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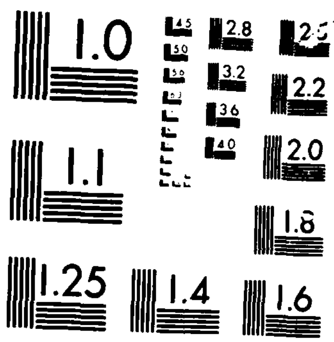

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AD-A169 189

Metal Ion-Promoted Syntheses of Boranes and Carboranes

Final Report

June, 1986

U. S. Army Research Office

Contract DAAG29-83-K-0030

University of Virginia

Charlottesville, Virginia

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

boron	arene-metal complex
boranes	iron-carborane complex
carboranes	cobalt-carborane complex
metallacarboranes	nickel-carborane complex
metal complex	oxidative fusion

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Controlled synthetic routes to new boron hydrides, carboranes, and metal-carborane complexes have been developed and a number of structurally novel species have been prepared and characterized. The oxidative fusion method for synthesis of boranes and carboranes has been further extended and its mechanism explored. The chemistry of small (7-vertex) metallacarboranes having reactive metal centers has been examined. Practical routes to metal-arene-carborane sandwich complexes have been developed.

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I. Statement of Problem

This research was directed at the development of new synthetic routes to boron hydrides and carboranes. The work entailed fundamental studies in synthetic boron chemistry, centering on the use of transition-metal and main group-metal reagents to effect oxidative fusion or coupling of small boranes and carboranes.

II. Summary of Important Results

1. Oxidative Fusion as a Synthetic Tool. The method of metal-promoted carborane cage fusion, discovered in our laboratory in earlier work, was extended under the ARO Contract to boron hydrides and metallaboranes (Figure 1). This in turn led to a number of significant findings, including the synthesis and structural characterization of the first neutral B_{12} hydride ($B_{12}H_{16}$); the conversion of B_5H_9 to $B_{10}H_{14}$ via metal deprotonation and complexation; and the conversion of 1- and 2-$(C_5H_5)CoB_4H_8$ to isomers of $(C_5H_5)_2Co_2B_8H_{12}$, which are analogues of $B_{10}H_{14}$. The mechanism of fusion in these latter systems was investigated and the data were found to be consistent with base-to-base linkage of two square-pyramidal units (B_5 or CoB_4) followed by rearrangement to a 10-vertex nido basket.

Further insight into the oxidative fusion of $R_2C_2B_4H_4^{2-}$ ligands to form $R_4C_4B_8H_8$ (studied earlier for R = CH_3, C_2H_5, and n-C_3H_7) was gained from the R = $C_6H_5CH_2$ case (C,C'-dibenzylcarborane, discussed below). The $(C_6H_5CH_2)_4C_4B_8H_8$

product is non-fluxional, in contrast to its tetraalkyl analogues, and the cage geometry is the same as that in $(C_2H_5)_4C_4B_8H_8$.

2. Studies of (X)(Y)M($R_2C_2B_4H_4$) Metallacarboranes with Reactive Metal Centers [M = Fe, Co, Ni; X = Cl, Br, CN; Y = $P(C_6H_5)_3$, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$]. The preparation and chemistry of 7-vertex MC_2B_4 cages containing halo or cyano ligands was studied, as outlined in Figure 2. In addition to the chemistry shown, X-ray structural analyses of the diamagnetic species 1 and 2 and the paramagnetic complex 3 were conducted.

3. Synthesis and Chemistry of Arene-Metal-Carborane Sandwich Complexes. Methods have been developed for the synthesis of specific desired air-stable solid metallacarboranes in which the metal is π-coordinated to an arene ligand. Compounds of this type are of potential value in the areas of VHBR (very high burning rate) propellants, low-dimensional electrical conductors, and new reagents for organic synthesis. A wide variety of complexes containing the pyramidal $R_2C_2B_4H_4^{2-}$, cyclic planar $R_2C_2B_3H_5^{2-}$, or other carborane ligands, in conjunction with arenes and metals, has been prepared and structurally characterized. Figure 3 outlines the major developments in this chemistry under the ARO Contract.

Among the more important achievements in this work are the bench-scale synthesis of C,C'-dibenzyldicarbahexaborane(8), an air-stable nonvolatile liquid which serves as a versatile precursor to numerous metal complexes (see Figure 3), and the designed preparation of a number of stable complexes containing metal-bound polyarene ligands including naphthalene, fluorene, phenathrene, and [2.2]paracyclophane. This work provides a foundation for continuing investigation in this laboratory.

FIGURE 1. OXIDATIVE FUSION IN SYNTHESIS

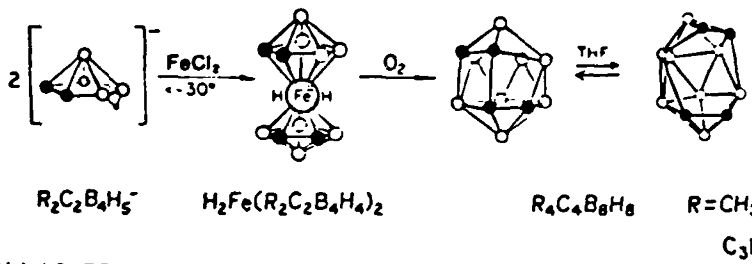
Pre-ARO work

[a]Maxwell, Miller, and Grimes, J. Am. Chem. Soc. 96, 7116 (1974), and Inorg. Chem. 15, 1343, 1976.

[b]Wong, Bowser, Pipal, and Grimes, J. Am. Chem. Soc. 100, 5045 (1978)

OBH ●CR • H

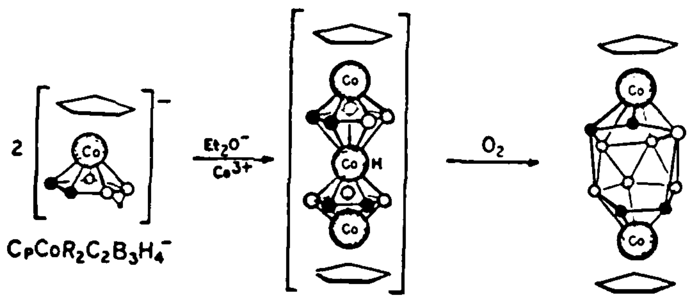
CARBORANES



(A)

R = CH_3, C_2H_5, C_3H_7, $CH_2C_6H_5$

METALLACARBORANES



$Cp_2Co_2R_4C_4B_6H_6$
(R = CH_3)

(B)

Work supported by ARO Contract

[a]Brewer and Grimes, J. Am. Chem. Soc. 107, 3552 (1985).

[b]Brewer, Swisher, Sinn, and Grimes, J. Am. Chem. Soc. 107, 3558 (1985).

BORANES

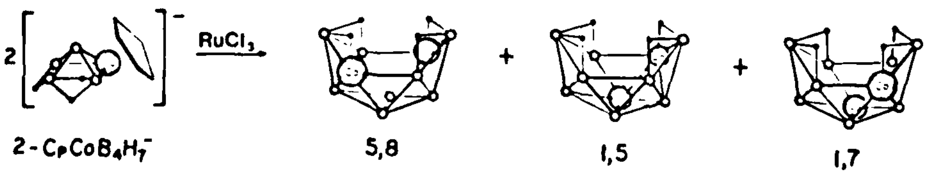
(C)

(D)

METALLABORANES

$2,4\text{-}Cp_2Co_2B_8H_{12}$

(E)



$Cp_2Co_2B_8H_{12}$ ISOMERS

(F)

Figure 2. Synthesis and Chmistry of 7-Vertex $(X)(Y)M(R_2C_2B_4H_4)$ Metallacarboranes

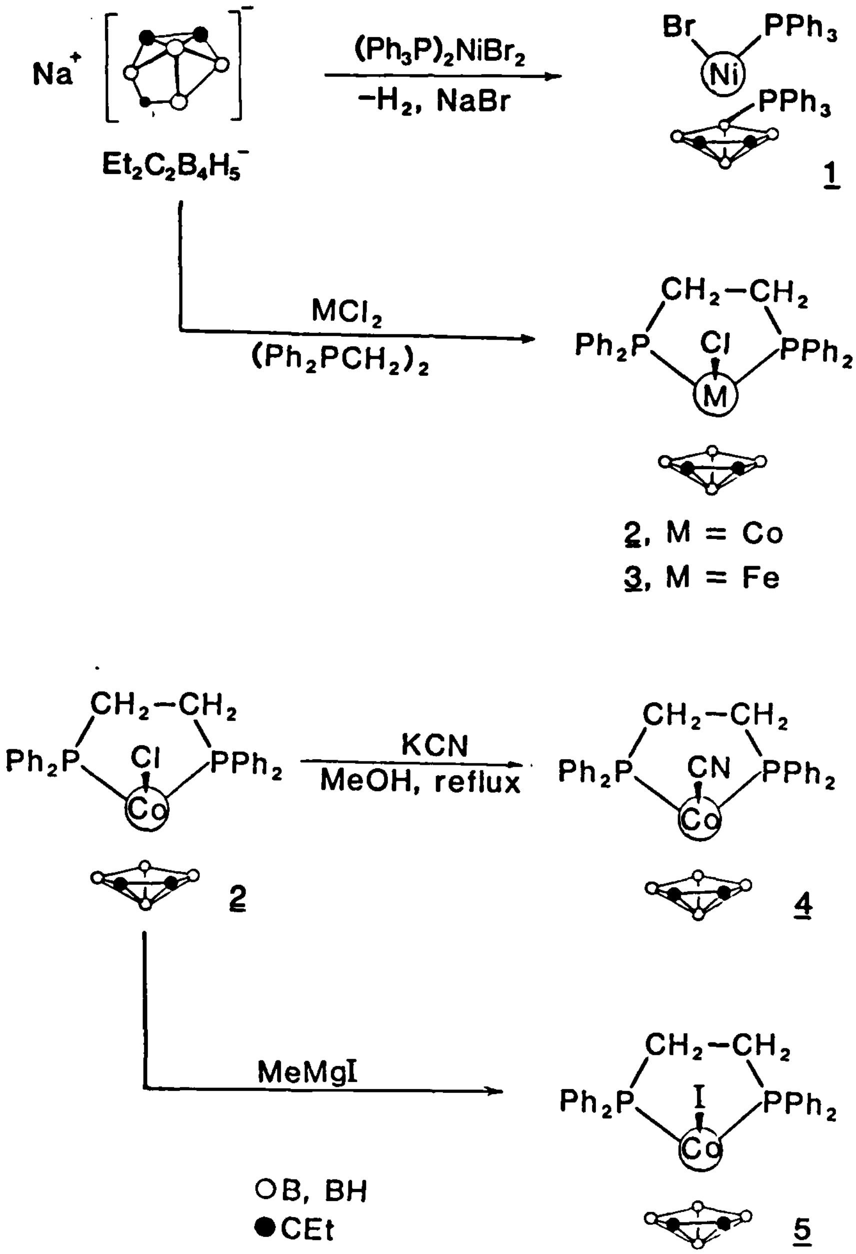
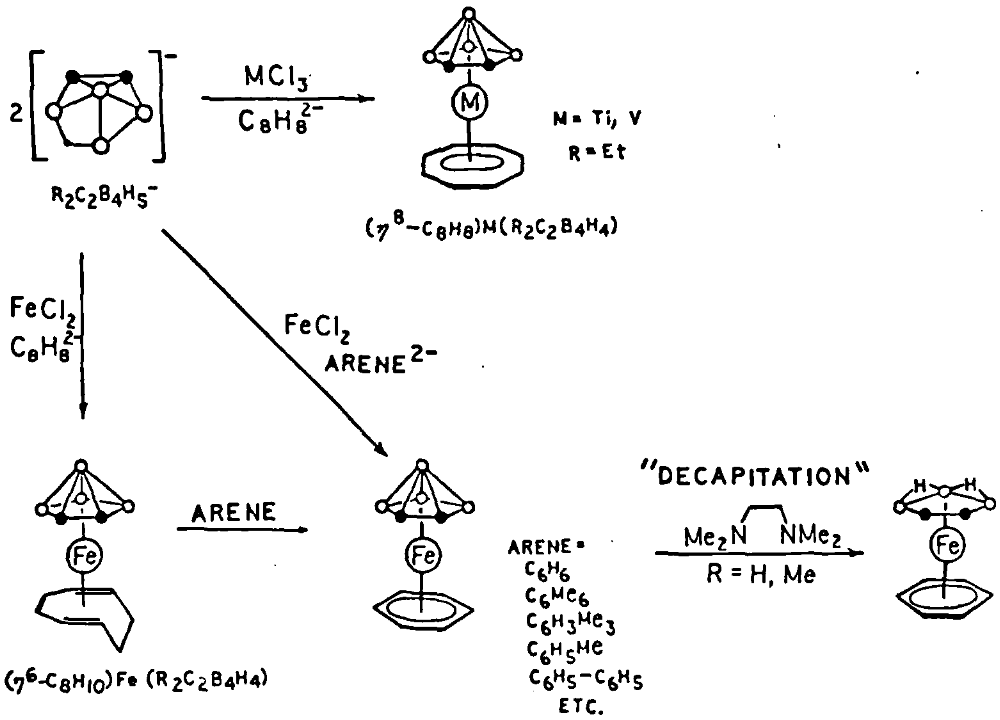


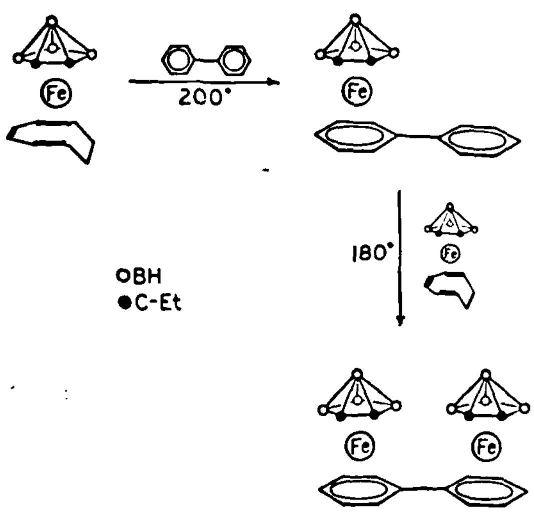
FIGURE 3

Synthesis of Arene-Metal-Carborane Sandwich Complexes

1. General Routes



2. Polycyclic Arene- and Multiidecker- Complexes



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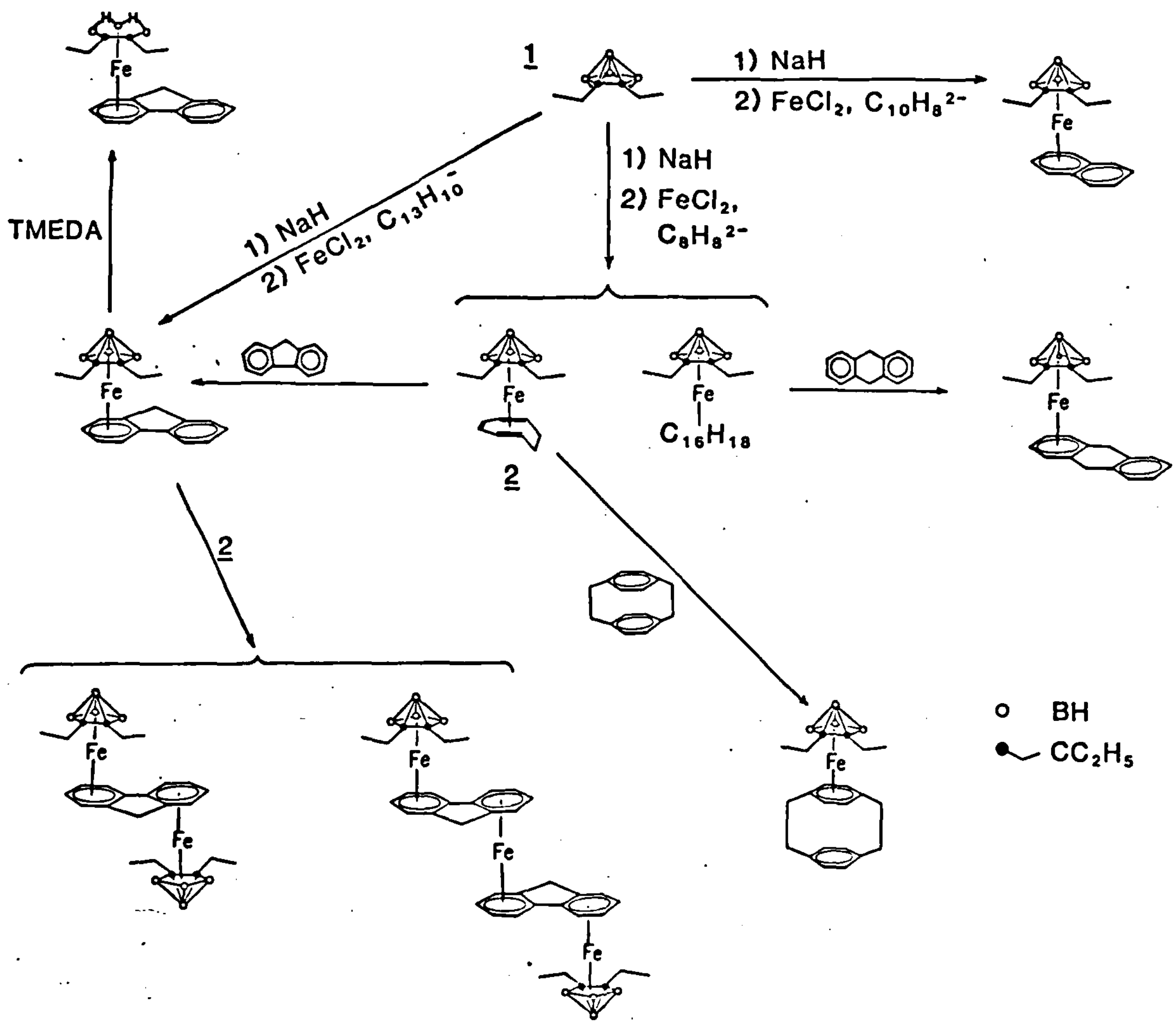
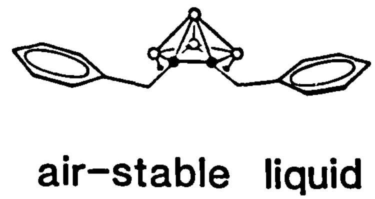
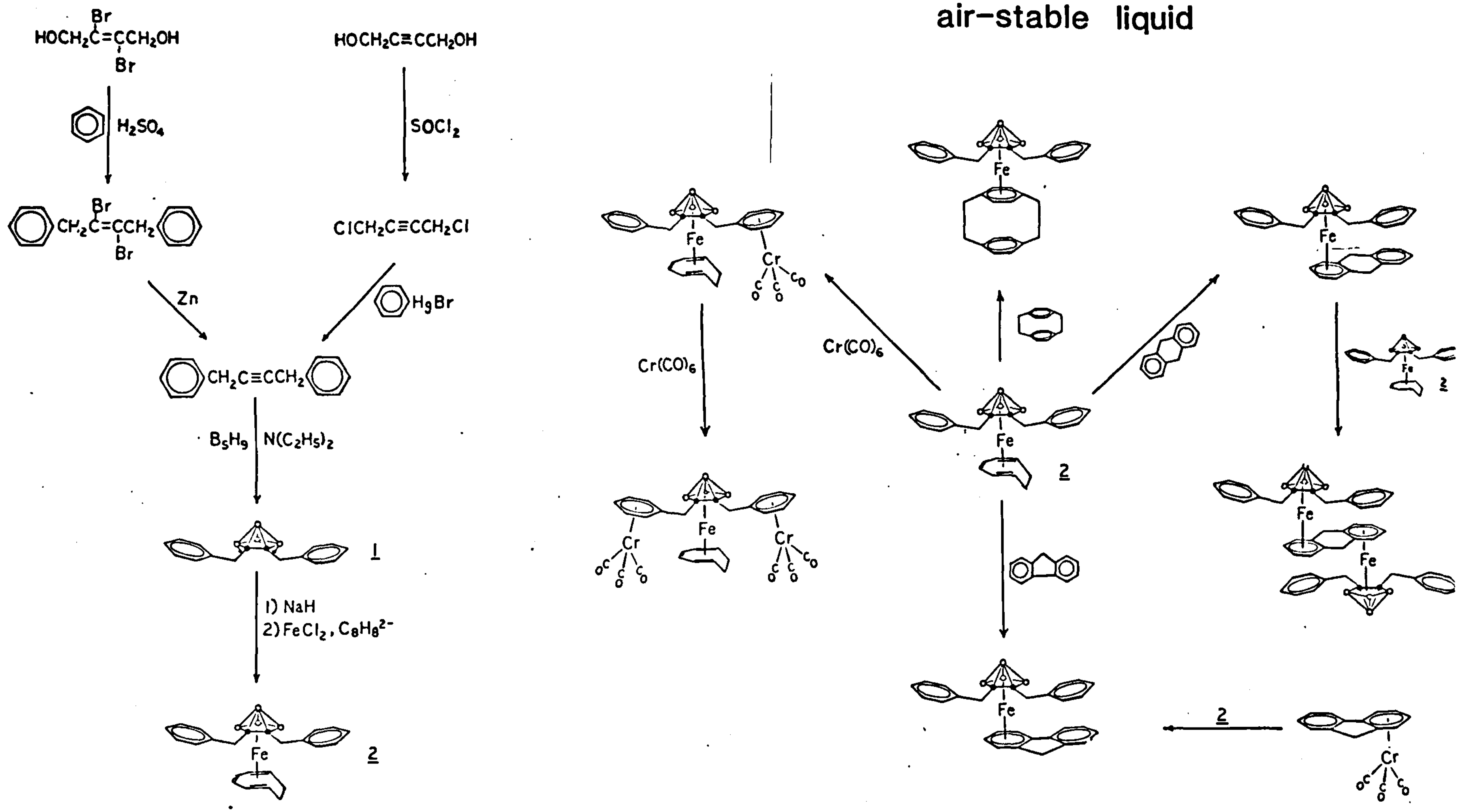
Polycyclic Arene- and Multiidecker- Complexes (cont'd)



C,C′-Dibenzyl-$C_2B_4H_6$ and its Chemistry





III. List of Publications

H. A. Boyter, Jr., R. G. Swisher, E. Sinn, and R. N. Grimes, "Seven-Vertex (Phosphino)(halo)metallacarboranes of Iron, Cobalt, and Nickel: Syntheses, Structures, and Reactions", Inorg. Chem., 1985, 24, 3810.

C. T. Brewer and R. N. Grimes, "Metal-Promoted Fusion and Linkage of $B_5H_8^-$, $1\text{-}XB_5H_7^-$ (X = D, CH_3), $B_{10}H_{13}^-$, and $(\eta^5\text{-}C_5H_5)CoB_4H_7^-$. Facile Routes to $B_{10}H_{14}$ and $(\eta^5\text{-}C_5H_5)_2Co_2B_8H_{10}$ Isomers", J. Am. Chem. Soc. 1985, 107, 3552.

C. T. Brewer, R. G. Swisher, E. Sinn, and R. N. Grimes, "Metal-Promoted Fusion of $B_6H_9^-$. Directed Synthesis and Structural Characterization of Dodecaborane(16), $B_{12}H_{16}$", J. Am. Chem. Soc. 1985, 107, 3558.

C. T. Brewer and R. N. Grimes, "Metal-Induced Oxidative Fusion of Boranes. Synthesis of $B_{12}H_{16}$, the First Neutral Dodecaborane", J. Am. Chem. Soc., 106, 2722 (1984).

R. G. Swisher, R. J. Butcher, E. Sinn, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 5. Studies on (η^6-Arene)iron(carborane) Complexes of Benzene and Biphenyl. Crystal Structures of $(\eta^6\text{-}C_6H_5\text{-}C_6H_5)Fe(Et_2C_2B_4H_4)$ and $1,2\text{-}[(\eta^6\text{-}C_6H_6)Fe(Et_2C_2B_4H_3)]_2\text{-}CH(CH_3)CH_2$, a Hydrocarbon-Linked Bisferracarborane," Organometallics, 4, 882 (1985).

R. N. Grimes, "Synthesis and Structure of Large Boron Cages and Multi-Decker Metal-Carborane Sandwich Complexes", in Boron-Rich Solids, American Institute of Physics Conference Proceedings No. 140, D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, eds., American Institute of Physics, New York, 1986.

J. T. Spencer and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 8. Mono-, Di-, and Triiron Polyarene Sandwich Complexes of $Et_2C_2B_4H_4^{2-}$ Containing Fluorene, 9,10-Dihydroanthracene or [2.2]Paracyclophane Ligands", submitted.

J. T. Spencer and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 9. Nido-2,3-Dibenzyl-2,3-dicarbahexaborane(8) $[(PhCH_2)_2C_2B_4H_6]$, a Versatile Multifunctional Nido-Carborane: Iron-Polyarene Sandwich Compounds and Chromium Tricarbonyl π-Complexes", submitted.

J. T. Spencer, M. R. Pourian, R. J. Butcher, E. Sinn, and R. N. Grimes, Organotransition-Metal Metallacarboranes. 10. π-Complexation of nido-$(PhCH_2)_2C_2B_4H_6$ at the C_2B_3 and C_6 Rings. Synthesis and Crystal Structures of Nido-$2,3\text{-}[(CO)_3Cr(\eta^6\text{-}C_6H_5)CH_2]_2\text{-}2,3\text{-}C_2B_4H_6$ and $(PhCH_2)_4C_4B_8H_8$, a Nonfluxional C_4B_8 Cluster", submitted.

IV. Participating Scientific Personnel

Principal Investigator: Russell N. Grimes, Professor of Chemistry

Postdoctoral Associates: Robert Swisher
Mohammad Pourian

Graduate Students: Henry Boyter (M.S. Chemistry, M.S. August 1984)
Cynthia Brewer (Ph.D. Chemistry, August 1984)
Kathleen Kahler

Undergraduate Student: Mark Fessler

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