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NEW SYNTHETIC ROUTES TO
BORON CAGE COMPOUNDS

FINAL REPORT
LARRY G. SNEDDON

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U. S. ARMY RESEARCH OFFICE
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This project was concerned with the development of new synthetic routes to polyhedral boron cage compounds. This work resulted in the development of new synthetic routes to several important classes of compounds, including small cage carboranes, alkenyl-substituted boranes and carboranes, large cage mono-carbon carboranes and multi-cage boranes and carboranes.		

Summary of Scientific Goals and Results

Polyhedral boron cage compounds have been recognized as having numerous potentially important practical applications due to their unique chemical and physical properties. Unfortunately this potential has been largely unrealized because of the non-selective, low yield synthetic methods required to obtain these compounds. The principle thrust of the work performed under ARO sponsorship was to investigate the fundamental processes involved in the formation of these types of compounds and to apply these techniques to the development of new high yield, low energy, selective synthetic routes.

Our work has demonstrated (1) new catalytic, high yield syntheses of alkenyl boranes and alkenyl carboranes (2) the high yield thermally initiated conversion of alkenylpentaboranes into small cage carboranes (2) new routes to large cage mono-carbon carboranes (3) new catalytic routes to multi-cage compounds and (4) the synthesis of a range of new hybrid cluster systems with unique structural properties.

These results have been described in detail in the publications and progress reports listed below:

Publications:

1. A.J. Borelli, Jr., J.S. Plotkin and L.G. Sneddon, "Structural Characterization of 6:4',5'-[(η -C₅H₅)Co-2,3-(CH₃)₂C₂B₄H₃][2',3'-(CH₃)₂C₂B₄H₃]: A Coupled-Cage Cobaltacarborane Complex Containing a Three-Center Boron Linkage", *Inorg. Chem.*, 21, 1328-1331 (1982).
2. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 4. A One-Step Synthesis of the Coupled Cage Borane, 1:2'-[B₅H₈]₂", *Inorg. Chem.*, 22, 182 (1983).
3. R.J. Astheimer and L.G. Sneddon, "Pyrolysis Reactions of 1,5-C₂B₃H₅ and 1,6-C₂B₄H₆. Isolation of a New Four Carbon Carborane, C₄B₇H₁₁, and the Boron Carbon Bonded Dimer and Trimers of 1,5-C₂B₃H₅. Improved Synthesis of the Mixed Cage Carborane, 2':2'1',5'-C₂B₃H₄11,6-C₂B₄H₅]", *Inorg. Chem.* 22, 1928-1934 (1983).
4. R.P. Micciche, J.S. Plotkin and L.G. Sneddon, "Structural Characterization of 3':2'-[2',4'-C₂B₃H₆][1,8,5,6-(η -C₅H₅)₂Co₂C₂B₃H₆]: A Coupled-Cage Cobaltacarborane Containing a Boron-Boron Linkage", *Inorg. Chem.*, 22, 1765-1768 (1983).
5. R.P. Micciche and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 3. Synthesis and Structural Characterization of an Arene-Ferracarborane Complex: 1-(η^6 -CH₃C₆H₅)Fe-2,3-(C₂H₄)₂C₂B₄H₄", *Organometallics*, 2, 674-678 (1983).
6. G.J. Zimmerman and L.G. Sneddon, "Structural Characterization of 1,2-Dimethyl-3-cyclopentadienylcobalt-2,3-dicarbaoctaborane", *Acta Cryst.*, C39, 856-858 (1983).

7. T. Davan, E.W. Corcoran and L.G. Sneddon, "Transition-Metal-Promoted Reactions of Boron Hydrides 5. Palladium Promoted Pentaborane(9)-Olefin Coupling Reactions: A New, Mild Synthetic Route to Alkenylpentaboranes", *Organometallics*, 2 1693-1694 (1983).
8. J.A. Anderson, R.J. Astheimer, J.D. Odom and L.G. Sneddon, "The Use of Nuclear Magnetic Resonance to Investigate Bonding Between Quadrupolar Nuclei. Boron-Boron Spin-Spin Coupling Constants in Linked Polyhedral Borane and Carborane Cages", *J. Amer. Chem. Soc.*, 106, 2275-2283 (1984).
9. R.J. Astheimer and L.G. Sneddon, "Photochemical Reactions of Hexafluoroacetone with Pentaborane(9) and 2,4-Dicarbaheptaborane(7)", *Inorg. Chem.* 23, 3207-3212 (1984).
10. R.J. Micciche, J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 4. Direct Synthesis of (η^6 -Arene)Ferracarborane Clusters From Alkynes and Boranes. Structural Characterization of Four Carbon (η^6 -Arene)Metallacarboranes: 1-[(η^6 -(CH₃)₆C₆)Fe-4,5,7,8-(CH₃)₄C₄B₅H₃] and 2-[(η^6 -CH₃C₆H₅)Fe-6,7,9,10-(CH₃)₄C₄B₅H₃]. *Organometallics*, 3, 1396-1402 (1984).
11. R.J. Micciche, J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 5. Synthesis of the First (η^6 -Arene)Metallaborane and (η^6 -Arene)Metallaioxaborane Clusters. Structural Characterizations of 5-[(η^6 -C₆(CH₃)₃H₃)FeB₇H₁₃] and 2-[(η^6 -C₆(CH₃)₃H₃)Fe-6-OB₈H₁₀]. *Inorg. Chem.* 23, 3992-3999 (1984).
12. E.W. Corcoran, Jr. and L.G. Sneddon, "Transition Metal Promoted Reactions of Boron Hydrides 6. Platinum(II) Bromide Catalyzed Borane and Carborane Dehydrodimerization Reactions: A New Synthetic Route to Boron-Boron Linked Multi-Cage Boranes and Carboranes" *J. Amer. Chem. Soc.* 106, 7793-7800 (1984).
13. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 6. Synthesis and Structural Characterization of a Coupled Diborane-Metallacarborane Cluster: 5:1',2'-[1-(η -C₅H₅)Co-2,3-(Me₃Si)₂C₂B₄H₃][B₂H₃]" *Organometallics*, in press.
14. R.J. Micciche, P.J. Carroll and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 7. Synthesis and Structural Characterization of an Open-Cage Triple-Decker Metallathiorborane Cluster 4,6-(η -C₅H₅)₂-Co₂-3,5-S₂B₂H₂" *Organometallics*, submitted.
15. J.J. Briguglio and L.G. Sneddon, "Metal Atom Synthesis of Metalla-Boron Clusters 8. Synthesis of New Iron, Cobalt and Nickel Clusters Derived From 2,6-C₂B₇H₁₁. Structural Characterizations of 2-[(η^6 -C₆(CH₃)₃H₃)Fe-1,6-C₂B₇H₉], 6-[(η^6 -C₆(CH₃)₃H₃)Fe-9,10-C₂B₇H₁₁] and 5,7,8-(CH₃)₃ 11,7,8,10 [(η^3 -C₄(CH₃)₄H)NiC₃B₇H₇] in preparation.

Progress Reports

No.

1. 1/1/82-6/30/82
2. 7/1/82-12/31/82
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Participating Scientific Personnel

Larry G. Sneddon, Principal Investigator
Thomas Davan, Postdoctoral
Ned Corcoran, Graduate Students
Robin Ernest
Mario Mirabelli
Robert Astheimer

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