THE CHEMISTRY OF NITROGEN-CONTAINING HIGHER BORON HYDRIDE DERIVATIVES

LEE J. TODD, JOHN KESTER, BOB CHAPMAN, JOHN L. LITTLE, AND MIKE WHITESELL

JANUARY 16, 1989

U.S. ARMY RESEARCH OFFICE

DAAG29-85-K-0047

INDIANA UNIVERSITY

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.
Several synthetic studies of heteroborane cage compounds containing group 15 elements (N, P, As, Sb and Bi) have been completed. The synthesis of B$_9$H$_{11}$NH from B$_{10}$H$_{14}$ has been improved. The first closo azaboranes, B$_9$H$_{11}$NH and CpCo(NHB)$_9$H$_9$, have been prepared and their properties investigated. The new phosphaborane derivatives 1,2-P$_2$B$_{10}$H$_{14}$, 6-(triethylamine)-2-PB$_9$H$_8$, Na(B$_9$H$_{11}$P) and 2-(triethylamine)-1PB$_{11}$H$_{10}$ have been prepared and characterized. Several new metalloarsaboranes including 1,2-AsEB$_{11}$H$_{10}$ (E = Sn and Pb) have been prepared and characterized. The first boron hydride cage molecules containing the element bismuth have been prepared. The compounds 1,2-Bi$_2$B$_{10}$H$_{14}$ and N(CH$_3$)$_3$[BiB$_{11}$H$_{11}$] are unusually stable to heat in the solid state.
STATEMENT OF THE PROBLEM STUDIED

Initially, we studied the synthesis and chemistry of azaboranes. This class of compounds had been very little studied before our investigations. Subsequent studies have involved a more general investigation of group 15 (N, P, As, Sb, Bi) heteroborane chemistry.

A SUMMARY OF THE MOST IMPORTANT RESULTS

I. Azaborane Chemistry

We have done an extensive investigation of the reaction of $\text{B}_{10}\text{H}_{14}$ with sodium nitrite to form $\text{Na}[\text{B}_9\text{H}_{12}\text{NH}]$. This azaborane anion was oxidized with $I_2$ to form the very useful starting material, $\text{B}_9\text{H}_{11}\text{NH}$ in 57% yield (based on $\text{B}_{10}\text{H}_{14}$). The nido-$\text{B}_9\text{H}_{11}\text{NH}$ was converted to $\text{B}_9\text{H}_{9}\text{NH}$ and $\text{B}_9\text{H}_{9}\text{NH(CoCp)}$, the first two closo azaboranes. Further chemical and $^{14}\text{N}$ NMR studies of the nitrogen unit in these closo azaboranes has been completed and published.

II. Phosphaborane Chemistry

Although arsaborane compounds are well known, the corresponding phosphaboranes have been little studied due to the complex nature of the reaction product mixture. The diphosphaborane, $1,2\text{-P}_2\text{B}_{10}\text{H}_{10}$ has been prepared in low yield from $\text{B}_{10}\text{H}_{14}$ using $\text{PCl}_3$ as the source of phosphorus. This reaction gives several other products, one of which is 6-(triethylamine)-2-$\text{P}_{9}\text{H}_8$, which has been fully characterized, including a single crystal X-ray structure determination. The thermal conversion of $1,2\text{-P}_2\text{B}_{10}\text{H}_{10}$ to $1,7\text{-P}_{7}\text{H}_{10}\text{H}_{12}$ occurred at 560-590 °C in a sealed tube. Aqueous base rapidly removed one phosphorus atom from $1,2\text{-P}_2\text{B}_{10}\text{H}_{10}$ to form the $7\text{-P}_{7}\text{H}_{10}\text{H}_{12}$ ion.
Treatment of Na[B₁₁H₁₄] with triethylamine and PCl₃ formed both Na[B₁₁H₁₁P] and 2-(triethylamine)-1-PB₁₁H₁₀.

III. Arsaborane Chemistry

Methods have been developed to improve the yield of 7-AsB₁₀H₁₂⁻ and 1,2-As₂B₁₀H₁₀ to 50% based on B₁₀H₁₄. The icosahedral anion, B₁₁H₁₁As⁻ has been obtained in 48% yield from B₁₁H₁₄⁻. The metalloarsaboranes, 3,1,2-(dppe)Ni(As₂B₉H₉), 3,6,1,2-[(C₅H₅)Co]₂As₂B₆H₈ and 1,2-AsEB₁₀H₁₀⁻ (E = Sn and Pb) have been prepared and characterized.

IV. Bismaborane Chemistry

The first boron hydride structures containing the element bismuth have been prepared. The compound 1,2-Bi₂B₁₀H₁₀ was obtained in low yield from the reaction of B₁₀H₁₄ with triethylamine and BiCl₃. In the solid state, 1,2-Bi₂B₁₀H₁₀ starts to decompose at 350° and is surprisingly heat stable. Other bismaboranes that have been prepared and characterized are 1,2-EB₁₀B₁₀H₁₀ (E = P, As and Sb) and N(CH₃)₄[BiB₁₁H₁₁].
List of Publications


Participating Scientific Personnel

Lee J. Todd  Professor of Chemistry
Jeff Baer  B.S. Chemist (completed degree 5-15-85)
Tanya Curtis  B.S. candidate
Kevit Hart  B.S. Chemist (completed degree 5-15-86)
Wyatt J. Mills  Ph.D. candidate
John G. Kester  Ph.D. candidate
Bob Chapman  B.S. Chemist (completed degree 6-1-88)
Chris Sutton  Ph.D. candidate