ORGANOMETALLICS

Volume 19, Number 14, July 10, 2000

## Reviews

# Systematic Metallaborane Chemistry

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*Received April 24, 2000*

Monocyclopentadienyl metal chlorides of transition metals of groups 5−9 react with monoboranes ($LiBH_4$ or $BH_3THF$) to give metallaboranes (and LiCl or $BH_2Cl$). The composition of the metallaborane produced depends on the nuclearity of the metal complex, the number of chlorides (oxidation state of the metal), and the monoborane used. For both monoboranes, a monocyclopentadienyl metal polyborohydride is implicated as the key intermediate, which is competitively converted into either a metal hydride or a metallaborane. The comparative reaction chemistry of these metallaboranes exhibits a dependence on transition metal properties for borane addition, metal fragment addition, and dihydrogen elimination. In addition, base degradation and small molecule reactivity promise similar metal dependencies. These observations suggest that control of borane chemistry with transition metals, analogous to that achieved in organometallic chemistry, can be realized.

## Introduction

In retrospect, the potential of the chemistry of compounds containing direct transition metal−boron bonding could have been recognized in the years when organometallic chemistry was rapidly developing into an independent discipline. However, much of the early understanding of the metal−carbon bond was based on the successful principles of coordination chemistry.[1] The carbon moieties were designated as ligands and therefore electron-rich Lewis bases. Indeed many organic ligands were assigned formal negative charges, and the discussion of metal oxidation state still occupies a significant position in organometallic texts.[2] For this reason, early examples of compounds containing M−B bonds (metallaboranes) were viewed as curious species.[3] Why should an “electron-deficient” species behave as an electron donor toward a metal center?

With a modicum of carbon added to a boron framework the situation was much clearer.[4] From the 12-vertex cage, $C_2B_{10}H_{12}$, the anionic free ligand $[C_2B_9H_{11}]^{2-}$ was generated and found to possess such a versatile coordination chemistry that derivatives of transition metals throughout the periodic table could be accessed.[5] The key concept, derived by comparison with metallocene chemistry, was the identification of this carborane dianion as a six-electron, $\eta^5$-ligand analogous to

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10.1021/om000355r CCC: $19.00 © 2000 American Chemical Society
Publication on Web 06/02/2000

the $[\eta^5\text{-}C_5H_5]^-$ ligand. Indeed, Hawthorne's chemistry associated with this organic ligand analogue was one of those featured in the first perspectives volume of *The Journal of Organometallic Chemistry*.[6] Other carborane ligands, with smaller cages, additional p-block elements, and/or one or three carbon atoms, have substantive known metal chemistries as well.[7−12] Even more easily identified as ligands are the heterocyclic rings containing boron.[13−15]

Understandably, then, the early approach to metallaboranes focused on the reaction of anionic boranes.[3,7,16] Indeed the reaction of monoanionic boranes with metal−halogen bonds in the manner of borohydrides works well for mononuclear metal derivatives, e.g., compounds derived from the reactions of $[B_3H_8]^-$ with metal halides.[17,18] Extension of this approach to larger boranes has demonstrated its generality, e.g., coordination of the $[B_4H_9]^-$ ion.[19,20] More recently, phosphine borane adducts have been shown to function as ligands in the manner of the borohydride ion.[21] Species such as $B_2H_4(PR_3)_2$ possess sufficiently basic hydrides to function as chelating ligands to transition metal centers.[22] Despite these positive results, and the interesting derivatives produced, there was no corresponding surge of chemistry comparable to that generated by carborane ligands. The accessibility of borane anions and polyborane base adducts is certainly one factor that contributes to the difference, but there is also a conceptual problem.

A weakness in the ligand approach to metallaborane synthesis is the formal charge assigned to the borane. For example, viewed as a $\pi$-ligand analogue, a borane need have a higher charge than a hydrocarbon analogue, e.g., the $\pi$-allyl $[C_3H_5]^-$ vs borallyl $[B_3H_7]^{2-}$ ligands.[23] Carborane dianions are more readily accessed than those of boranes. In fact, borane dianions are rare.[24] Furthermore, some fascinating metallaboranes were generated in low yield from neutral boranes with no transparent connection between reactants and products, e.g., $CpCo(B_4H_8)$[25] and $Fe_2(CO)_6B_3H_7$[26] derived from $B_5H_9$. Even some pathways involving anionic boranes are difficult to envision, e.g., the formation of $HMn_3(CO)_{10}B_2H_6$.[27] The existence of such compounds, including high nuclearity systems such as $Cp_4Co_4B_4H_4$[28−30] and early transition metal compounds such as $[(Cp_2Zr)_2B_5H_8][B_{11}H_{14}]$,[31] challenges our understanding of the nature of metal−boron bonding. Do these compounds contain borane ligands? The puzzle whets the curiosity and fuels the search for alternative, more logical routes.

The synthetic approach we pursued was fostered by the realization that some metallaboranes are not appropriately viewed as metal ligand complexes; for example, based on the geometry of the borane fragment, $Fe_2(CO)_6B_3H_7$ does not contain a borallyl ligand even though the compound can be formally partitioned as $[Fe_2(CO)_6{}^{2+}][B_3H_7{}^{2-}]$.[32] Thus, these compounds are better considered as heteroatom metal clusters in which covalent bonding dominates. Indeed, in terms of electronegativity, boron is a better match to metals than is carbon—an advantage for strong covalent M−B bonds. The compatibility of the bonding requirements of transition metal and borane fragments is expressed in the substantial number of known metallaboranes.[33−38] Deeper understanding comes from the skeletal electron counting rules for cages/clusters[39−43] combined with the isolobal principle relating the frontier orbitals of main group and transition metal fragments.[44,45] With these for guides, sets of seemingly disparate compound stoichiometries are seen to have similar numbers of skeletal bonding electron pairs (sep) or cluster valence electrons (cve) and geometries; for example, $B_5H_9$, $Fe(CO)_3B_4H_8$, and $Fe_2(CO)_6B_3H_7$ all have 7 sep and square pyramidal geometries. Combined, the compounds and the simple theory reveal a close connection between metallaborane chemistry on one hand and borane, carbocation, organometallic, and metal cluster chemistries on the other. Various aspects of these interrelationships are emphasized in several monographs and edited books.[37,46−48]

But these beautiful structural connections offered no obvious answer to the question of how one makes

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compounds containing metal−boron covalent bonds. For me, the initial impetus to pursue a solution to the synthetic problem arose as a consequence of a comparison of the photochemical reactivity of $Fe(CO)_3(\eta^4\text{-}C_4H_4)$[49] with that of isoelectronic and structurally analogous $Fe(CO)_3B_4H_8$.[50] The former reacts with RC≡CR to yield 1,2-$C_6H_4R_2$, whereas the latter gives principally $C_4R_4B_4H_4$.[51] Thus, the promise of synthesizing unusual carboranes combined with an understandable desire to avoid heating $B_5H_9$ with $Fe(CO)_5$ at 200 °C in a closed system (the only known route to $Fe(CO)_3B_4H_8$) led to our initial forays into metallaborane syntheses.

The trail leading to the method discussed below was a meandering one, but over time the overall problem became defined. Controlled formation of compounds with M−B bonds required both active boranes and active metal fragments. Rather than follow the organometallic paradigm and use polyborane ligands, we decided to concentrate on the use of commercially available monoborane base adducts, e.g., $BH_3$THF and $LiBH_4$, and build the polyborane fragment on a metal scaffold, i.e., take advantage of stepwise cluster-building reactions known both for boranes[52] and for metal clusters.[53] Besides commercial availability and compatibility with needle techniques, monoboranes could be used in a dual role: activation of the metal as well as a source of the borane fragments for the metallaborane.[54] However, selectivity was only achieved with metal reagents that could be activated at room temperature or below: the low barriers associated with metallaborane reactivity required low temperatures in order to achieve kinetic control.[55] In the end, activation of a general type of organometallic compound by monoboranes was achieved thereby permitting a range of transition metal effects to be observed for a single set of metal ancillary ligands.[56] It is wryly amusing, however, that although many compounds have been synthesized, we still have not found a good alternative route to $Fe(CO)_3B_4H_8$.

## Synthesis

The description of the synthetic route that follows is based on our understanding of a continuing exploration of the reaction of monocyclopentadienyl metal halides with monoboranes. Conventional wisdom accommodates the reaction of monocyclopentadienyl metal halides with nucleophiles but not electrophiles.[57] Thus, the route to metallaboranes via $[BH_4]^-$ is more easily rationalized than that via $BH_3$THF. In the end, although significant details remain to be resolved, the overall pathway in each case is a straightforward one based on established chemical principles and one new reaction. Mechanistic considerations aside, the practical fact is that the new pathway provides good yields of pure crystalline compounds from readily accessible starting materials via simple Schlenk line techniques often with no chromatography or fractional crystallization.

The discovery by Ting and Messerle that the reaction of $[Cp^*TaCl_2]_2$, Cp* = $\eta^5$-$C_5Me_5$, with 2 mol of $LiBH_4$ gives the metallaborane $(Cp^*TaCl)_2B_2H_6$, rather than a borohydride or hydride,[58] pointed us in the direction of monocyclopentadienyl metal halides as sources of metal fragments. Given the fact that monocyclopentadienyl metal halides of nearly all the transition metals are known,[57] and boranes coordinated to bases other than $H^-$ were commercially available, e.g., $BH_3$THF, Kathryn Deck and I decided that the investigation of $[Cp^*CoCl]_2$ (to access the compounds of Grimes[8]) and $[Cp^*CrCl]_2$ (to look at possible borane analogues of Theopold's organometallic compounds[59]) would make a good thesis project. It did![60−64] She and her contemporary, Yasushi Nishihara, laid a foundation for the development of this theme by the enthusiastic group of talented co-workers who followed.

The reaction pathway involving lithium borohydride is treated first. Compare the first formed metallaborane observed for $Cp^*MCl_n$, where M is varied through the group 9 triad (Figure 1) and the group 6 triad (Figure 2). For cobalt, $(Cp^*Co)_2B_2H_6$ is the first product derived from $[Cp^*CoCl]_2$; however, it was characterized only as an intermediate on the way to a mixture of metallaboranes containing the Cp*Co fragment.[64] $[Cp^*RhCl_2]_2$ forms $(Cp^*Rh)_2B_2H_6$, which is stable enough to be isolated in good yield.[65,66] Reduction to $[Cp^*RhCl]_2$ precedes metallaborane formation. Iridium provides the most varied behavior. $[Cp^*IrCl_2]_2$ is not reduced but produces a monohydride that goes on to form $(Cp^*IrH_2)B_3H_7$ and $Cp^*IrH_4$. On the other hand, $[Cp^*IrHCl]_2$ yields $(Cp^*IrH)_2B_2H_6$, which, however, exhibits no tendency for $H_2$ loss to form $(Cp^*Ir)_2B_2H_6$, the analogue of the Co and Rh diborane derivatives.[67]

For $[Cp^*CrCl]_2$ and $[Cp^*CrCl_2]_2$, only paramagnetic borohydrides are observed. Heating produces an inseparable mixture of chromaboranes and paramagnetic species.[68] For molybdenum, rapid $Cp^*MoCl_5$ reduction to $[Cp^*MoCl_2]_2$ precedes formation of $(Cp^*MoCl)_2B_2H_6$, a direct analogue of $(Cp^*TaCl)_2B_2H_6$ with a formal single M−M bond.[69−71] $Cp^*WCl_5$, which is less easily

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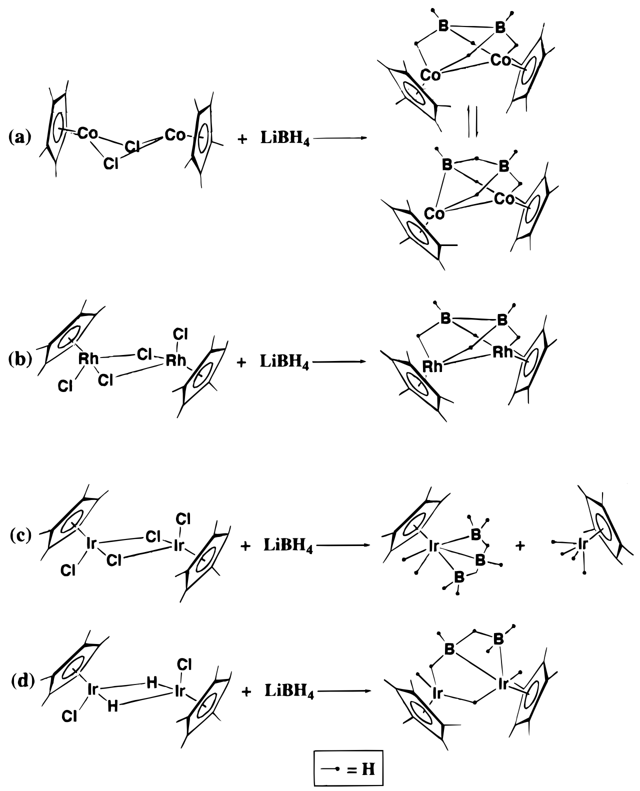

**Figure 1.** The first observed metallaborane products for the reaction of monocyclopentadienyl metal chorides of (a) cobalt, (b) rhodium, and (c) iridium with $LiBH_4$ and (d) the mixed hydride of iridium with $LiBH_4$.

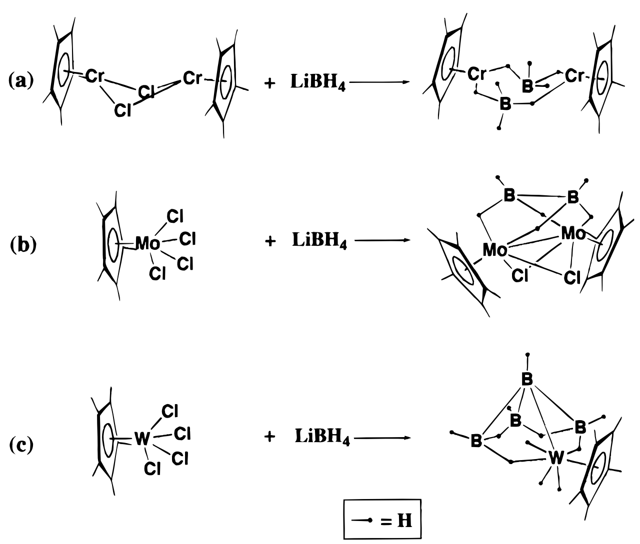

**Figure 2.** The first observed metallaborane products for the reaction of monocyclopentadienyl metal chorides of (a) chromium, (b) molybdenum, and (c) tungsten with $LiBH_4$.

reduced than its molybdenum analogue, yields 2-($Cp^*WH_3$)$B_4H_8$, via two intermediates. $[Cp^*WCl_2]_2$, examined independently, behaves much like the molybdenum system.[72]

A simple set of sequential and competitive reactions account for these observations. Rapid metathesis of $Cl^-$ by $BH_4^-$ (eq 1) is followed by competition between metallaborane formation by $H_2$ elimination (eq 2) and hydride formation by borane displacement by a Lewis base, e.g., solvent (eq 3). Reductive elimination of $H_2$ from the hydride (eq 4) effectively converts a metal

$$Cp^*MCl_n + x\ BH_4^- \rightarrow Cp^*MCl_{n-x}(BH_4)_x + x\ Cl^- \tag{1}$$

$$Cp^*MCl_{n-x}(BH_4)_x \rightarrow Cp^*MCl_{n-x}(BH_3)_x + 1/2x\ H_2 \tag{2}$$

$$Cp^*MCl_{n-x}(BH_4)_x \rightarrow Cp^*MCl_{n-x}H_x + x\ BH_3 \tag{3}$$

$$Cp^*MCl_{n-x}H_x \rightarrow Cp^*MCl_{n-x} + 1/2x\ H_2 \tag{4}$$

polyhalide to a lower halide, which can reenter the reaction manifold. Reaction 2, $H_2$ elimination from a polyborohydride which competes with borane elimination, constitutes the new chemistry—all the other reactions are ancient history. Because metallaborane formation competes with hydride formation (and metal reduction), the metallaboranes formed for a given metal depend on the properties of the metal. Reaction 1 has a low barrier in all cases. The barriers for both eq 2 and eq 3 are high for $[Cp^*CrCl]_2$. The barrier of eq 2 is much lower than that of eq 3 for $Cp^*WCl_5$, but the other way around for $Cp^*MoCl_5$, and so forth. It follows that the number of boron atoms in the final product is determined by the number of chlorides present in the species for which the rate of eq 2 dominates that of eq 3. Thus, $[Cp^*RhCl_2]_2$ cleanly yields $(Cp^*Rh)_2B_2H_6$ via $[Cp^*RhCl]_2$, whereas $[Cp^*RuCl_2]_2$ yields $(Cp^*RuH)_2B_3H_7$ because it is the mixed valence complex $[Cp^*_2Ru_2Cl_3]$ for which the rate of eq 2 dominates that of eq 3.[66]

The reaction of $BH_3THF$ with $Cp^*MCl_n$ to form $BH_2Cl$ and metallaboranes was not observed prior to our synthesis of $(Cp^*Co)_2B_3H_7$ from $[Cp^*CoCl]_2$.[63] The nature of this reaction was obscure in the beginning because the second metal investigated provides the only exception to $BH_2Cl$ as the chlorine sink. (The coproduct of $(Cp^*Cr)_2B_4H_8$ formed from $[Cp^*CoCl]_2$ and $BH_3THF$ is $[Cp^*CoCl_2]_2$.)[61] However, as the number of metals investigated increased, the broad outlines of the reaction pathway became clear.

With $BH_3THF$ a greater number of boron atoms is found in the isolated product than observed for the reaction of $Cp^*MCl_n$ with $LiBH_4$. Facile borane fragment growth on the first formed metallaborane is implied. Support comes from the fact that clean, nearly quantitative borane fragment growth reactions on this type of metallaborane has been observed for metallaboranes with $B_1$ to $B_4$ fragments (see below also).

$$(Cp^*IrH)_2BH_5 + BH_3THF \rightarrow (Cp^*IrH)_2B_2H_6 + H_2{}^{73} \tag{5}$$

$$(Cp^*Rh)_2B_2H_6 + BH_3THF \rightarrow 2,3\text{-}(Cp^*Rh)_2B_3H_7 + H_2{}^{65,66} \tag{6}$$

$$(Cp^*RuH)_2B_3H_7 + BH_3THF \rightarrow 1,2\text{-}(Cp^*Ru)_2HB_4H_9 + H_2{}^{66,74} \tag{7}$$

$$(Cp^*Cr)_2B_4H_8 + BH_3THF \rightarrow (Cp^*Cr)_2B_5H_9 + H_2{}^{75} \tag{8}$$

Given that chloroborohydrides are formed from borane

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and metal chlorides[76] and a mononuclear chloroborohydride of a group 8 metal has recently been characterized,[77] the following set of reactions constitute a reasonable pathway.

$$\mathrm{Cp^*MCl}_n + x\,\mathrm{BH_3THF} \rightarrow \mathrm{Cp^*MCl}_{n-x}(\mathrm{BH_3Cl})_x \quad (9)$$

$$\mathrm{Cp^*MCl}_{n-x}(\mathrm{BH_3Cl})_x \rightarrow \mathrm{Cp^*MCl}_{n-x}(\mathrm{H})_x + x\,\mathrm{BH_2Cl} \quad (10)$$

$$\mathrm{Cp^*MCl}_{n-x}(\mathrm{H})_x + x\,\mathrm{BH_3THF} \rightarrow \mathrm{Cp^*MCl}_{n-x}(\mathrm{BH_4})_x \quad (11)$$

$$\mathrm{Cp^*MCl}_{n-x}(\mathrm{BH_4})_x \rightarrow \text{reactions 9–11 or 2–4}$$

Generally reactions 9−11 are complete before reactions 2−4 kick in, and the product metallaborane is chloride free. However, the reaction of $[Cp^*RhCl_2]_2$ with $BH_3$-THF gave 1-Cl-2,3-$(Cp^*Rh)_2B_3H_6$.[65,66] In this case the last chloroborohydride intermediate, $(Cp^*Rh)_2(BH_4)(BH_3Cl)$, undergoes $H_2$ elimination (eq 2) more rapidly than chloride exchange (eqs 10 and 11). The resulting $(Cp^*Rh)_2(B_2H_5Cl)$ intermediate adds $BH_3THF$ to give the observed product. Note that reaction 6 provides a route to chloride-free 2,3-$(Cp^*Rh)_2B_3H_7$.

Although we cannot rule out reactions 10 and 11 taking place in a single step, a sequential two-step pathway suggests the possibility of isolating the metal hydride intermediate utilizing lower $BH_3THF$ stoichiometries. The recent isolation of a new tungsten hydride in good yield using a less than stoichiometric amount of borane adds weight to this suggestion. That is, with excess borane, metallaborane formation is observed (eq 11), whereas with less borane an intermediate hydride is isolated (eq 12) that can be independently converted to the same metallaborane (eq 13).

$$\mathrm{Cp^*WCl_4} + \text{excess } \mathrm{BH_3THF} \rightarrow (\mathrm{Cp^*W})_2\mathrm{B_5H_9} + \mathrm{BH_2Cl} + \mathrm{H_2}^{72} \quad (11)$$

$$2\,\mathrm{Cp^*WCl_4} + 4\,\mathrm{BH_3THF} \rightarrow [\mathrm{Cp^*WHCl_2}]_2 + 4\,\mathrm{BH_2Cl} + \mathrm{H_2}^{78} \quad (12)$$

$$[\mathrm{Cp^*WHCl_2}]_2 + 9\,\mathrm{BH_3THF} \rightarrow (\mathrm{Cp^*W})_2\mathrm{B_5H_9} + 4\,\mathrm{BH_2Cl} + 6\,\mathrm{H_2} \quad (13)$$

These observations along with the example of a metal borohydride formed from a metal hydride and borane[79] combined with the photochemical generation of metallaboranes from metal hydrides and borane[80,81] suggest that metal hydrides may serve as another source of metallaboranes.

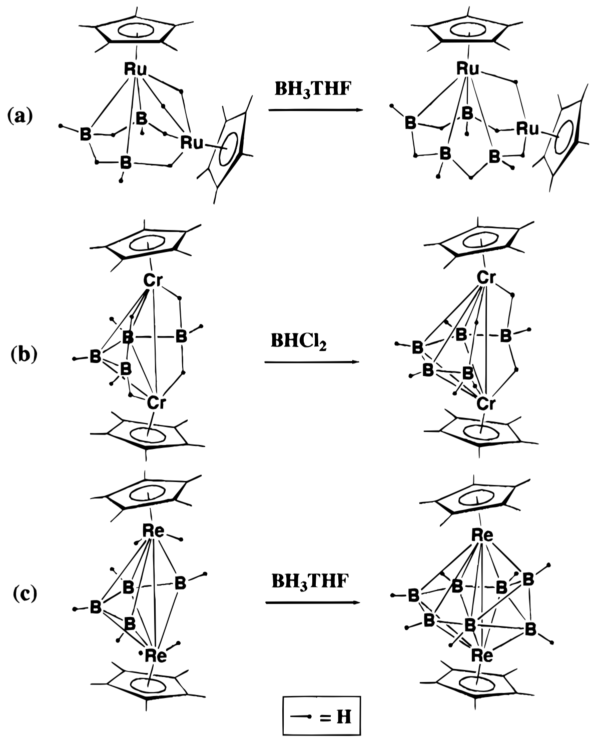

**Figure 3.** Examples of borane fragment growth for a (a) ruthenaborane, (b) chromaborane, and (c) rhenaborane.

## Systematic Reaction Chemistry

Although these new metallaboranes have fascinating structural aspects, e.g., electronically unsaturated $(Cp^*Cr)_2B_4H_8$,[82] it is the newly accessible reaction chemistry that constitutes the most exciting advance. In the following the dependence of three reaction types on transition metal type is established—a finding reminiscent of organometallic chemistry. Two other reaction types, in earlier stages of development, are also briefly described.

**Borane Expansion.** As already noted above, the reaction of $BH_3THF$ with a metallaborane can lead to growth of the borane fragment by one or more BH units. Let us take a closer look. As addition of BH increases the number of occupied vertexes by one and the sep count by one, the cluster structural type is unchanged. For example, 7 sep nido-$(Cp^*RuH)_2B_3H_7$ yields 8 sep nido-$(Cp^*Ru)_2HB_4H_9$, reaction 7, Figure 3a. The situation with electronically unsaturated $(Cp^*Cr)_2B_4H_8$ corresponds but with a subtle difference. Although the sep count defines the cluster shape ($n + 1$ sep → $n$ vertex deltahedron), it is possible for a cluster to accommodate a greater number of vertices via the capping effect (a capped $n$ vertex deltahedron requires only a sep of $n + 1$).[43] Thus we have 5 sep $(Cp^*Cr)_2B_4H_8$ with an observed bicapped tetrahedral structure (formally requiring 6 sep) being converted into 6 sep $(Cp^*Cr)_2B_5H_9$ with an observed bicapped trigonal bipyramidal structure (formally requiring 6 sep) (reaction 8, Figure 3b). Note that both $(Cp^*Mo)_2B_5H_9$[71,83] and $(Cp^*W)_2B_5H_9$[72] are known and are isostructural with $(Cp^*Cr)_2B_5H_9$. But both of these heavier congeners are formed directly in the

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synthesis reaction with $BH_3THF$, and no evidence is found for the heavier analogues of $(Cp^*Cr)_2B_4H_8$. Clearly, the barrier for addition of borane depends on metal properties, which suggests metal participation in the process.

Life becomes considerably more interesting with 6 sep $(Cp^*Re)_2B_4H_8$, with an observed bicapped tetrahedral structure (formally requiring 6 sep). In both the Ru and Cr examples above, the BH insertion reaction increases an open $(BH)_n$ ring fragment by one unit ($n = 3$ for Ru, $n = 4$ for Cr), leaving the metal environment largely the same. For the conditions examined, there is no evidence for further borane fragment growth. $(Cp^*Re)_2B_4H_8$ adds borane in a facile reaction to yield 7 sep $(Cp^*Re)_2B_7H_7$ (Figure 3c). One can envision $(Cp^*Re)_2B_5H_9$ as an intermediate (unobserved) followed by rapid replacement of the four ReH hydrogens by two additional BH fragments. As discussed in detail previously, $(Cp^*Re)_2B_7H_7$ requires a model of the cluster bonding lying outside of the electron-counting rules.[84,85] There are nine skeletal fragments but only 7 sep, and no simple capping model can account for the unprecedented geometry with cross-cluster Re–Re bonding. The analysis of the geometry and cluster bonding suggests a direct connection with the hypoelectronic Zintl clusters of Sevov and Corbett.[86] There is also a clear relationship with metallaboranes and carboranes designated as isocloso or hypercloso.[87–89] Access to additional members of this new class of highly condensed metallaborane clusters will be described below.

There appears to be a limit on the number of BH fragments, $n$, that can be added to a dimetal fragment under mild conditions—a limit that varies with the nature of the metal. For Cr, Mo, $n = 5$; W, $n = 8$; Re, $n = 7$; Ru, $n = 4$; Co, Rh, $n = 3$; Ir, $n = 4$. Going from earlier to later transition metals, $n$ decreases, whereas going down a given group, $n$ increases on going from the second to third row.

**Borane Degradation.** The addition of a Lewis base to a metallaborane (and borane[52] and metal cluster[53] as well) can have a number of consequences. Among these are adduct formation, thereby increasing the skeletal electron count (discussed in the section below on small molecule reactions); deprotonation, thereby forming an anion; and degradation, thereby generating a cluster of reduced size plus a borane base adduct and/or a mononuclear metal coordination compound.

Although we have only begun examining this aspect of reactivity, others have examined the ruthenium system. Prepared independently from the reaction of $[Cp^*RuCl]_4$ and $BH_3THF$, $(Cp^*RuH)_2B_3H_7$ is converted by $PMe_3$ into a diboron metallaborane, reaction 14.[74]

$$(Cp^*RuH)_2B_3H_7 + 2\ PMe_3 \rightarrow 1,2\text{-}(Cp^*Ru)_2(PMe_3)(H)B_2H_5 + BH_3PMe_3 \quad (14)$$

This suggests that in those cases where the cluster-building reaction directly yields boron-rich compounds, e.g., $(Cp^*W)_2B_5H_9$, the size of the borane fragment may be selectively reduced by degradation with an appropriate Lewis base.

**Metal Fragment Reactivity.** Since the salad days of metal cluster chemistry, the addition, replacement, and removal of metal cluster fragments has constituted a substantial fraction of the chemistry.[53] In reflecting their cluster-like character, metallaboranes undergo similar metal fragment reactions.[34,35] Reactions of metallaboranes of group 6–9 metals with two typical metal fragment sources, $Fe_2(CO)_9$ and $Co_2(CO)_8$, have now been investigated. Although the predominant pathway is metal fragment addition, the examples of metal fragment substitution and degradation emphasize the similarities with metal clusters. The following two systems demonstrate variation in reactivity with change in transition metal.

Metal derivatives of pentaborane(9) have been of interest to us since our first investigations; for example, $1\text{-}Fe(CO)_3B_4H_8$, mentioned above, is analogous to $B_5H_9$ in the sense that the apical BH is replaced by the isolobal $Fe(CO)_3$ fragment. The dimetal derivatives have three possible isomeric forms, and as indicated in Figure 4, different metals are found to possess different skeletal isomeric forms. In the case of rhodium, it is clear that the 2,3-isomer is more stable than the 1,2-isomer, as the 1,2- to 2,3-rearrangement has been observed spectroscopically.[65] Attempts to rearrange the 1,2-ruthenium and 2,4-cobalt isomeric forms have been unsuccessful, and they, too, likely constitute the most stable forms. With incomplete information, we originally suggested that steric factors drive the stability of $2,4\text{-}(Cp^*Co)_2B_3H_7$, as $1,2\text{-}\{Fe(CO)_3\}_2B_3H_7$ was the only comparable form known at that time.[63] However, the examples given in Figure 4 show that electronic factors must dominate. We wondered how this metal effect on structure would translate into reactivity.

As illustrated in Figure 4a, reaction of $2,4\text{-}(Cp^*Co)_2B_3H_7$ with metal carbonyl fragments generates $1,2\text{-}(Cp^*Co)\{Fe(CO)_3\}B_3H_7$ (metal fragment substitution) or $(Cp^*CoCO)B_3H_7$ (metal fragment loss).[90] In the case of $1,2\text{-}(Cp^*Ru)_2B_3H_7$ addition of a metal fragment gives $(Cp^*Ru)_2\{Co(CO)_4\}B_3H_6$. Subsequent $H_2$ elimination gives $(Cp^*Ru)_2\{Co(CO)_4\}B_3H_4$ (Figure 4b).[66] For $1\text{-}Cl\text{-}2,3\text{-}(Cp^*Rh)_2B_3H_6$, addition (with simultaneous $H_2$ elimination) produces $(Cp^*Rh)_2\{Co(CO)_3\}B_3H_3Cl$ (Figure 4c).[66] Although the net reaction for the addition of a single metal fragment is similar for the Ru and Rh metallaboranes, the Rh system adds both iron and cobalt fragments similarly and reacts with additional $Co_2(CO)_8$ to generate the unusual pentametal cluster $(Cp^*Rh)_2\{Co_3(CO)_8\}B_3HCl$ with a boride-like boron atom (Figure 4c).[91] Presumably metal fragment addition, e.g., $Co(CO)_4$, takes place with all three compounds; however, this is followed by metal fragment elimination in the case of $2,4\text{-}(Cp^*Co)_2B_3H_7$ but ancillary ligand (CO and $H_2$) elimination in the case of ruthenium and rhodium. Clearly differences in metal–metal, metal–hydrogen, and metal–boron bonding modulated by the steric repulsion of the Cp* ligands are important, but with

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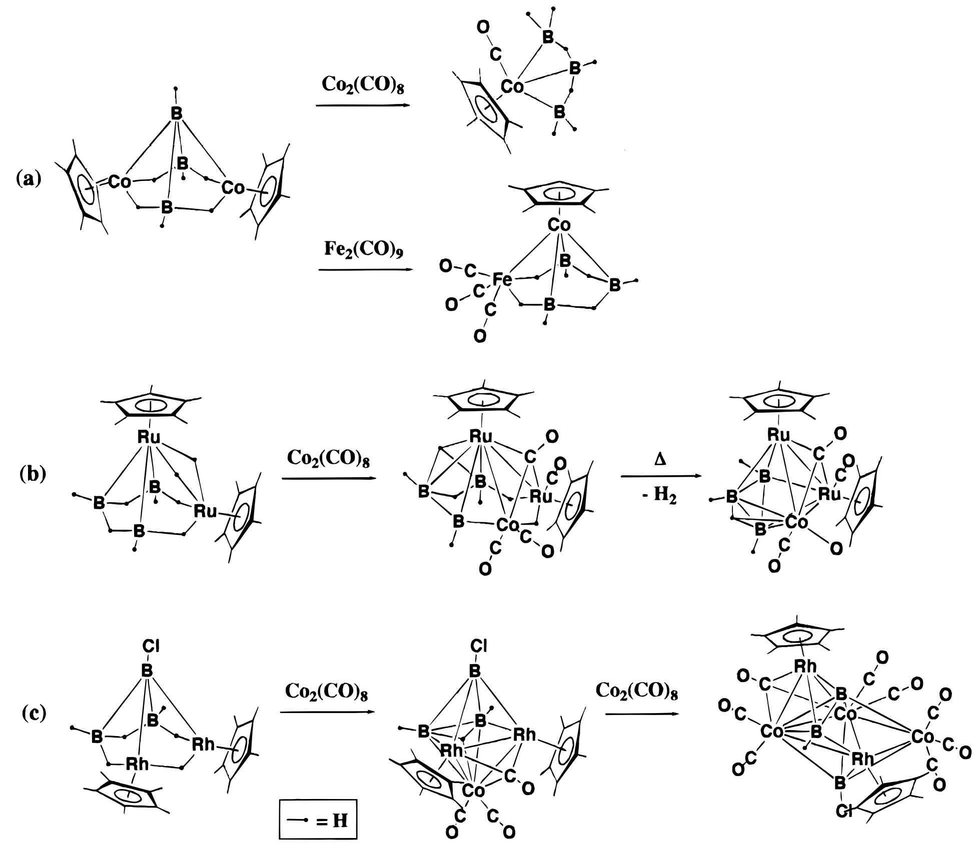

**Figure 4.** Examples of metal fragment growth for dimetallapentaborane(9)'s of (a) cobalt, (b) ruthenium, and (c) rhodium.

limited information the role played in each case remains obscure. However, it is clear that the identity of the transition metal is an important factor in determining the reactivity expressed.

In the second example, the reactions of a set of compounds, each with the molecular formula $(Cp^*M)_2B_4H_8$, M = Ir, Ru, Re, Cr, with $Co_2(CO)_8$ are compared. As indicated in Figure 5, the decreasing sep on going from group 9 to group 6 metals causes a systematic change in structure. 8 sep nido-$(Cp^*Ir)_2B_4H_8$ exhibits the pentagonal pyramidal structure expected based on the electron-counting rules. 7 sep $(Cp^*Ru)_2B_4H_8$ adopts a capped square pyramidal structure rather than the octahedral structure often observed. 6 sep $(Cp^*Re)_2B_4H_8$, bicapped tetrahedron, and 5 sep $(Cp^*Re)_2B_4H_8$, unsaturated, bicapped tetrahedron, were discussed above.

$(Cp^*Ir)_2B_4H_8$ reacts with $Co_2(CO)_8$ but produces only low yields of products containing boron. $(Cp^*Ru)_2B_4H_8$ undergoes metal addition with $Fe_2(CO)_9$ to give $(Cp^*Ru)_2\{Fe(CO)_4\}B_4H_4$, a 7 sep capped octahedron, in a reaction reminiscent of the cluster-building reactions of the group 8 and 9 metallaboranes discussed above (Figure 5b).[66] The group 7 representative $(Cp^*Re)_2B_4H_8$ shows a distinct difference. Two cobalt fragments add to close the open, four-membered borane ring in the starting material (Figure 5c). The 6 sep $(Cp^*Re)_2Co_2(CO)_5B_4H_4$ product with cross-cage Re–Re bonding constitutes another example of a hypoelectronic metallaborane (see above).[92] $(Cp^*Cr)_2B_4H_8$ adds a metal fragment with the loss of one hydrogen atom to yield a compound viewed as a metallaborane adduct of Co (Figure 5d).[93] As with the borane addition reaction, the rhenaborane exhibits considerably more reactivity than the chromaborane. In fact, the chromaborane adduct serves as a reasonable model for an intermediate in the formation of $(Cp^*\text{-}Re)_2Co_2(CO)_5B_4H_4$. It is important to emphasize that the ancillary ligand on the transition metal is identical in all four compounds, and the differences in chemistry can only be due to differences caused by the metals. A flaw in the comparison arises as the metals are from the first, second, and third rows. The dramatic differences in reactivity must be substantially due to differing geometric structure that reflects cluster electron count; however, additional differences similar to those found for, for example, Rh vs Co, are to be expected if the compounds can be prepared.

**$H_2$ Elimination.** The cluster electron count for a given compound includes the endo hydrogen atoms which are usually found in bridging positions. Hence, formal sequential loss of $H_2$ from 8 sep arachno $B_5H_{11}$ with a core structure based on a pentagonal bipyramid missing two vertices leads to 7 sep nido $B_5H_9$ based on an octahedron missing one vertex and then 6 sep closo $B_5H_7$ based on a trigonal bipyramid, i.e., a hypothetical borane but one formally generated by protonation of $B_5H_5^{2-}$. In fact, $B_5H_9$ shows little tendency for thermal loss of $H_2$, a property mimicked by the metallaborane analogue 2-$CpCoB_4H_8$, which rearranges at ~200 °C to 1-$CpCoB_4H_8$.[94,95]

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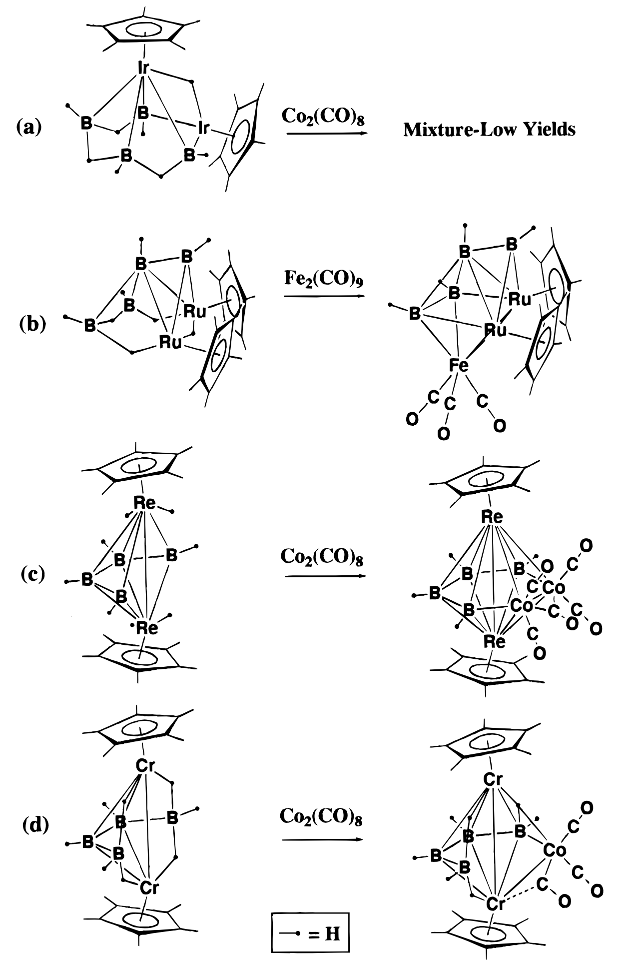

**Figure 5.** Examples of metal fragment growth for metallaboranes of composition $(Cp^*M)_2B_4H_8$ for M = (a) Ir (8 sep), (b) Ru (7 sep), (c) Re (6 sept), and (d) Cr (5 sep) ruthenium and rhodium.

A group 9 metal Cp*M fragment is viewed as a three-orbital−two-electron cluster fragment like a BH fragment. To satisfy the cluster electron counting rules, clusters built with the same type of metal fragment but with metals of group 8 and lower will need an additional source of skeletal electrons to exhibit the same shape. In the absence of any other electron donors, we observe in our chemistry that the needed electron count is made up by eliminating fewer hydrogens from the hydrogen-rich precursors. This is clearly illustrated by the tungsten system. With the exception of the borohydride complex, all of the species listed in reactions 15−18 have

$$Cp^*WCl_4 + 4\ LiBH_4 \rightarrow Cp^*W(BH_4)_4 + 4\ LiCl \quad (15)$$

$$Cp^*W(BH_4)_4 \rightarrow 1\text{-}Cp^*WH_3B_4H_{10} + 3/2\ H_2 \quad (16)$$

$$1\text{-}Cp^*WH_3B_4H_{10} \rightarrow 1\text{-}Cp^*WH_3B_4H_8 + H_2 \quad (17)$$

$$1\text{-}Cp^*WH_3B_4H_8 \rightarrow 2\text{-}Cp^*WH_3B_4H_8 \quad (18)$$

been observed spectroscopically and shown by time-dependent multinuclear NMR to be members of this consecutive set of reactions.[72] 7 sep nido-2-$Cp^*WH_3B_4H_8$, originally prepared by others (with $\eta^5$-$C_5H_4{}^iPr$),[83] is analogous to the stable 2-$Cp^*CoB_4H_8$ metallaborane. However, the extra hydrogens looked like they might be more labile than the rest, and we wondered what would happen if they were eliminated.

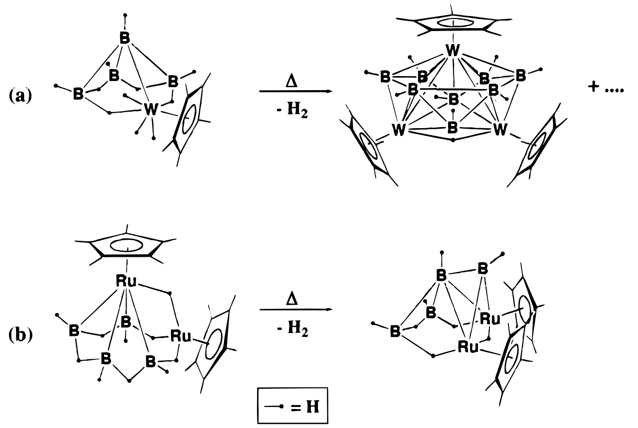

**Figure 6.** Examples of cage condensation by loss of hydrogen for (a) tungsten and (b) ruthenium.

The results are summarized in Figure 6a. In addition to 7 sep $(Cp^*W)_3HB_8H_8$, 7 sep $(Cp^*WH)_2B_7H_7$ (isoelectronic with $(Cp^*Re)_2B_7H_7$) and $(Cp^*W)_2B_5H_9$ are produced. Both of the first two products are hypoelectronic clusters (see above). The loss of the extra hydrogens associated with the Cp*W fragment drastically reduces the cluster sep count and generates cross cluster bonded, highly condensed metallaboranes. As suggested by the large number of bonding interactions, these new compounds are very stable and unreactive. They are, in fact, molecular analogues of refractory metal borides.[96−99]

Less dramatic, but fundamentally similar, is the conversion of 8 sep nido-1,2-$(Cp^*Ru)_2HB_4H_9$ into 7 sep $(Cp^*Ru)_2B_4H_8$, which has a nido-2,3-$(Cp^*Ru)_2B_3H_7$ core with a BH fragment capping the $Ru_2B$ face (Figure 6b) Apparently this alternative to an uncapped octahedral cluster is preferred, perhaps due to the presence of four bridging hydrogens.[100] If one compares 1,2-$(Cp^*Ru)_2$-$HB_4H_9$ with $B_6H_{10}$, one finds that Cp*Ru + H corresponds to one BH, as expected. Formally, it is these extra hydrogens that are easily eliminated. The fact that 8 sep nido-2-$(Cp^*Ir)_2B_4H_8$ shows no similar tendency to lose $H_2$ again confirms that the intrinsic stability of a nido pyramidal cluster skeleton is not substantially changed by metal vertex subrogation.[73]

**Small Molecule Coordination and Reduction.** The argued similarities of metallaboranes with organometallic compounds suggests that the reactions of these compounds with small organic substrates be investigated. Until now, only $(Cp^*Cr)_2B_4H_8$ has been explored in any detail. Because it is formally electronically unsaturated, we expected it to react with a variety of electron donors. Disappointingly the number of successful reactions thus far observed is limited to the reactions with CO and $CS_2$. Further, the reaction rates for CO addition are substantially lower than those

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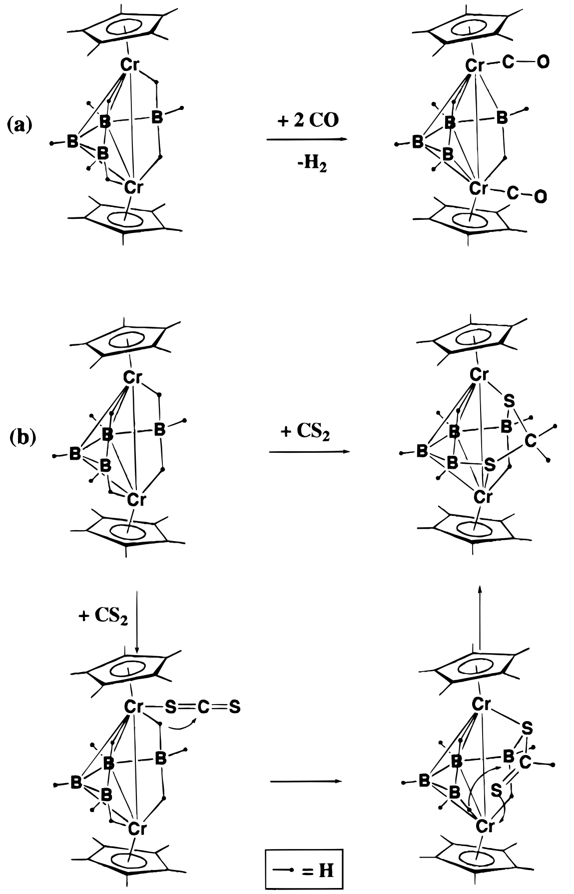

**Figure 7.** Examples of (a) CO addition to $(Cp^*Cr)_2B_4H_8$ and (b) $CS_2$ addition to $(Cp^*Cr)_2B_4H_8$ (with a suggested pathway for the double hydroboration).

exhibited in ongoing investigations of electronically saturated $(Cp^*Re)_2B_4H_8$.

As shown in Figure 7a, the reaction of CO with 5 sep $(Cp^*Cr)_2B_4H_8$ generates 6 sep $(Cp^*CrCO)_2B_4H_6$, in which the addition of two CO ligands to the metal sites is accompanied by elimination of $H_2$ from the BHCr sites.[68] The stoichiometry reflects a greater stability for the electronically saturated product. On addition of $CS_2$ to $(Cp^*Cr)_2B_4H_8$, reduction of both C═S bonds takes place to give a $(Cp^*Cr)_2(S_2CH_2)B_4H_6$ product in which the newly formed $H_2CS_2$ ligand bridges the open face of the starting material (Figure 7b).[101] The pathway shown is based on the pair of results: coordination of $CS_2$ via S to one Cr site; intramolecular hydroboration of one C═S bond; coordination of the other S to the other Cr site; hydroboration of the second C═S bond. Attempts to displace or eliminate the bound $H_2CS_2$ species were unsuccessful.

The recent stoichiometric,[102,103] photocatalytic,[104] and thermal catalytic boron functionalization of alkanes[105] provide beautiful examples of what can be accomplished when organometallic chemistry and metal−boron chemistry take place at the same metal site. Although the reactivity of the chromaborane is less extensive than expected, the situation for the related metallaboranes described remains to be investigated.

## Future Prospects

The work described has a limited focus: a single type of metal fragment, Cp*M, transition metals from group 5 to 9, mainly dinuclear metal compounds, and a small selection of derivative reaction types. Considering the large effect of the ancillary ligands on metal properties, the very different properties of the very early and very late transition metals, and the distinctiveness of post-transition metal chemistry, the work described only scratches the surface of what is possible in metallaborane reaction chemistry. To realize the potential, other efficient routes to metallaboranes need be developed, as the synthetic method described has several limitations. We already know, for example, that a strongly bound ancillary ligand like Cp* is required, that for Fe and Mn there is an insufficient barrier separating the metallaboranes from the slippery slope to metallocenes (e.g., $Cp^*_2Mn$ and $Cp^*_2Fe$), and that for easily reduced metals only elemental metal is produced (e.g., Ni). On the other hand, the approach may well be applicable to other group 13 hydrides, and we are beginning to explore the synthesis of compounds containing direct transition metal aluminum bonds from monocyclopentadienyl metal halides.

**Acknowledgment.** This account is a tribute to the excellent experimental chemistry of K. Deck, Y. Nishihara, J. Ho (Co, Cr); H. Hashimoto (Cr, Ta); S. Aldridge (Cr, Ta, Mo); K. Kawamura (Cr); X. Lei (Co, Rh, Ir, Ru); A. Weller (W, Re); M. Peldo (W); and S. Ghosh (Re). The contributions of Dr. M. Shang to the crystallography are also appreciated, and the continued support of the National Science Foundation made this chemistry possible.

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