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Rearrangement in Reduced Carboranes

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We recently discussed theoretical bases for the opening of deltahedral (closo) borane and heteroborane frameworks to nido and arachno molecules of lower symmetry upon addition of electrons to the polyhedral skeleton.[1] The potential energy surface along symmetry-allowed rearrangement coordinates was analyzed by extended Hückel MO calculations for $B_5H_5^{n-}$ (n = 2, 4, 6) molecules with the implication that these models were extendable to isoelectronic boranes and heteroboranes. Here we report similar work concerning the possible isomers of the known *closo*-carboranes $C_2B_3H_5$ and $C_2B_4H_6$,[2,3] isoelectronic with the unknown $B_5H_5^{2-}$ and the known $B_6H_6^{2-}$.[4] The results[5] have implications regarding the mode of intramolecular rearrangement and preferred geometry of the two-electron reduction products of these carboranes.

Hoffmann and Lipscomb[6] also have employed LCAO calculations to speculate on the nature of reduced carboranes. They noted that in D_{3h} symmetry (both C atoms axial in a trigonal-bipyramidal structure) $C_2B_3H_5^{2-}$ has orbital degeneracy and should not be stable. However, the isomeric forms of $C_2B_3H_5^{2-}$ of different symmetry were deemed "energetically inaccessible". Our results confirm this "inaccessibility" *if* the isomeric forms which are considered retain a nominally trigonal-bipyramidal framework and the symmetry is lowered from D_{3h} by varying the C atom placement to axial–equatorial (C_s) or equatorial–equatorial (C_{2v}). However, if descent in symmetry is realized by distortion from the trigonal-bipyramidal geometry to a square-pyramidal skeleton, we find that all of the isomeric forms of $C_2B_3H_5^{2-}$ are energetically accessible. The isomeric forms of square-pyramidal $C_2B_3H_5^{2-}$ are interconvertible by sds (square–diamond–square) rearrangements.[6] With the aid of symmetry considerations such as those discussed by Pearson[7] and Bartell[8] we find sds rearrangements to be symmetry allowed; however, on the basis of our EHMO calculations they appear to be relatively high-energy paths and alternate, symmetry-allowed, low-energy paths are proposed. Figure 1 summarizes the results for $C_2B_3H_5^{2-}$. The symmetry-allowed "low-energy" mode of interconversion between the isomeric square-pyramidal forms of $C_2B_3H_5^{2-}$ amounts to an arcing of one atom position as shown in Figure 1. These EHMO results suggest that the nominally square-pyramidal isomers of $C_2B_3H_5^{2-}$ decrease in stability in the order trans basal–basal, cis basal–basal, and apical–basal (−377.32, −376.34, and − −375.67 eV, respectively). This result appears to be in direct conflict with the fact that the only known isomer of $C_2B_3H_7$ (isoelectronic with $C_2B_3H_5^{2-}$) has the C atoms in apical and basal positions.[9] However, addition of protons to the "square" face of $C_2B_3H_5^{2-}$ so as to give two bridge hydrogens in the apical–basal isomer and two BH_2 groups in the basal–basal isomers changed the relative stabilities to apical–basal > trans basal–basal > cis basal–basal (−390.30, −389.70, and −389.46 eV, respectively). These results corroborate Williams' empirical observation that the placement of extra hydrogens as bridging hydrogens in heteroboranes appears to have precedence over the placement of electron-rich heteroatoms at low-coordinate vertices.[10] In the present case of $C_2B_3H_7$, even though a trans basal placement of the carbon atoms would be anticipated, such placement would preclude the possibility of bridge hydrogens since they have never been observed to bridge other than boron positions and bridge preferentially on nontrigonal faces. The apical–basal placement of the carbon atoms is the only one which can accommodate both extra hydrogens in bridging positions in the nido deltahedral fragment.[11]

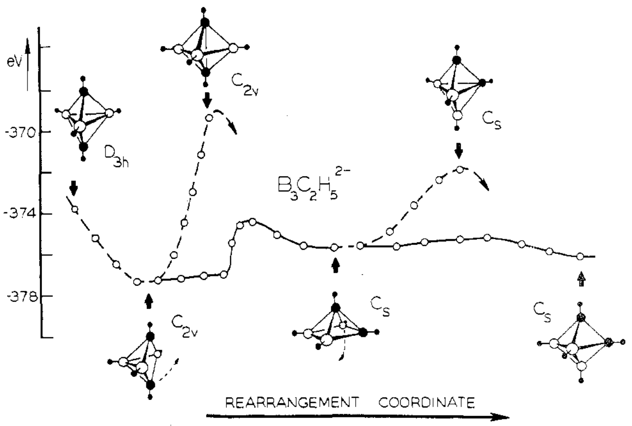

Figure 1. Energy as a function of geometry for $C_2B_3H_5^{2-}$. The solid line represents the interconversion of the isomeric forms of $C_2B_3H_5^{2-}$ via symmetry-allowed arcing movements of the designated atoms. The broken line designates the inconversion via a dsd mechanism. During the rearrangements all interatomic distances were maintained at their idealized values[5] except for that portion of the structure where the major rearrangement occurred.

The interconversion of the two isomeric forms of $C_2B_4H_6$ (cis and trans carbons in a nominally octahedral framework) has been suggested to occur through either a pentagonal-pyramidal intermediate or perhaps a trigonal prism.[6] However, one study mitigates against either of the latter intermediates and suggests a more complex potential surface.[12] In the case of $C_2B_4H_6^{2-}$ instability was implied for the trans isomer because of orbital degeneracy and it was suggested that the cis isomer was energetically accessible.[6] Our EHMO results suggest that *cis*- and *trans*-$C_2B_4H_6^{2-}$ are very similar in energy (ca. −430.5 eV). Likewise, the three trigonal-prismatic forms of $C_2B_4H_6^{2-}$ are similar in energy (ca. −433.5 eV). However, all of the pentagonal-pyramidal isomers of $C_2B_4H_6^{2-}$ are more stable (apical–basal, −434.4; ortho basal, −436.8; meta basal, −438.1 eV). The results for $C_2B_4H_6^{2-}$ suggest, as in the case of $B_3C_2H_5^{2-}$, that the more open, pyramidal form of the molecule is preferred over any deltahedral structure.[11] Finally, it is interesting to note that Hoffmann's extensive study of the potential surface for $C_5H_5^+$, isoelectronic with $C_2B_3H_5^{2-}$, also indicates a square-pyramidal structure[13] as had been anticipated previously on empirical grounds.[14]

Based on previous studies[1,15] and the results presented here, it is our suspicion that the two-electron reduction of *closo*-carboranes in general opens the deltahedron to the corresponding nido counterpart. However, at least for reduced $C_2B_{10}H_{12}$ molecules, there appears to be some controversy regarding the latter contention vs. the role of subsequent protonation in the opening of the icosahedron upon formation of $C_2B_{10}H_{13}^-$.[16,17]

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Registry No. $C_2B_3H_5^{2-}$, 54844-32-5; $C_2B_4H_6^{2-}$, 54844-33-6.

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Spectrophotometric Study of the Cobalt Chloride–Aluminum Chloride Vapor Complex

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We have recently made a spectrophotometric study of the blue gaseous complex formed by the reaction of solid cobalt chloride with gaseous aluminum chloride. Shortly after submission of our results we discovered that a report of another study of this system was about to be published. Our results are, for the most part, in agreement with those of Papatheodorou[1] but with some significant differences. Also our treatment of the data is somewhat different. We now present an abbreviated account of our work.

Anhydrous $CoCl_2$ was prepared by passing dry gaseous HCl over AR $CoCl_2{\cdot}6H_2O$ at 200°. Pure anhydrous $AlCl_3$ was prepared by distillation from a molten, approximately 6:4 by moles, mixture of AR $AlCl_3$ and AR NaCl. The $AlCl_3$ distilled off ranged in color from almost pure white to pale yellow. Both the $CoCl_2$ and $AlCl_3$ were sealed into previously flamed glass tubes awaiting use.

The absorption cells for the spectrophotometric measurements were constructed of silica and were approximately 7 cm long and 14 mm in diameter, with flat end windows. They were extensively flamed and degassed before being loaded in a N_2 flushed drybox.

The spectrophotometric measurements were done on a Cary 17 spectrophotometer. A special furnace capable of fitting into the cell compartment was constructed. It was designed so as to locate reproducibly in the spectrophotometer when lowered in for a measurement. The furnace was fitted with end-window heaters to ensure that the cell windows always remained slightly hotter than the cell body to prevent condensation.

Four 7-cm cells that had been previously flamed and degassed were each loaded with an excess of anhydrous $CoCl_2$ and varying known amounts of $AlCl_3$. The temperature range of this study was such that the $AlCl_3$ was present entirely as the vapor.[2] Also at the temperature used, the vapor pressure of $CoCl_2$ is virtually zero[2] and thus all measured absorbances were due to the complex. $AlCl_3$ itself has no absorption in the visible region in question. Spectra were scanned between 500 and 700 nm over the temperature range 550–750 K. Care was taken to ensure adequate time for equilibration. At any temperature a number of spectra were run over an extended period to ensure constant absorbance.

The details of the four experiments are given in column 1 of Table I and the results are given as plots of log (AT) vs. $10^3/T$ in Figure 1. The purpose of the plots in Figure 1 is to improve the data for subsequent treatment (see later). The spectrum of the complex at various temperatures in experiment 4 is shown in Figure 2.

The solid phase was shown to be $CoCl_2$ by X-ray diffraction. At the end of any experiment the cell was cooled in the furnace with the ends cooling somewhat faster. This caused the transport of some blue crystals from the center to the ends of the cell. That this material had been transported was indicated by its highly crystalline nature in contrast to the amorphous appearance of the original $CoCl_2$. Later in the cooling process white $AlCl_3$ was deposited. One cell was opened and the powder pattern for the blue crystals showed only diffraction lines attributable to $CoCl_2$.[3]

The molar absorptivity, ϵ_c, of the complex was determined from the two experiments summarized in Table II. In each experiment a cell was loaded with a known amount of $AlCl_3$ and an amount of $CoCl_2$ sufficiently small so as to ensure that all the $CoCl_2$ was in the vapor phase. The absorbance at the absorption maximum of 633 nm was recorded over the temperature range 650–750 K. At the end of each experiment the cell was opened and washed out with a known volume of dilute acid; the amount of $CoCl_2$ was determined by atomic absorption. The cell volumes were determined by filling with water and weighing. Our values of ϵ_c are considerably lower than the value of approximately 125 M^{-1} cm^{-1} found by Papatheodorou[1] and this affects the values of the complex formation constant subsequently calculated. The variation of ϵ_c with temperature might be taken as indicating the existence of more than one complex species. While our other data do not entirely rule out this possibility, we favor the idea of a single complex and believe that most if not all of the variation in ϵ_c is inherent in the complex itself and arises possibly from the fact that the spectrum of the complex is the result of a number of overlapping transitions. A similar decline in ϵ_c with rise