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Lawrence Barton, *University of Missouri–St. Louis*

Oleg Volkov, *University of Missouri–St. Louis*

Mitsuhiro Hata, *University of Missouri–St. Louis*

Paul McQuade, *University of Missouri–St. Louis*

Nigam P. Rath, *University of Missouri–St. Louis*



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Reactions of boranes and metallaboranes with phosphines*

Lawrence Barton[‡], Oleg Volkov, Mitsuhiro Hata, Paul McQuade, and Nigam P. Rath

Department of Chemistry and Biochemistry and the Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121, USA

Abstract: This paper reports extensions of the well-established field of phosphine–borane chemistry. Linked clusters, for example, $\{[(PPh_3)_2(CO)OsB_4H_7-3-BH_2-PPh_2]_2[Fe(C_5H_4)_2]\}$, are formed in reactions of rigid backboned bidentate phosphines with $\{2,2,2-(PPh_3)_2(CO)-nido-2-OsB_5H_9\}$. Reaction of bidentate phosphines with the unsaturated clusters $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$ and $[9,9-(PPh_3)_2-nido-9,7,8-RhC_2B_8H_{11}]$ leads to the isolation of novel species such as $\{1-(PPh_3)[1,3-(\mu-dppm)]-closo-1,2-RhSB_9H_8\}$, with a dppm molecule bridging adjacent metal and boron vertices in the cage, $[1,1-(\eta^2-dppe)-3-(\eta^1-dppm)-closo-1,2-RhSB_9H_8]$, a mixed ligand system, and $\{9,9-\eta^2-[(\eta^2-BH_3)PPh_2PCH_2PPh_2]-nido-9,7,8-RhC_2B_8H_{11}\}$ which contains a bidentate dppm·BH₃ moiety. The formation of bidentate phosphine-linked main group transition-metal moieties such as $[BH_3 \cdot PPh_2(CH)_n PPh_2 \cdot IrCp^*Cl_2]$ is also described as is an example of a bidentate phosphine-polyhedral borane adduct $[NR_4][B_{11}H_{12} \cdot (dppm)]$ in which the borane cage is isoelectronic with $[B_{11}H_{14}]^-$. Finally, a novel oxidative coupling reaction promoted by $Cp_2ZrCl_2/n-BuLi$ to form the new nonaborane cage system, *arachno*- $B_9H_{11} \cdot (PPh_3)_2$, an unusual homolog of the well-known species $B_{10}H_{12} \cdot (PPh_3)_2$, is reported.

INTRODUCTION

The study of base adducts of boranes represents some of the most classical aspects of boron hydride chemistry [1]. Although perhaps not studied so much as the amine adducts, phosphine boranes are more useful for the study of the reactions of bases with boranes due to their amenability for study by NMR spectroscopy. Reaction of boranes with bases may lead to the formation of adducts [2], to degradation or simple cleavage of the molecule [3], or to more complex rearrangement processes [4]. This paper will cover several aspects of recent work, all of which involves the formation of phosphorus to boron bonds or reactions of phosphine boranes. At IMEBORON X [5], we described work which was stimulated by some results we obtained from studies of the reactions of the metallahexaborane $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_5H_9]$ (**I**) with phosphines and the extensions of that work to reaction with bidentate phosphines [6]. We also described further extensions of the work to reactions of bidentate bases with the unsaturated cluster $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$ (**II**) [7]. Herein, we focus on the extensions of this work and on some more conventional phosphine–borane chemistry. Included below are sections describing the formation of linked clusters based on reaction of rigid backboned bidentate phosphines with $[(PPh_3)_2(CO)OsB_5H_9]$, reaction of bidentate bases with the unsaturated clusters $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$ (**II**) and $[9,9-(PPh_3)_2-nido-9,7,8-RhC_2B_8H_{11}]$ (**III**), [8] the formation of metal complexes of bidentate phosphines bonded to a single borane moiety, and subsequent chemistry, and the formation of nonaborane- and undecaborate-phosphine adducts.

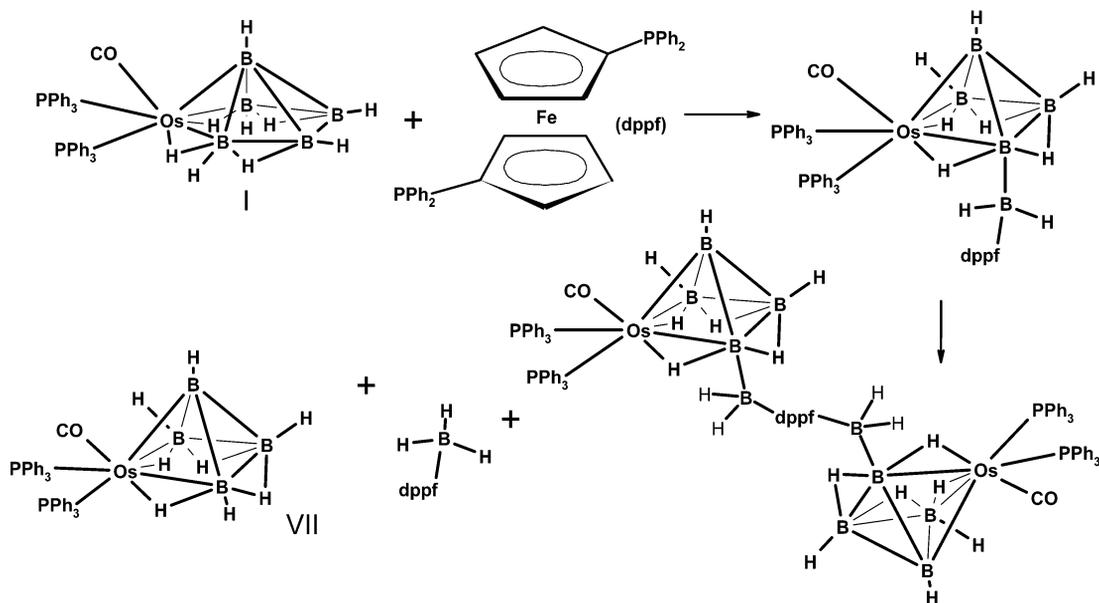
*Lecture presented at the XIth International Meeting on Boron Chemistry (IMEBORON XI), Moscow, Russia, 28 July–2 August 2002. Other presentations are published in this issue, pp. 1157–1355.

[‡]Corresponding author

RESULTS AND DISCUSSION

Reactions of [(PPh₃)₂(CO)OsB₅H₉] (I) with rigid-backboned bidentate phosphines

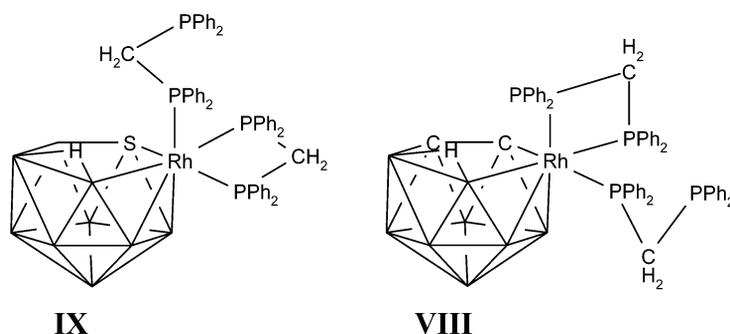
The reaction of phosphines with (I) gives species of the type [2,2,2-(PPh₃)₂(CO)-*nido*-2-OsB₄H₇-3-BH₂·PR₃] (IV) which contain a pendent BH₂·PR₃ group. Reactions with the bidentate bases dpmm, dppe, and dppp afford similar products to IV, e.g., {[(PPh₃)₂(CO)OsB₄H₇][BH₂·(dppe)]} (V) [6]. However, in the case of dppe and dppp, the species of the type V undergo intramolecular substitution to afford a second species [(PPh₃)₂(CO)OsB₄H₇-η²-3,2-{BH₂·(dppe)}] (VI). Species V is amenable to further reaction at the pendent PR₂ position with both borane-containing and transition-metal-containing moieties. In addition species of the type IV and V are subject to degradation in solution to afford [(PPh₃)₂(CO)OsB₄H₈] (VII) and phosphine-borane. In order to preclude the formation of products of the type VI, and allow further reactions at the pendent PPh₂ group in species of type V, a series of studies involving rigid backbone bidentate bases was performed [9]. In such cases, formation of a species with a pendent PPh₂ group may react with a second mole of I to give linked clusters. Reaction of I and [Fe(C₅H₄PPh₂)₂] (abbreviated as dppf) thus gives three types of phosphine-boranes: {[(PPh₃)₂(CO)OsB₄H₇](BH₂·dppf)}, {[(PPh₃)₂(CO)OsB₄H₇BH₂]₂-(dppf)}, and (dppf·BH₃) as indicated in Scheme 1.



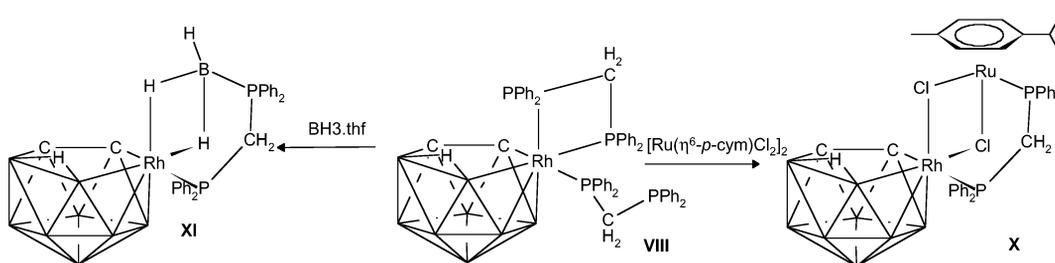
Scheme 1

Reactions of bidentate phosphines with [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] and subsequent chemistry

Reaction of [9,9-(PPh₃)₂-*nido*-9,7,8-RhC₂B₈H₁₁] (III), with the bidentate phosphine dpmm proceeds analogously to such reactions of II, affording a species in which two dpmm ligands have replaced the PPh₃ ligands on Rh. One is bidentate and the other monodentate [10]. The species formed, [9,9-(η²-dpmm)-9-(η¹-dpmm)-*nido*-9,7,8-RhC₂B₈H₁₁] (VIII), was completely characterized by multinuclear NMR spectroscopy, HR-MS, elemental analysis and a crystal structure determination. The structure of VIII, shown here, is similar to that we previously reported for {8,8-[η-(η²-dpmm)-8-(η¹-dpmm)]-*nido*-8,7-RhSB₉H₁₀} (IX), [11] also shown, but the orientation of the ligands in the two species is different. We have developed the chemistry of VIII and discovered that it and its derivatives are not as easy to work with as IX. Thus, reaction of III with other bidentate bases gave products difficult to character-



ize, but reaction of **VIII** with $[\text{Ru}(\eta^6\text{-}p\text{-cym})(\mu\text{-Cl})_2]_2$ affords $\{9,9\text{-}\eta^2\text{-}[(\mu\text{-Cl})_2\text{Ru}(p\text{-cym})\text{dppm}]\text{-nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}\}$ (**X**), which contains the moiety $[(\mu\text{-Cl})_2\text{Ru}(\eta^6\text{-}p\text{-cym})\text{dppm}]$ that coordinates in a multidentate mode to Rh. Reaction of **VIII** with $\text{BH}_3\cdot\text{thf}$ affords $\{9,9\text{-}\eta^2\text{-}[\eta^2\text{-}(\text{BH}_3)\cdot\text{dppm}]\text{-nido-}9,7,8\text{-RhC}_2\text{B}_8\text{H}_{11}\}$ (**XI**), which contains the bidentate ligand $[(\text{BH}_3)\cdot\text{dppm}]$ that coordinates to the Rh center via a PPh_2 group and also via a $\eta^2\text{-BH}_3$ group [12]. The species **X** and **XI**, whose formation is shown in Scheme 2 are quite similar in that they contain ligands which bond to the Rh through a donor P atom and also via two bridging atoms such that the ligand supplies 6 electrons to the cluster. In **XI**, the two BH moieties contribute a pair of electrons each to the Rh atom and in **X** the two Ru-Cl moieties do the same. The difference is that in **X** the interaction involves two 2-center, 2-electron bonds whereas in **XI** there are two 3-center, 2-electron bonds.



Scheme 2

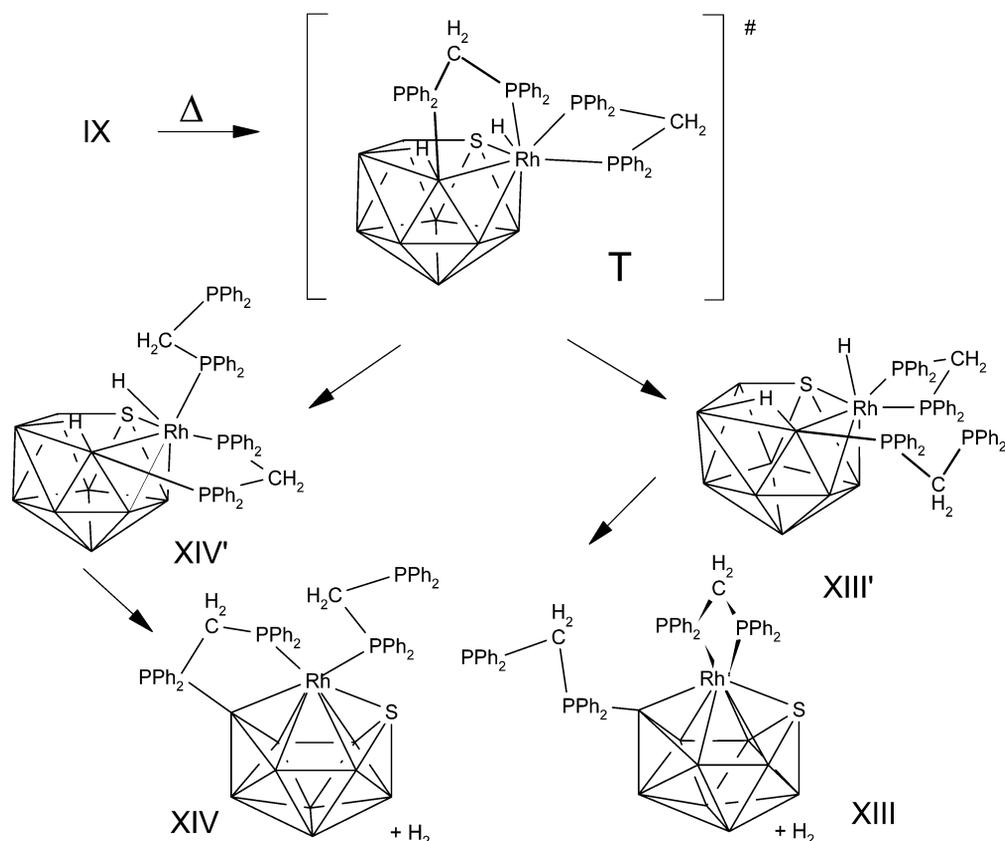
Some chemistry of $\{8,8\text{-}[\eta^2\text{-}(\text{dppm})_2]\text{-}8\text{-}[\eta^1\text{-}(\text{dppm})]\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}\}$ (**IX**)

Degradation and rearrangement reactions

Species **IX** is yellow, but on standing for several days in solution, a red compound is formed which initially eluded characterization [11]. A key to the identity of this species was obtained when **IX** was allowed to react with **II**. A red compound was isolated and characterized as $\{1\text{-}(\text{PPh}_3)\text{-}[1,3\text{-}(\mu\text{-dppm})]\text{-}closo\text{-}1,2\text{-RhSB}_9\text{H}_8\}$ (**XII**), which is illustrated later on. It consists of a *closo*-1,2-RhSB₉H₈ 11-vertex cluster with a PPh₃ ligand on Rh and a dppm ligand bridging the Rh atom and the closest B atom at position 3 [13]. Presumably, during the ligand exchange process between the *nido*-species **IX** and **II**, loss of H₂ also occurs resulting in the formation of *closo*-**XII**. The “red” species is also formed in small amounts during the preparation of **IX**. Reaction of **XII** with dppm in CH₂Cl₂ at room temperature afforded the red compound for which elemental analysis and low-resolution mass spectra indicate the composition $(\text{dppm})_2\text{RhSB}_9\text{H}_8$. NMR spectroscopy suggested a mixture, but HR-MS confirmed a composition corresponding to C₅₀H₅₂B₉P₄RhS; a RhSB₉H₈ cage with two additional dppm ligands attached. The electron count conforms to a *closo*-cluster, assuming that one of the PPh₂ groups is not coordinated to the cage. Our experience and the NMR spectra of the red compound, suggested that it is a

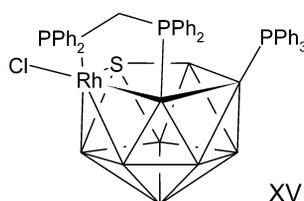
mixture of [1,1-(η^2 -dppm)-3-(η^1 -dppm)-*closo*-1,2-RhSB₉H₈] (**XIII**) and [1-(η^1 -dppm)-1,3-(μ -dppm)-*closo*-1,2-RhSB₉H₈] (**XIV**).

We propose a reaction scheme leading to species for which analytical data conforms to that expected for the red compound **XIII/XIV**, as shown in Scheme 3 below. This would involve the transfer of the dangling PPh₂ group on dppm to the cage to form **T**, a transition state containing a very crowded 20-valence electron Rh atom in an electron-rich cluster. Subsequent detachment of a PPh₂ group from Rh can go either to **XIII'** or **XIV'**. This can be followed by loss of H₂ to afford species [1-(η^1 -dppm)-1,3-(μ -dppm)-*closo*-1,2-RhSB₉H₈] **XIV** from **XIV'** or [1,1-(η^2 -dppm)-3-(η^1 -dppm)-*closo*-1,2-RhSB₉H₈] **XIII** from **XIII'**. If species **XIII** and **XIV** 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 **XIII** and **XIV** in Scheme 3, as **XIII'** and **XIV'**. Many attempts to solve the structure from diffraction patterns of the nice red crystals, which were easy to grow, were unsuccessful. Attempts at purification allowed isolation of one of the components in ca. 90 % purity, which allowed tentative assignments of the resonances in the ³¹P NMR spectrum to each isomer [13].



Scheme 3

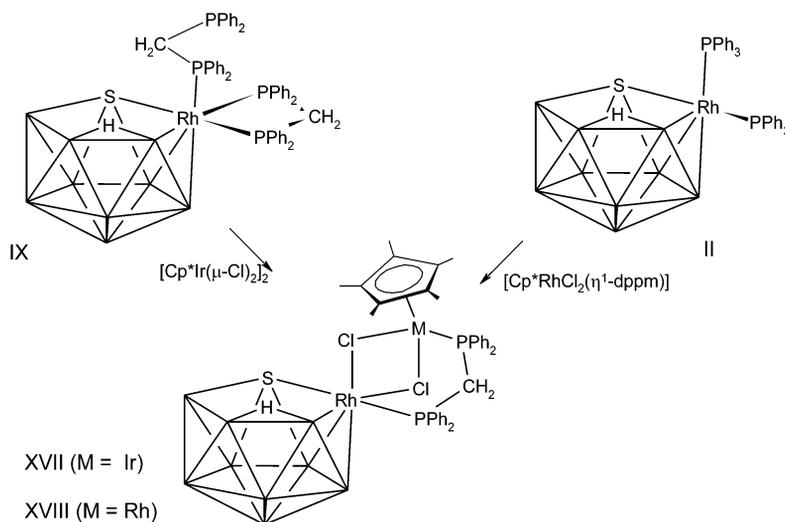
Some support for the proposed mechanism given in Scheme 3 came from the reaction of **IX** with the metal reagents [IrCl(CO)(PPh₃)₂] or [RhCl(PPh₃)₃]. The former gave traces of **XII** as the major product along with unidentified material, but reaction with the latter was more informative. The initial product from the reaction of [RhCl(PPh₃)₃] with **IX** is **XII**, but if the reaction is allowed to proceed for extended periods, a new species [8-Cl-{8,9-(μ -dppm)-10-PPh₃-*nido*-8,7-RhSB₉H₇}] (**XV**) is observed as



the major product [14]. The structure of **XV** is illustrated, and it clearly relates to that of our proposed intermediate shown in Scheme 3.

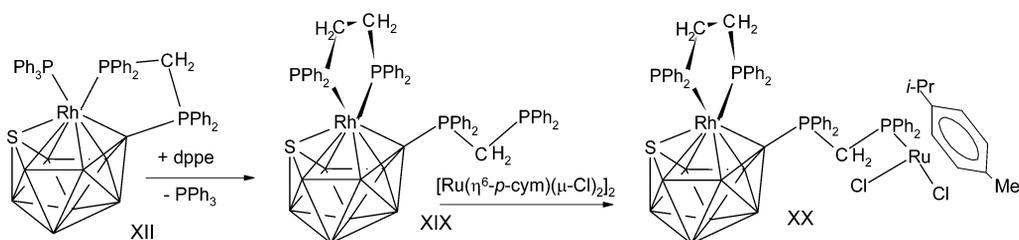
Formation of transition-metal derivatives

Although the reaction between **IX** and either $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ or $[\text{RhCl}(\text{PPh}_3)_3]$ did not lead to the isolation of transition bimetallic derivatives, such were obtained from reactions with other metal-containing reagents. Thus reaction with $[\text{Ru}(\eta^6\text{-}p\text{-cym})(\mu\text{-Cl})_2]_2$ affords the species $\{8,8\text{-}\eta^2\text{-}[(\mu\text{-Cl})_2\text{-Ru}(\eta^6\text{-}p\text{-cym})(\text{dppm})]\text{-nido-8,7-RhSB}_9\text{H}_{10}\}$ (**XVI**) [15]. Similar chemistry using $[\text{Cp}^*\text{Ir}(\mu\text{-Cl})_2]_2$ $\{\text{Cp}^* = [\eta^5\text{-C}_5(\text{CH}_3)_5]\}$ affords the related species $\{8,8\text{-}\eta^2\text{-}[(\mu\text{-Cl})_2\text{Cp}^*\text{Ir}(\text{dppm})]\text{-nido-8,7-RhSB}_9\text{H}_{10}\}$ (**XVII**), and $\{8,8\text{-}\eta^2\text{-}[(\mu\text{-Cl})_2\text{Cp}^*\text{Rh}(\text{dppm})]\text{-nido-8,7-RhSB}_9\text{H}_{10}\}$ (**XVIII**) is obtained from the reaction between **II** and $[\text{Cp}^*\text{RhCl}_2(\eta^1\text{-dppm})]$. The formation of these species, and their structures, are illustrated in Scheme 4 [14].



Scheme 4

The species **XII**, $\{1\text{-}(\text{PPh}_3)[1,3\text{-}(\mu\text{-dppm})]\text{-}closo\text{-}1,2\text{-RhSB}_9\text{H}_8\}$, was described above. We discovered that reaction of **XII** with dppe afforded $[1,1\text{-}(\eta^2\text{-dppe})\text{-}3\text{-}(\eta^1\text{-dppm})\text{-}closo\text{-}1,2\text{-RhSB}_9\text{H}_8]$ (**XIX**), which on treatment with $[\text{Ru}(\eta^6\text{-}p\text{-cym})(\mu\text{-Cl})_2]_2$ affords $\{1,1\text{-}(\eta^2\text{-dppe})\text{-}3\text{-}\eta^1\text{-}[(\text{dppm})\text{Ru}(\eta^6\text{-}p\text{-cym})\text{Cl}_2]\text{-}closo\text{-}1,2\text{-RhSB}_9\text{H}_8\}$ (**XX**). This is a new type of heterobimetalaborane, and its formation is given in Scheme 5 [14].

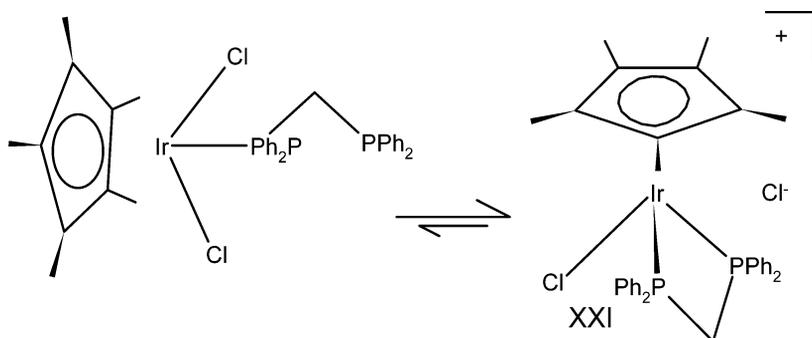


Scheme 5

Formation of borane complexes of transition metal-ligated bidentate phosphines

Preparation of derivatized bis-phosphines

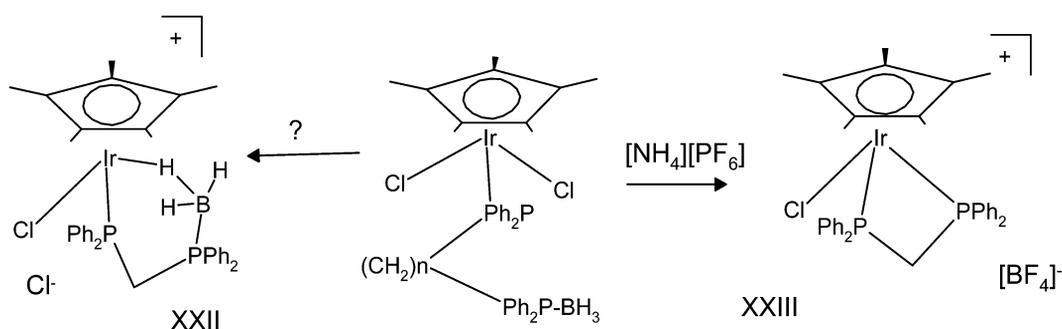
We have prepared a series of systems with the general formula $\text{PPh}_2(\text{linker})\text{-PPh}_2\cdot\text{ML}_n$. These include species with the linkers CH_2 , C_2H_4 , C_3H_6 , C_6H_{12} , $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$; and CC , with ML_n (ligated transition-metal groups) Cp^*IrCl_2 , Cp^*RhCl_2 , $\text{Ru}(\eta^6\text{-}p\text{-cym})\text{I}_2$ and $\text{Ru}(\eta^6\text{-}p\text{-cym})\text{Cl}_2$. Our initial work involved the latter metal moiety in the preparation of metal-ligated diphosphines for studies of such reagents in reactions with metallaboranes. In the case of dppm , we found it difficult to obtain $[\eta^1\text{-}(\text{dppm})\cdot\text{RuCl}_2(\eta^6\text{-}p\text{-cym})]$ because it appeared that some of the species $[\eta^2\text{-dppm}\cdot\text{RuCl}(\eta^6\text{-}p\text{-cym})]^+\text{Cl}^-$ was always present in the product mixture. We were also unable to conveniently obtain either species pure. We discovered that for other metals it was easier to push the equilibrium shown in Scheme 6, to afford bidentate dppm species of type **XXI** using $[\text{PF}_6]^-$ salts. We also derivatized the same series of phosphines with BH_3 at one end and a metal moiety at the other end to form such species as $\text{BH}_3\cdot\text{PPh}_2(\text{linker})\text{PPh}_2\cdot\text{ML}_n$ [16]. One goal of this series of experiments was to compare these species with those involving more complex borane moieties such as those described above.



Scheme 6

Attempts to form simple bidentate phosphine–borane metal complexes

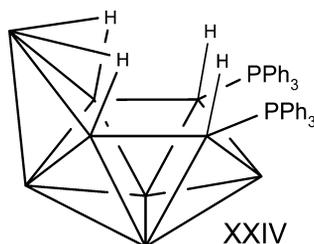
The other goal was to see if we could convert a species of the general formula $\text{BH}_3\cdot\text{PPh}_2(\text{linker})\text{PPh}_2\cdot\text{ML}_n$ into ones involving bidentate coordination of the metal by the borane-diphosphine species as indicated in Scheme 7. This would be analogous to our formation of species such as **XI** above. Such a possibility is illustrated on the left side of Scheme 7 as compound **XXII**. However, our attempts using Cp^*Rh or Ir resulted in an unusual fluorination of the BH_3 moiety and conversion to $[\text{BF}_4]^-$, as illustrated by **XXIII** on the right-hand side of Scheme 7 [17]. Our goal was achieved by Weller et al. [18] using another system during the time we were doing this work, so we abandoned this project.



Scheme 7

Formation of the new nonaborane cage system, *arachno*-B₉H₁₁·(PPh₃)₂, a homolog of the well-known species B₁₀H₁₂·(PPh₃)₂

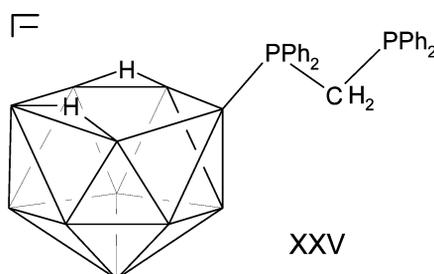
We recently prepared the species μ -(Cp₂ZrCl)₂B₅H₈ and [(Cp₂Zr)₂B₅H₈][B₁₁H₁₄] from reactions of [B₅H₈]⁻ with Cp₂ZrCl₂ [19]. There was only one other group 4 derivative of a small polyhedral borane known [20]. We were attempting to prepare more conventional zirconahexaboranes. When a suspension of Cp₂ZrCl₂ in THF is treated with 2 equiv of *n*-BuLi at -78 °C, metathesis occurs to give Cp₂ZrBu₂. The latter affords Cp₂Zr(CH₂ = CH₂) and BuH via β -hydride elimination on warming to 0 °C. This complex serves as a convenient precursor to zirconocene “Cp₂Zr” due to the lability of the π -ligand [21]. Therefore, in the presence of the borane cluster, we expected that “Cp₂Zr” might be incorporated into the cluster cage since, as a vertex a 14e metal fragment, it should supply two skeletal electrons, as does a BH fragment. We obtained an unstable metallaborane product, and in order to stabilize it we added PPh₃ and found that we could isolate [B₉H₁₁(PPh₃)₂] (XXIV) in 35 % yield if we also bubbled air through the solution [22]. This procedure is related to the well-known oxidative coupling used in many laboratories, but pioneered in polyhedral borane chemistry by Grimes [23]. The species XXIV was identified by its NMR and mass spectra, by elemental analysis, and by a crystal structure determination. The structure is given below with the *exo*-hydrogens omitted.



XXIV is only the second member of the important class of *arachno*-borane clusters to which belongs the species *arachno*-B₁₀H₁₂L₂, where L is a Lewis base such as CH₃CN or Me₂S. Species, which are described by the formula L₂B_nH_{n+2} are not known for any other borane clusters [24]. Probably no boron hydride cluster has seen more applications than the series of compounds described by the general formula B₁₀H₁₂L₂ and the species for which they are precursors [25]. It is reasonable to expect similar chemistry for XXIV. The species B₁₀H₁₂L₂ is the precursor to the best known of the carboranes C₂B₁₀H₁₂ [26] and also may be converted to *closo*-[B₁₀H₁₀]²⁻ [27]. Thus, B₉H₁₁L₂ may be potentially a very useful synthon in polyhedral borane chemistry, perhaps not as the stable PPh₃ adduct but involving a weaker donor base, Me₂S or Me₂NC₆H₅. Studies on this fascinating species continue.

Formation of $[\text{NEt}_3\text{Bz}][\text{B}_{11}\text{H}_{12}(\text{dppm})]$

Acidification of $[\text{NEt}_3\text{Bz}]_2[\text{B}_{11}\text{H}_{11}]$ [28] with CF_3COOH affords the species $[\text{NEt}_3\text{Bz}][\text{B}_{11}\text{H}_{12}]$ [29], which, when treated with dppm in CH_2Cl_2 , allows the isolation of the crystalline salt $[\text{NEt}_3\text{Bz}][\text{B}_{11}\text{H}_{12}(\text{dppm})]$. The species was fully characterized and has the structure depicted as **XXV**, herein. It contains two bridging H atoms, and the pendent PPh_2 group is a site for potential chemistry analogous to that described above. Work on this system continues with a view to metallating the pendent PPh_2 group and thence incorporating the metal moiety into the cage.



CONCLUSIONS

We have extended the chemistry of phosphine boranes in a range of related but differing studies. Thus, reactions of phosphines with small metallaboranes as well as with larger metallaheteroboranes afford novel results. In the case of the small metallaborane, we showed that the phosphine reacts with a cage boron atom, and by modifying the linking atoms in a bidentate phosphine, we can modify the reaction pathway. We have demonstrated that both diphosphine–boranes and metalladiphosphines may act as novel ligands to metals in metallaheteroboranes. For the latter systems, attack by the phosphine at either the metal center or a cage boron site provides differing options. We have prepared a series of bidentate phosphines with metal moieties, borane, or both, coordinated to them and explored routes to metal chelation through the borane and the phosphine functionalities. We have also prepared new phosphine–boranes based on 9- and 11-vertex systems and have demonstrated that there is much potential for further work in the general area of reactions of phosphines with boranes and metallaboranes.

ACKNOWLEDGMENTS

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