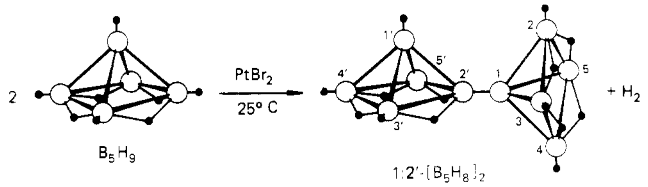
Transition-Metal-Promoted Reactions of Boron Hydrides. 4.[1] A One-Step Synthesis of the Coupled Cage Borane 1:2′-$[B_5H_8]_2$

Sir:

We have recently reported[1,3,4] the use of various transition-metal reagents to promote the reactions of boron hydrides and carboranes with acetylenes, illustrating the potential importance of transition metals as catalysts in polyhedral boron cage chemistry. We have now extended our studies to include other classes of metal-promoted reactions and report here the first example of a transition-metal-catalyzed dehydrodimerization reaction of a boron hydride.

In a typical reaction 1.057 g of dried $PtBr_2$ powder (Aldrich) (2.98 mmol) was stirred with 19.0 mmol of pentaborane(9) at room temperature in vacuo. After 24 h the reaction mixture was separated by vacuum-line techniques to give 0.073 g (0.58 mmol) of 1:2′-$[B_5H_8]_2$, 0.72 mmol of H_2, and 17.5 mmol of unreacted B_5H_9. The $PtBr_2$ catalyst appeared to be unchanged with no indication of the formation of platinum metal. The remaining B_5H_9 was then recondensed over the $PtBr_2$ and the reaction continued with daily removal of product and hydrogen. After 7 days it was found that a total of 3.86 mmol of 1:2′-$[B_5H_8]_2$ and 4.09 mmol of H_2 had been produced and 8.4 mmol of B_5H_9 had reacted. This corresponds to a 92% yield of 1:2′-$[B_5H_8]_2$ based on consumed B_5H_9. Analysis by GLC and NMR confirmed the identity and purity of 1:2′-$[B_5H_8]_2$. There was no evidence for the formation of either of the symmetrical isomers 2:2′-$[B_5H_8]_2$ or 1:1′-$[B_5H_8]_2$ in the reaction.

The observed stoichiometry of the reaction is consistent with eq 1 and thus corresponds to a $PtBr_2$-catalyzed dehydrodimerization of pentaborane(9), giving the compound 1:2′-$[B_5H_8]_2$ in essentially quantitative yields. This unusual coupled cage compound, which has a structure composed of two pentaborane(9) cages linked by a single boron–boron bond between apex and basal positions of the two cages, was originally characterized by Gaines,[5] who discovered the compound in the lower volatile residues of pentaborane(9) storage tanks. No synthetic route to this compound was available, however, until 1979 when Gaines reported[6] its synthesis in 20% yield by the reaction of NaB_5H_8 with 1-BrB_5H_8. We have also reported[7] that 1:2′-$[B_5H_8]_2$ can be obtained along with 2:2′-$[B_5H_8]_2$ and 1:1′-$[B_5H_8]_2$, by the mercury-sensitized photolysis of pentaborane(9). Although the reaction reported herein is relatively slow (~0.55 mmol of 1:2′-$[B_5H_8]_2$/day, ~0.19 catalyst turnover/day), the high yields and simplicity of reaction and product isolation make this route a significant improvement over existing methods. Furthermore, the reaction should be readily adaptable to larger scales, thereby increasing the rate of product formation.



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It is indeed surprising that only one of the three possible isomers of $[B_5H_8]_2$ is produced in the reaction. Although the mechanism of reaction is still undetermined, this unique selectivity suggests that both electrophilic attack, which would lead to apex cage substitution, and oxidative addition of pentaborane(9) at the metal, which would lead to basal cage substitution, are important in the overall reaction.

We are now investigating both the mechanism of this reaction and the potential applications of dehydrodimerization catalysts for the production of other types of multicage polyhedral boron cluster compounds.

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Registry No. 1:2-$[B_5H_8]_2$, 31831-99-9; $PtBr_2$, 13455-12-4; B_5H_9, 19624-22-7.

Department of Chemistry and
Laboratory for Research on the
Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104

Edward W. Corcoran, Jr.
Larry G. Sneddon*[2]

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