APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 409–420
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.448

Organometallic chemistry on rhodaheteroborane clusters: reactions with bidentate phosphines and organotransition metal reagents†

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Received 14 January 2003; Revised 20 January 2003; Accepted 29 January 2003

This article reviews our recent work on the reactions of the rhodaheteroboranes [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (1) and [9,9-$(PPh_3)_2$-*nido*-9,7,8-$RhC_2B_8H_{11}$] (2), and their derivatives, with the bidentate phosphines, dppe [$(CH_2)_2(PPh_2)_2$], dppp [$(CH_2)_3(PPh_2)_2$], and dppm [$CH_2(PPh_2)_2$], and also with organotransition metal reagents. Simple substitution of the two PPh_3 ligands by a single bidentate phosphine takes place when a 1:1 molar ratio of base (dppe or dppp) to rhodathiaborane (1) is used. However, in the presence of an excess of dppe or dppp, products containing 1 or 2 mol of base are formed. These products include a bidentate ligand on the metal and a monodentate ligand on the cage. The displaced hydrogen atom from the cage has moved to the metal center. These bis(ligand) species are unstable with respect to the loss of dihydrogen, affording *closo*-11 vertex clusters with a pendent phosphine ligand on the cage. In concentrated solutions, the pendent phosphine attacks another cage to afford linked clusters. Under both sets of conditions, when dppm is used, only one product is observed. This species has two dppm ligands coordinated to the metal: one in a unidentate mode and the other bidentate. A similar product is obtained in the reaction of 2 with dppm, although the arrangement of the ligands on the metal in the product is different. Ligand exchange experiments on the dppm–thiaborane system lead to results that provide keys to the reaction pathways in some of these processes. The bis(dppm) derivatives of 1 and 2 are amenable to further derivatization. A second metal may be added, either as an *exo*-polyhedral atom in a *nido* cluster in which the metal is part of a bidentate ligand, in the case of 1 and 2, or in a *closo* cluster derivative of 1 in which the metal is bonded to a dangling PPh_2 moiety. Thus, it was possible to add the metals iridium, rhodium or ruthenium to the cluster, in the case of 1 and ruthenium in the case of 2. However, the reaction of more electrophilic organotransition metal reagents, such as Wilkinson's catalyst, with the dppm derivative of 1 affords species resulting from removal of ligand rather than incorporation of metal, and the products shed light on the rearrangement processes in these systems.

KEYWORDS: boranes; metallaboranes; carboranes; thiaboranes; clusters; organometallic; rhodium

INTRODUCTION

This article reviews our recent work on the reactions of bidentate bases and organotransition metal reagents with unsaturated heterometallaboranes. The motivation for this project was based on our previous success in the interaction of small metallaboranes with bidentate bases wherein pendent phosphine ligands, which exhibit the potential to form linked clusters, were observed.[1] Two substrates came to mind for such a study: [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$][2,3] (**1**) and [9,9-$(PPh_3)_2$-*nido*-9,7,8-$RhC_2B_8H_{11}$] (**2**; Scheme 1),[4,5]

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Contract/grant sponsor: National Science Foundation; Contract/grant number: CHE-9727570.
Contract/grant sponsor: Missouri Research Board.
Contract/grant sponsor: UM–St Louis Center for Molecular Electronics.
†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.
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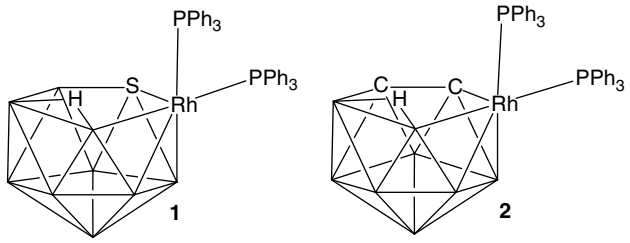
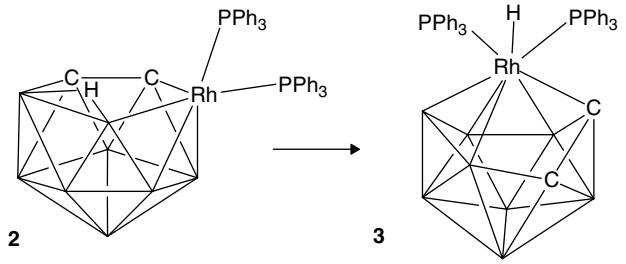
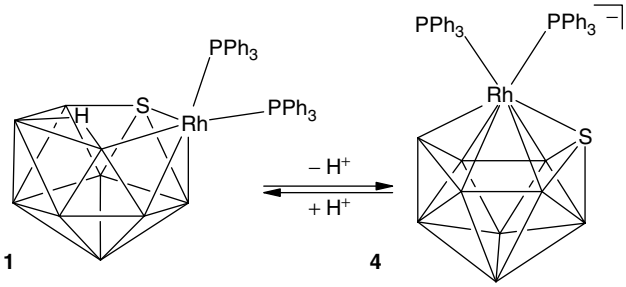


Scheme 1.



Scheme 2.

compounds that are formally isoelectronic and are two electrons short of the number notionally required to satisfy the polyhedral skeletal electron pair theory (PSEPT).[6–8] Unlike the rhodacarborane **2**, which is less stable and may rearrange to a more closed configuration[4] (Scheme 2), the rhodathiaborane **1** is stable, easily prepared and has been more extensively studied.[2,3,9–13] There are novel features associated with compound **1**. The unsaturation has been questioned, and the presence of two unusual *ortho*-CH···Rh agostic interactions have been suggested[9,12,13] to account for this apparent anomaly. Also, rearrangement of **1** to a *closo*-system is promoted by deprotonation,[12,13] as indicated in Scheme 3. Molecule **1** undergoes interesting fluxional behavior in solution[2] (Scheme 4) and is reactive towards both electrophiles and nucleophiles. In particular, the reactions of **1** with Lewis bases L (where L = CO, PMe_2Ph or CH_3CN) result in either addition of the ligand, L, to the metal center or addition and substitution, giving rise to species such as [8-L-8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (where L = CO[3] or CH_3CN[9]) and [8,8,8-$(PMe_2Ph)_3$-*nido*-8,7-$RhSB_9H_{10}$].[10] Among the latter species, only [8-(CO)-8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] has been studied further, and in refluxing benzene it forms [1-(CO)-1,3-$(PPh_3)_2$-*closo*-1,2-$RhSB_9H_8$], which when treated with an excess of PMe_2Ph at reflux temperature in benzene affords [1-(CO)-1-(PMe_2Ph)-3-L-*closo*-1,2-$RhSB_9H_{10}$] (where L = PMe_2Ph or PPh_3).[3] Other reaction patterns, such as terminal hydrogen substitution at the 9-position by an OEt group[11] and an unusual metal incorporation to form a 12-vertex bimetallic species, have also been reported.[3] Herein, we summarize our studies of the reactions of **1** and **2**



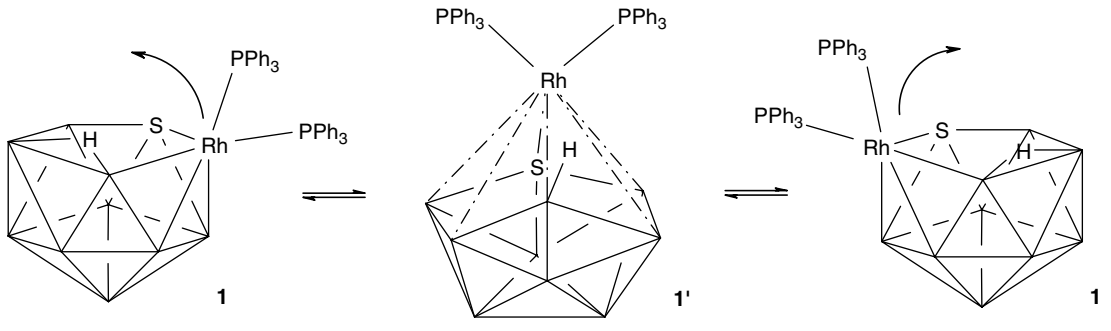
Scheme 3.

and their derivatives with bidentate phosphine bases and organotransition metal reagents.

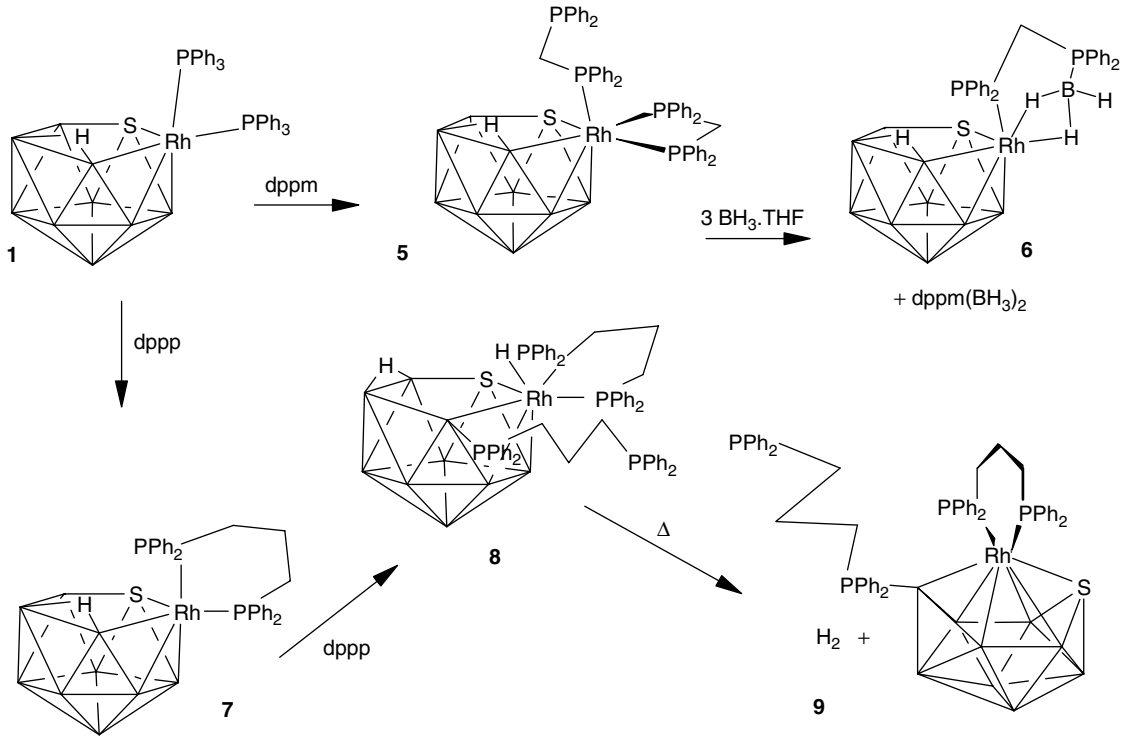
CHEMISTRY OF THE RHODATHIABORANE, [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (1) AND ITS DERIVATIVES

Reactions of [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (1) with bidentate phosphines

Reaction between [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**) and dppm (i.e. $[CH_2(PPh_2)_2]$), in CH_2Cl_2 at room temperature, affords the saturated rhodathiaborane cluster [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-$RhSB_9H_{10}$] (**5**).[14–16] Compound **5**, shown in Scheme 5, contains both a bi- and a mono-dentate dppm ligand, and was obtained as a yellow crystalline solid in 48% yield along with another species, a red crystalline material that initially eluded characterization.



Scheme 4.



Scheme 5.

Compound **5** was identified by high-resolution mass spectrometry, multinuclear magnetic resonance spectroscopy and a single crystal structure determination. This species is clearly a saturated cluster, since the additional phosphine donor on the rhodium center provides another pair of electrons to the cluster. Thus, it contains 13 skeletal electron pairs and 11 vertices, appropriate for a *nido*-cluster.[6–8]

In order to see if compound **5**, which contained a dangling PPh_2 group, would form links to other main group moieties, we treated **5** with excess BH_3·thf in CH_2Cl_2 at room temperature. An air-stable orange crystalline solid **6** was obtained in 71% yield, along with an equimolar amount of [dppm$(BH_3)_2$]. Compound **6** was characterized by NMR spectroscopy, elemental analysis, mass spectrometry and a crystal structure determination, to be [8,8-η^2-{η^2-$(BH_3)Ph_2PCH_2PPh_2$}-*nido*-8,7-$RhSB_9H_{10}$]. The structure of **6**, illustrated in Scheme 5, is unique in that it contains the $[(BH_3)Ph_2PCH_2PPh_2]$ ligand, which chelates to the rhodium as a six-electron donor. The ligand bonds to the rhodium atom through a phosphine group and a borane unit. The BH_3 terminus of this ligand can be regarded as a neutral phosphine–borane that coordinates the rhodium atom, through the BH_3 in a bidentate mode, via two Rh–H–B three-center two-electron bonds. The $^1H\{^{11}B\}$ NMR spectrum of **6**, at room temperature, exhibits a single resonance for the hydrogen atoms of the BH_3 group at −1.37 ppm. As the temperature is lowered, this peak broadens and finally splits into three signals at +2.73, −0.24 and −0.52 ppm. This suggests that the BH_3 group is fluxional in solution, probably undergoing rotation about the B–P bond, rendering the two bridging and the terminal hydrogen atoms equivalent on the NMR time scale ($\Delta G^{\ddagger} \approx 37$ kJ mol^{-1}). More recently, another system containing a bidentate $[(BH_3)Ph_2PCH_2PPh_2]$ ligand that also chelates a rhodium center was reported.[17]

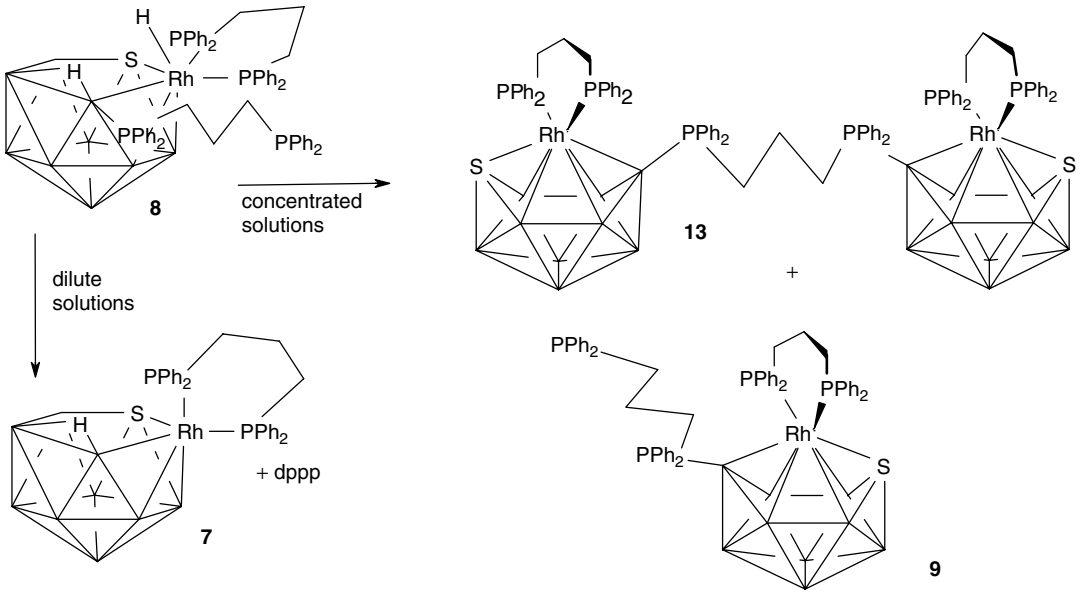
Reactions of [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**) with dppp or dppe (i.e. $[(CH_2)_n(PPh_2)_2]$, where $n = 3$ or 2 respectively) proceed quite differently from reactions with dppm.[16] When a 1:1 molar ratio of phosphine to rhodathiaborane is used, simple substitution to form [8,8-(η^2-dppp)-*nido*-8,7-$RhSB_9H_{10}$] (**7**) or [8,8-(η^2-dppe)-*nido*-8,7-$RhSB_9H_{10}$] (**10**), as yellow and orange air stable solids respectively, is observed. Compound **10** is known and was prepared previously from the reaction between $[RhCl(dppe)]_2$ and Cs[6-*arachno*-SB_9H_{12}];[18] but compound **7** was new, and complete characterization, including a crystal structure determination, identified the material. The properties of compounds **7** and **10** are quite similar to those of the starting material **1**. NMR spectra for **7** at different temperatures suggest an intramolecular dynamic process, which resembles the fluxional behavior observed for the previously studied species, **1** and **10**, the isoelectronic platinacarborane, [8,8-$(PMe_2Ph)_2$-*nido*-8,7-$PtCB_9H_{11}$],[19] and the rhodaazaborane, [8,8-$(PPh_3)_2$-*nido*-8,7-$RhNB_9H_{11}$].[20] It is thought that all these species undergo fluxional motion similar to that illustrated in Scheme 4 for compound **1**, involving a *closo*-type transition state. The activation energy $\Delta G^{\ddagger}$ calculated for the process observed for **7** at the coalescence temperature of 310 K in the ^{31}P NMR spectrum, is 53 kJ mol^{-1}. This compares well with values for

the previously studied species. The transition state shown in Scheme 4 is comparable to the species in solution equilibrium with the *nido*-metallacarborane analogue of **2**, [9,9-$(PEt_3)_2$-9,7,8-$RhC_2B_8H_{11}$] and its *isonido*-isomer,[4,5] [1,1,1-$H(PEt_3)_2$-1,2,4-$RhC_2B_8H_{10}$]. It is also related to the *isonido*-species, [1,1,1-$H(PMe_3)_2$-1,2,4-$IrC_2B_8H_{10}$], formed from the thermolysis of [9,9,9-$CO(PMe_3)_2$-*nido*-9,7,8-$IrC_2B_8H_{11}$].[21,22] Further support for the *closo*-type transition state comes from the observation of the reversible *nido* to *closo* change that compound **1** undergoes on deprotonation, which is illustrated in Scheme 3.[9,12,13]

When the reactions of compound **1** with dppe and dppp are carried out in 1:3 metallathiaborane to phosphine molar ratios, compounds **7** and **10** are formed together with the yellow *nido*-rhodathiaboranes, [8,8-(η^2-dppp)-9-(η^1-dppp)-*nido*-8,7-$RhSB_9H_{10}$] (**8**) and [8,8-(η^2-dppe)-9-(η^1-dppe)-*nido*-8,7-$RhSB_9H_{10}$] (**11**). The new species, **8** and **11**, are formed by substitution reactions at the metal center, and the addition of a second ligand at the 9-position in the cluster. They were characterized by NMR spectroscopy and mass spectrometry. The proposed structure for **8** is illustrated in Scheme 5. The ^{11}B NMR spectra consist of seven peaks of relative intensity 2:1:1:1:1:2:1 for **8**, and five broad peaks of relative intensity 1:1:4:2:1 for **11**. $^1H\{^{11}B(sel)\}$ experiments assigned eight different terminal hydrogen atoms to their directly bound boron atoms, indirectly resolving the ^{11}B spectra. One of the boron atoms has no terminal hydrogen atom, since it bears a PPh_2 terminus of the monodentate diphosphine substituent. The ^1H NMR spectra include peaks at −2.39 and −11.96 ppm for **8**, and at −1.39 and −11.97 ppm for **11**. The signals at the highest frequencies in the negative region of the spectra, which are broad singlets, are assigned to B–B bridging hydrogen atoms on the cluster, whereas the peaks at the lowest frequencies, observed as multiplets, are assigned to rhodium-bonded hydrides. The $^{103}Rh-^1H$ coupling is clearly visible. The observed spectroscopic data suggest molecular structures as shown in Scheme 5 for **8**.

The formation of **8** and **11** from **1** would appear to involve substitution of the PPh_3 groups by a chelating ligand followed by the addition of a second ligand at the 9-position on the cage with concomitant migration of the hydrogen atom to the rhodium atom. However, we cannot rule out a mechanism with an initial step, similar to the formation of **5**, in which two ligands first coordinate to the metal followed by transfer of the unidentate one to the electrophilic site at B(9). The higher nucleophilicity of the PPh_2 group on dppe or dppp and a more favorable stereochemistry mitigate in favor of a higher tendency for concerted transfer of a ligand to the cage than would be the case for dppm from compound **5**, although more recent results, described below, tend to muddy the waters. However, we have no explanation for the apparently different behaviors of the dppm-coordinated clusters with respect to the dppe- and dppp-coordinated systems.

Compounds **8** and **11** are unstable in solution and tend to lose dihydrogen to form 11-vertex *closo*-clusters [1,1-(η^2-dppp)-3-(η^1-dppp)-*closo*-1,2-$RhSB_9H_8$] (**9**) and [1,1-(η^2-dppe)-3-(η^1-dppe)-*closo*-1,2-$RhSB_9H_8$] (**12**) respectively. Indeed the *closo*-species of the type indicated as **9** in Scheme 5 are often formed during attempts to isolate **8** and **11**. However, the situation is more complex. When a dilute solution of **8** is heated at reflux temperature, in CH_2Cl_2 for 1 day, the resultant solution contains a mixture of the precursor rhodathiaborane **7** and free phosphine. However, when a concentrated solution of **8** in $CDCl_3$ is heated at 40 °C in an NMR tube, a mixture of **7** and free dppp, as minor products, and two new compounds, **9** and **13**, are isolated (see Scheme 6). Similar chemistry is



Scheme 6.

observed for **10**, except that in this case we did not observe the formation of an analogue of **13**; only **12** was obtained, although we did not look very hard. The *closo*-11vertex rhodathiaborane clusters of type **9** had previously been reported, although these species contain either monodentate ligands[5] or multihapto-ligands on the metal.[23]

The new species **9**, **12** and **13** were identified by multinuclear magnetic resonance spectroscopy and mass spectrometry. **12**, which was identified spectroscopically as [1,1-(η^2-dppe)-3-(η^1-dppe)-*closo*-1,2-$RhSB_9H_8$], also afforded crystals suitable for X-ray analysis. NMR spectra for **9** and **12** are very similar to each other and, indeed, very similar to those for **13**, so crystals of **9** were not grown. The ^{11}B NMR spectra for **9** consist of five resonances of relative intensity 1 : 1 : 3 : 2 : 2 and $^1H\{^{11}B(sel)\}$ data show eight terminal hydrogen atoms in a 1 : 2 : 1 : 2 : 2 relative intensity pattern, indirectly resolving the ^{11}B spectra. The ^{31}P NMR spectra are diagnostic of the molecular structures of these compounds. For compounds **9** and **12** a sharp doublet is found in the region corresponding to the chelating phosphine ligands, a singlet and a doublet due to the dangling PPh_2 groups, for **9** and **12**, respectively, and a broad signal for the phosphorus atom bonded to a cage boron atom are observed. The ^{31}P NMR spectrum of **13** exhibits a doublet, assigned to a dppp chelating ligand, and a very broad signal typical of a phosphorus atom directly bonded to boron; the two signals appear in 2 : 1 relative intensity ratio respectively. The ^{31}P NMR spectrum of **13** does not exhibit signals corresponding to either dangling PPh_2 or the PPh_2O groups often observed for systems with pendent $C_2H_4PPh_2$ groups. These data, and the X-ray structure for **9**, suggest that **13** is composed of two 11-vertex *closo*-clusters linked by an inter-cage bridging dppp ligand, as shown in Scheme 6. This conclusion is supported by mass spectrometry, which shows the correct molecular ion, $[M]^+$, centered at $m/z = 1718.9$, with an isotopic distribution that conforms to the calculated values for the proposed formulation of **13** as [{1,1-(η^2-dppp)-*closo*-1,2-$RhSB_9H_8$}$_2$-3,3′-(μ-dppp)].

Formation of an *isonido*-rhodathiaborane

The formation of the linked pair of clusters **13** suggested that such species might be reasonable synthetic targets. Thus, our first attempt to prepare linked rhodathiaborane clusters involved the reaction between the *nido*-clusters **1** and **5**. We did not obtain linked clusters in these studies but obtained most interesting results.[24] These results afforded novel products and also provided clues to the identity of the 'red compound' always formed during the preparation of **5**. Stirring equimolar mixtures of [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**) and [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-$RhSB_9H_{10}$] (**5**) for 3 days in CH_2Cl_2 allowed the isolation of another red species, identified as [1-(PPh_3){1,3-(μ-dppm)}-*closo*-1,2-$RhSB_9H_8$] (**14**). NMR spectra, elemental analysis, and high-resolution mass spectrometry were consistent with the formulation, which was confirmed by a single crystal X-ray diffraction study (Fig. 1). It consists of a *closo*-1,2-$RhSB_9$ 11-vertex cluster with a PPh_3 ligand on Rh and a dppm ligand bridging the rhodium atom and the closest boron atom at position 3. Presumably, during the ligand exchange process between the *nido*-species **1** and **5**, loss of dihydrogen also occurs, resulting in the formation of the *closo*-type species **14**. The ^{31}P NMR spectrum exhibits the expected three signals. These are a doublet of doublets of doublets at 45.8 ppm assigned to the phosphorus atom from dppm on rhodium, a doublet of doublets at 47.2 ppm assigned to the PPh_3 group on rhodium and a single broad resonance assigned to the phosphorus atom of the dppm ligand bound to a cage boron atom. The ^{11}B spectrum exhibits the 1 : 1 : 1 : 2 : 2 : 2 pattern expected for the symmetrical *closo*-$RhSB_9$ cage and the $^1H\{^{11}B\}$ spectrum exhibits three resonances assigned to B*H* nuclei in 2 : 2 : 4 ratio, reflecting some overlap.

A close examination of the structure of **14**, especially the way it is presented in Fig. 1, reveals that it is not a simple 11-vertex *closo*-structure. There is no Rh(1)–B(5) bond in the cage. This renders an open quadrilateral 'face' to the molecule reminiscent of the series of *isonido*-11-vertex clusters that have been discovered in recent years.[2,3,21,22,25–32] The difference between our observed structure of **14** and that for an idealized 11-vertex cluster is illustrated in Scheme 7. The cage is quite distorted in the vicinity of the open face

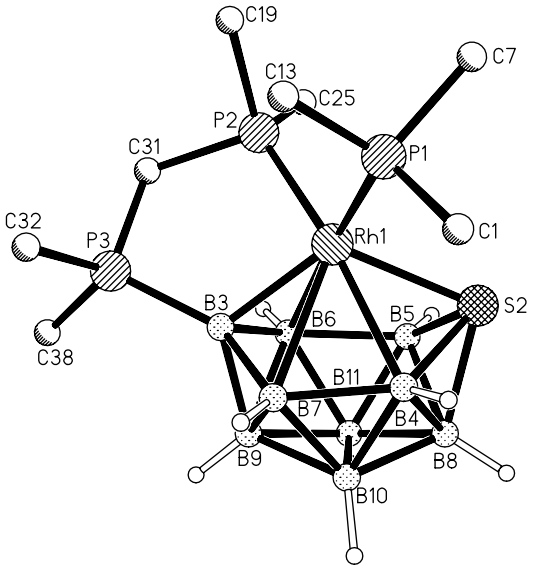
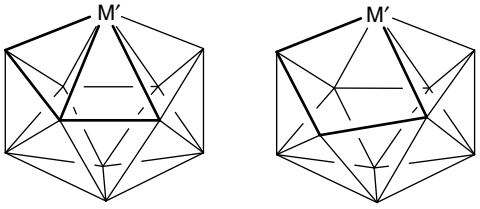


Figure 1. The structure of [1-(PPh_3){1,3-(μ-dppm)}-*closo*-1,2-$RhSB_9H_8$] (**14**).



Scheme 7.

S(2)–Rh(1)–B(6)–B(5). The non-bonded distance Rh(1)–B(5) is 2.678(3) Å, whereas if it were bonding it would be of the order 2.4–2.5 Å, as observed for compound **12**[16] and also for **15**[32] described below. The stretching of the Rh(1)–B(5) axis is reflected in the shortening of the S(2)–B(6) distance to 3.178(3) Å, whereas in **15**, a normal octadecahedron, the distance is longer at 3.366(4) Å. The confirmation of **14** as an *isonido*-species with an open square face adds to the number of examples of what may be considered structurally to be 'frozen' intermediates or transition states proposed[33] for the known fluxional process that renders all the vertices in the closed 11-vertex borane $[B_{11}H_{11}]^{2-}$ equivalent on the NMR time scale.[34,35] The process is thought to involve diamond–square–diamond rearrangements and the square-faced species is the transition state for such processes. Since the NMR spectra of **14** do not provide evidence for the structural distortion, in that they indicate a plane of symmetry in the $RhSB_9$ cage, the species must be fluxional in solution. In [1,1-(η^2-dppe)–3-(η^1-dppe)-*closo*-1,2-$RhSB_9H_8$] (**12**) the plane including the two phosphorus atoms of the bidentate ligand on rhodium, and the rhodium atom, is essentially orthogonal to the plane described by the atoms S(2)–Rh(1)–B(3). In the *isonido*-species **14**, however, the system is constrained by the bridging dppm ligand, and thus the angle between the planes B(3)–Rh(1)–S(2) and P(2)–Rh(1)–P(1) is 60.3°, suggesting substantial strain in the molecule. Also, the angle between the planes P(3)–B(3)–Rh(1) and C(31)–P(3)–B(3) is 146.7°, whereas if the dppm ligand were free at the distal end the angle would be expected to be close to 180°. Another measure of the extent of strain in the system is the angle Rh(1)–B(3)–P(3) = 118°, whereas in related systems, e.g. **7**[16] and **15** described below, such angles range from 129 to 136°. Clearly, **14** is a strained system, and whether this has anything to do with the distortion of the cage is not clear, but it certainly is true that **14** is the first example of an *isonido* 11-vertex metallathiaborane.

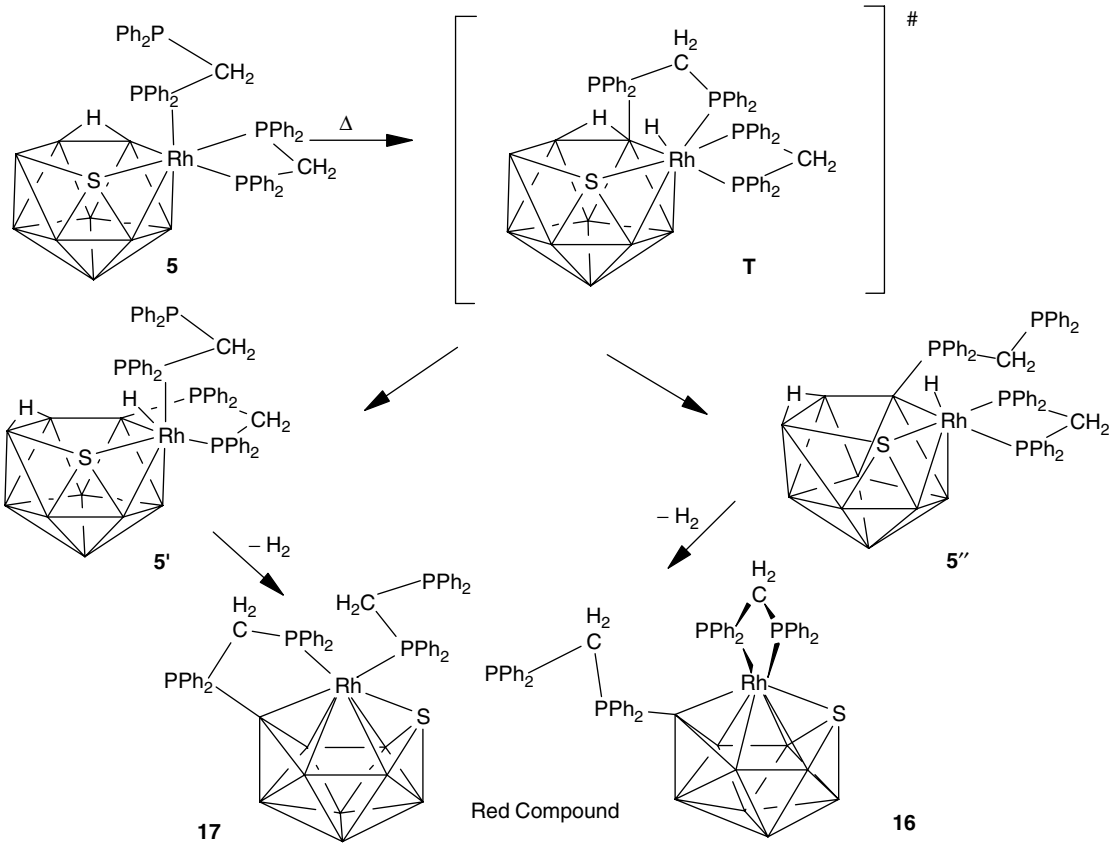
Clues to the identity of the 'red compound' formed in the preparation of 5

That the structure of **14** turned out to be [1-(PPh_3){1,3-(μ-dppm)}-*closo*-1,2-$RhSB_9H_8$], as shown in Fig. 1, was quite a surprise to us. We had not expected to observe the dppm ligand bridging between the rhodium atom and the boron atom at position 3 in **14**. We had thought that such bridging might be an intermediate in the hypothetical transfer of a second dppe or dppp ligand from heretofore unobserved dppe or dppp analogues of **5** to form the species **8** shown in Scheme 5. However, we rejected the possibility of such an intermediate for the dppm system in view of the ligand size, and also from the fact that we observed no analogues of **8** in the case of dppm. We had surmised previously[16] that dppm analogues of such species were not observed because of the shorter dppm ligand disfavoring such a transfer from the rhodium in the precursor **5** to the 9-position on the cage. Reaction of **14** with dppm in CH_2Cl_2 at room temperature afforded the same red compound that was observed as a minor impurity in the reaction of [8,8-(PPh_3)$_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**) with dppm. This suggests that perhaps this elusive red species is an analogue of **14** with a dangling dppm moiety on rhodium. Transformation of **5** to the same red compound occurred if allowed to remain in solution at room temperature for 7 days. Elemental analysis and mass spectrometric data conform to a species with the formula $(dppm)_2RhSB_9H_8$. NMR spectroscopy suggested a mixture, but high-resolution mass spectrometry and elemental analysis indicated a composition corresponding to $C_{50}H_{52}B_9P_4RhS$: an $RhSB_9H_8$ cage with two additional dppm ligands attached. The electron count conforms to a *closo*-cluster, assuming that one of the PPh_2 groups is not coordinated to the cage. That would be 12 skeletal electron pairs for an 11-vertex cluster.[6–8] Our experience suggested that we may have a mixture of [1,1-(η^2-dppm)-3-(η^1-dppm)-*closo*-1,2-$RhSB_9H_8$] (**16**), which is analogous to **9**, and [1,1-(η^2-dppm)-1,3-(μ-dppm)-*closo*-1,2-$RhSB_9H_8$] (**17**), which is analogous to **14**.

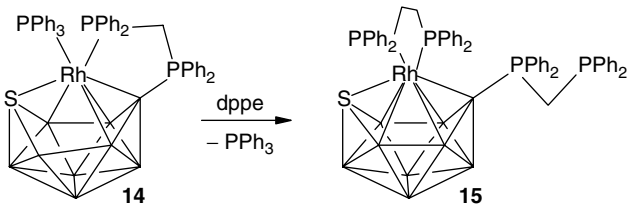
One can propose a reaction mechanism leading to species for which analytical data conform to that expected for the red compound **16**/**17**, as shown in Scheme 8. This would involve the transfer of the dangling PPh_2 group on dppm to the cage to form **T**, a transition state containing a very crowded 20 valence electron rhodium atom in an electron-rich cluster. Subsequent detachment of a PPh_2 group from rhodium can go either to **5′** or **5″**. This can be followed by loss of dihydrogen to afford species [1-(η^1-dppm)-1,3-(μ-dppm)-*closo*-1,2-$RhSB_9H_8$] (**17**) from **5′** or [1,1-(η^2-dppm)-3-(η^1-dppm)-*closo*-1,2-$RhSB_9H_8$] (**16**) from **5″**. If species **16** and **17** are not interchanging in a solution equilibrium process, then different intermediates are required, and this possibility is where we identify the two potential precursors to **16** and **17** in Scheme 8, as **5″** and **5′**. Many attempts to solve the structure from diffraction patterns of the nice red crystals, which were easy to grow, were unsuccessful. One attempt at purification allowed isolation of one of the components in *ca* 90% purity, which allowed tentative assignments of the resonances in the ^{31}P NMR spectrum to each isomer.

An examination of the structures of **16** and **17**, given in Scheme 8, indicates that there should be seven resonances in the ^{31}P NMR spectrum. **16** should have four resonances in 1 : 1 : 1 : 1 ratio and **17** should have three resonances in 2 : 1 : 1 ratio. We observe seven resonances and, on the basis of the isolation of **16** in *ca* 90% purity, we are able to assign the spectra and provide tentative assignments. Clearly we do not have the definitive answer to the identity of our 'red' compound, but our tentative conclusions are consistent with our observations that it is a mixture of **16** and **17**.

Possible interchange between **16** and **17** was suggested by the next experiment we performed. Adding a 50% excess of dppe to a solution of **14** in CH_2Cl_2, and stirring for 1 h, allows the formation of the ligand exchange product [1,1-(η^2-dppe)-3-(η^1-dppm)-*closo*-1,2-$RhSB_9H_8$] (**15**), as indicated in Scheme 9. **15** is formed in 87% yield and identified by elemental analysis, NMR and mass spectrometry, and a crystal structure determination. What is interesting about



Scheme 8.



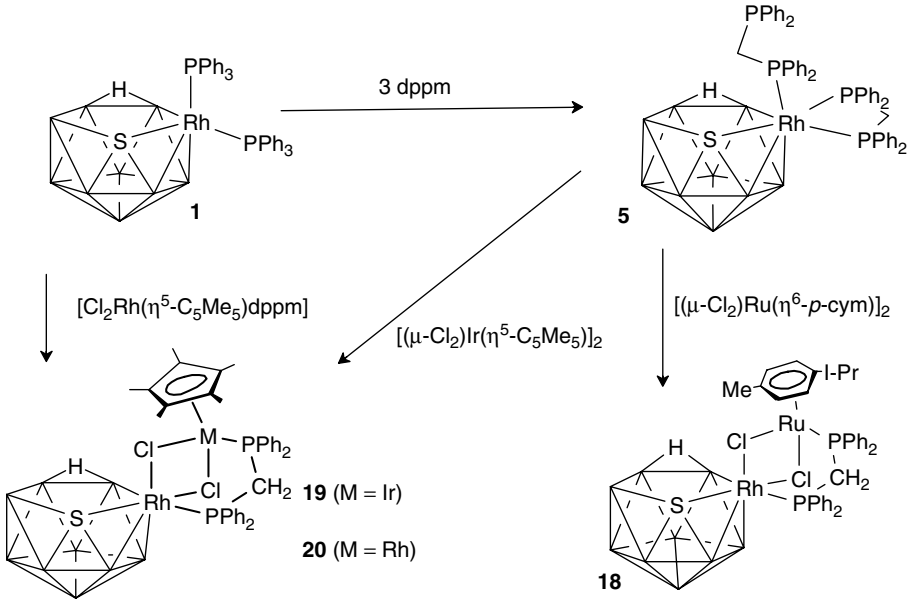
Scheme 9.

this system is that the dppe ligand that has replaced the PPh_3 ligand is now bidentate at the 1-position and the dppm ligand is dangling. Thus, the dppm and the dppe ligands have effectively changed places, as indicated in Scheme 9. This can arise from a possible mutual rearrangement of pairs of species analogous to **16** and **17**.

An alternative possibility is that there is no such intermolecular exchange between species types **16** and **17** but that, in the case of addition of dppe to **14**, initially the PPh_3 is replaced by the dppe ligand, which would be expected to become bidentate from considerations of the chelate effect and the greater stability of bidentate dppe versus dppm. Also, the PPh_2 group on a dppe ligand is more nucleophilic than one on a dppm ligand; thus, the species **15** is the expected thermodynamic product of this reaction. In other words, a dangling PPh_2 group on dppm is more favorable than one on dppe. Species **15** is a conventional 11-vertex *closo*-cluster, unlike **14**, with the dppe ligand essentially orthogonal to the B(3)–Rh(1)–S(2) plane; the angle between the two planes B(3)–Rh(1)–S(2) and Rh(1)–P(1)–P(2) is 92.6°.

Addition of a second metal to the rhodathiaborane cluster

The reaction between $[Ru(\eta^6 - p\text{-cym})(\mu\text{-Cl})_2]_2$ and [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-$RhSB_9H_{10}$] (**5**) in CH_2Cl_2 affords a red crystalline product that was characterized as [8,8-η^2-{(μ-Cl)$_2$Ru(η^6-*p*-cym)(dppm)}-*nido*-8,7-$RhSB_9H_{10}$] (**18**), in 77% yield.[36,37] Elemental analysis, NMR and mass spectral data support the formulation and a crystal structure determination confirmed it. Compound **18** has the molecular structure drawn in Scheme 10 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 chlorine ligands on the ruthenium atom. The multidentate ligand is formally a neutral dppm molecule with one of the PPh_2 groups coordinated to the ruthenium atom in the [Ru(η^6-*p*-cym)Cl_2] moiety. The orientation around the rhodium atom in **18** is pseudo-octahedral, as it is in the starting complex **5**; the angles around rhodium conform quite well to octahedral geometry. One chlorine ligand is in the plane of the open face of the cluster, *trans* to a

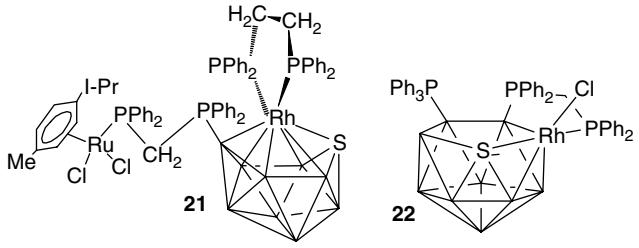


Scheme 10.

boron atom, and the other is perpendicular to the open face, *trans* to a B–B axis in the lower pentagonal belt. The orientation around the ruthenium atoms is not unusual, also conforming to a pseudo-octahedral arrangement, as is seen in typical [Ru(η^6-*p*-cym)Cl_2]–phosphine complexes,[38] and the four-atom ring Ru–Cl–Rh–Cl is almost a perfect square. Thus the structure of **18** is novel. The dppm-ligated ruthenium moiety [$RuCl_2$(η^6-*p*-cym)(dppm)] coordinates to the rhodium atom through a PPh_2 group and also through two chlorine ligands on ruthenium, thus forming an Rh–(μ-$Cl)_2$–Ru moiety in which the two metals are also linked through a bridging dppm ligand. In the formation of **18**, replacement of the bidentate dppm on **5** by the two chlorine ligands maintains the electronic configuration of the octahedrally coordinated rhodium 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 functions as a six-electron donor. **18** is thus similar to the species [8,8-η^2-{(η^2-BH_3)(dppm)}-*nido*-8,7-$RhSB_9H_{10}$] (**6**) described above,[14,15] and shown in Scheme 5. The latter contains a $BH_3 \cdot$dppm moiety that functions as a multidentate ligand, but in that case the BH_3 group uses two of its hydrogen atoms in three-center two-electron bonds to rhodium, whereas in **18** the interactions are normal two-electron two-center bonds. During the formation of **18**, presumably the [Ru(η^6-*p*-cym)(μ-$Cl)_2]_2$ dimer is cleaved by the dangling PPh_2 group on **5**. This is then followed by replacement of the bidentate dppm ligand in **5** by a lone pair of electrons on each of the two chlorine ligands on ruthenium. The additional [$RuCl_2$(η^6-*p*-cym)] moieties remaining in solution would complex to the dppm released.

The reaction between **5** and [Cp*Ir(μ-$Cl)_2]_2$ in CH_2Cl_2 at ambient temperature affords the analogous species [8,8-η^2-{(μ-$Cl)_2$Cp*Ir(dppm)}-*nido*-8,7-$RhSB_9H_{10}$] (**19**) as a yellow solid in 47% yield. Although we were unable to obtain crystals suitable for X-ray analysis, the elemental analysis, high-resolution mass spectrometry and multinuclear magnetic resonance spectroscopy also supported our formulation of the species whose proposed structure is given in Scheme 10. The ^{11}B spectrum exhibits nine signals whose chemical shift values are very close to those for **18**, and the ^1H spectrum exhibits signals corresponding to ten cage-bonded hydrogen atoms including a bridging hydrogen atom at very similar chemical shifts to those for **18**. The rhodium analogue of **19**, [8,8-η^2-{(μ-$Cl)_2$Cp*Rh(dppm)}-*nido*-8,7-$RhSB_9H_{10}$] (**20**), was obtained from the reaction between [Cp*$RhCl_2$(η^1-dppm)] and [8,8-($PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**) in CH_2Cl_2 under dinitrogen. The isolated and purified orange product was characterized as **20** and obtained in 65% yield. We again were unable to grow crystals suitable for X-ray analysis, but the spectral and analytical data support the proposed structure drawn in Scheme 10.

An alternative mode of incorporation of a second metal atom into one of the rhodathiaboranes would be to add an electrophilic metal moiety to a species with a dangling phosphine moiety. An ideal candidate for such chemistry is **15**, which contains only one reactive site, the pendent PPh_2 group. Treatment of **15** with [Ru(η^6-*p*-cym)(μ-Cl_2)]$_2$ in CH_2Cl_2 allowed the isolation of an orange solid, [1,1-(η^2-dppe)-3-η^1-{(dppm)Ru(η^6-*p*-cym)Cl_2)}-*closo*-1,2-$RhSB_9H_8$] (**21**), in 79% yield. A drawing of **21** is given in Scheme 11. Species **21** was completely characterized as a *closo*-$RhSB_9H_8$ 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 **21** is very similar to that of **15**.



Scheme 11.

Other reactions of organotransition metal reagents with the rhodathiaborane cluster 5

The reaction between **5** and other coordinatively unsaturated organometallic reagents provided new insights into the chemistry of this system. Reaction between **5** 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-$RhSB_9H_8$] (**14**) and other unidentifiable products. It appeared that the iridium reagent served to remove dppm from the metal center prior to subsequent chemistry. However, if [RhCl(PPh_3)$_3$] is added to a solution of freshly prepared **5** in CH_2Cl_2, and the reaction mixture stirred for 2 h, the only isolable product, in 66% yield, is **14**. Apparently, some exchange of PPh_3 for dppm on the rhodium center occurs and the metal reagent serves to coordinate dppm. If the reaction mixture is stirred for 3 days prior to work-up, two products are obtained. One was compound **14**, 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 hydrogen atoms. The ^{31}P spectrum indicated the presence of three phosphorus atoms, one bonded to rhodium 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-$RhSB_9H_7$] (**22**) and the structure is given in Fig. 2 and also illustrated in Scheme 11.[37]

The structure of **22** is that of a *nido*-rhodathiaborane cluster with a dppm ligand bridging the metal and the adjacent boron atom in the open face. A PPh_3 molecule is bonded to the boron atom adjacent to the latter, also in the open face, and the rhodium atom bears a chlorine ligand. The orientation around rhodium is essentially square planar and presumably reflecting a 16-electron metal center. For such 16-electron square planar metallaboranes containing platinum, palladium or rhodium, the electron count is typically two electrons short of the count required by the PSEPT.[39–42] This is the case for **22**, in which the seven BH groups contribute 14 electrons, the sulfur atom contributes 4 electrons, the two B·PR_3 groups contribute six electrons, and the Cl–Rh–PR_3 moiety, presuming it is rhodium (I), does not contribute any skeletal electrons to the cluster. Thus, **22** (which contains 11 vertices) has 12 skeletal electron pairs and, since it has a *nido*-structure, it is two electrons short of the required number.[6–8]

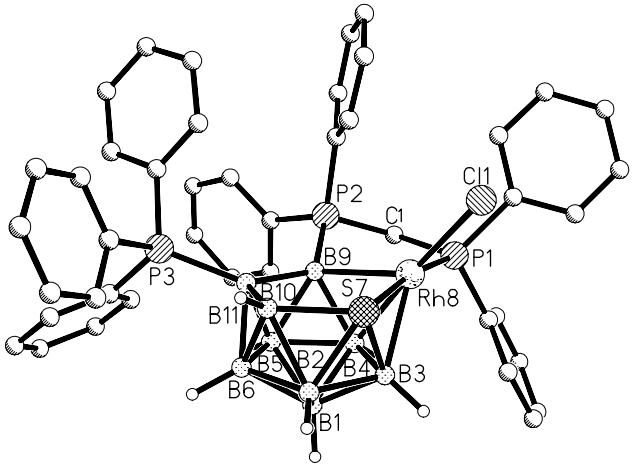


Figure 2. The structure of [8-Cl-{8,9-(μ-dppm)}-10-PPh_3-*nido*-8,7-$RhSB_9H_7$] (**22**).

22 is certainly unusual, in that there are no bridging hydrogen atoms in the open face and the electron deficiency due to the metal vertex not contributing any skeletal electrons to the cluster is compensated for by the additional PPh_2 group's contribution.

It is of interest to ask why reactions proceed differently when [IrCl(CO)(PPh_3)$_2$] or [RhCl(PPh_3)$_3$] are allowed to react with **5**, as opposed to when the chloride dimers [Ru(η^6-*p*-cym)(μ-Cl)$_2$]$_2$, [Cp*Ir(μ-Cl)$_2$]$_2$, or presumably [Cp*Rh(μ-Cl)$_2$]$_2$, react with **5**. It appears that reactions of **5** with the organometallic reagents differ in accord with the ability of the latter to remove dppm by coordinating it in a bidentate mode. The monomeric rhodium or iridium reagents can remove dppm, which becomes bidentate as the resulting complex loses a mole of PPh_3. This PPh_3 is available in solution for further reaction with **5**, allowing the formation of ([1-PPh_3-{1,3-(μ-dppm)}-*closo*-1,2-$RhSB_9H_8$] (**14**), 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 dihydrogen as the free PPh_2 group of the dppm coordinates to the cage, would result in the formation of **14**. The dihydrogen would come from loss of a terminal hydrogen atom and the bridging hydrogen atom. Reaction between **5** and [RhCl(PPh_3)$_3$] for extended periods of time results in the formation of species **22**, perhaps from reaction with a precursor to **14**. A plausible route to **22** 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 they release PPh_3. Thus, a different reaction pathway is followed and formation of bimetallic clusters is observed.

The structure of **22**, especially the dppm moiety bridging the rhodium atom and the adjacent boron in the open face

of the cage, adds credence to our proposals summarized in Scheme 8. In Scheme 8 we invoke the involvement of the intermediate or transition state, species **T**, which has two electrons more than the 'saturated' species **5** and contains a dppm ligand bridging the metal and the adjacent boron position on the cage. We suggest that our observation of this bridging ligand in **22** adds credence to our proposal that **T**, or a very similar species, is the precursor to **16** and **17**. These results clearly stimulate additional research in this area.

REACTIONS INVOLVING THE RHODADICARBABORANE, [9,9-$(PPh_3)_2$-*nido*-9,7,8-$RhC_2B_8H_{11}$] (2)

The species [9,9-$(PPh_3)_2$-*nido*-9,7,8-$RhC_2B_8H_{11}$] (**2**)[2,3] is isoelectronic with [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**),[10] since the CHCH moiety in the open face of **2**, (see Scheme 1) provides the same number of electrons for cluster bonding as does the BHS moiety of **1**. Thus, we expected to observe chemistry for **2** similar to that we observed for **1**. This was indeed the case, as we outline below.

Reactions of [9,9-$(PPh_3)_2$-*nido*-9,7,8-$RhC_2B_8H_{11}$] (2) with bidentate bases

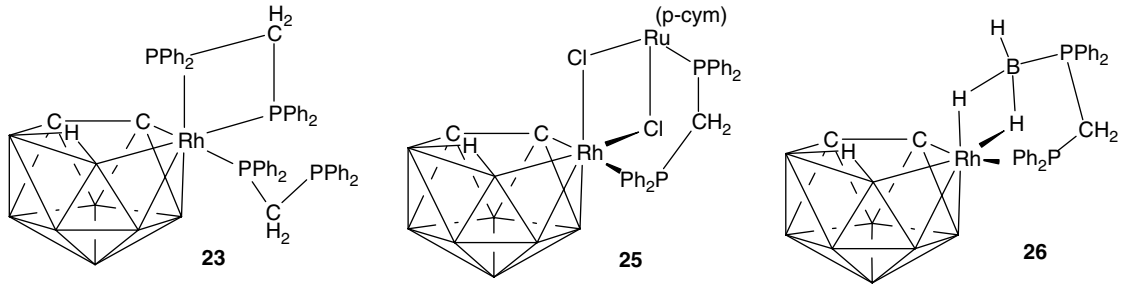
Reaction of **2** with dppm in CH_2Cl_2 affords the species [9,9-(η^2-dppm)-9-(η^1-dppm)-*nido*-9,7,8-$RhC_2B_8H_{11}$] (**23**) as a yellow crystalline in 73% yield.[43] Compound **23** is analogous to [8,8-(η^2-dppm)-8-(η^1-dppm)-*nido*-8,7-$RhSB_9H_{10}$] (**5**), described above, but, as we show later, the structure is different. It was identified by conventional spectral and analytical methods and by a crystal structure determination. The NMR data are completely consistent with the structure seen in Scheme 12, and resemble those for **5**. They indicate the presence of eight boron atoms and 11 protons associated with the cage. The ^{11}B resonances in 2:1:1:1:1:1:1 ratio, in the ascending frequency direction, suggest a cage with no symmetry, a conclusion supported by the proton spectra. As expected, four signals are observed in the ^{31}P spectrum. The structure, shown in Scheme 12, clearly resembles that of **5**, but an important difference is that the bidentate ligand in **5** lies in the plane of the open face of the $RhSB_9$ cage, whereas in **23** the bidentate dppm ligand bridges axial and equatorial positions and the monodentate one occupies the other equatorial (in the plane of the open face) position. Actual bond distances and angles are very similar in **5** and **23** and we have no explanation for the difference in structure. In both **5** and **23**, the orientation around the rhodium atom is pseudo-octahedral and very similar indeed, in spite of the differing arrangement of ligands. In both molecules an Rh–P vector is directed perpendicular to the open face of the cage, again in spite of the fact that in **23** the phosphorus atom is part of a bidentate ligand whereas for **5** the phosphorus atom has the freedom of a monodentate ligand. If there is a constraining aspect of the coordination around the rhodium, then perhaps there would be a difference in the P–C–P angles in the dppm ligands; however, these are quite similar, at 97.1° and 96.0° respectively in **23** and **5**.

Reaction of dppe with **2** under the same conditions as used in the reaction with dppm gave an unstable product, identified by as [9,9-(η^2-dppe)-9-(η^1-dppe)-*nido*-9,7,8-$RhC_2B_8H_{11}$] (**24**). NMR spectra suggested a rhodadicarbaundecaborane cage with two dppe ligands bonded to the rhodium, one in a bidentate manner and the other monodentate. The ^1H and ^{11}B spectra are very similar to those for **23**: the ^{11}B spectrum indicates the presence of eight boron atoms and the ^1H spectrum identifies eight terminal BH groups, two CH groups and a bridging hydrogen atom. The ^{31}P NMR spectra were key to identifying the coordination details and conform to a structure similar to that shown for **23** in Scheme 12. We were unable to grow crystals suitable for X-ray analysis, nor were we able to obtain satisfactory elemental analysis. **24** is quite unstable, and the related species obtained from dppp was even more difficult to handle. Mass spectral data for **24** are consistent with the formulation and we are confident that we indeed isolated and characterized **24**. On the other hand, it is not clear to us why the chemistry of the dppe and dppp adducts of the RhC_2B_8 cage are so different from those of the $RhSB_9$ cage.

Reactions of the cluster [9,9-(η^2-dppm)-9-(η^1-dppm)-*nido*-9,7,8-$RhC_2B_8H_{11}$] (23)

An important consequence of the preparation of **23** is that the range of chemistry exhibited by **5** is potentially available for **23**. The molecular cage is effectively the same as **5**, except that the S–BH moiety in the open face is replaced by an HC–CH group. Thus, **5** (similar to **23**, with three electron pair donors on the rhodium atom) has 26 skeletal electrons and thereby conforms to the *nido* classification both structurally and electronically. We had originally avoided the carborane system **2** because species containing less-crowded phosphine ligands have a tendency to rearrange to afford the *isonido* species,[2] but this was not reported for the PPh_3 derivatives and we observed no such rearrangement.

Reaction between [Ru(η^6-*p*-cym)Cl_2]$_2$ and [9,9-(η^2-dppm)-9-(η^1-dppm)-*nido*-9,7,8-$RhC_2B_8H_{11}$] (**23**) in CH_2Cl_2 affords a brown crystalline product, [9,9-η^2-{(μ-Cl)$_2$Ru(*p*-cym)$Ph_2PCH_2PPh_2$}-*nido*-9,7,8-$RhC_2B_8H_{11}$] (**25**) in 70% yield. The species is identified by elemental analysis, NMR spectrometry and a crystal structure determination. The structure is drawn in Scheme 12. Presumably, formation of **25** proceeds in an analogous manner to the formation of **18**. The orientation of the [(μ-Cl)$_2$Ru(*p*-cym)$Ph_2PCH_2PPh_2$] ligand in **25** is illustrated in the view given in Fig. 3. This view shows the open face of the cage pointing away from the reader, such that the axis B(1)–B(2) is perpendicular to the plane of the page; showing the view illustrates the nature of the two six-membered rings, Ru–P(1)–C(11)–P(2)–Rh–Cl. The ring involving Cl(1) is a distorted chair conformation and that involving Cl(2) is a distorted boat. The distortions arise from the octahedral arrangement around rhodium rendering



Scheme 12.

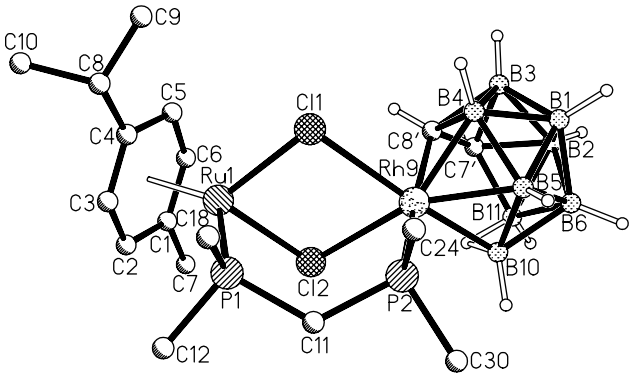


Figure 3. The structure of [9,9-η^2-{(μ-Cl)$_2$Ru(*p*−cym)Ph$_2$PCH$_2$PPh$_2$}-*nido*-9,7,8- RhC$_2$B$_8$H$_{11}$] (**25**).

the three angles in each ring involving the chlorine atoms relatively close to 90°. The other angles in the six-membered rings are normal; the interesting one, P(2)–C(11)–P(1), is *ca* 123°, in contrast to the angle P(1)–C(1)–P(2) in **23**, which is *ca* 97°. The former angle is slightly larger than typical bond angles at the CH_2 group for dppm ligands that are bridging two centers, e.g. in A-frame complexes,[44] but that latter conforms well to such angles for dppm ligands chelating a metal center.[45]

Reaction of BH_3·thf with **23** in CH_2Cl_2 under nitrogen affords an orange solid, which we identified as [9,9-η^2-{η^2-(BH_3)·dppm}-*nido*-9,7,8-RhC$_2$B$_8$H$_{11}$] (**26**), in 76% yield. The species was fully characterized, including a crystal structure determination. The data were all quite similar to those for **6**. The ^{1}H NMR spectral behavior of the BH_3 group mirrors that in **6**. The ^{11}B NMR chemical shift values are very similar; that for **6** is −24.1 ppm and that for **26** is −23.6 ppm, and the protons of the BH_3 are similarly fluxional, with $\Delta G^{\ddagger} \approx 42$ kJ mol^{-1}. Thus, it appears that these two isoelectronic species, **6** and **26**, are very similar in their chemistry.

An interesting feature is that the orientation of the two [dppm·BH_3] ligands in **6** and **26** and the two [dppm Ru(η^6-*p*-cym)Cl$_2$)] ligands in **18** and **25** are essentially the same in each species, although the relative positions of the two dppm ligands in **5** and **23** are not. In **5**, the bidentate dppm ligand lies in the same plane as the open face of the RhSB$_9$H$_{10}$ cluster and the monodentate one is located perpendicular to the plane. However, in **23**, the bidentate ligand spans sites on the rhodium atom both perpendicular to and in the plane of the open face, and the monodentate ligand lies essentially in the plane.

Clearly, we have demonstrated that similar chemistry is available for the two systems **1** and **2**, and we expect to note more similarities in their derivative chemistry. Species derived from **2** are less stable then those derived from **1**, and thus we have seen less success in developing the chemistry of **2** than we did of **1**. We expect to be reporting further on the derivative chemistry of **1** and **2**.

CURRENT AND FUTURE DIRECTIONS

The species [8,8-(PPh$_3$)$_2$-*nido*-8,7-RhSB$_9$H$_{10}$] (**1**) and [9,9-(PPh$_3$)$_2$-*nido*-9,7,8-RhC$_2$B$_8$H$_{11}$] (**2**), and their derivatives, are certainly novel and have led to some interesting chemistry. Aspects that are clearly not completely understood nor studied include the chemistry of [1-(PPh$_3$){1,3-(μ-dppm)}-*closo*-1,2-RhSB$_9$H$_8$] (**14**), the first example of an *isonido*-thiaborane, and that of the species [8-Cl-{8,9-(μ-dppm)}-10-PPh$_3$-*nido*-8,7-RhSB$_9$H$_7$] (**22**), a remarkably unusual electron-deficient cluster. There is much potential to prepare linked clusters from these systems, and the chemistry of the borane complexes [8,8-η^2-{η^2-(BH_3)·dppm}-*nido*-8,7-RhSB$_9$H$_{10}$] (**6**) and [9,9-η^2-{η^2-(BH_3)·dppm}-*nido*-9,7,8-RhC$_2$B$_8$H$_{11}$] (**26**) begs development. In addition, the incorporation of metals into and onto these cluster systems are significant goals. All of these features are represented in our current and future plans for this area.

Acknowledgements

We acknowledge the NSF (grant no. CHE-9727570), the Missouri Research Board and UM–St Louis for research grants to LB, and the NSF, the UM–St Louis Center for Molecular Electronics and the Missouri Research Board for funds that helped purchase NMR, X-ray diffraction and Mass spectrometry facilities.

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