 2 h. After this time, the solution was filtered over silica gel, and an orange component was collected. Recrystallization in CH$_2$Cl$_2$/pentane gave rise to the isolation of a product characterized as [8,8-η^2-{(μ-Cl)$_2$Cp*Rh(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$]·1.5CH$_2$Cl$_2$ (**6**: 16 mg, 0.017 mmol; 58%). Anal. Calcd for C$_{35}$H$_{47}$B$_9$Cl$_2$P$_2$Rh$_2$S(CH$_2$Cl$_2$)$_{1.5}$: C, 41.24; H, 4.74. Found: C, 41.44; H, 4.81. ^{11}B NMR: δ 15.1 (v br, 1B), 10.3 (d, J(H,B) = 125 Hz, 1B), 8.1 (v br, 1B), 1.9 (v br, 1B), −1.2 (v br, 1B), −18.5 (d, J(H,B) = 135 Hz, 1B), −20.6 (d, J(H,B) = 125 Hz, 1B), −22.4 (d, J(H,B) = 145 Hz, 1B), −32.2 (v br, 1B). ^{31}P{^{1}H} NMR: δ 33.9 (dd, J(P,Rh) = 153 Hz, J(P,P) = 7 Hz, 1P), 28.6 (dd, J(P,Rh) = 144 Hz, J(P,P) = 7 Hz, 1P). ^{1}H{^{31}P} NMR (500 MHz, CD$_2$Cl$_2$, 25 °C): δ 7.79−6.98 (m, 20H; C$_6$H$_5$), 4.32 and 3.32 (each d, J(H,H) = 14 Hz, 2H; Ph$_2$PCH$_2$PPh$_2$), 1.33 (s, 15H; C$_5$(CH$_3$)$_5$). Additional ^{1}H{^{11}B} NMR: δ 3.80 (1H, BH), 3.51 (1H, BH), 2.89 (2H, BH), 2.55 (1H, BH), 2.52 (1H, BH), 1.81 (1H, BH), 1.12 (1H, BH), 0.96 (1H, BH), −2.07 (1H, μ-H). HR-MS (FAB with 3-NBA/CsI) m/z calcd for C$_{35}$H$_{47}$B$_9$Cl$_2$CsP$_2$Rh$_2$S: 1068.0320 (M + Cs$^+$), found 1068.0341. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements.

Preparation of [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-Rh-SB$_9$H$_8$] (7) from 2 and [RhCl(PPh$_3$)$_3$]. dppm (50 mg, 0.130 mmol) was added to a solution of **2** (50 mg, 0.065 mmol) in CH$_2$Cl$_2$ (ca. 20 mL) under N$_2$, and the reaction mixture was stirred at room temperature for 15 min. After this time, [RhCl-(PPh$_3$)$_3$] (70 mg, 0.076 mmol) was added, and the reaction mixture was stirred for 2 h. Then the red solution was filtered over SiO$_2$ to remove chromatographically immobile components and reduced in volume. Addition of pentane resulted in the isolation of 38 mg of orange solid, characterized by mass and NMR spectra as the previously reported [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$]^{16d} (**7**: 0.043 mmol, 66%).

Preparation of [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (8). dppm (50 mg, 0.130 mmol) was added to a solution of **2** (50 mg, 0.065 mmol) in CH$_2$Cl$_2$ (ca. 20 mL) under N$_2$, and the reaction mixture was stirred at room temperature for 15 min. Then [RhCl(PPh$_3$)$_3$] (60 mg, 0.065 mmol) was added

to the reaction mixture, and the resulting red solution was stirred at room temperature for 3 days. Subsequent preparative column chromatography, using CH$_2$Cl$_2$ as the eluent, afforded two products characterized as [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$]^{16d} (**7**: 21 mg, 0.024 mmol; 37%) and [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (**8**: 15 mg, 0.016 mmol; 25%). Single crystals of **8** were obtained by slow diffusion of Et$_2$O into CH$_2$Cl$_2$ solution. Anal. Calcd for C$_{43}$H$_{44}$B$_9$-ClP$_3$RhS: C, 56.05; H, 4.81. Found: C, 55.92; H, 4.90. ^{11}B NMR: δ 20.2 (v br, 1B), 1.2 (v br, 1B), −1.7 (v br, 1B), −2.7 (v br, 1B), −5.8 (d, J(H,B) = 130 Hz, 1B), −8.5 (d, J(H,B) = 110 Hz, 1B), −23.2 (d, J(H,B) = 105 Hz, 1B), −25.2 (d, J(H,B) = 138 Hz, 1B), −27.4 (v br, 1B). ^{31}P{^{1}H} NMR: δ 35.2 (dd, J(P,Rh) = 160 Hz, J(P,P) = 85 Hz, 1P), 21.9 (v br, 1P), 18.6 (br d, 1P). ^{1}H NMR: δ 8.11−6.53 (m, 35H; C$_6$H$_5$), 3.90 (br m, 1H; Ph$_2$PCH$_2$PPh$_2$), 2.93 (br m, 1H; Ph$_2$PCH$_2$PPh$_2$). Additional ^{1}H{^{11}B} NMR: δ 4.73 (1H, BH), 2.78 (2H, BH), 2.24 (2H, BH), 1.87 (1H, BH), 1.35 (1H, BH). HR-MS (FAB with 3-NBA) m/z calcd for C$_{43}$H$_{44}$B$_9$ClP$_3$RhS: 921.2026 (M$^+$), found 921.1923. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements.

Preparation of [1,1-(η^2-dppe)-3-η^1-{(dppm)Ru(η^6-*p*-cym)Cl$_2$)}-*closo*-1,2-RhSB$_9$H$_8$] (10). [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$ (22 mg, 0.036 mmol) was added to a solution of [1,1-(η^2-dppe)-3-(η^1-dppm)-*closo*-1,2-RhSB$_9$H$_8$] (**9**) (30 mg, 0.029 mmol) in CH$_2$Cl$_2$ (ca. 25 mL). After 3 h stirring under N$_2$ at room temperature, the solution was reduced in volume, and an orange solid was precipitated when EtOH was added. Recrystallization in CH$_2$Cl$_2$/pentane gave rise to the isolation of 32 mg of a product which was characterized as [1,1-(η^2-dppe)-3-η^1-{(dppm)Ru(η^6-*p*-cym)Cl$_2$)}-*closo*-1,2-RhSB$_9$H$_8$]·CH$_2$Cl$_2$ (**10**: 0.023 mmol, 79%). Crystals suitable for X-ray analysis were grown by layering a CH$_2$Cl$_2$ solution of the product with pentane. Anal. Calcd for C$_{61}$H$_{68}$B$_9$Cl$_2$P$_4$RhRuS(CH$_2$Cl$_2$): C, 52.65; H, 4.99. Found: C, 52.33; H, 4.97. ^{11}B NMR: δ 38.0 (d, J(P,B) =112 Hz, 1B), 26.9 (d, J(H,B) = 138, 1B), 0.9 (v br, 3B), −16.9 (v br, 2B), −27.4 (v br, 2B). ^{31}P{^{1}H} NMR: δ 60.9 (br d, J(P,Rh) = 154 Hz, 2P), 25.7(v br, 1P), 24.6 (br d, J(P,P) = 48 Hz, 1P). ^{1}H NMR: δ 7.52−6.79 (m, 40H; C$_6$H$_5$), 5.09 and 4.94 (each d, each 2H; MeC$_6$H$_4$CHMe$_2$), 4.33, 2.59, and 2.34 (each br m, each 2H; Ph$_2$PCH$_2$PPh$_2$ and Ph$_2$PCH$_2$-CH$_2$PPh$_2$), 2.35 (sept, J(H,H) = 7 Hz, 1H; MeC$_6$H$_4$CHMe$_2$), 1.79 (s, 3H; MeC$_6$H$_4$CHMe$_2$), 0.92 (d, J(H,H) = 7 Hz, 6H; MeC$_6$H$_4$-CHMe$_2$). Additional ^{1}H{^{11}B} NMR: δ 2.66 (1H, BH), 1.96 (3H, BH), 0.49 (2H, BH), −0.02 (2H, BH). HR-MS (FAB with 3-NBA/CsI) m/z calcd for C$_{61}$H$_{68}$B$_9$Cl$_2$CsP$_4$RhRuS: 1462.1437 (M + Cs$^+$), found 1462.1416. The mass envelopes for the measured masses match quite well with those calculated from the known isotopic abundances of the constituent elements.

Structure Determination. Crystals were mounted on glass fibers in random orientations. Preliminary examination and data collection were performed using a Bruker SMART CCD detector system using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) equipped with a sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 45 narrow frame (0.3° in ω) scans. The data set collected typically consists of 3636 frames with a frame width of 0.3° in ω and 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^{33a} 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. Collected data were corrected for systematic errors

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Table 1. Crystal Data and Structure Refinement for [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (4), [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (8), and [1,1-(η^2-dppe)-3-η^1-{(dppm)Ru(η^6-*p*-cym)Cl$_2$}]-*closo*-1,2-RhSB$_9$H$_8$] (10)

	4	8	10
empirical formula	C$_{41}$H$_{55}$B$_9$Cl$_2$N$_3$P$_2$RhRuS	C$_{45.5}$H$_{49}$B$_9$Cl$_6$P$_3$RhS	C$_{62}$H$_{70}$B$_9$Cl$_4$P$_4$RhRuS
fw	1056.05	1133.72	1414.19
temp/K	223(2) K	180(2) K	223(2) K
wavelength/Å	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
α/Å	12.781(3)	16.4160(4)	14.7117(7)
β/Å	13.405(4)	20.7474(5)	20.0133(10)
χ/Å	28.450(7)	16.8186(4)	22.9074(12)
α/deg	90	90	90
β/deg	91.480(18)	115.631(2)	107.165(3)
γ/deg	90	90	90
V/Å^{-3}	4873(2)	5164.6(2)	6444.2(6)
Z	4	4	4
D(calc)/Mg m^{-3}	1.440	1.458	1.458
abs coeff/mm^{-1}	0.900	0.808	0.827
cryst size/mm	0.30 × 0.26 × 0.14	0.30 × 0.22 × 0.14	0.16 × 0.08 × 0.04
F(000)	2144	2300	2880
θ range for data collcn/deg	1.43 to 28.00	1.96 to 26.37	1.79 to 28.00
index ranges	$-16 \leq h \leq 16$	$-20 \leq h \leq 18$	$-19 \leq h \leq 18$
	$-17 \leq k \leq 17$	$-25 \leq k \leq 25$	$-26 \leq k \leq 26$
	$-37 \leq l \leq 37$	$-21 \leq l \leq 21$	$-30 \leq l \leq 30$
no. of reflens collected	89319	101621	87223
no. of ind reflens	11587 [R(int) = 0.09]	10519 [R(int) = 0.12]	15447 [R(int) = 0.09]
max. and min. transmn	0.8844 and 0.7740	0.8953 and 0.7936	0.9677 and 0.8790
no. of data/restraints/params	11587/38/569	10519/3/632	15447/3/781
goodness-of-fit on F^2	1.053	1.061	1.012
final R indices [$I > 2\sigma(I)$] R1	0.0680	0.0704	0.0612
wR2 (all data)	0.2004	0.1903	0.1044
largest diff peak and hole/e Å^{-3}	1.403 and -2.242	1.343 and -1.393	0.665 and -0.596

using SADABS[33b] 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.[33c] The structures were solved by direct methods and refined successfully in the space group $P2_1/n$ (**4**) and $P2_1/c$ (**8** and **10**). 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 boron cage hydrogen atoms were located and refined freely. Other hydrogens were treated using an appropriate riding model (AFIX m3). All the three compounds contain solvent of crystallization. The crystal lattice of **8** contains a molecule of CH$_2$Cl$_2$, **4** crystallizes with three molecules of CH$_3$CN, and **10** crystallizes with 2.5 molecules of CH$_2$Cl$_2$. The final residual values and other structure refinement parameters are listed in Table 1. The structures of the molecules, showing the atom labeling, are presented in Figures 1, 2, and 3 for compounds **4**, **8**, and **10**, respectively, and selected bond lengths and angles are given in Tables 2–4.

Complete listings of the atomic coordinates for the non-hydrogen atoms and the geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms, and anisotropic displacement coefficients for the non-hydrogen atoms are deposited with the Cambridge Crystallographic Data Center (CCDC #XXX, YYY, and ZZZ for **4**, **8**, and **10**, respectively).

Results and Discussion

The reaction between [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$ and [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] (**3**) in CH$_2$Cl$_2$, followed by passage through silica gel, affords a red crystalline product, which was characterized as [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (**4**), in 77% yield. Unidentified materials that were slow to move on silica are assumed to be [dppm-RuCl$_2$(η^6-*p*-

Table 2. Selected Bond Distances (Å) and Angles (deg) in [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (4)

Rh(8)−B(9)	2.145(7)	Rh(8)−B(4)	2.145(7)
Rh(8)−S(7)	2.338(2)	Rh(8)−B(3)	2.155(8)
Rh(8)−P(1)	2.264(2)	Rh(8)−Cl(1)	2.593(2)
Rh(8)−Cl(2)	2.489(2)	Ru(1)−P(2)	2.320(2)
Ru(1)−Cl(1)	2.386(1)	Ru(1)−Cl(2)	2.414(2)
B(9)−B(10)	1.841(11)	B(10)−B(11)	1.844(13)
B(11)−S(7)	1.913(9)	Ru(1)−centroid	1.705(6)
B(9)−Rh(8)−B(4)	50.4(3)	B(9)−Rh(8)−S(7)	90.5(2)
B(4)−Rh(8)−S(7)	90.7(2)	B(9)−Rh(8)−B(4)	50.4(3)
B(4)−Rh(8)−B(3)	49.6(3)	S(7)−Rh(8)−B(3)	54.1(2)
B(9)−Rh(8)−P(1)	86.4(2)	B(4)−Rh(8)−P(1)	86.4(2)
S(7)−Rh(8)−P(1)	171.96(6)	B(3)−Rh(8)−P(1)	119.0(2)
B(9)−Rh(8)−Cl(1)	178.9(2)	B(4)−Rh(8)−Cl(1)	129.3(2)
S(7)−Rh(8)−Cl(1)	88.44(6)	B(3)−Rh(8)−Cl(1)	91.7(2)
P(1)−Rh(8)−Cl(1)	87.67(5)	B(9)−Rh(8)−Cl(2)	101.8(2)
B(4)−Rh(8)−Cl(2)	151.7(2)	S(7)−Rh(8)−Cl(2)	94.73(6)
B(3)−Rh(8)−Cl(2)	147.9(2)	P(1)−Rh(8)−Cl(2)	91.40(5)
Cl(1)−Rh(8)−Cl(2)	78.64(4)	P(2)−Ru(1)−Cl(2)	85.83(5)
C(1)−P(1)−C(8)	105.4(3)	C(20)−P(2)−Ru(1)	109.31(18)
C(8)−P(1)−Rh(8)	115.6(2)	C(20)−P(2)−C(1)	99.8(3)
C(2)−P(1)−C(2)	99.3(3)	C(14)−P(2)−Ru(1)	118.8(2)
P(2)−Ru(1)−Cl(2)	85.83(5)	Cl(1)−Ru(1)−Cl(2)	84.30(5)
Ru(1)−Cl(1)−Rh(8)	97.24(5)	Ru(1)−Cl(2)−Rh(8)	97.24(5)
S(7)−B(3)−Rh(8)	67.5(2)	B(4)−B(9)−Rh(8)	64.8(3)
B(9)−B(4)−B(1)	108.8(6)	B(9)−B(4)−B(5)	59.2(5)
B(9)−B(4)−Rh(8)	64.8(3)	B(5)−B(4)−Rh(8)	116.3(5)
B(1)−B(4)−Rh(8)	117.3(5)	B(1)−B(3)−Rh(8)	116.8(5)
B(11)−S(7)−Rh(8)	110.6(3)	B(10)−B(9)−Rh(8)	110.7(8)

cym)] complexes. We have noted previously that such species tend to move very slowly during chromatography or actually stick to the plate.[34] Elemental analysis and high-resolution mass spectrometry support the formulation of **4**. Single crystals of **4**·(CH$_3$CN)$_3$, suitable for X-ray crystallography, precipitated from CH$_3$CN/Et$_2$O

(34) (a) McQuade, P.; Barton, L. Unpublished results. (b) McQuade, P. *Spec. Publ.−R. Soc. Chem.* **2000**, *253*, 271.
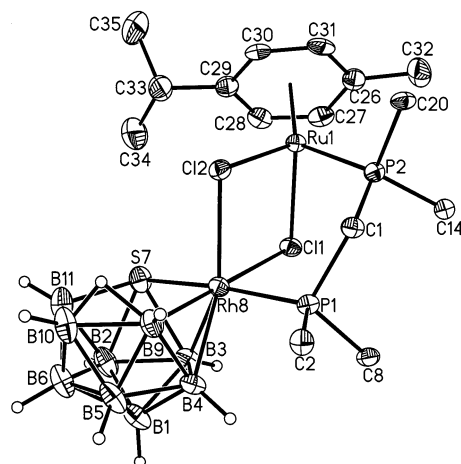
Table 3. Selected Bond Distances (Å) and Angles (deg) in [8-Cl-{8,9-(μ-dppm)}-10-PPh₃-*nido*-8,7-RhSB₉H₇] (8)

Rh(8)−B(3)	2.173(7)	P(1)−C(1)	1.855(6)
Rh(8)−B(9)	2.183(6)	P(2)−C(1)	1.811(6)
Rh(8)−P(1)	2.274(2)	P(2)−B(9)	1.926(6)
Rh(8)−S(7)	2.330(2)	P(3)−B(10)	1.949(7)
Rh(8)−Cl(1)	2.370(2)	B(9)−B(10)	1.731(9)
S(7)−B(11)	1.925(7)	B(10)−B(11)	1.746(9)

B(3)−Rh(8)−B(9)	83.6(2)	B(9)−Rh(8)−S(7)	88.8(2)
B(3)−Rh(8)−B(4)	48.9(2)	P(1)−Rh(8)−S(7)	171.8(1)
B(9)−Rh(8)−B(4)	47.9(2)	B(34c)−Rh(8)−Cl(1)	153.2(2)
B(3)−Rh(8)−P(1)	117.5(2)	B(9)−Rh(8)−Cl(1)	136.6(2)
B(9)−Rh(8)−P(1)	93.1(2)	P(1)−Rh(8)−Cl(1)	94.35(6)
B(4)−Rh(8)−P(1)	84.3(2)	S(7)−Rh(8)−Cl(1)	89.77(5)
B(3)−Rh(8)−S(7)	54.7(2)	B(9)−Rh(8)−S(7)	88.8(2)
B(11)−S(7)−Rh(8)	105.8(2)	C(14)−P(2)−C(20)	109.8(3)
C(8)−P(1)−C(2)	102.2(3)	B(10)−B(9)−P(2)	128.0(4)
C(8)−P(1)−C(1)	105.8(3)	B(10)−B(9)−Rh(8)	119.7(4)
C(2)−P(1)−C(1)	102.0(3)	P(2)−B(9)−Rh(8)	103.5(3)
C(8)−P(1)−Rh(8)	119.7(2)	B(9)−B(10)−B(11)	109.1(5)
C(2)−P(1)−Rh(8)	116.8(2)	B(9)−B(10)−P(3)	132.4(4)
C(1)−P(1)−Rh(8)	108.5(2)	B(11)−B(10)−P(3)	114.4(4)
C(14)−P(2)−C(1)	103.9(3)	P(2)−C(1)−P(1)	108.8(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) in [1,1-(η²-dppe)-3-η¹-{(dppm)Ru-(η⁶-*p*-cym)Cl₂}]-*closo*-1,2-RhSB₉H₈] (10)

Rh(1)−B(3)	2.115(5)	Rh(1)−P(2)	2.2670(11)
Rh(1)−S(2)	2.3611(11)	Rh(1)−P(1)	2.2794(11)
Rh(1)−B(7)	2.395(5)	Rh(1)−B(6)	2.374(5)
Rh(1)−B(5)	2.468(5)	Rh(1)−B(4)	2.410(5)
Ru(2)−Cl(1)	2.3985(12)	Ru(2)−P(4)	2.3687(12)
S(2)−B(5)	1.929(5)	Ru(2)−Cl(2)	2.4085(12)
B(3)−B(7)	1.714(6)	S(2)−B(4)	1.953(6)
B(3)−B(6)	1.711(7)	P(3)−B(3)	1.927(5)
B(5)−B(6)	1.855(7)	B(4)−B(7)	1.839(7)

B(3)−Rh(1)−S(2)	120.55(13)	C(1)−C(2)	1.527(5)
B(7)−Rh(1)−B(4)	44.99(17)	P(2)−Rh(1)−P(1)	84.44(4)
P(4)−Ru(2)−Cl(1)	86.78(4)	B(6)−Rh(1)−B(7)	68.10(17)
C(57)−Ru(2)−Cl(2)	160.28(15)	B(4)−Rh(1)−B(5)	68.78(18)
C(53)−Ru(2)−Cl(2)	112.14(13)	C(56)−Ru(2)−Cl(2)	122.56(15)
C(55)−Ru(2)−Cl(2)	93.39(15)	C(54)−Ru(2)−Cl(2)	89.55(14)
Cl(1)−Ru(2)−Cl(2)	88.91(4)	C(52)−Ru(2)−Cl(2)	148.51(13)
B(5)−S(2)−Rh(1)	69.42(16)	P(4)−Ru(2)−Cl(2)	85.86(4)
B(8)−S(2)−Rh(1)	99.00(16)	B(5)−S(2)−B(4)	90.5(2)
C(9)−P(1)−C(1)	106.2(2)	B(4)−S(2)−Rh(1)	67.17(15)
C(1)−P(1)−C(3)	101.47(19)	C(9)−P(1)−C(3)	101.62(19)
C(1)−P(1)−Rh(1)	109.11(14)	C(9)−P(1)−Rh(1)	121.04(14)
C(21)−P(2)−C(2)	105.09(19)	C(3)−P(1)−Rh(1)	115.36(14)
C(2)−P(2)−C(15)	102.0(2)	C(21)−P(2)−C(15)	100.08(19)
C(2)−P(2)−Rh(1)	108.34(14)	C(21)−P(2)−Rh(1)	121.92(14)
C(28)−P(3)−C(34)	108.29(18)	C(15)−P(2)−Rh(1)	117.15(15)
C(34)−P(3)−C(27)	107.04(18)	C(28)−P(3)−C(27)	109.21(19)
C(34)−P(3)−B(3)	114.67(19)	C(28)−P(3)−B(3)	110.58(19)
C(40)−P(4)−C(46)	104.9(2)	C(27)−P(3)−B(3)	106.89(19)
C(46)−P(4)−C(27)	107.06(19)	C(40)−P(4)−C(27)	107.61(19)
P(3)−B(3)−Rh(1)	138.8(2)	C(40)−P(4)−Ru(2)	115.48(16)
C(46)−P(4)−C(27)	107.06(19)	C(46)−P(4)−Ru(2)	111.21(14)
B(6)−B(3)−B(7)	102.5(3)	C(27)−P(4)−Ru(2)	110.18(13)
B(6)−B(3)−Rh(1)	75.9(2)	B(9)−B(3)−P(3)	110.9(3)
B(9)−B(3)−Rh(1)	110.3(3)	B(7)−B(3)−Rh(1)	76.7(2)
S(2)−B(4)−Rh(1)	64.53(15)	B(7)−B(4)−S(2)	126.4(3)
S(2)−B(5)−Rh(1)	63.56(16)	B(6)−B(5)−S(2)	124.4(3)
C(1)−C(2)−P(2)	107.6(3)	C(2)−C(1)−P(1)	109.4(3)

Figure 1. Molecular structure of [8,8-η²-{(μ-Cl)₂Ru(η⁶-*p*-cym)(dppm)}-*nido*-8,7-RhSB₉H₁₀] (**4**). Displacement ellipsoids are drawn at the 50% level. The phenyl rings on phosphorus, *ipso*-carbon atoms excepted, are omitted for clarity, as are all the H atoms on carbon.

starting complex **3**. One Cl ligand, Cl(1), is in the plane of the open face of the cluster, *trans* to B(9), and the other, Cl(2), is perpendicular to the face, *trans* to the B(3)−B(4) axis, with the Cl−Rh−Cl angle ca. 79°. The P atom coordinated to Rh is *trans* to S. The other angles around Rh conform quite well to octahedral geometry: Cl(1)−Rh−B(9) is 179°, P(1)−Rh−S is 172°, B(9)−Rh−S is 90°, and P(1)−Rh−Cl(1) is 88°. The orientation around the Ru atoms is not unusual, also conforming to a pseudo-octahedral arrangement, as is seen in typical [Ru(η⁶-*p*-cym)Cl₂]-phosphine complexes,[35] and the orientations around the two P atoms are those of somewhat distorted tetrahedra. Interestingly, the four-atom ring Ru−Cl(2)−Rh−Cl(1) is almost a perfect square, with the internal angles, centered at the previously listed atoms, being 84.3°, 99°, 79°, and 97°, respectively. The cage dimensions do not deviate from those found in related systems, except that the bonds to Rh are shorter by 0.05−0.08 Å, presumably due to the electron-withdrawing influence of the Cl ligands.[16a,b,19,22,24,25]

NMR spectral data for **4** are consistent with the structure given in Figure 1. The ¹¹B NMR spectrum consists of nine broad signals in the range δ = +14.9 to −31.8. Three of them are very broad, and presumably are those bonded to Rh. The noncage protons associated with the *p*-cymene group, the phenyl groups on P, and the CH₂ group on dppm were all identified in their NMR spectra, and additional resonances, assigned to nine boron-bonded terminal hydrogen atoms and one bridging hydrogen atom (−2.08 ppm), were observed. The expected two ³¹P{¹H} resonances were also observed: a broad doublet assigned to the P atom on Rh *trans* to the sulfur atom at 31.8 ppm (J³¹P−¹⁰³Rh = 153 Hz) and a doublet at 26.6 ppm (J³¹P−³¹P = 4 Hz) assigned to the P atom coordinated to the Ru atom.

During the formation of **4**, presumably the [Ru(η⁶-*p*-cym)(μ-Cl)₂]₂ dimer is cleaved by the dangling PPh₂ group on **3**. This is then followed by replacement of the bidentate dppm ligand in **3** by a lone pair of electrons

solutions. Compound **4** has the molecular structure depicted in Figure 1, and it can be described as an 11-vertex *nido*-rhodathiaundecaborane with an *exo*-polyhedral ligand that chelates the rhodium through a phosphine and a pair of Cl ligands on the Ru atom. The multidentate ligand is formally a neutral dppm molecule with one of the PPh₂ groups coordinated to the Ru atom in the [Ru(η⁶-*p*-cym)Cl₂] moiety. The orientation around the Rh atom in **4** is pseudo-octahedral, as it is in the

(35) Serron, S. A.; Nolan, S. P.; Abramov, Yu. A.; Brammer, L.; Petersen, J. L. *Organometallics* **1998**, *17*, 104.

Scheme 2
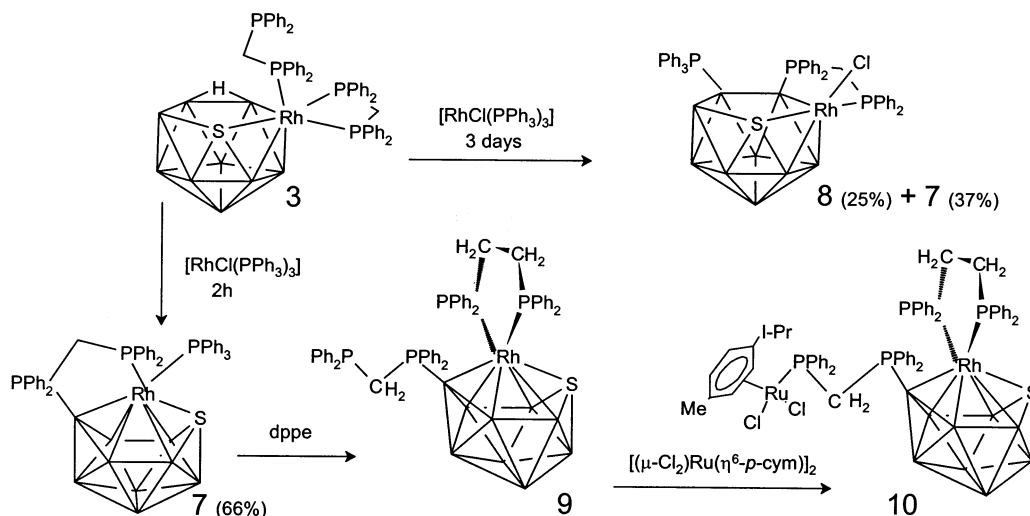
on each of the two Cl ligands on Ru. The additional [RuCl$_2$(η^6-*p*-cym)] moieties remaining in solution would complex to the released dppm. The structure of **4** is novel. The dppm-ligated Ru moiety [RuCl$_2$(η^6-*p*-cym)-(dppm)] coordinates to the Rh atom through a PPh$_2$ group and also through two Cl ligands on Ru, thus forming a Rh−(μ-Cl)$_2$−Ru moiety in which the two metals are also linked through a bridging dppm ligand. In the formation of **4**, replacement of the bidentate dppm on **3** by the two Cl ligands maintains the electronic configuration of the octahedrally coordinated Rh atom as an 18-electron metal center. This satisfies the metal center electronically and also maintains the correct *nido*-skeletal electron count of the cluster, the ligand functioning as a six-electron donor. **4** is similar to the species [8,8-η^2-{(η^2-BH$_3$)(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$], which we described previously,[16a] and is shown as structure **E** in Chart 1. The latter contains a BH$_3$·dppm moiety, which functions as a multidentate ligand, but in that case the BH$_3$ group uses two of its H atoms in three-center two-electron bonds to Rh, whereas in **4** the interactions are normal two-electron two-center bonds.

The reaction between **3** and [Cp*Ir(μ-Cl)$_2$]$_2$ in CH$_2$-Cl$_2$ at ambient temperature affords the analogous species [8,8-η^2-{(μ-Cl)$_2$Cp*Ir(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (**5**) as a yellow solid in 47% yield. Although we were unable to obtain crystals suitable for X-ray analysis, elemental analysis and high-resolution mass spectrometry indicated the composition and NMR spectra also supported our formulation of the species whose proposed structure is given in Scheme 1. The ^{11}B spectrum exhibits nine signals, whose chemical shift values are very close to those for **4**. Similarly the ^{1}H spectrum exhibits signals corresponding to 10-cage-bonded H atoms at chemical shifts very similar to those for **4**. The bridging H atom is observed at −2.01 ppm. The rhodium analogue of **5**, [8,8-η^2-{(μ-Cl)$_2$Cp*Rh(dppm)}-*nido*-8,7-RhSB$_9$H$_{10}$] (**6**), was obtained from the reaction between [Cp*RhCl$_2$(η^1-dppm)] and [8,8-(PPh$_3$)$_2$-*nido*-8,7-RhSB$_9$H$_{10}$] (**2**) in CH$_2$Cl$_2$ under N$_2$. The isolated and purified orange product was characterized as **6** and obtained in 65% yield. We carried out the reaction of the preformed ligand [Cp*RhCl$_2$(η^1-dppm)] with **2** to see if we obtained the same type of product as **5**, and indeed we did. The NMR spectral data for **6** are very similar to those for **5**,

and the formulation was confirmed by elemental analysis and high-resolution mass spectrometry. We again were unable to grow crystals suitable for X-ray analysis, but we are confident that the structure of **6** is the same as that depicted in Scheme 1.

The reaction between **3** and other coordinatively unsaturated organometallic reagents provided new insights into this system. Reaction between **3** and [IrCl-(CO)(PPh$_3$)$_2$] afforded unstable product mixtures containing small amounts of the previously reported species [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$] (**7**)[16d] and other unidentifiable products. It appeared that the Ir reagent served to remove dppm from the metal center prior to subsequent chemistry. If [RhCl(PPh$_3$)$_3$] is added to a solution of freshly prepared **3** in CH$_2$Cl$_2$, and the reaction mixture stirred for 2 h, the only isolable product, in 66% yield, is **7**. The reaction is illustrated in Scheme 2. Apparently some exchange of PPh$_3$ for dppm on the Rh center occurs, and the metal reagent serves to coordinate dppm. If the reaction mixture is stirred for 3 days prior to workup, two products are obtained. One was compound **7**, obtained in 37% yield. The ^{11}B NMR spectrum of the second product exhibits nine resonances, five of which were very broad, but the proton spectrum exhibited resonances corresponding to seven cage hydrogen atoms, none of which were assignable to bridging H atoms. The ^{31}P spectrum indicated the presence of three phosphorus atoms, one bonded to Rh and the other two bonded to boron. A crystal structure determination identified the species as [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (**8**), and the structure is given in Figure 2 and also illustrated in Scheme 2.

The structure of **8** is that of a *nido*-rhodathiaborane cluster with a dppm ligand bridging the metal and the B(9) position in the open face. A PPh$_3$ molecule is bonded to B(10), also in the open face, and the Rh atom bears a Cl ligand. The orientation around Rh is essentially square planar. We and others have noted that for such 16-electron square planar metallaboranes containing Pt, Pd, or Rh the electron count is two electrons short of the count required by the PSEPT.[23] This is the case for **8**, in which the seven BH groups contribute 14 e$^-$, the S atom contributes 4 e$^-$, the two B·PR$_3$ groups contribute 6 e$^-$, and the Cl−Rh−PR$_3$ moiety does not contribute
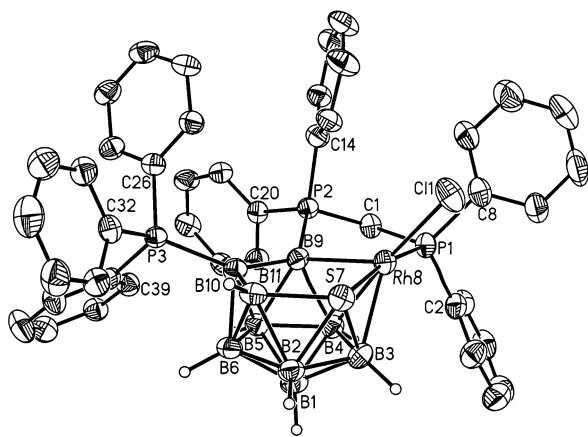
Figure 2. Molecular structure of [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (**8**). Displacement ellipsoids are drawn at the 50% level. The H atoms on carbon are all omitted for clarity.

any skeletal electrons to the cluster. Thus **8**, which contains 11 vertexes, has 12 skeletal electron pairs, and since it has a *nido*-structure, it is two electrons short of the required number. This compound is isoelectronic with **7**, whose structure is that of a *closo*-11 vertex cluster, with an open four-sided "face" reminiscent of the series of *iso-nido* 11-vertex clusters which have been discovered in recent years.[36]

The angles around Rh in **8** reflect the near square-planar geometry. The angles B(9)−Rh−P(1) and Cl−Rh−P(1) are close to the required 90° at ca. 94.3° and 93.1°, respectively. Also the axis S−Rh−P(1) is almost linear at 171.8°, but distortion from the idealized geometry is seen by the angle B(9)−Rh−Cl, which is ca. 136°. Other interesting features of the structure of **8** are the bond distances in the open face of the cage and the Rh−P distances. They are all slightly shorter than those in **3** and also in the related species **2**. This may be due to the inductive effects of the phosphine ligands on the cage boron atoms and also the absence of a bridging H atom in **8**. High-resolution mass spectrometry also confirmed the formulation of **8**, and elemental analysis data attested to the purity of the material we isolated.

Reactions proceed differently when [IrCl(CO)(PPh$_3$)$_2$] or [RhCl(PPh$_3$)$_3$] is allowed to react with **3**, as opposed to when the chloride dimer [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$, [Cp*Ir-(μ-Cl)$_2$]$_2$, or presumably [Cp*Rh(μ-Cl)$_2$]$_2$ reacts with **3**. It appears that the reaction of **3** with the organometallic reagents differs in accord with the ability of the latter to remove dppm from **3** and coordinates dppm in a bidentate mode. The monomeric Rh and Ir reagents can remove dppm, which become bidentate as the resulting complex loses a mole of PPh$_3$. This PPh$_3$ is available in solution for further reaction with **3**, allowing the formation of [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$], **7**, which we observe in the cases involving [IrCl(CO)-(PPh$_3$)$_2$] or [RhCl(PPh$_3$)$_3$]. Accordingly, addition of PPh$_3$

to the metal center in the rhodathiaborane cluster, along with concomitant loss of H$_2$ as the free PPh$_2$ group of the dppm coordinates to the cage, would result in the formation of **7**. The H$_2$ would come from loss of a terminal and the bridging H atom. Previously we prepared **7** in a ligand exchange reaction between **2** and **3**.[16d] Reaction between **3** and [RhCl(PPh$_3$)$_3$] for extended periods of time results in the formation of species **8**. Perhaps this reaction occurs with a precursor to **7**, although there are obvious unanswered questions about the formation of **8**. A plausible route to **8** would involve replacement of PPh$_3$ with the more nucleophilic Cl$^-$, thereby releasing more PPh$_3$, which then attacks a cage boron atom. The dimeric bridging-chloride reagents cannot abstract dppm to form stable species in which dppm bonds in a bidentate mode nor, of course, can it release PPh$_3$. Thus a different reaction pathway is followed and formation of bimetallic clusters is observed.

Of particular interest to us was the structure of **8**, especially the dppm moiety bridging the Rh atom and position 9 in the open face of the cage. We have noted previously that **3** thermally converts to a mixture of two red species, which we have been unable to separate completely.[16d] Our conclusions are described elsewhere and are summarized in Scheme 3. In the scheme we propose that **3** converts to either [3-(η^1-dppm)-1,1-(η^2-dppm)-*closo*-1,2-RhSB$_9$H$_8$] (**11′**) or [1-(η^1-dppm)-1,3-(μ-dppm)-*closo*-1,2-RhSB$_9$H$_8$] (**11″**) via the species **T**, which has two electrons more than the "saturated" species **3** and contains a dppm ligand bridging the metal and the 9-position on the cage. We suggest that our observation of this bridging ligand in **8** adds credence to our proposal that **T** or a very similar species is the precursor to **11′** and **11″**.

We had also previously noted that the reaction between [1-PPh$_3$-{1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$] (**7**) and dppe affords [1,1-(η^2-dppe)-3-(η^1-dppm)-*closo*-1,2-RhSB$_9$H$_8$] (**9**),[16d] as illustrated in Scheme 2. As part of our study of potential metal derivatives of the RhSB$_9$ cluster, we decided to see if we could metalate **9** at the pendant PPh$_2$ position. Treatment of **9** with [Ru(η^6-*p*-cym)(μ-Cl$_2$)]$_2$ in CH$_2$Cl$_2$ followed by workup allows isolation of an orange solid, [1,1-(η^2-dppe)-3-η^1-{(dppm)-Ru(η^6-*p*-cym)Cl$_2$}-*closo*-1,2-RhSB$_9$H$_8$] (**10**), in 79% yield. The reaction is illustrated in Scheme 2. ^{11}B NMR spectra indicate the presence of nine boron atoms, and the proton spectrum exhibits four resonances assignable to eight terminal boron-bonded atoms on the cage. The ^{31}P NMR spectrum shows the expected four P atoms in 2:1:1 ratio. Elemental analysis and high-resolution mass spectrometry supported the proposed formulation, and crystals suitable for X-ray analysis afforded a structure that confirmed it. The structure is given in Figure 3, and it is a *closo*-RhSB$_9$H$_8$ cluster in which the rhodathiaborane cage has a pendent metal-ligated dppm group at the 3-position.

The structure of the RhSB$_9$ cage in the bimetallic species **10** is very similar to that of **9**. Thus the angles B(9)−B(3)−P(3), Rh−B(3)−P(3), B(9)−B(3)−Rh, and S−Rh−B(3) are 110.9°, 138.8°, 110.3°, and 120.55° in **9**, respectively, and 114.79°, 136.6°, 112.8°, and 120.97° in **10**, respectively. The orientation of the pendant [(dppm)Ru(η^6-*p*-cym)Cl$_2$)] group relative to the cage is interesting. The planes defined by the atoms Rh−B(3)−

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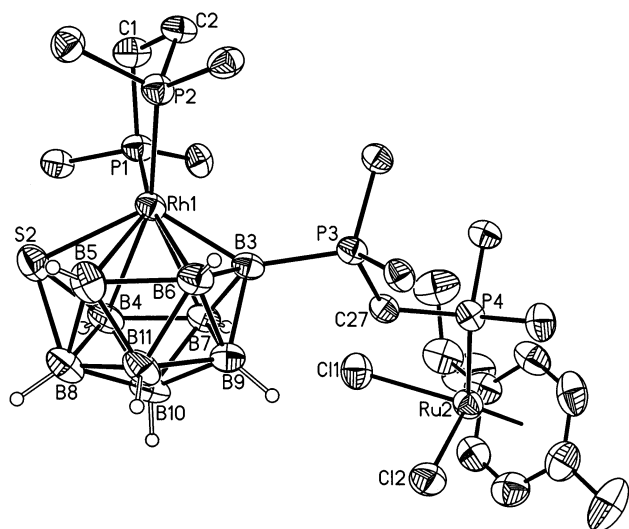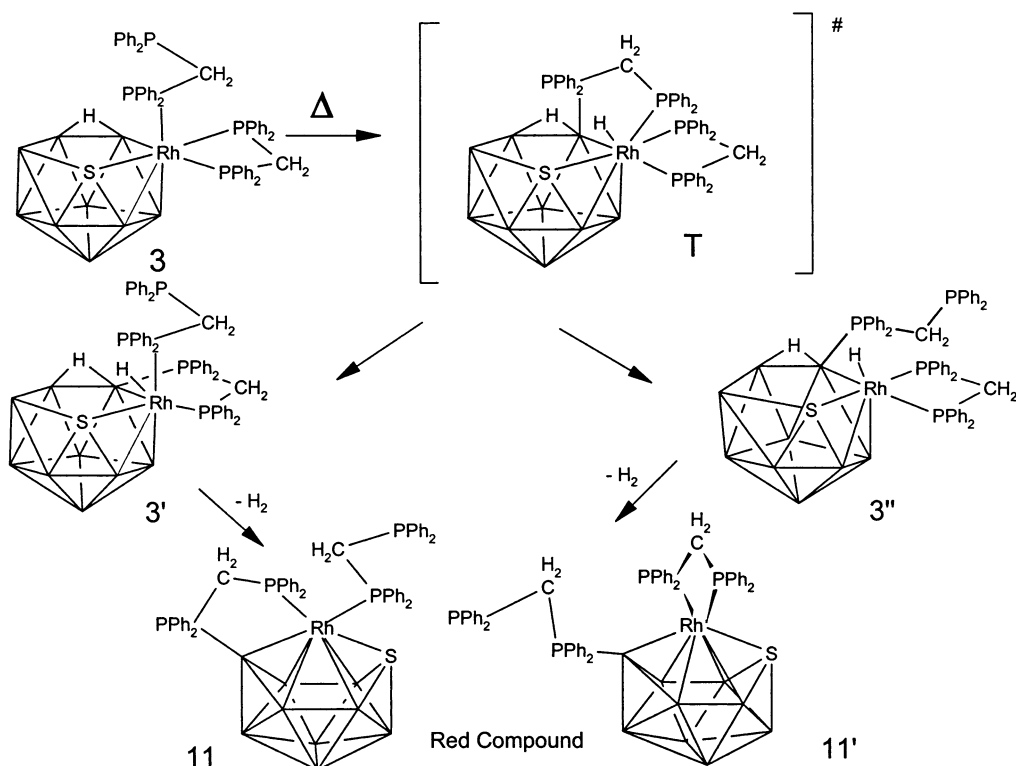
Scheme 3

Figure 3. Molecular structure of [1,1-(η^2-dppe)-3-η^1-{(dppm)Ru(η^6-*p*-cym)Cl$_2$)}-*closo*-1,2-RhSB$_9$H$_8$] (**10**). Displacement ellipsoids are drawn at the 50% level. The phenyl rings on phosphorus, *ipso*-carbon atoms excepted, are omitted for clarity, as are all the H atoms on carbon.

P(3) and B(3)−P(3)−C(27) lie at 116.4° to each other, reflecting minimization of steric crowding of the methylene H atoms on C(27). On the other hand, the planes defined by the atoms B(3)−P(3)−C(27) and P(3)−C(27)−P(4) deviate from coplanarity by 5.3°, and those defined by the atoms P(3)−C(27)−P(4) and C(27)−P(4)−Ru by 6.2°; thus the atoms B(3), P(3), C(27), and Ru all lie essentially on a plane. There is nothing unusual about the geometry around the atoms on the backbone of the pendant [(dppm)Ru(η^6-*p*-cym)Cl$_2$)] group. The orientation around the atoms P(3), P(4), and C(27) shows deviations from ideality which reflect steric factors. For

example the angles B(3)−P(3)−C(27) and C(27)−P(4)−Ru(2) are 106.89(19)° and 110.18(13)°, respectively, whereas P(3)−C(27)−P(4) is 130.7(2)°, reflecting the greater steric requirements of the PPh$_2$ groups relative to the CH$_2$ groups. As expected the Ru atom is pseudo-octahedrally coordinated by the two Cl atoms, P(4), and the "tricoordinate" (*p*-cym) ligand. Thus the angles Cl-(1)−Ru−Cl(2), Cl(1)−Ru−P(4), and Cl(2)−Ru−P(4) are all close to 90°, at 88.9°, 86.8°, and 85.9°, respectively. The cage itself is quite similar to analogous systems. The angle between the planes S(2)−Rh(1)−B(3) and P(1)−Rh(1)−P(2) is 101°, quite close to the ideal value of 90°.

Summary

We have exploited the chemistry of the novel species [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-RhSB$_9$H$_{10}$] (**3**) by preparing a series of bimetallathiaboranes on a RhSB$_9$ cluster template. These include *nido*-species containing the metal pairs Rh/Ru, Rh/Ir, and Rh/Rh. In addition we have prepared a *closo*-derivatives of **3** with a pendant ligated metal moiety, which may portend applications of these systems. Ligand exchange on **3** is stimulated by the use of the more electrophilic coordinatively unsaturated metal reagents [IrCl(CO)(PPh$_3$)$_2$] and [RhCl-(PPh$_3$)$_3$], and the products of these reactions provided us with support for our earlier suggestion for the reaction pathway for rearrangement of species **3**.

Supporting Information Available: X-ray structural data for **4**, **8**, and **10** including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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