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13. ABSTRACT *(Maximum 200 words)*

The project centered on the designed synthesis of small metallacarborane sandwich complexes for use as building-blocks in the construction of new families of electroactive, magnetoactive, and/or optically active materials. The compounds of interest exhibit generally high thermal and oxidative stability, chemical versatility, electronic tunability, and solubility in organic solvents. Synthetic routes were developed for several new classes of multi-metallic metallacarborane clusters that are bifunctional and suitable as precursors to novel metallopolymers. These include B-B, B-X-B (X = alkene, alkyne, or aryl), and M-M linked C_2B_4M clusters, arene- and carborane-endcapped multidecker sandwiches, and B-halo species. Strategies for preparing high molecular weight electronically active materials from these compounds were explored. Concurrently with the synthetic work, the electronic structures, nonlinear optical properties, and other aspects of selected systems were investigated in detail, partly in collaboration with other laboratories.

14. SUBJECT TERMS
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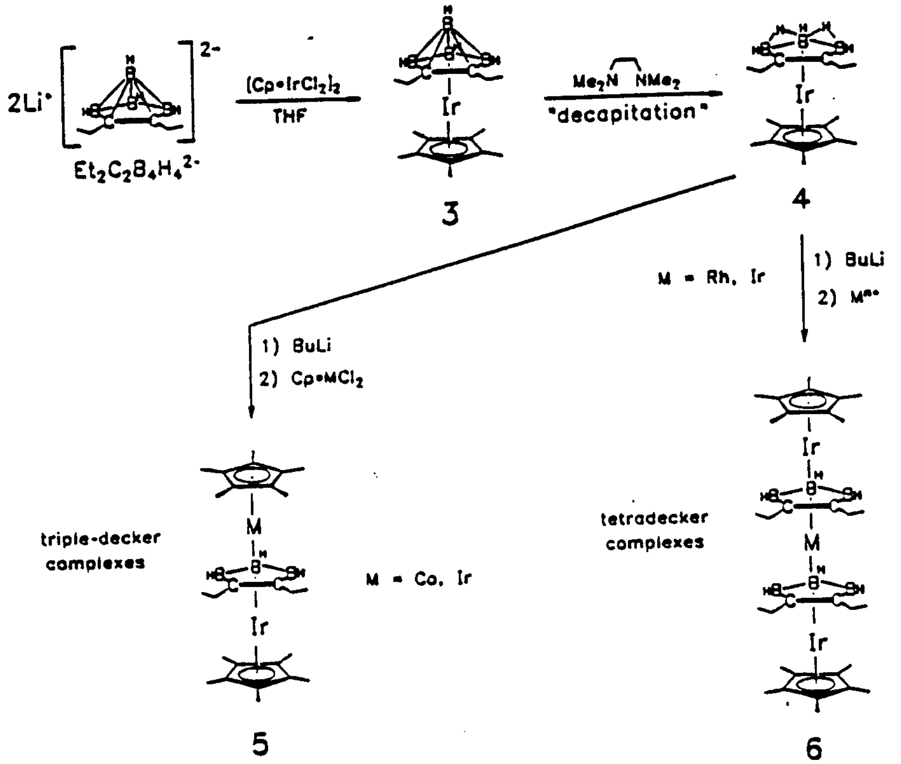
I. Statement of Problem

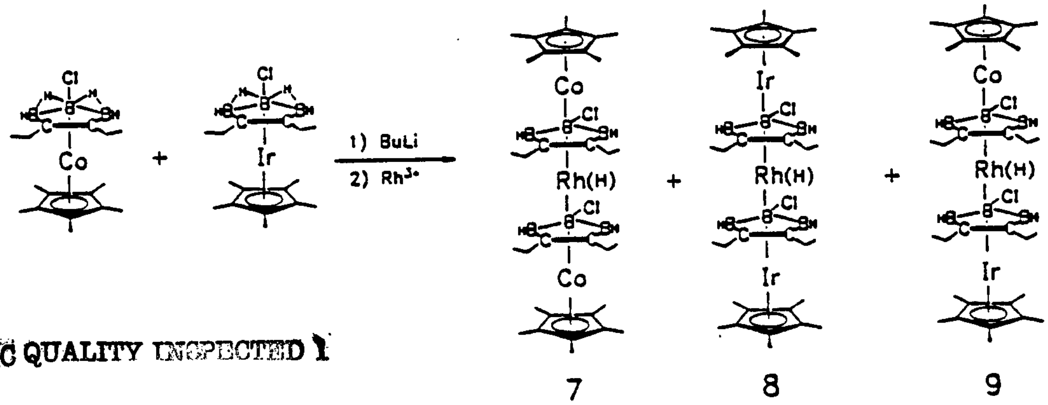
The main objective of this work was to design and synthesize small metallacarborane sandwich complexes that are suitable as building-blocks in the construction of new families of electroactive, magnetoactive, and/or optically active materials, and to conduct detailed studies of the electronic and molecular structure of selected systems of this class.

II. Summary of Important Results

1. Synthesis of Heavy Transition-Metal Metallacarborane Sandwich Complexes

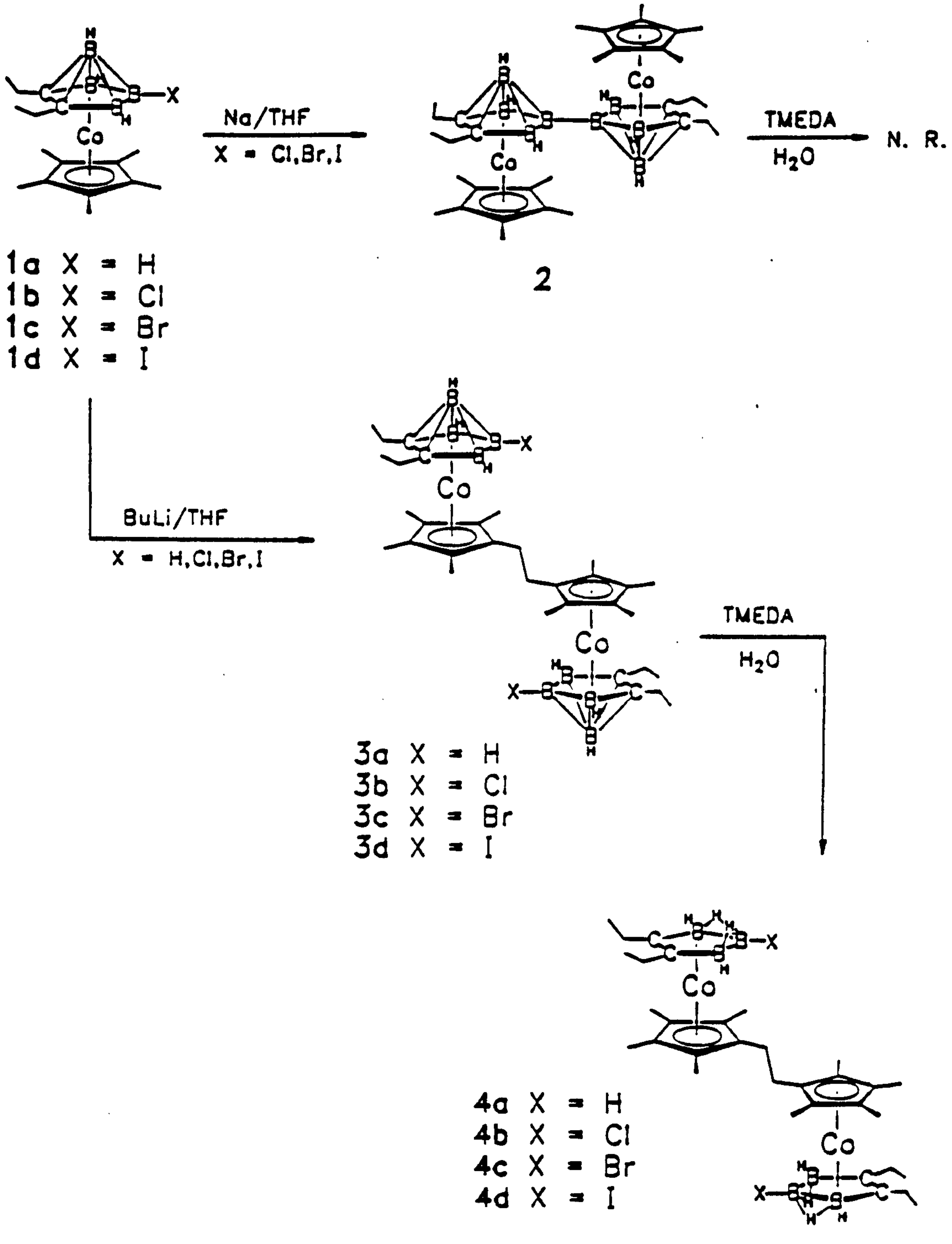
Synthetic routes to multidecker sandwich complexes of second- and third-row transition elements were developed. As an example, double-decker iridium and ruthenium complexes were prepared and employed as synthons for preparing several new classes of triple- and tetradeckers, including rhodium- and iridium-centered sandwiches including compound **9** ("Group9ocene"), a unique sandwich containing all three Group 9 metals. (For details see Interim Technical Report for February 1996, and publication 9 cited below).





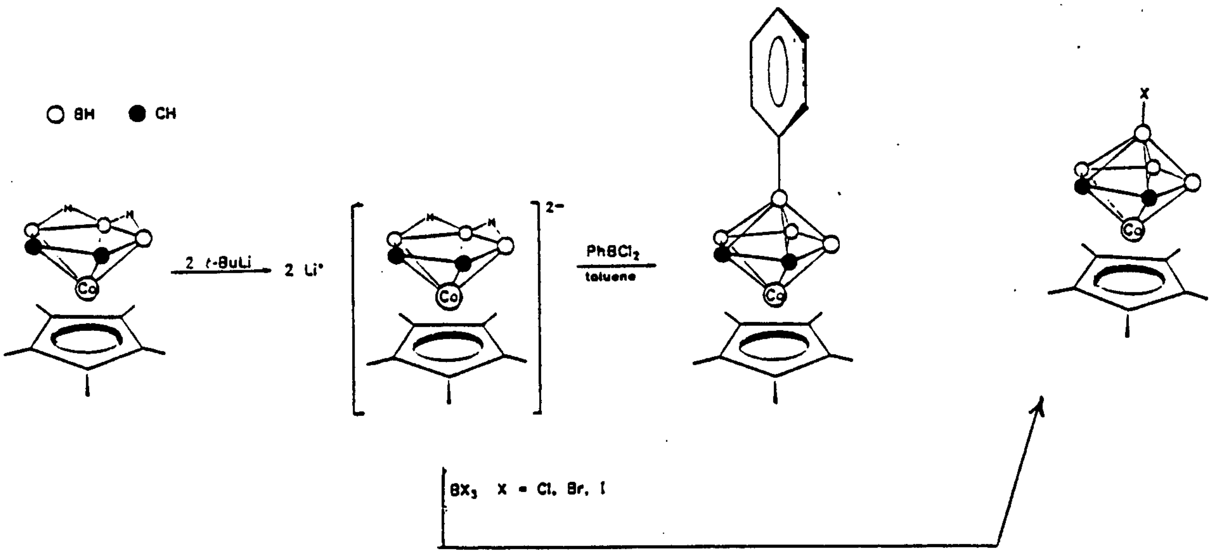
2. Cluster Linkage.

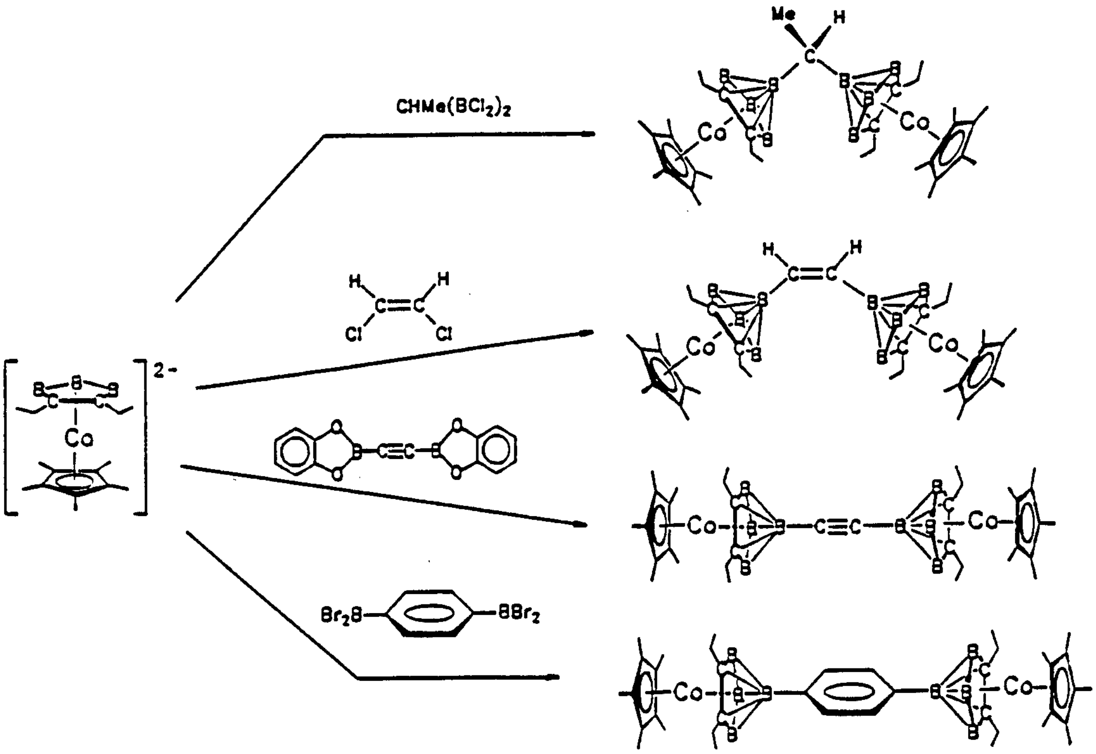
In a project begun during the previous 3-year grant and extended under the current project, we developed methods for linking metallacarborane clusters via B-B, C-C, and metal-metal (M-M) intercage bonds, for the purpose of eventually building extended electron-delocalized solid-state metallacarborane-based networks. Paper 4 cited below describes the B-B and C-C linking reactions, both of which are novel to boron chemistry:



3. Cage Recapitation.

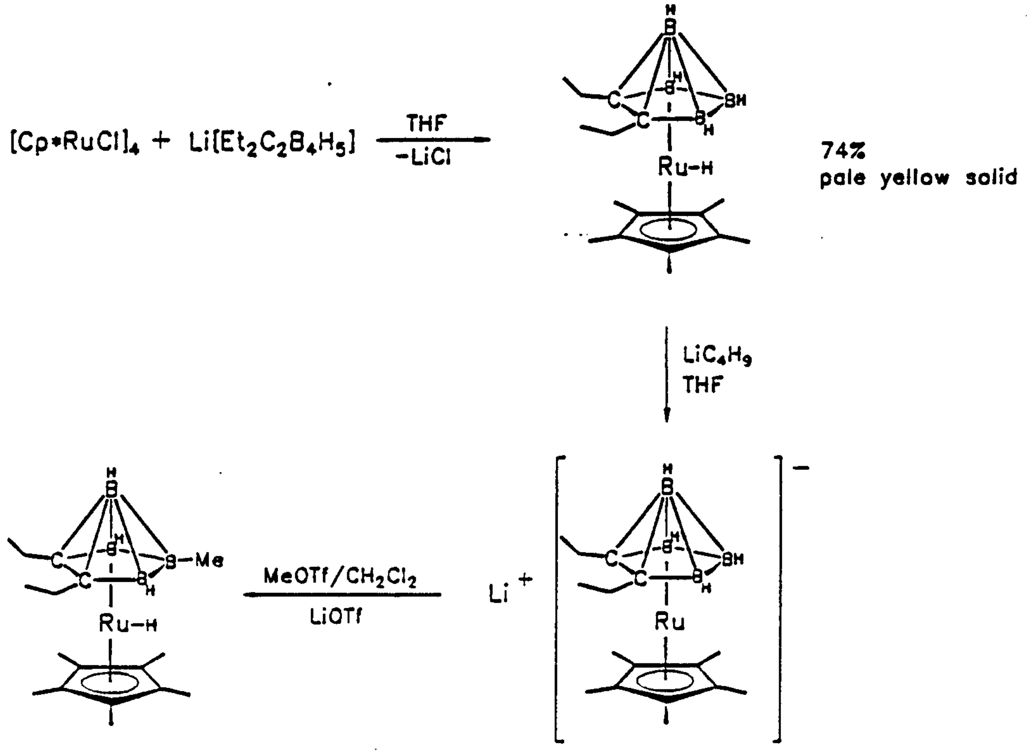
A further dimension to cluster linkage methodology was added via "recapitation", a process that is functionally the reverse of our "decapitation" reaction in which the apex BH in a closo-MC_2B_4 cage is removed to generate an open face which in turn can π-complex to metal ions (e.g., conversion of **3a-d** to **4a-d** shown above). In recapitation, illustrated here, a boron atom bearing a substituent is inserted into the open face to a B-X unit, thereby affording apex-substituted clusters that can be used to form apex-linked oligomers and polymers (paper 10). In collaborative work with Siebert and co-workers at the University of Heidelberg (paper 14), this approach was exploited to prepare and structurally characterize a series of linked biscobaltacarboranes:



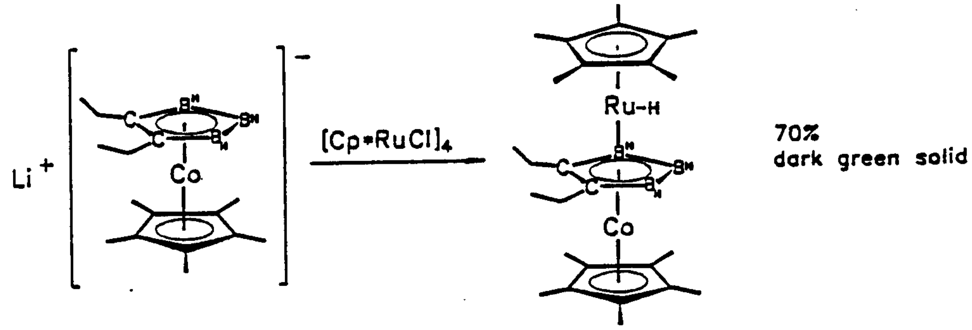


4. Metal Hydride Sandwich Complexes.

Manipulation of metal-bound protons in hydridometallacarboranes of iron and cobalt (e.g., their reversible deprotonation with accompanying redox processes at the metal centers) was explored in our laboratory as a means of controlling metal oxidation states. This approach has potential as a type of "molecular switch" that could be incorporated in organometallic polymers to alternate between conducting and insulating behavior. As described in paper 12, this work has been extended to ruthenium hydrides with the synthesis of the double-decker species Cp*Ru^{II}H($Et_2C_2B_4H_4$), which undergoes an unexpected B-alkylation on treatment with methyl triflate:

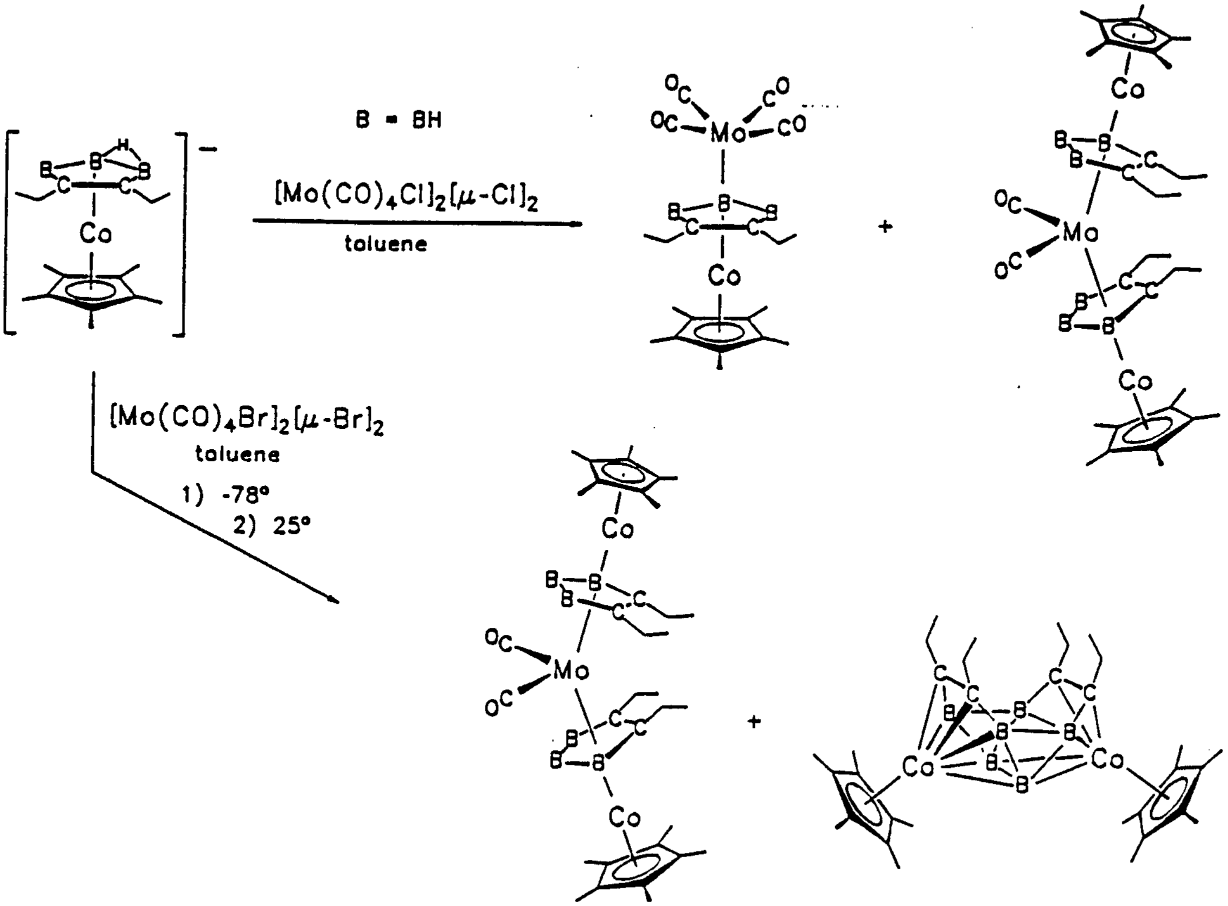


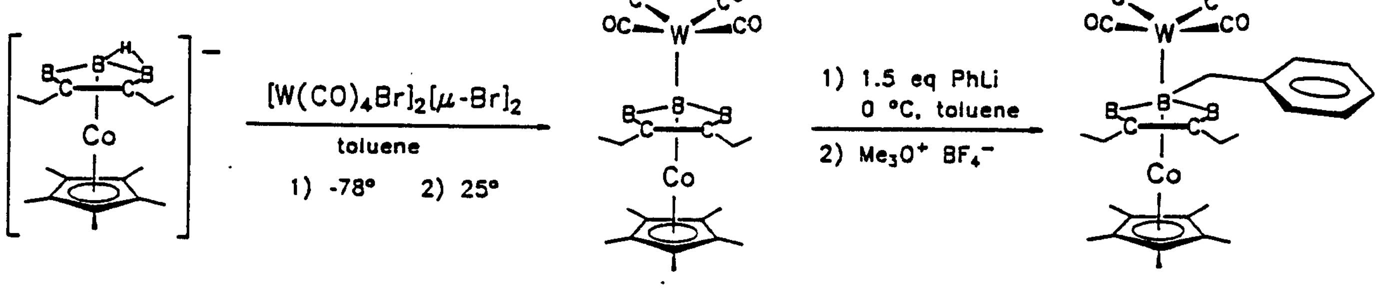
A heterobimetallic RuH-Co triple-decker was also synthesized as shown.



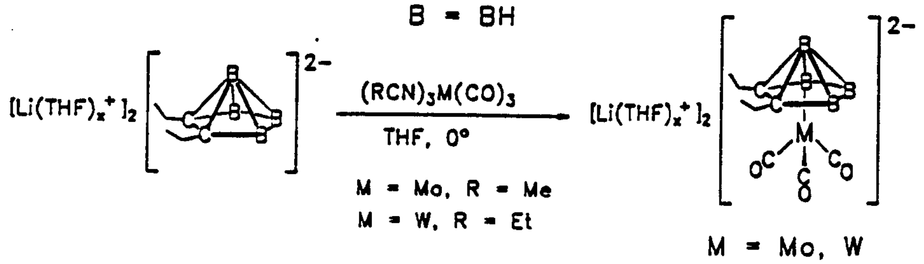
5. Metal Carbonyl-Based Chemistry and Metal-Metal-Bonded Clusters.

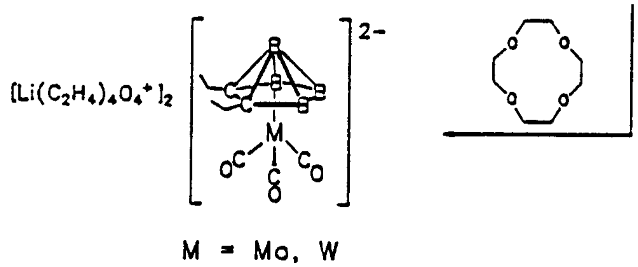
A different approach to metallacarborane sandwich synthesis, with implications for materials engineering, utilizes metal carbonyl complexes whose CO ligands are more easily displaced than hydrocarbon ligands such as Cp, Cp*, and arenes, and hence promote coupling reactions directly at the metal centers. The following schemes summarize our work on molybdenum and tungsten metallacarboranes which has generated some novel species including the first M-M linked small metallacarboranes (paper 15). X-ray crystallography has established several of the structures shown, including the bent tetradecker (the first of its genre in carborane chemistry).

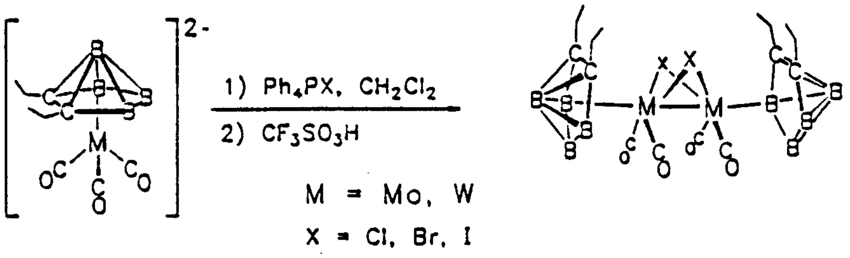


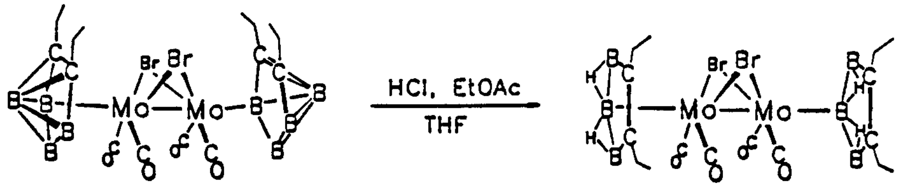


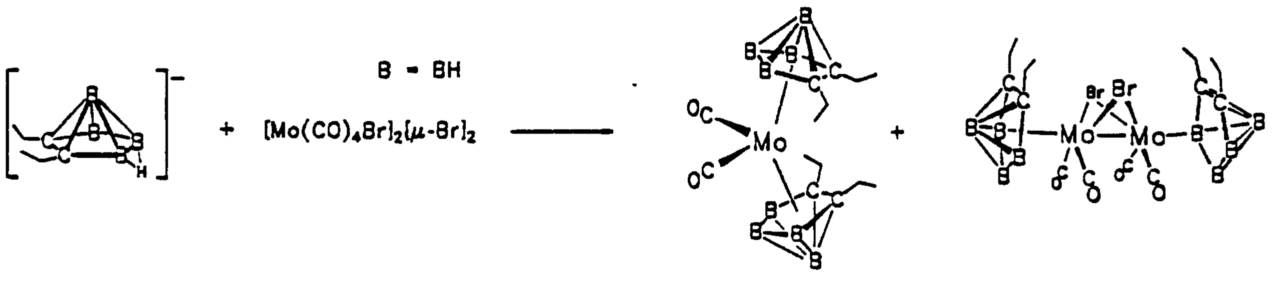
The principal significance of this work is twofold: (1) double-open-ended complexes such as the Mo_2 species shown, are potential precursors to linear M-M linked polymers which would be quite novel and may have interesting electronic and magnetic properties; (2) the absence of hydrocarbon ligands makes these species attractive candidates for conversion to graphite-free metal-boron solid-state materials.





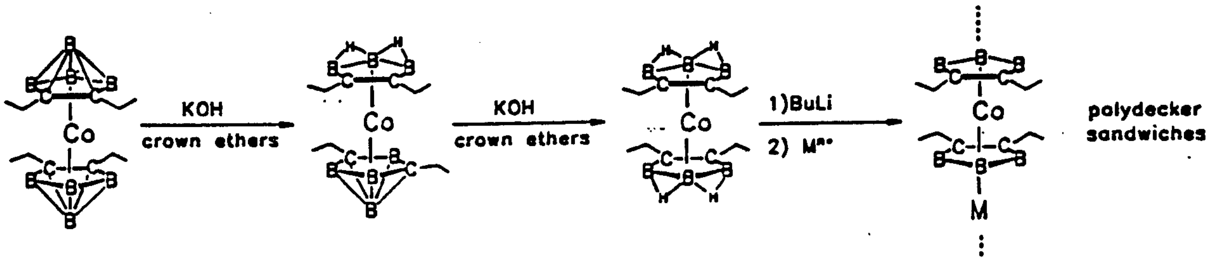






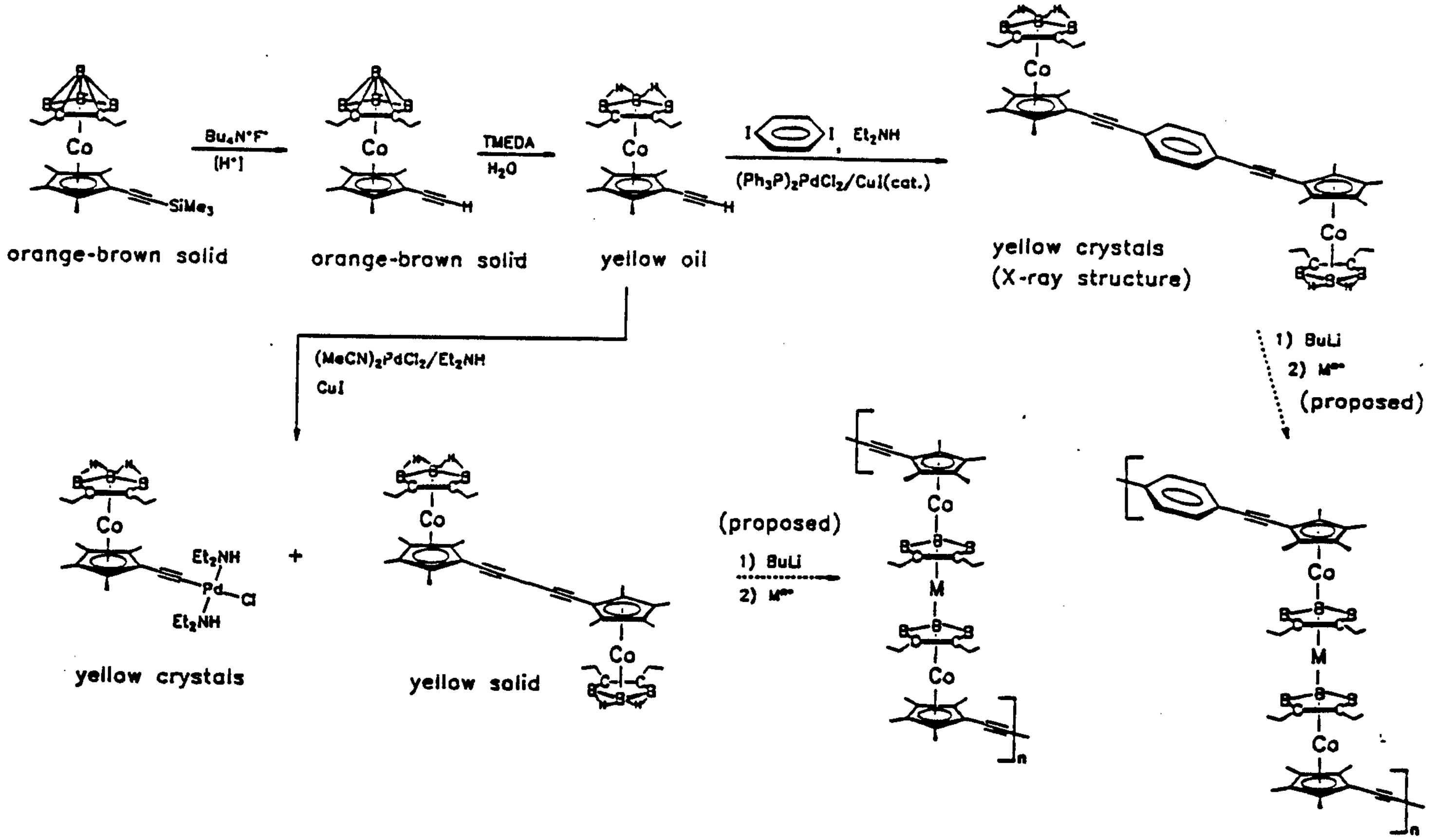
6. Double-Decapped Metallacarborane Synthon Complexes.

After an extended effort, we have found a way to prepare small double-decker complexes containing *two* open-faced C_2B_3 rings that can be deprotonated and reacted with metal ions to generate extended multidecker sandwiches, i.e., polydeckers. Such species have been a goal of this research for some time, and we are currently investigating the actual formation of such polydecker species.



7. Alkyne-Linked Systems.

Substantial progress has been achieved in the synthesis of metallacarboranes containing multiple metal centers with alkyne (bare carbon atom) connectors that are efficient conductors of electrons and are often called "molecular wires". The double-open-ended complexes shown are well positioned to serve as synthons for alkyne-linked conducting polymers, a prospect we are currently investigating.



III. Publications produced under this Contract

(1) "Cluster Forming and Cage Fusion in Metallacarborane Chemistry", Grimes, R. N., *Coord. Chem. Rev.* **1995,** *143,* 71.

(2) "Organotransition-Metal Metallacarboranes. 39. Arene-Capped Ruthenium-Carborane Tetradecker Sandwich Complexes", Greiwe, P.; Sabat, M.; Grimes, R. N., *Organometallics* **1995,** *14,* 3683.

(3) "Organotransition-Metal Metallacarboranes. 40. Regiospecific Halogenation of Transition Metal Small Carborane Complexes", Stockman, K. E.; Garrett, D. L.; Grimes, R. N., *Organometallics* **1995,** *14,* 4661.

(4) "Organotransition-Metal Metallacarboranes. 41. Synthesis and Structure of B-B and Cp*-Cp* Linked Cobaltacarborane Clusters", Wang, X.; Sabat, M.; Grimes, R. N., *Organometallics* **1995,** *14,* 4668.

(5) "Organotransition-Metal Metallacarboranes. 42. Synthesis and Cluster Fusion of Iron-Centered Tetradecker Sandwiches", Wang, X.; Grimes, R. N., *Inorg. Chem.* **1995,** *34,* 6509.

(6) "Organotransition-Metal Metallacarboranes. 43. Directed Synthesis of Carborane-Endcapped Multidecker Sandwiches", Wang, X.; Sabat, M.; Grimes, R. N., *J. Am. Chem. Soc.* **1995,** *117,* 12218.

(7) "Organotransition-Metal Metallacarboranes. 44. Synthesis and Structure of Pentadecker and Hexadecker Sandwiches", Wang, X.; Sabat, M.; Grimes, R. N., *J. Am. Chem. Soc.* **1995,** *117,* 12227.

(8) "Metal-Carborane Multidecker Sandwich Complexes as Building-Blocks for New Materials", Grimes, R. N., *Applied Organometallic Chemistry.*, **1995,** *10,* 209-225.

(9) "Organotransition-Metal Metallacarboranes. 46. Multidecker Sandwiches of the Group 9 Metals", Franz, D. A.; Houser, E. J.; Sabat, M.; Grimes, R. N., *Inorg. Chem.* **1996,** *35,* 7027.

(10) "'Recapitation' of Nido-Metallacarboranes as a Synthetic Tool: Preparation of Apically Substituted CoC_2B_4 Clusters via Boron Insertion", Curtis. M. A.; Sabat, M.; Grimes, R. N., *Inorg. Chem.* **1996,** *35,* 6703.

(11) "Metal-Carborane Sandwiches and Macromolecular Assemblies", Grimes, R. N., in *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1997, p. 321-332.

(12) "Organotransition-Metal Metallacarboranes. 45. Synthesis and Structure of Hydridoruthenacarborane Double-Decker and Triple-Decker Sandwich Complexes", Houser, E. J.; Curtis, M. A.; Sabat, M.; Grimes, R. N., *J. Organometal. Chem.* **1996,** *536/537,* 115.

(13) "Recent Advances in Metallacarborane Sandwich Chemistry: Controlled Linking, Stacking, and Cool Fusion", Grimes, R. N., in *The Borane-Carborane-Carbocation Continuum*, Casanova, J., Ed.; Wiley-Interscience, **1998**, Chapter 13, pp. 307-329.

(14) "Apically Linked Small Metallacarborane Clusters. Directed Synthesis and Structural Characterization of 7,7′-[$Cp^*Co(2,3\text{-}Et_2C_2B_4H_3]_2$ and $[Cp^*Co(2,3\text{-}Et_2C_2B_4H_3\text{-}7)]_2X$ Complexes (X = MeCH, HC=CH, or C≡C)", Curtis, M. A.; Müller, T.; Beez, V.; Pritzkow, H.; Siebert, W.; Grimes, R. N., *Inorg. Chem.* **1997,** *36,* 3602.

(15) "New Metallacarborane Chemistry: Molybdenum and Tungsten Carbonyl Multidecker Sandwiches. Cluster Dimers Linked via Metal-Metal Bonds", Curtis, M. A.; Houser, E. J.; Sabat, M.; Grimes, R. N., *Inorg. Chem.* **1998,** *37,* 102.

(16) "A Delocalized Analogue of the Bicobaltocene Cation Derived From Reduction of a d^6d^6 (Fulvalenediyl)bis(cobaltacarborane) Complex: Electrochemistry, ESR, Optical Spectroscopy, and IR Spectroscopy of the Carborane Group", Chin, T. T.; Grimes, R. N.; Geiger, W. E., *Inorg. Chem.* **1999,** *38,* 93.

Manuscript in press:

(17) "Small Carborane Ligands as Spectators and as Players", Grimes, R. N., *J. Organometal. Chem.*, in press.

Manuscript submitted:

(18) "A Novel Heterooctametallic Metallacarborane Tetramer", Parker, K. E.; Russell, J. M.; Sabat, M.; Grimes, R. N., submitted.

IV. Participating Scientific Personnel

"Studies in Metallacarborane Chemistry: Controlled Cluster Synthesis and Reagents for Organic Transformations", M. A. Curtis, Ph. D. University of Virginia, 1998

Principal Investigator: Russell N. Grimes, Professor of Chemistry

Postdoctoral Associates:
Keith Parker
Dennis Malaba

Graduate Students (degrees earned):
Michael Curtis (Ph.D. 1998)
Barbara Gilmore
Dana Kobeda

V. Inventions: none