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Facile Hydrometalation of Alkynes by *nido*-1,2-($Cp^*RuH)_2B_3H_7$ Yielding Novel Ru−B Edge-Bridging Alkylidenes. Stepwise Conversion of HC≡CC(O)OMe into *nido*-1,2-($Cp^*RuH)_2$-3-HOB-4-MeC-5-MeOC-BH_3, Cp* = η^5-C_5Me_5

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The myriad ways in which boron hydrides and transition metal hydrides can be used to manipulate organic substrates, for example, hydroboration[1] and hydrometalation,[2] make them valuable reagents for chemical transformations. A natural question concerns how B−H and M−H moieties would behave if it were possible for them to act in concert as an integral part of a single reagent? Metallaboranes containing both B−H and M−H sites provide a vehicle for answering this question experimentally; however, until recently, the vast majority of metallaboranes known incorporated only B−H terminal and B−H−M bridge hydrogens.[3−7]

With the development of the reaction of monocyclopentadienylmetal halides with monoboranes as a route to metallaboranes of groups 5−9, metallaboranes, which contain earlier metals plus the extra metal hydrides needed to satisfy the cluster skeletal electron pair (sep) count for the geometry adopted,[8,9] became accessible.[10] For example, square pyramidal, 7 sep 2-$Cp^*WH_3B_4H_8$, Cp* = η^5-C_5Me_5,[11,12] analogous to 2-$Cp^*CoB_4H_8$,[13] and square pyramidal, 7 sep 1,2-$(Cp^*RuH)_2B_3H_7$, **1**,[14,15] analogous to 1,2-$(Cp^*Rh)_2B_3H_7$,[16] are "hydrogen-rich" clusters with additional hydrogen atoms associated with the metal atoms. Unimolecular decomposition of hydrogen-rich metallaboranes gives rise to hypoelectronic metallaboranes.[17,18] The work described below concerns bimolecular reactions of the diruthenapentaborane.

We have already reported that reaction of $(Cp^*Rh)_2B_3H_7$ with terminal or internal alkynes leads to catalytic cyclotrimerization, whereas **1** reacts with internal alkynes to undergo kinetically controlled insertion chemistry yielding metallacarboranes of new types.[16,19] As described below, terminal alkynes permit a reaction pathway in which cluster edge-bridging alkylidenes are produced. To demonstrate the impressive capabilities of a hydridic, oxyphilic metallaborane in transforming an organic substrate, we present the example of methyl acetylene monocarboxylate.

The reaction of **1** with HC≡CC(O)OMe at room temperature leads to two primary products. The first is *nido*-1,2-$(Cp^*RuH)_2$-5-C(O)OMe-4,5-$C_2B_2H_5$ resulting from insertion of the alkyne and loss of $[BH_3]$.[16] This path is also observed for internal alkynes.[19] The second, *nido*-1,3-μ-Me{C(O)OMe}C-1,2-$(Cp^*Ru)_2B_3H_7$, **2**, in which the alkyne has been converted into a μ-alkylidene, is unique to terminal alkynes. This compound exists as a pair of isomers, **2a**, **2b**, and the structure of **2b** is shown in Figure 1. Isomer **2a** has the positions of the substituents on the μ-alkylidene carbon atom reversed as shown in Scheme 1.[20] The two hydrogen atoms that generate a $-CH_3$ group from ≡CH most likely arise from one terminal BH and one bridging RuHRu. Hence, we view the formation of **2** as arising from hydroboration followed by hydroruthenation[21] or the reverse. The regiochemistry of the alkyne reduction is predominantly Markovnikoff; however, a small amount of the anti-Markovnikoff product has been isolated and characterized. Phenyl acetylene generates a μ-alkylidene as well, showing an activated alkyne is not necessary.

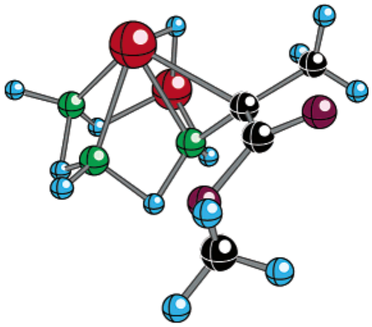
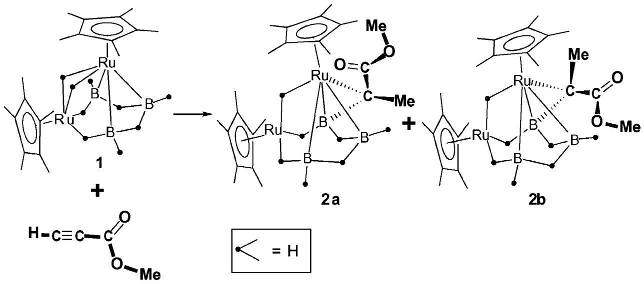


Figure 1. Framework of **2b** (Cp* omitted); Ru-red, B-green, H-blue, C-black, O-purple.

Scheme 1



Compound **2** is novel. We are unaware of any previous characterization of compounds containing metal-boron μ-alkylidenes, although a M−M bridging CR_2 fragment is a common feature in transition metal organometallic chemistry.[2] There is one example of a carbenoid moiety bridging a B−B bond of a carborane; however, in this case, the sp^2 CR_2 moiety is contributing a single orbital to the three-center bridge bond.[22] Note that the formation of **2** takes place on the cluster framework of **1** without any net change in sep. Compound **1** is a 7 sep nido diruthenapentaborane, and, as a two electron μ-alkylidene replaces two one electron hydrogen atoms, **2** is also a 7 sep nido diruthenapentaborane.

Heating **2a** or **2b** leads to rearrangement into a single product, *arachno*-2,3,-μ(*C*)-5-η^1(*O*)-Me{C(O)OMe}C-1,2-$(Cp^*Ru)_2B_3H_7$, **3**, in high yield (Figure 2, Scheme 2). The carbonyl oxygen has coordinated to a boron atom and opened a basal BHB edge of **2**. The pair of electrons contributed by the oxygen atom increases the sep to 8 consistent with the observed structure. Coordination results in the C=O distance increasing ~0.1 Å and ν(C=O) decreasing ~150 cm^{-1}. The conversion of **2b** is much more facile ($t_{1/2}$ = 10

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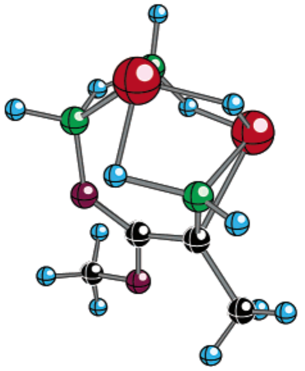
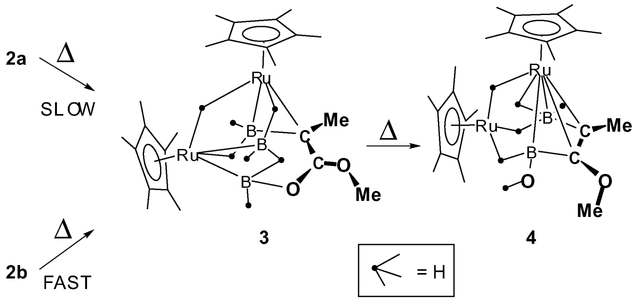


Figure 2. Framework of **3** (Cp* omitted); Ru-red, B-green, H-blue, C-black, O-purple.

Scheme 2



min at 80 °C) than that of **2a** ($t_{1/2} = 8$ h at 80 °C). Monitoring the conversion of **2a** into **3** did not reveal **2b** as an intermediate. As the carbonyl oxygen is positioned for attack of the borane fragment in **2b** but not in **2a**, we suggest that **2a** slowly rearranges to **2b** which rapidly converts to **3**.

Heating **3** for 48 h at 80 °C leads to loss of a [BH] fragment and the production of *nido*-1,2-(Cp*RuH)$_2$-3-HOB-4-MeC-5-MeOC-BH$_3$, **4**, as the final product in high yield (Figure 3, Scheme 2). The carbonyl oxygen bond has been completely cleaved, and the carbonyl carbon, as well as the adjacent carbon of the original acetylene fragment, has been inserted into the metallaborane framework to yield an 8 sep nido diruthenadicarbahexaborane. The oxygen atom is found as a terminal BOH adjacent to the former carbonyl carbon. The sequence of reactions has resulted in reduction of ≡CH to CH$_3$, insertion of a carbonyl oxygen into a BH bond, and insertion of a C$_2$ fragment into the cluster. Individually, all are known processes (an exemplar of insertion of CO into a BH bond is the reaction of CO with B$_2$H$_6$ catalyzed by BH$_4^-$ to yield methyl boroxime),[23,24] but here all three take place sequentially on a metallaborane framework.

As might be expected with such a reactive alkyne, additional products are produced when the alkyne is used in excess and the temperature is raised. A complete description of this chemistry and that of less activated alkynes will be presented in the full paper.

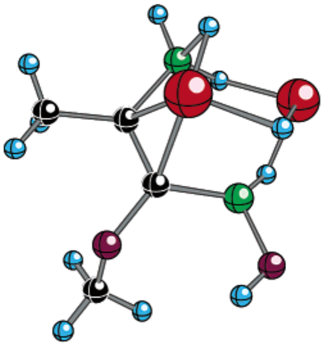


Figure 3. Framework of **4** (Cp* omitted); Ru-red, B-green, H-blue, C-black, O-purple.

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Supporting Information Available: Experimental procedures, spectroscopic and X-ray data for all of the compounds reported, including ORTEP drawings of **2**−**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Brown, H. C. *Hydroboration*; Benjamin: New York, 1962.
(2) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: New York, 1989.
(3) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519.
(4) Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211.
(5) Housecroft, C. E.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57.
(6) Grimes, R. N. *Acc. Chem. Res.* **1978**, *11*, 420.
(7) Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982; p 269.
(8) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.
(9) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F.; Kaesz, H. D.; Adams, R. D., Eds.; VCH: New York, 1990.
(10) Fehlner, T. P. *Organometallics* **2000**, *19*, 2643.
(11) Weller, A. S.; Shang, M.; Fehlner, T. P. *Organometallics* **1999**, *18*, 53.
(12) Bullick, H. J.; Grebenik, P. D.; Green, M. L. H.; Hughes, A. K.; Leach, J. B.; McGowan, P. C. *J. Chem. Soc., Dalton Trans. (1972−1999)* **1995**, 67.
(13) Venable, T. L.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 887.
(14) Lei, X.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1999**, *121*, 1275.
(15) Kawano, Y.; Matsumoto, H.; Shimoi, M. *Chem. Lett.* **1999**, 489.
(16) Yan, H.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4498.
(17) Weller, A. S.; Shang, M.; Fehlner, T. P. *Organometallics* **1999**, *18*, 853.
(18) Lei, X.; Shang, M.; Fehlner, T. P. *Organometallics* **2001**, *20*, 1479.
(19) Yan, H.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2578.
(20) For characterization and X-ray data, see Supporting Information.
(21) Alcock, N. W.; Cartwright, J.; Hill, A. F.; Marcellin, M.; Rawles, H. M. *Chem. Commun.* **1995**, 369.
(22) Mirabelli, M. G. L.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 592.
(23) Rathke, M. W.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 2606.
(24) Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975.

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