

Reactions of alkynes with metallaboranes: Novel reactivities lead to new structure types*

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Abstract: The reactions of alkynes with *nido*-dimetallaboranes containing monocyclopentadienyl metal fragments are highly dependent on metal identity. Typical metals from groups 6 and 7 do not react under mild conditions, Rh gives exclusively alkyne cyclotrimerization via a cluster-catalyzed reaction, and Ru reacts predominantly via insertion to give new ruthenacarborane clusters. The facile reaction observed for Ru permits the characterization of intermediates exhibiting novel structural features, e.g., external cluster-bridging mono-borane or alkylidene fragments. Despite the large differences in reactivity, circumstantial evidence suggests the alkyne adds to and opens the metallaborane to an *arachno*-structure. The metal present determines the character of the metallaborane, which in turn determines whether further reaction occurs. For Ru, it is the hydrogen-rich character fostered by the metal fragment that leads to the copious chemistry observed.

Keywords: boranes; transition metals; alkynes; rhodium; ruthenium; cyclotrimerization; metallacarboranes; metallaboranes; catalysis.

ALKYNES IN CHEMISTRY

Alkynes with one or more C≡C triple bonds are much more reactive than saturated hydrocarbons. Alkynes, and organic compounds with this functional group, readily undergo addition reactions leading to loss of multiple bonding. Hence, they are classified with the descriptor “unsaturated”. This high reactivity often leads to their selection as one substrate in the initial investigations of the reaction properties of new classes of compounds. Frequently, further novel compounds are produced and the definition of the bonding and structure of the class of compound of interest begins to develop. High reactivity often is accompanied by low selectivity; hence, interest rapidly diminishes in the face of the inevitable low yields and unanswered questions of mechanism. But one should not undervalue the information gained on reactivity as it often shows the way to related chemistry that is selective and of potential value. What follows is an overview of what has been learned from the reaction of metallaboranes with alkynes. To introduce the topic, some background on the reactions of boranes and metal complexes with alkynes is pertinent.

Alkynes plus boranes

The story of the reactions of boranes with organic functional groups is a fascinating one that has been told in many reviews and books [1,2]. Alkynes have had a role, albeit a somewhat limited one for rea-

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sons already stated above. Addition of the B–H bond to the triple bond (hydroboration) is very fast, and stopping the reaction at the initial vinyl product is difficult. Alternatively, for terminal alkynes, formation of a B–C bond and H₂ can occur through protolysis if the B–H bond is sufficiently hydridic. In the context of this article, the reaction of alkynes with polyboranes is more relevant. The first systematic studies of small carborane cages arose from their synthesis in mixtures from the reaction of acetylene with B₅H₉ under vigorous conditions [3]. Later studies showed that insertion is promoted by base [4] and that vinyl polyboranes could be generated via metal-promoted reactions [5]. Vinyl polyboranes yield substituted one carbon carboranes on heating, but energy barriers are large [6].

Alkynes plus transition-metal complexes

The explosion of chemistry in the mid-20th century arising from the combination of organic moieties with transition metals included reactions with alkynes [7]. New classes of compounds (e.g., “flyover” complexes) created a stir and forced the expansion of old and development of new ideas of metal-carbon bonding [8]. Likewise, when multinuclear metal cluster systems were developed, some of the earliest reaction chemistry involved alkynes [9]. Alkyne addition and incorporation into the cluster-bonding network, alkyne cleavage, carbyne-carbyne, and carbyne-CO coupling and other reactions were observed in the interactions of metal clusters with alkynes [10].

The reaction of carboranes, either neutral or anionic, with transition-metal fragment sources led to the development of the broad area of metallacarborane chemistry [11,12]. This chemistry can be viewed as derived secondarily from alkynes as the most common carborane type contains two carbon fragments derived from an alkyne, i.e., alkyne plus borane yields carborane, which then is combined with a metal fragment. Viewed in this fashion, this leads one to think about the alternative: borane plus metal yields metallaborane, which then adds alkyne to give what? One very logical answer was generated in the early days of metallaborane chemistry when it was shown that the pentaborane(9) analog, 2-CpCoB₄H₈, reacts with an alkyne to generate the metallacarborane *nido*-1,2,3-CpCoRR'C₂B₃H₅ [13,14]. Little development followed because (a) convenient routes to metallaboranes were not yet available, (b) the reaction required long pyrolysis at high temperature similar to those required for the reaction of borane clusters with alkynes, and (c) the metallacarborane had already been made in better overall yield by adding a metal fragment to a preformed carborane. This situation changed when a route to metallaboranes via monocyclopentadienyl metal halides and monoboranes proved to be both selective and general for the synthesis of dinuclear compounds [15].

ALKYNES PLUS METALLABORANES

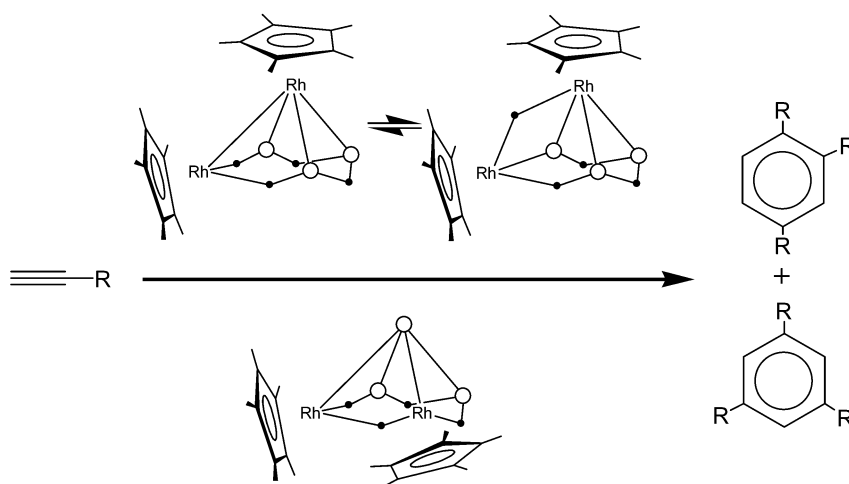
Expectations of the reactivity of metallaboranes with alkynes are colored by the known reactivities of boranes and metal clusters as well as the early work on metallaboranes mentioned in the introduction. Thus, addition, hydrometallation, and insertion are all likely consequences. Why, then, even bother? That is, how can the work be justified? Consider insertion to yield metallacarboranes. The existing route to metallacarboranes is to add metal fragments to carboranes. As the carborane framework is a robust one, the majority of products contain a single metal center and the carborane fragment is justifiably viewed as a variant of a polyhaptic organic ligand. The reverse strategy, whereby the weaker boron and metal interactions are formed first and the metal/boron and carbon interactions second, has the possibility of allowing milder conditions. Mild conditions give more kinetic control and access to a greater variety of products. Further, metallaborane clusters often have more than a single metal atom and compounds with M:B:C ratios approaching 1:1:1 are accessible. In such species, the balanced competition between the bonding characteristics of each element may well lead to novel structures. Finally, the combination of both borane and metal cluster properties in a single reagent might also lead to reactivity not seen in either borane or metal system separately

Survey of metallaborane reactivity

As part of a study of reactivity as a function of transition metal, the set of *nido*-metallaboranes $\{\text{Cp}^*\text{Cr}\}_2\text{B}_4\text{H}_8$, $\{\text{Cp}^*\text{M}\}_2\text{B}_5\text{H}_9$, $\text{M} = \text{Mo}, \text{W}$, $\{\text{Cp}^*\text{Re}\}_2\text{B}_4\text{H}_8$, $\{\text{Cp}^*\text{RuH}\}_2\text{B}_3\text{H}_7$, $\{\text{Cp}^*\text{Co}\}_2\text{B}_3\text{H}_7$, and $\{\text{Cp}^*\text{Rh}\}_2\text{B}_3\text{H}_7$ were tested for alkyne reactivity [16]. To our surprise, only two showed evidence of activity under mild reaction conditions. No doubt some activity to produce stable metallacarboranes would be observed at higher temperatures for those metallaboranes of sufficient thermal stability to survive long enough to react with the alkyne. However, as described above, vigorous thermolysis would largely invalidate one important objective of this work.

Rhodaboranes [17,18]

Monitoring the reaction of *nido*-1,2- $\{\text{Cp}^*\text{Rh}\}_2\text{B}_3\text{H}_7$, which exists as an equilibrium mixture of two tautomers (Scheme 1, where in each scheme the solid dots are H atoms and the open circles are BH fragments) with an alkyne with ^{11}B NMR showed neither loss or change of the signals due to the metallaborane. But a ^1H NMR study revealed that a chemical reaction was taking place. Loss of alkyne and formation of copious amounts of new products identified as substituted benzenes was observed. Clearly, the presence of the rhodaborane promoted alkyne cyclotrimerization. In fact, it was demonstrated that the reaction is catalyzed by the rhodaborane or a species derived from it.



Scheme 1

Significant turnover numbers were observed at room temperature (at room temperature and a rhodaborane to alkyne ratio of 1:260 a 40 % yield of cyclotrimerized product was isolated). To attack the difficult problem of identification of the true catalytic species, the activities and selectivities for cyclotrimerization of terminal alkynes were observed for both *nido*-1,2- $\{\text{Cp}^*\text{Rh}\}_2\text{B}_3\text{H}_7$ and *nido*-2,3- $\{\text{Cp}^*\text{Rh}\}_2\text{B}_3\text{H}_7$ cluster isomers for a variety of alkyne substituents. Importantly, the two isomeric rhodaborane catalysts showed different activities and modestly differing selectivities. If formed, catalytically active degradation products should be the same and the two rhodaborane cluster isomers should give similar activities and selectivities. The real differences observed suggest the active catalysts are the rhodaboranes themselves and not degradation products.

The common mechanism for cyclotrimerization of alkynes catalyzed by organometallic compounds is a catalytic cycle in which the first step is addition of the first mole of alkyne. Hence, one requirement of the catalytically active species is a site of unsaturation. It is either present or must be gen-

erated in the course of the reaction. This might be viewed as a problem as the cluster bonding of *nido*-1,2- $\{\text{Cp}^*\text{Rh}\}_2\text{B}_3\text{H}_7$ is saturated. However, any species that can be thought to require multicenter two-electron bonding possesses an intrinsic unsaturation. In fact, a *nido*-cluster can add a ligand and open up (*nido*- to *arachno*-) or lose a ligand and close up (*nido*- to *closo*-). Hence, by adding a Lewis base addition/cluster opening step, the standard mechanism for cyclotrimerization catalyzed by organometallic complexes adequately explains the results. These first two steps are outlined at the top of Scheme 6, which summarizes the mechanistic information for the isoelectronic rhodium and ruthenium cluster systems.

Presumably the other *nido*-metallaboranes that do not react easily with alkynes can also add the alkyne in a reversible step. We can conclude from this that for these metallaboranes reaction barriers leading to metallacarboranes, cyclotrimerization, or other products must be large under the reaction conditions examined. Why does cyclotrimerization take place for the rhodaborane rather than insertion and metallacarborane formation? To seek information that addresses this question, we need to look at a metallaborane that does produce metallacarboranes.

Ruthenaboranes [17,19–23]

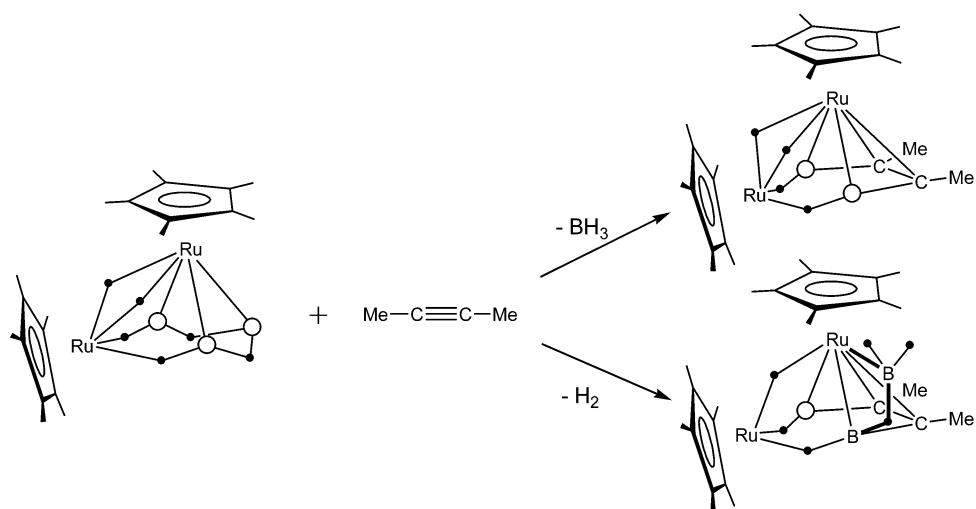
In contrast to the other metallaboranes, the ruthenaborane *nido*-1,2- $\{\text{Cp}^*\text{RuH}\}_2\text{B}_3\text{H}_7$ produced a plethora of compounds in which the metal, boron, and alkyne fragments were combined. The most prominent compounds differed depending on the alkyne (terminal vs. internal and alkyne substituent), the reaction time and temperature and, to some extent, reactant ratios. The sheer complexity of the system at first sight defies mechanistic explanation. However, tracing the various threads back to early reaction times, aided by the spectroscopic characterization of intermediates, and even, in some instances, their isolation and solid-state structure determination showed how a fairly simple primary reaction of alkyne with metallaborane can lead to a complex array of products. As several of the products illustrate new cluster concepts, the first section following describes the major findings in terms of composition and structure. The summary of mechanistic ideas in the succeeding section completes the story. Details will be found in the complete account of the work.

New structural concepts

The isolation of intermediates in a reaction is fundamentally limited by the magnitude of the smallest free energy barrier separating the intermediate from other products relative to RT. It follows that the lower the temperature the better the chance of isolating such species. The reaction temperature, in turn, is determined by the free energy barrier separating reactants and intermediates. In the case of the ruthenaborane studied, this barrier is low for reaction with alkynes; hence, the species that were isolated and structurally characterized provide new fundamental ideas of cluster mechanisms.

Bridging monoborane intermediates

The reaction of *nido*-1,2- $\{\text{Cp}^*\text{RuH}\}_2\text{B}_3\text{H}_7$ with 2-butyne at room temperature leads to insertion and formal loss of BH_3 to give *nido*-1,2- $\{\text{Cp}^*\text{RuH}\}_2$ -4,5- Me_2 - $\text{C}_2\text{B}_2\text{H}_4$ (and the isomer *nido*-1,2- $\{\text{Cp}^*\text{RuH}\}_2$ -4-Et- $\text{C}_2\text{B}_2\text{H}_5$) by one pathway and insertion and formal loss of H_2 to give *nido*-1,2- $\{\text{Cp}^*\text{Ru}\}_2$ -4,5- Me_2 - $(\mu\text{-BH}_2)\text{C}_2\text{B}_2\text{H}_5$ by a parallel path (Scheme 2). The cluster frameworks of both product types are structurally and compositionally similar, containing two metal, two boron, and two carbon atoms. It is in the external cluster bonding that they differ. The structure of *nido*-1,2- $\{\text{Cp}^*\text{RuH}\}_2$ -4,5- Me_2 - $\text{C}_2\text{B}_2\text{H}_4$ can be viewed as standard. Despite its M:B:C ratio of 1:1:1, it exhibits a pentagonal pyramidal cluster structure consistent with its 7 skeletal electron pairs (sep).

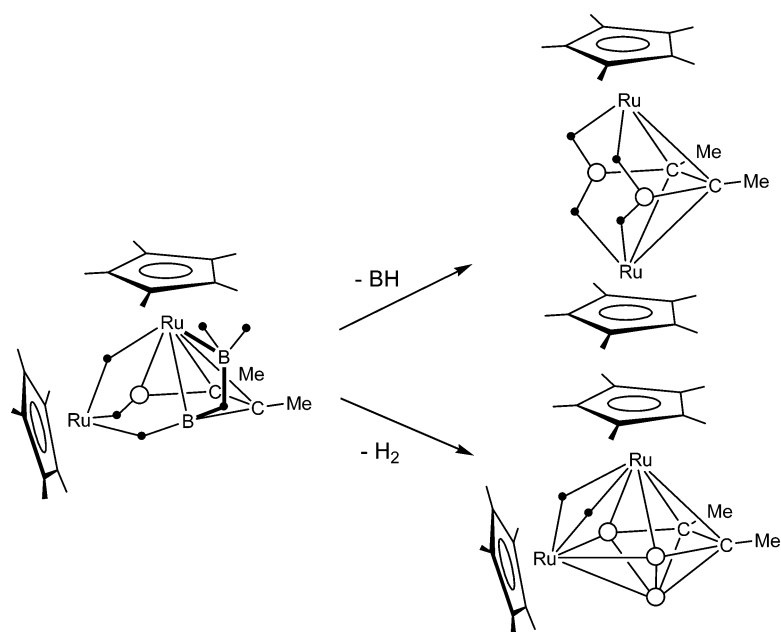


Scheme 2

The other product type, *nido*-1,2- $\{\text{Cp}^*\text{Ru}\}_2$ -4,5- Me_2 - $(\mu\text{-BH}_2)\text{C}_2\text{B}_2\text{H}_5$, has the same geometry and presumably the same sep count. Hence, one Ru–H–Ru on the former and the bridging BH_2 on the latter must count the same. Note, however, that this bridging BH_2 is joined to the basal B–H by forming a B–H–B bridge with its terminal B–H. Hence, it could equally well be described as a BH_3 group bridging a Ru and bare boron atom. This product type is found with all of the alkynes studied and has since been discovered in the cluster-building reaction of metallaboranes by borane [24]. It is shown to be an intermediate in both cases as illustrated in the next section for the metallacarborane.

Novel cluster isomers

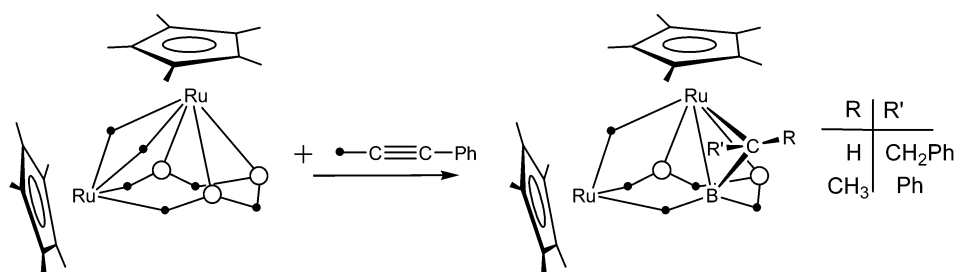
Heating *nido*-1,2- $\{\text{Cp}^*\text{Ru}\}_2$ -4,5- Me_2 - $(\mu\text{-BH}_2)\text{C}_2\text{B}_2\text{H}_5$ generates two products (Scheme 3). In one, loss of H_2 and cluster closing generates a 7 sep, 7 vertex *closo*-cluster. In the other, loss of BH leads to *nido*-1,7- $\{\text{Cp}^*\text{RuH}\}_2$ -4,5- Me_2 - $\text{C}_2\text{B}_2\text{H}_4$ if one numbers the fundamental deltahedron the same way for this compound and *nido*-1,2- $\{\text{Cp}^*\text{RuH}\}_2$ -4,5- Me_2 - $\text{C}_2\text{B}_2\text{H}_4$ produced in the room temperature reaction of the ruthenaborane and alkyne. With the same composition, they are isomers but of a new type. Both are based on a pentagonal bipyramid with one vertex unoccupied; however, in one case it is an apical (5-connect) vertex, whereas in the other it is a basal (4-connect) vertex that is unoccupied. The former is the rule for borane clusters so the novel isomer must reflect the perturbation of the heteroatoms in that the discrimination of a transition metal for 4- vs. 5-connect vertices is not as large as for a main group atom. Curiously, the isomers do not interconvert below their decomposition temperatures and would not have been observed unless the two different pathways to the same composition (+ alkyne – BH_3 vs. + alkyne – H_2 followed by – BH) could be accessed. The metallaborane route to metallacarboranes does have an advantage.



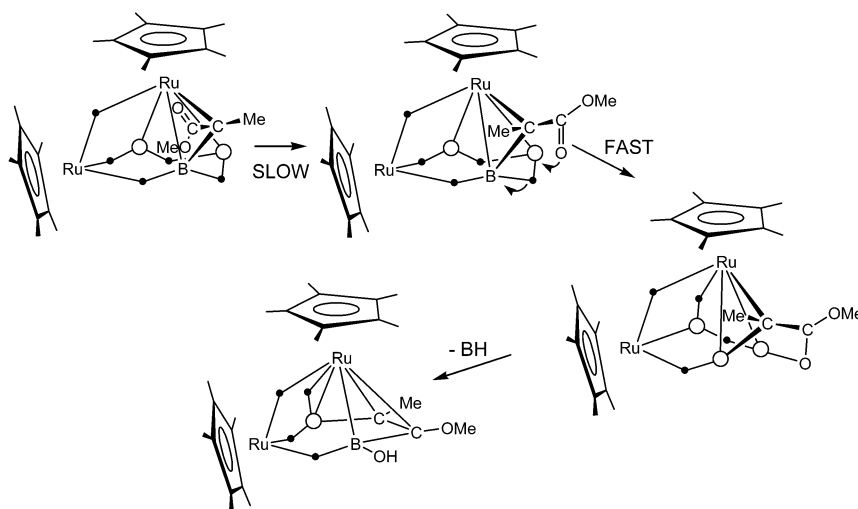
Scheme 3

Bridging alkylidenes

With terminal alkynes, although the two product types described above are the major ones, another novel product type is observed. In this one, addition of the alkyne takes place with no loss of atoms. As shown in Scheme 4, in this parallel path insertion does not occur, rather the alkyne ends up as a reduced alkylidene bridging a metal boron edge of the unchanged ruthenaborane *nido*-cluster. For $\text{HC}\equiv\text{CPh}$, both Markovnikoff and anti-Markovnikoff addition of the two cluster hydrogen atoms is observed and yields both Me, Ph, and H, CH_2Ph substituent pairs on the alkylidene bridging carbon atom. The same is true for $\text{HC}\equiv\text{CC}(\text{O})\text{OMe}$ except now the Markovnikoff product also possesses two isomeric forms with the Me group pointing toward and away from the Ru–Ru bond. As shown in Scheme 5, further reactivity ensues due to the presence of the $-\text{C}(\text{O})\text{OMe}$ substituent on the alkyne. The isomer with an orientation of the carbonyl oxygen favorable for insertion into the borane fragment reacts more rapidly than the isomer with unfavorable orientation, ultimately resulting in cleavage of the $\text{C}=\text{O}$ bond and insertion of two carbyne fragments. Once again, the stable $\text{Ru}_2\text{B}_2\text{C}_2$ framework is produced albeit one carbon is derived from a carbonyl fragment rather than one from the original alkyne.



Scheme 4



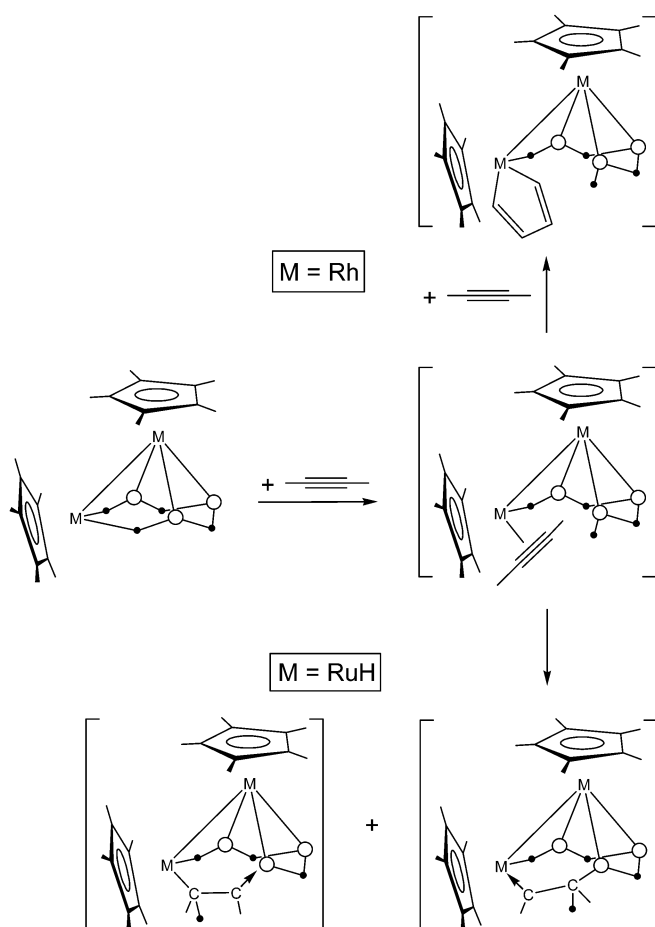
Scheme 5

Reaction pathway

It should be clear from the nature of the products discussed above that the mechanism of the reaction of alkyne with ruthenaborane clusters is complex. However, full characterization of these and related products for three different alkynes generated a set of NMR parameters empirically characteristic of cluster type and substituent pattern. With this information, it was possible to move to early reaction times and “isolate” in time the NMR signatures of four major intermediates that could not be isolated. These provided the key to unlocking the nature of the first reaction steps. The postulated structures of two of these species, connected in time by the NMR experiments, rationalize the major products at room temperature. The first steps in the pathway and the two crucial intermediates observed by NMR are shown in Scheme 6. Now it can be seen that the first step is addition of the alkyne and identical to that for the isoelectronic rhodaborane. In contrast to the rhodaborane, the hydrogen-rich ruthenaborane facilitates hydrometallation, which starts the incorporation of the alkyne into the cluster framework.

In contrast to the rhodaborane, hydroboration must be more facile than cyclotrimerization. It is noteworthy that there is spectroscopic evidence for low yields of hydrogenated alkyne as well as cyclotrimer with the ruthenaboranes. Clearly, the balance between the two pathways is a fine one. Once hydroboration has been achieved rearrangement to the bridging alkyldiene, insertion and loss of H_2 or BH_3 or addition of more alkyne if available, takes place to yield the major isolated products.

Comparison of the reactivities of the entire set of metallaboranes up until now suggest that the reactivities can be correlated with the number and nature of the hydrogen atoms on the cluster framework. In the case of alkynes, it appears that the “extra” hydrogen per Cp^*Ru fragment is the source of its rich reaction chemistry. Relative to *nido*-1,2- $\{Cp^*Rh\}_2B_3H_7$, these two hydrogen atoms compensate for the fact that each Cp^*Ru is a one-electron cluster fragment. From the structure and electron counts of other ruthenaboranes [25], we know that these extra hydrogens are not absolutely required. This is just another way of saying they can be easily lost via reaction. “Hydrogen-poor” metallaboranes like $\{Cp^*Cr\}_2B_4H_8$ are expected to behave differently and do.



Scheme 6

FUTURE PROSPECTS

The chemistry of metallaboranes can be understood as a combination of that of boranes and metal clusters. Hence, one can begin to search for reactions that serve a practical purpose. Although the continued development of the corpus of inorganic chemistry is necessary and needs no justification within the profession of chemistry, practical applications provide more immediate arguments for support a capitalistic society demands. The discouraging behavior encountered with the majority of the metallaboranes in terms of alkyne reactivity led us to think about ways of activating these clusters for reaction. As some metals “do it” and others do not, the thought occurred that hetero-metal promoted alkyne addition might be possible for the recalcitrant metallaboranes. Indeed, such chemistry is possible [5] and we now have evidence that the molybdenum center in *nido*-1,2- $\{\text{Cp}^*\text{Ir}\}\{(\text{CO})_3(\text{THF})\text{Mo}\}\text{B}_4\text{H}_8$ promotes the addition and insertion of two alkynes [26]. But that work is still under development and will be a story for another time [27].

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