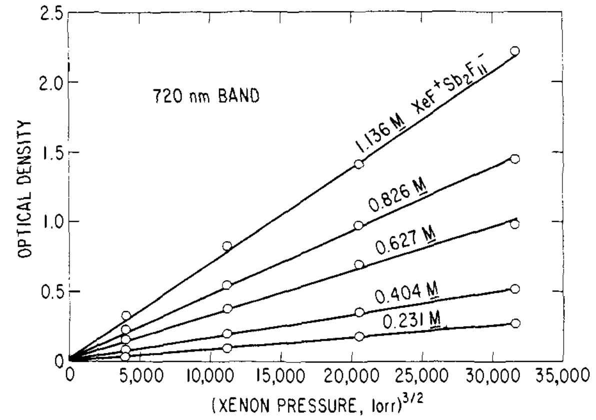

Figure 2. Optical density of the 720-nm band plotted as a function of the $^3/_2$ power of xenon pressure. Each line was obtained at a constant concentration of $XeF^+Sb_2F_{11}^-$, shown in the figure. The spectra were recorded with a Cary 14 spectrometer, using a 0.1-cm-path-length cell for all measurements except those of the most dilute solution. Measurements of the 0.231 M solution were made with a 1.0-cm-path-length cell and were divided by 10 for purposes of representation in this figure.

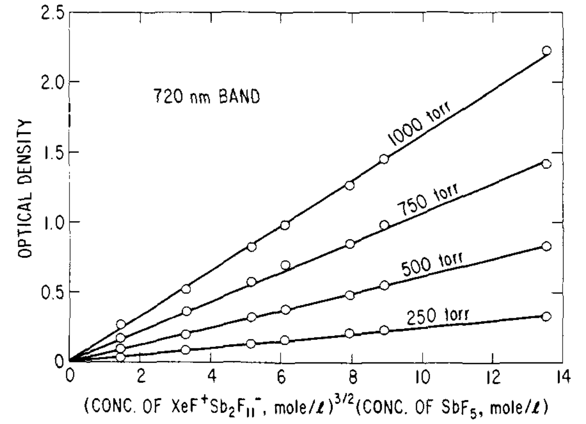

Figure 3. Optical density of the 720-nm band plotted as a function of the product of the $^3/_2$ power of $XeF^+Sb_2F^{11-}$ concentration and first power of the SbF_5 concentration; the latter concentration is not an independent variable but is required for the equilibrium in eq 3. Each line was obtained at a constant pressure of xenon, shown in the figure. The measurements were made in the same manner as those described in Figure 2.

that the concentration of Xe_2^+, measured by the optical density at 720 nm, is proportional to approximately the $^3/_2$ power of both the xenon pressure (Figure 2) and the $XeF^+Sb_2F_{11}^-$ concentration (Figure 3), and the first power of the antimony pentafluoride concentration. We therefore conclude that the cation is strongly bound in a complex with excess oxidant (eq 2). The overall reaction resulting from both oxidation and complexation is shown in eq 3. Our spectral data yield a uniform equilibrium constant for this reaction over a sixteenfold range of xenon pressure and fourfold range of $XeF^+Sb_2F_{11}^-$ concentration, when an arbitrary value for the molar extinction coefficient of dixenon cation is used. We are currently endeavoring to measure the extinction coefficient and establish a value for this constant.

$$Xe_2^+Sb_2F_{11}^- + XeF^+Sb_2F_{11}^- \rightleftharpoons Xe_2^+Sb_2F_{11}^-\cdot XeF^+Sb_2F_{11}^- \quad (2)$$

$$3Xe + 3XeF^+Sb_2F_{11}^- + 2SbF_5 \rightleftharpoons 2Xe_2^+Sb_2F_{11}^-\cdot XeF^+Sb_2F_{11}^- \quad (3)$$

The original methods for the production of dixenon cation[3]—reduction of xenon(II) with metals or water—involve irreversible reactions. A number of new reductants, including lead monoxide, arsenic trioxide, finely divided silica, glass wool, sulfur dioxide,[5] phosphorus trifluoride, and carbon monoxide, have been found to react in analogous fashion with solutions of $XeF^+Sb_2F_{11}^-$ in antimony pentafluoride. These irreversible reactions produce both Xe_2^+ and elemental xenon in various nonequilibrium ratios. Hence they proceed independently of the reversible reaction described in this communication.

Acknowledgments. We thank A. J. Downs, A. R. Minihan, E. H. Appelman, and J. G. Malm for stimulating discussions of these findings.

References and Notes

(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.
(2) This method for the production of dixenon cation was first described in a paper presented at the Fourth Winter Fluorine Conference, Daytona Beach, Fla., Jan 28–Feb 2, 1979, by L. Stein in collaboration with J. R. Norris, A. J. Downs, and A. R. Minihan; it has more recently been described in greater detail by the present authors at the Ninth International Symposium on Fluorine Chemistry, Avignon, France, Sept 3–7, 1979.
(3) Stein, L.; Norris, J. R.; Downs, A. J.; Minihan, A. R. *J. Chem. Soc., Chem. Commun.* **1978**, 502–504.
(4) The band at 720 nm is very broad and has a non-Gaussian shape, which suggests that it may encompass two overlapping bands. However, this is an artifact caused by the nonlinearity in energy of the wavelength scale; when converted to a wavenumber scale, the band assumes a Gaussian shape. The center of this band was previously reported at 710 nm in ref 3.
(5) Minihan, A. R., private communication.
(6) Undergraduate Research Participant from Westminster College, New Wilmington, Pa., spring term, 1979.

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Transition Metal Catalyzed Reactions of Alkynes and Boron Hydrides: Synthesis of 2-(*cis*-2-Butenyl)pentaborane(9) and Its Conversion into Monocarbon Carboranes

Sir:

Conventional small carborane syntheses have usually involved the thermal reactions[1a] of pentaborane(9) with alkynes and have generally resulted in both cage fragmentation and the formation of numerous products.[1b] The initial step in these reactions has been proposed[2] to be the hydroboration of the alkyne to produce the corresponding alkenyl-substituted pentaborane(9) derivative, although no such compounds have heretofore been isolated. We now report the development of a transition metal catalyzed synthesis of these compounds under mild conditions and that, furthermore, these alkenyl-substituted pentaborane(9) derivatives can be converted in high yields into monocarbon carboranes.

In a typical reaction equimolar amounts of pentaborane(9) and dimethylacetylene are heated in the liquid phase at 75 °C in the presence of 10 mol % of dimethylacetylene dicobalthexacarbonyl, $(CH_3)_2C_2Co_2(CO)_6$. After 1 h, vacuum line fractionation of the reaction products revealed a 22% conversion[3] of pentaborane(9) into 2-(*cis*-2-butenyl)-pentaborane(9) (I). This compound, which has not been detected in uncatalyzed experiments, can then be further purified by GLC[4] to give an air-sensitive liquid which slowly decomposes to polymeric material under vacuum.

The composition of I is supported by exact mass measurements on the parent ion (mass calculated, 118.1643; found, 118.1650) and its proposed structure is consistent with the spectroscopic data. Thus, the ^{11}B NMR[5] consists of three doublets at −14.4 (J = 160 Hz), −18.6 (J = 167 Hz), and −50.9 (J = 174 Hz) and a singlet at 3.2 ppm with relative intensities of 2:1:1:1, confirming substitution at the 2 boron position. Likewise, the ^{11}B spin decoupled ^1H NMR spectrum[6] is in agreement with this formulation showing broad resonances from the protons bound to the boron cage at 2.52

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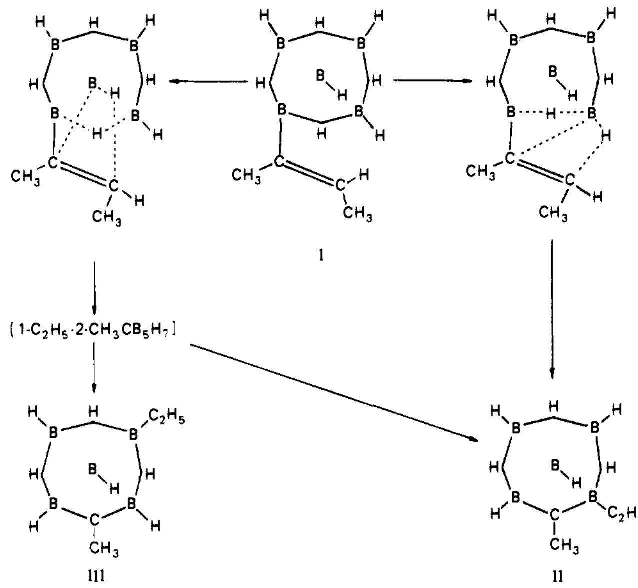
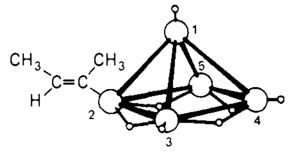
Scheme I. Proposed Mechanism for the Conversion of 2-(*cis*-2-Butenyl)pentaborane(9) (I) into $2\text{-}CH_3\text{-}3\text{-}C_2H_5CB_5H_7$ (II), and $2\text{-}CH_3\text{-}4\text{-}C_2H_5CB_5H_7$ (III).

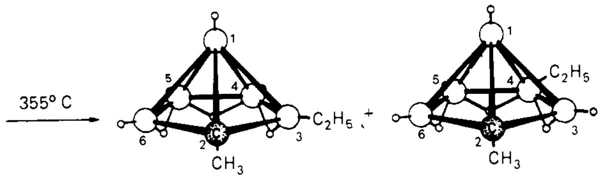


($B_{3,5}$-H, 2 H), 2.32 (B_4-H, 1 H), 1.03 (B_1-H, 1 H), −1.33 (H_{Br}, 2 H), and −2.52 ppm (H_{Br}, 2 H), as well as the resonances expected from the butenyl group at 5.76 (q, $J = 6.9$ Hz, CH), 1.71 (s, CH_3), and 1.61 ppm (d, $J = 6.9$ Hz, CH_3). Cis addition at the alkyne was confirmed by the reaction of I with excess glacial acetic acid. Analysis of the resulting 2-butene by GLC[7] indicates a cis/trans ratio of 97.2:2.8.

Since compounds such as I have been proposed as the first step intermediates in thermally induced carborane syntheses, it was expected that I could be converted into carboranes easily. The thermolysis reactions of I were therefore investigated, and it was found that the quick passage of I through a heated tube (355 °C) in vacuo indeed results in an 86% conversion of I into carborane products. The two major products are $2\text{-}CH_3\text{-}3\text{-}C_2H_5CB_5H_7$ (II, 37%) and $2\text{-}CH_3\text{-}4\text{-}C_2H_5CB_5H_7$ (III, 39%) as shown.



I



II III

Compound II was previously known[8] and was identified by comparison of its ^{11}B and ^{1}H NMR spectra with literature values. Compound III is a previously unreported isomer, the structure of which was deduced from the spectroscopic data.[9]

Previously, CB_5H_9 and its alkyl derivatives were synthesized in only low yields from the thermal reactions of pentaborane(9) and acetylene,[2a] or in moderate yields from the reaction of $2,5\text{-}C_2B_6H_8$ with tetramethylammonium borohydride.[8] Thus, the combined discovery of a metal assisted synthesis of alkenylpentaborane(9) derivatives and their subsequent conversion into the corresponding alkyl derivatives of CB_5H_9 provides an attractive new route to this unusual monocarbon carborane.

The formation of II and III as major products in this reaction is consistent with the reaction sequence originally proposed by Williams[2b] for the corresponding thermal reaction. This mechanism is shown in Scheme I and involves an internal hydroboration of the butenyl group by an adjacent B-H group (boron positions 1 or 3) followed by an ethyl group migration to generate II and $1\text{-}C_2H_5\text{-}2\text{-}CH_3CB_5H_7$. The latter compound may then readily rearrange under the reaction conditions in a manner similar to the thermal rearrangement of 1-alkylpentaboranes to 2-alkylpentaboranes[10] to yield both II and III.

The results presented above are important not only because they provide further insight into the mechanism of the reactions of boron hydrides and alkynes, but, in addition, they illustrate a new direction of potentially great importance in boron cage chemistry, that is, the use of transition metal complexes as catalytic reagents to induce reactions which previously could be carried out only under severe conditions.[11] Indeed, we have now obtained results similar to those described above with a variety of catalysts and boron cage systems and this will be discussed in a future publication.

Acknowledgment. We thank the Karcher and Busch Foundations for fellowships (R.W.) and the Army Office of Research for support of this work.

References and Notes

(1) (a) R. N. Grimes, "Carboranes", Academic Press, New York, 1970, Chapters 3 and 4. (b) As an alternative to the thermally induced formation of small carboranes, an improved Lewis-base-promoted reaction of alkynes with pentaborane(9) at or below room temperature has been reported; however, this synthesis is limited to the formation of C-substituted derivatives of the small carborane $C_2B_4H_8$ [see Onak et al., *Inorg. Chem*, **3**, 1686 (1964), and N. S. Hosmane and R. N. Grimes, *ibid.*, **18**, 3294 (1979)]

(2) (a) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88**, 2061 (1966). (b) R. E. Williams in "Progress In Boron Chemistry", Vol. 2, R. J. Brotherton and H. Steinberg, Eds., Pergamon Press, New York, 1970, Chapter 2.

(3) Recently, higher percent conversions and turnover rates have been observed for this reaction using other transition metal catalysts: R. Wilczynski and L. G. Sneddon, unpublished work.

(4) Tricresyl phosphate (TCP), 6% on 60–80 mesh Chromosorb W; 80 °C; $R_V(B_5H_9) = 1.0$, $R_V(I) = 15.0$.

(5) Relative to $BF_3 \cdot O(C_2H_5)_2$ with positive sign indicating shift to lower field.

(6) Relative to Me_4Si with positive sign indicating shift to lower field.

(7) Durapak phenyl isocyanate/Proacil C; 80–100 mesh; 35 °C.

(8) G. B. Dunks and M. F. Hawthorne, *Inorg. Chem*, **8**, 2667 (1969).

(9) (a) Calcd for $C_4H_{15}B_5$: B, 46.11. Found: B, 46.12. (b) High resolution mass measurement for $^{12}C_4{}^{1}H_{15}{}^{11}B_5$ calcd for *m/e* 118.1643, found 118.1640. (c) ^{11}B NMR (ppm, C_6D_6): 13.7 (d, 2, $B_{3,6}$, $J_{BH} = 141$ Hz), 11.7 (s, B_4), −4.9 (d, B_5, $J_{BH} = 172$ Hz), −48.4 (d, B_1, $J_{BH} = 156$ Hz). ^{1}H NMR (δ, C_6D_6, ^{11}B spin decoupled): 4.34 (br s, 2, $B_{3,6}$–H), 3.25 (br s, B_5–H), 2.23 (s, 3, CH_3), 1.08 (s, 5, CH_2CH_3), −0.43 (br s, 2, B_1–H and H_{Br}), −1.70 and −2.14 (br s, H_{Br}).

(10) T. P. Onak and F. J. Gerhart, *Inorg. Chem.*, **1**, 742 (1962).

(11) In this regard, Fehlner has reported the stoichiometric reaction of a transition metal complex, $B_4H_8Fe(CO)_3$, with 2-butyne under photolytic conditions to form a four carbon carborane; see T. P. Fehlner, *J. Am. Chem. Soc.*, **99**, 8355 (1977).

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Preparation of a "Stabilized Formyl" Complex from Carbon Monoxide and Hydrogen and the Crystal Structure of a Derivative in Which the C–O Bond Has Been Cleaved

Sir:

There is now good evidence that a formyl complex is unstable with respect to a hydrido carbonyl complex when a coordination site is vacant.[1] Therefore to form one from a