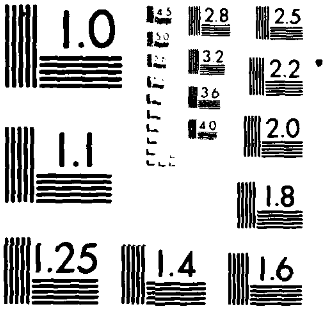
AD-A092 270 VIRGINIA UNIV CHARLOTTESVILLE DEPT OF CHEMISTRY F/G 7/3
MERCURY-BRIDGED COBALTACARBORANE COMPLEXES CONTAINING B-HG-B TH--ETC(U)
NOV 80 D C FINSTER, R N GRIMES N00014-75-C-0305
UNCLASSIFIED TR-36 NL

1 of 1
AD
A092270

END
DATE
FILMED
1 81
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

OFFICE OF NAVAL RESEARCH

(12)

CONTRACT NO. (15) N00014-75-C-0305

SC

(9) TECHNICAL REP[redacted]T NO. 36 (14) TR-36

(6) Mercury-Bridged Cobaltacarborane Complexes Containing B-Hg-B Three-Center Bonds. Synthesis and Structure of μ,μ'-[(η^5-C_5R_5)Co$(CH_3)_2C_2B_3H_4$]$_2$Hg, μ-[(η^5-C_5R_5)Co$(CH_3)_2C_2B_3H_4$]HgCl, (R=H, CH_3) and Related Compounds.

(10) David C. Finster [redacted] Russell N. Grimes

Department of Chemistry
University of Virginia
Charlottesville, Va. 22901

Prepared for Publication in

Inorganic Chemistry

(11) Nov[redacted]80 (12) 43

401145

Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, VA 22901

Mercury-Bridged Cobaltacarborane Complexes Containing B-Hg-B Three-Center Bonds. Synthesis and Structure of μ,μ'-$[(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$, μ-$[(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$, (R=H, CH_3) and Related Compounds[1]

David C. Finster and Russell N. Grimes*

Abstract. Reactions of the nido-cobaltacarborane anions $(\eta^5$-$C_5H_5)Co(CH_3)_2C_2B_3H_4^-$ and $[\eta^5$-$C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4^-$ with $HgCl_2$ in tetrahydrofuran give initially the unstable adducts $[(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4 \cdot HgCl_2]^-$ (R = H, CH_3), which lose Cl^- to form the isolable HgCl-bridged complexes μ-$[(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$; the latter species undergo symmetrization to generate the bis(cobaltacarboranyl)mercury complexes μ,μ'-$[(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$. In the cyclopentadienyl system (R = H), the formation of the μ,μ' complex is rapid, giving high yields within minutes; in contrast, the pentamethylcyclopentadienyl species reacts much more slowly, requiring days to form the μ,μ' complex in isolable quantity. Thus, the characterization of the mono (cobaltacarboranyl)mercury complex is readily achieved with the $C_5(CH_3)_5$-substituted cobaltacarborane. The structural characterization of the Hg-bridged complexes is based on pulse Fourier transform ^1H and ^{11}B NMR, ir, and mass spectra, and single-crystal X-ray diffraction studies of μ-$[\eta^5$-$C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4$-HgCl and μ,μ'-$[(\eta^5$-$C_5H_5)Co(CH_3)_2C_2B_3H_4]_2Hg$. The mono(cobaltacarboranyl) complex crystallizes as a dimer with weak intermolecular Hg···Cl interactions. Crystal data: $HgCoClC_{14}B_3H_{25}$,

mol wt 520.76, space group $P2_1/n$, Z = 2; a = 9.634(2), b = 14.05(1), c = 13.862(7) Å; β = 96.71(3)°; V = 1863 $Å^3$; R = 0.044 for 1607 reflections having $F_o^2 > 3\sigma(F_o^2)$. $HgCo_2C_{18}B_6H_{30}$, mol wt 629.75, space group $P2_1/n$, Z = 2; a = 8.456(8), b = 11.334(7), c = 11.77(1) Å; β = 100.12(9)°; V = 1110 $Å^3$; R = 0.081 for 1441 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

A recent report[2] from these laboratories described the preparation of the mercury-bridged complexes μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ (I), μ,μ'-$(B_5H_8)_2Hg$ (II), and some chemistry based on these species. In the proposed structures[2] of I and II, a mercury atom interacts with a B-B edge on the open face of the nido-carborane or -borane ligand, forming a two-electron, three-center B-Hg-B bond. The general principle of boron-metal-boron bridging in nido-boranes and -carboranes is well established;[3] in addition to I and II, there are several known complexes in which a metal (or nonmetal) atom participates in B-M-B bridge-bonding on two separate ligands.[4] However, previous examples of well-characterized B-Hg-B bridging are virtually nonexistent.[5]

The cobaltacarboranes 1,2,3-$(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_4H_6$ (III, R = H;[10] IV, R = CH_3[11]) are direct analogues of the nido-carborane $(CH_3)_2C_2B_4H_6$ in which a $Co(C_5R_5)$ unit replaces the apex BH, and are readily available to us. Hence it appeared worthwhile to explore the synthesis of mercury-bridged derivatives of III and IV (which would be analogues of complex I, mentioned above) in order to assess the influence of the apical $Co(C_5R_5)$ unit on complexation. An additional motivation was the hope of producing crystals of mercury-bridged complexes suitable for X-ray diffraction studies, inasmuch as no definitive structural characterization of a complex containing discrete B-Hg-B three-center bridges had been reported.

Results and Discussion

Synthesis of Mercury-Bridged Cobaltacarboranes. As has been described previously,[10] the nido-cobaltacarborane 1,2,3-(η^5-C_5H_5)Co$(CH_3)_2C_2B_3H_5$ (III) reacts easily with sodium hydride in tetrahydrofuran (THF) at room temperature, eliminating one of its two bridging protons to form the $(C_5H_5)Co(CH_3)_2C_2B_3H_4^-$ anion (Figure 1); the reaction is analogous to the bridge-deprotonation[12] of 2,3-$C_2B_4H_8$ to give $C_2B_4H_7^-$. The pentamethylcyclopentadienyl counterpart, IV, also undergoes bridge deprotonation but much more slowly (i.e., a matter of hours for IV vs. minutes in the case of III). Treatment of the $(\eta^5$-$C_5R_5)Co(CH_3)_2C_2B_3H_4^-$ anions (R = H or CH_3) with $HgCl_2$ in THF proceeds as shown in Figure 1, generating initially an $HgCl_2$-bridged unstable intermediate VA (R = H) or VB (R = CH_3); these species in turn lose Cl^- to give the corresponding yellow-orange HgCl-bridged complexes VI A and VI B.

Further reaction of VI A and VI B with a second mole equivalent of the cobaltacarborane anion produces the respective yellow-orange μ,μ'-bis(cobaltacarboranyl) complexes VII A and VII B; again, there is a notable difference in the reactivity of the $C_5H_5^-$ vs the $C_5(CH_3)_5^-$ containing species, with the former (VI A) adding a second cobaltacarborane ligand much more rapidly (Table I). As a consequence, the HgCl-bridged $C_5(CH_3)_5$ derivative (VI B) was isolated and fully characterized, whereas its cyclopentadienyl counterpart (VI A) was detected only in trace amounts. Similarly, the C_5H_5 complex VII A was generated rapidly in high yield while the $C_5(CH_3)_5^-$ containing species VII B required days to form in isolable quantity (Table I). The unstable $HgCl_2$-bridged intermediates (V A and V B) were only partially characterized from mass spectral and (in the case of V B) proton NMR data as described below.

Spectroscopic Characterization. The ^{11}B and ^{1}H FT NMR data (Tables II and III) and ir spectra (Table IV) of the three isolable species VI B, VII A, and VII B, are consistent with, but do not in themselves confirm, the structures shown in Figure 1. The ambiguity arises, in part, from the fact that the bridging mercury atom does not cause major perturbations in chemical shifts relative to those of the parent (unbridged) cobaltaborane;[10,11] thus, the ^{11}B NMR spectra exhibit only two resonances in a 2:1 area ratio instead of the expected three equal-area signals. However, the inequivalence of the cage $C-CH_3$ units is evident in the proton spectra of VB and VII A, and the split B-H absorption near 2500 cm^{-1} in the ir spectra of the compounds is characteristic of heteroatom-bridged derivatives of nido-carboranes.[2,13] The structures of these compounds were unequivocally established from X-ray crystal structure analyses of VI B and VII A, as described in the following section.

The geometries of the proposed $HgCl_2$-bridged anionic intermediates V A and V B, shown in Figure 1, are not certain but are suggested by the conditions of synthesis and the known structures of subsequent products. These species are evidently salts in view of their low TLC R_f values (0.05 to 0.2 in 1:1 CH_2Cl_2/hexane) and the absence of mass spectral peaks at probe temperatures less than

$\sim$290°C (neutral metallacarboranes typically have sufficient volatility to exhibit mass spectra below 200°C). The mass spectra obtained for V A and V B at 290°C exhibit high mass cutoffs at m/e 700 and 840 respectively, corresponding to $(C_5R_5)_2Co_2(CH_3)_4$ $C_4B_6H_4Cl_2Hg^+$ ions (R = H, CH_3) which are assumed to form by pyrolysis of the ionic samples; the presence of $(C_5R_5)Co(CH_3)_2C_2B_3H_3^+$ and Hg^+ fragments is clearly evident. The 100-MHz ^1H FT NMR spectrum of V B is consistent with an Hg-bridged CoC_2B_4 complex and is very similar to that of the structurally established species VI B which forms from V B on standing. Thus, complexes V A and V B are formulated as Na^+ salts of $HgCl_2$-bridged adducts[14] of the respective $(C_5R_5)Co(CH_3)_2C_2B_3H_4 \cdot HgCl_2^-$ anions with the proposed structures depicted in Figure 1.

Molecular Structures of μ-[η^5-$C_5(CH_3)_5$]$Co(CH_3)_2C_2B_3H_4$]HgCl (VI B) and μ,μ'-[(η^5-C_5H_5)$Co(CH_3)_2C_2B_3H_4$]$_2$Hg (VII A). The geometries and unit cell packing of VI B and VII A are shown in Figures 2-5 and the relevant crystallographic data are given in Tables V-IX. The molecular structures of both compounds conform to those proposed from spectroscopic data, and contain a mercury atom bridging a B-B edge on the open face of a pyramidal CoC_2B_3 unit. In the HgCl-bridged species VI B, the two enantiomeric forms of the molecule crystallize in centrosymmetric pairs (Figure 2) with the HgCl moieties parallel to each other and within weakly bonding distance [3.155(3) Å]; this intermolecular Hg-Cl separation can be compared with the intramolecular Hg-Cl distance of 2.349(3) Å, which reflects strong covalent bonding. The dimerization of VI B in the solid state is not unusual, since many organomercury compounds adopt crystal structures in which there are weak intermolecular Hg···X interactions,[15] as shown by Hg-X distances significantly less than the sum of van der Waals radii (4.10 Å for Hg and Cl). Thus, in $HgCl_2$ itself[16] each mercury atom is surrounded by three pairs of chlorine atoms at distances of 2.25, 3.34, and 3.63 Å, the last two being intermolecular.

In both VI B and VII A, the mercury atom is regarded as sp hybridized and is linearly bonded to its coordinated ligands. As indicated in Table VII, the corresponding distances in the two structures are, in general, closely similar though there are a few differences; thus, the mercury atom is slightly closer to the carborane cage in VI B than in VII A. The similarity of the molecules is particularly evident in a comparison of the dihedral angles between mean planes, as given in Table IX. However, a notable exception is found in the positions of the B-H-B hydrogen bridges [H(56)]. In compound VI B, the dihedral angle subtended by the B(5)-H(56)-B(6) plane and the C_2B_3 ring is 46.2°, whereas in VII A it is 66.5°; the difference is shown more dramatically by the deflection of H(56) from the Co-B(5)-B(6) plane, which in VI B is 9.5° outward (<u>away</u> from Hg) but in VII A is 10.9° inward (<u>toward</u> Hg) as shown in Figure 6. As a consequence, the H(56)-Hg distance is only 2.42(1) Å in VII A as compared to 2.79(1) Å in VI B. While the determination of hydrogen atoms in the vicinity of mercury from X-ray data must be viewed with considerable caution, there are strong indications that the effect shown in Figure 6 is real. First, the ^1H NMR spectra of both VI B and VII A exhibit ^{199}Hg satellites on the H(56) resonance, but the magnitude of the $^{199}Hg-^1H$ coupling constant (J) is larger in VII A (113 Hz) than in VI B (67 Hz). Second, in VII A, not only is the B-H-B bridge tilted toward Hg as suggested above, but in addition H(56) is skewed toward B(5), the boron adjacent to mercury; thus, B(5)-H(56) is 1.55(1) Å while B(6)-H(56) is 1.63(1) Å. In VI B the opposite is true, as shown by the B(5)-H(56) and B(6)-H(56) distances of 1.53(2) and 1.36(1) Å, respectively. In both structures, the B-Hg-B bridge is significantly asymmetric, with Hg closer to B(4) than to B(5), but the Hg-B(5) distance is longer in VII A than VI B.

All of these observations are consistent with a weak, but real, bonding interaction between mercury and the bridging hydrogen atom in VII A. We emphasize that it is <u>weak</u>, since the 2.42 Å Hg···H distance is 0.6 Å larger than the sum of covalent radii for Hg and H. It is nonetheless interesting to note that in the copper-bridged species[17] μ-$[(C_6H_5)_3P]_2Cu$-$B_5H_8Fe(CO)_3$, in which an established Cu···H interaction exists, the Cu-H distance (1.96 Å) is 0.5 Å greater than the sum of covalent radii. In the copper complex, the bridging Cu attracts a <u>terminal</u> B-H hydrogen whereas in the present species VII A, the bridging Hg interacts with a <u>bridging</u> hydrogen. It is not obvious why this effect should be felt more strongly in VII A than in VI B, but we can eliminate direct H(56)···Cl (intermolecular) linkage in VI B inasmuch as that distance (3.54 Å) is far too great for even a weak bonding interaction.

The locations of the methyl groups in VI B and VII A require comment. Hoffman, Mingos, and coworkers[18] have shown that when polyene or polyenyl ligands $(CR)_n$, $n = 3-8$, are face-bonded to a metal atom, the R substituents will tend to bend either toward or away from the metal atom depending on ring size (n). The effect arises from the optimization of the overlap of polyene bonding MO's with the metal d orbitals, and it has been calculated that for $n > 5$ the substituents will tilt toward the metal while for $n < 5$ they will bend away. When $n = 5$, either is possible and structure determinations have produced examples[18] of both types of bending. In the present species VI B, the methyl groups on the $C_5(CH_3)_5$ ring show an average tilt of 3° away from the cobalt atom.

Somewhat surprisingly, in both VI B and VII A the methyl groups on the C_2B_3 rings all tilt toward the cobalt atom, i.e., by 4.6 and 4.8° in VI B and by 5.8 and 8.4° in VII A. This observation is curious since the $C_5R_5^-$ and $(CH_3)_2C_2B_3H_4^{3-}$ ligands are formally isoelectronic and, one would assume, roughly isolobal. Moreover, in VI B the $C_5(CH_3)_5$ and $(CH_3)_2C_2B_3H_3$ rings are nearly eclipsed, so that the bend of the carboranyl methyl groups occurs despite a repulsive steric interaction, albeit a weak one with an inter-methyl C-C distance of ca. 3.9 Å.

Finally, we comment briefly on the observation of a single conformer in the bis(cobaltacarboranyl)mercury complex, VII A. Since the $(\eta^5-C_5H_5)Co(CH_3)_2C_2B_4H_5^-$ ligand occurs as a racemic mixture, complexation of two such groups to mercury via B-Hg-B bridging should generate two distinguishable stereoisomers, one of which has idealized C_2 symmetry (the one observed as VII A). In the other, the bridging Hg and H atoms on one ligand are reversed relative to VIIA, producing idealized C_s (mirror) symmetry. In each of these isomers, which are analogous to those proposed for μ,μ'-$(C_2B_4H_7)_2SiH_2$,[4a] there is presumably free rotation about the mercury atom, thus giving rise to a number of different conformers in solution.

One must assume that both the C_2 and C_s stereoisomers are produced during synthesis, although they are probably indistinguishable via NMR spectroscopy, as is the case[2] with the bis(carboranyl)mercury complex (I) mentioned earlier. Hence, the fact that only the C_2 isomer of VII A is observed in the crystal structure analysis must reflect differences in the molecular packing of the two forms. Conceivably the C_2 isomer crystallizes more readily, or was fortuitously present in the crystal selected for data collection.

As compounds VI B and VII A are the first metallacarboranes containing B-Hg-B bridge bonds to be crystallographically characterized, further exploration of these stereochemical effects must await additional structure determinations in this class of compounds.

Experimental Section

Materials. Pentamethylcyclopentadiene (Alfa) was used as received and all other chemicals were reagent grade. Tetrahydrofuran (THF) was rigorously dried over $LiAlH_4$ prior to use. N-Butyllithium was obtained from Alfa as a hexane solution and determined to be 1.8 M by the method of Silveira.[19] NaH (Alfa, 50% in mineral oil) was washed with pentane prior to use. $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ was prepared as described below, and $[\eta^5\text{-}C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_5$ was similarly prepared as described elsewhere.[11] Thin layer chromatography (TLC) was conducted on precoated plates of silica gel F-254 (Brinkmann Instruments, Inc.)

Instrumentation. ^{11}B (32 Mhz) and ^1H (100 MHz) pulse Fourier transform NMR spectra were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Broadband heteronuclear decoupling was employed. Unit-resolution mass spectra (EI) were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Infrared spectra were recorded on a Beckman IR-8 instrument.

Synthesis of $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ (III). $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_5$ was prepared via degradation of $(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_4H_4$ in basic THF or CH_3CN.[10] In a typical reaction, about 250 mg

$(\eta^5$-$C_5H_5)Co(CH_3)_2C_2B_4H_4$ was dissolved in 20 ml CH_3CN to which 15 ml 2M NaOH was added with stirring. The progress of the reaction was monitored by spot TLC in 1:1 CH_2Cl_2/hexanes [1,2,3-$(\eta^5$-$C_5H_5)Co(CH_3)_2C_2B_4H_4$, R_f = 0.6; III, R_f = 0.9] and after 1 hr the reaction was stopped by removal of most of the CH_3CN by rotary evaporator. The cobaltacarboranes were extracted from the remaining slurry with CH_2Cl_2 and purified by TLC to give about 200 mg III (83% yield) and a small amount of the starting material. Use of THF instead of CH_3CN generally gave lower yield of III (50%) and trace yields of the other characterized cobaltacarboranes,[10,20] 1,7,2,3-$(\eta^5$-$C_5H_5)_2Co_2(CH_3)_2C_2B_3H_3$ and $(\eta^5$-$C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$, isomer V.

Synthesis of pentamethylcyclopentadienylcobaltacarboranyl mercury compounds (VIB, VIIB). A tip-in sidearm flask was charged with 60 mg [η^5- $C_5(CH_3)_5$]$\cdot Co(CH_3)_2C_2B_3H_5$, IV, 0.21 mmol)[11] and 50 mg NaH (0.25 mmol). The flask was evacuated and about 20 ml dry THF was distilled in vacuo into the flask at -196 °C. The flask was warmed to 23 °C with no reaction (yellow solution) and then warmed to 60 °C for 15 min with no reaction. The solution was allowed to stir at 23°C for 12 hr (giving a yellow/orange color) whereupon it was filtered in vacuo into a flask containing 67 mg $HgCl_2$ (0.25 mmol). No immediate reaction being observed, the solution was stirred for 2 days at 23 °C producing a dark, flocculent yellow suspension and a gray precipitate. The THF was removed in vacuo and the system was exposed to the air. Extracts using CH_2Cl_2 and hexane were purified via TLC to give 22 mg yellow/orange μ,μ'-$\{[(\eta^5$-$C_5(CH_3)_5$ $]Co(CH_3)_2C_2B_3H_4\}_2Hg$ (VIIB, 0.028 mmol, 27% yield; R_f = 0.2 in hexane; m/e = 772; m.p. = 255 °C dec) and 34 mg yellow/orange μ-$[\eta^5$- $C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4HgCl$ (VIB, 0.065 mmol, 31% yield; R_f = 0.5 in 1:1 CH_2Cl_2/hexane; m/e = 524; m.p. = 173 °C dec), 3 mg of the starting material, and a trace of VB, formulated as the sodium salt of the adduct $[\eta^5$- $C_5(CH_3)_5]$ $Co(CH_3)_2C_2B_3H_4\cdot HgCl_2^-$ (R_f = 0.05 in 1:1 CH_2Cl_2/hexane). All of these compounds are moderately air-stable; the slow decomposition of VB to VIB has been noted.

A similar reaction in which the NaH deprotonation step involved stirring for 2 hr (possibly incomplete) and the reaction with $HgCl_2$ was stirred only 10 min, gave a 4.3% yield of VIB , 19% yield of VB, and 49% recovery of the starting compound. Other compounds (in trace yield) of similar color and R_f as that of VB gave mass spectra indicating the addition of extra chlorine atoms.

Synthesis of cyclopentadienylcobaltacarboranyl mercury compounds (VIA, VIIA). The syntheses are similar to those described above for VIB and VIIB. In dry THF, 50 mg of $(\eta^5$-$C_5H_5)$ $Co(CH_3)_2C_2B_3H_5$ (III, 0.23 mmol) was deprotonated in vacuo with 55 mg NaH (2.3 mmol) over a period of 30 min with H_2 evolution and a color change from yellow to orange. After freezing the solution, the H_2 (not measured) was removed by evacuation. The salt was then filtered at 23 °C in vacuo into a flask containing 63 mg $HgCl_2$ (0.23 mmol) effecting an immediate color change back to yellow. The solution was stirred for 10 min at 23 °C and the THF removed in vacuo. The flask was exposed to the air, and CH_2Cl_2 and hexane extracts were purified via TLC to give 48 mg yellow/orange μ,μ'-$[(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ (VIIA), 0.076 mmol, 66% yield; R_f = 0.2 in hexane, 0.85 in 1:1 CH_2Cl_2/hexane; m/e = 632, m.p. = 190 °C dec), a trace of yellow/orange μ-$[(\eta^5\text{-}C_5H_5)Co(CH_3)_2C_2B_3H_4]HgCl$ (VIA , R_f = 0.7 in 33% acetone in hexane, m/e = 452), a trace of starting material, and salts analogous to those described above (R_f = 0.2-0.3 in 1:1 CH_2Cl_2/hexane.)

A similar reaction conducted over a period of 4 days gave no compounds in isolable yields.

X-ray Crystal Structure Determinations on VIB and VIIA. The crystals used were grown by slow evaporation of solvent: compound VIB from 10% CH_2Cl_2 in hexane at 10 °C and compound VIIA from CH_2Cl_2 at 10 °C. The crystals were mounted on glass fibers in arbitrary orientations and examined by preliminary precession photographs which indicated acceptable crystal quality. Crystal data follow: $HgCoClC_{14}B_3H_{25}$ (VIB), molecular weight 520.76; space group $P2_1/n$, Z = 2; a = 9.634(2), b = 14.046(10), c = 13.862(7) Å; β

$= 96.71(3)^{\circ}$; $V = 1863\ \text{Å}^3$; $\mu(\text{MoK}\alpha) = 94.6\ \text{cm}^{-1}$, $\rho(\text{calcd}) = 1.86\ \text{g cm}^{-1}$. Crystal dimensions (mm from centroid): (010) 0.06 , $(0\bar{1}0)$ 0.06, (101 0.125, $(\bar{1}0\bar{1})$ 0.125, $(10\bar{1})$ 0.14, $(\bar{1}01)$ 0.14. $\text{HgCo}_2\text{C}_{18}\text{B}_6\text{H}_{30}$ (VIIA), molecular weight 629.75; space group $P2_1/n$, $Z = 2$, $a = 8.456(8)$, $b = 11.334(7)$, $c = 11.76(1)\ \text{Å}$, $\beta = 100.12(9)^{\circ}$, $V = 1110\ \text{Å}^3$, $(\text{MoK}\alpha) = 85.8\ \text{cm}^{-1}$, $\rho(\text{calcd}) = 1.88\ \text{g cm}^{-1}$. Crystal dimensions (mm from centroid): (100) 0.06, $(\bar{1}00)$ 0.06, (011) 0.145, $(0\bar{1}\bar{1})$ 0.145, $(01\bar{1})$ 0.145, $(0\bar{1}1)$ 0.145.

For each crystal the Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide approximate cell dimensions. Refined cell dimensions and their estimated standard deviations were obtained from 28 accurately centered reflections. The mosaicity of the crystals was examined by the ω scan technique and judged to be satisfactory. The space groups were chosen based on systematic absences and chemical and spectroscopic information. In each case, successful solution and refinement of the structure confirmed the choice of space group.

Collection and Reduction of the Data. Diffraction data were collected at 295°K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer using MoKα radiation from a highly oriented graphite crystal monochrometer. The θ-2θ scan technique was used to record the intensities of all reflections for which $1.0 < 2\theta < 48^\circ$ for VIB and $1.0 < 2\theta < 50^\circ$ for VIIA. Scan widths were calculated from the formula $Sw = (A + B\tan\theta)$, where A is estimated from the mosaicity of the crystal and B compensates for the increase in the width of the peak due to $K\alpha_1 - K\alpha_2$ splitting. The values of A and B are 0.60 and 0.35 for VIB and 0.60 and 0.30 for VIIA, respectively. The calculated scan angle was extended at each side by 25% for background determination (BG1 and BG2). The net count (NC) was then calculated as NC = TOT-2(BG1+BG2), where TOT is the estimated peak intensity.

The intensities of four standard reflections, at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and then for absorption, (minimum transmission factor 0.21, maximum 0.55 for VIB ; minimum 0.28, maximum 0.46 for VIIA), resulting in 2274 reflections for VIB and 1851 relections for VIIA of which 1607 for VIB and 1441 for VIIA had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o)$ was estimated from counting statistics ($\rho = 0.03$).[21] Only the 3σ data were used in the final refinement of the structural parameters.

Solution and Refinement of the Structures. Full-matrix least squares refinement was based on F, and the function minimized was $w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[22] and those for hydrogen from Stewart, et al.[23] The effects of anomolous dispersion for all non-hydrogen atoms were included in F using the values of Cromer and Ibers[24] for $\Delta f'$ and $\Delta f''$.

The positions of the mercury and cobalt atoms in VIB were determined from three-dimensional Patterson functions calculated from all intensity data. The intensity data were phased sufficiently well by these positional coordinates to permit location of the remaining non-hydrogen atoms from Fourier difference functions. A small amount of positional disorder was observed in the $(CH_3)_5C_5$ ring, but the disordered positions could not be adequately established and contributed little to the overall scattering. This disorder is also unimportant in terms of the interesting structural features of the molecule and was therefore not pursued further. The molecule was found to be dimerized about a crystallographic inversion center via a pair of Hg - Cl interactions. Anisotropic temperature factors were introduced for all nonhydrogen atoms. The position of the bridging hydrogen, H(56), was calculated and included in the refinement, except during the final three cycles. A final Fourier difference map was featureless. The esd of an observation of unit weight was 2.49.

For compound VIIA the positions of the cobalt and mercury atoms were determined from a three-dimensional Patterson function. The Hg atom was found to be at a center of inversion, thus requiring solution for only half of the molecule.

The intensity data were phased sufficiently well by the coordinates of the Hg and Co atoms to permit location of the remaining non-hydrogen atoms from Fourier difference functions. After introducing anisotropic thermal parameters for all nonhydrogen atoms, some hydrogen atoms were found on Fourier difference maps, and those remaining were calculated and inserted. All hydrogen atoms were included in the refinement for three cycles and thereafter held fixed. A final Fourier difference map was featureless. The esd of an observation of unit weight was 4.62.

The models converged to $R = 0.044$ and $R_w = 0.055$ for VIB, and $R = 0.061$ and $R_w = 0.094$ for VIIA, where $R = ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2}$. Tables of observed and calculated structure factors are available (see paragraph at end of paper on supplementary material.) The computing system and programs are described elsewhere.[25]

Acknowledgments. This work was supported by the Office of Naval Research and the National Science Foundation, Grant No. 79-09948. We are grateful to Professor Ekk Sinn for assistance in the X-ray crystallographic structure determinations.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Based in part on a Ph.D. dissertation (University of Virginia, 1980) by D.C.F.

(2) Hosmane, N.S.; Grimes, R.N. *Inorg. Chem*. **1979**, *18*, 2886.

(3) (a) Greenwood, N.N.; Ward, I.M. *Chem. Soc. Rev.* **1974**, *3*, 231; (b) Wegner, P.A. in "Boron Hydride Chemistry"; Muetterties, E.L., Ed.; Academic Press: New York, 1975, Chapter 12.

(4) (a) Tabereaux, A.; Grimes, R.N. *Inorg. Chem*. **1973**, *12*, 792; (b) Davison, A.; Traficante, D.D.; Wreford, S.S. *J. Am. Chem. Soc*. **1974**, *96*, 2802; (c) Denton, D.L.; Clayton, W.R.; Mangion, M.; Shore, S.G.; Meyers, E.A. *Inorg. Chem*. **1976**, *15*, 541; (d) Brennan, J.P.; Schaeffer, R.; Davison, A.; Wreford, S.S. *J. Chem. Soc., Chem. Commun*. **1973**, 354; (e) Shore, S.G. *Abstracts of Papers, XIX Int. Conf. on Coord. Chem. Prague*, Sept. 1978; (f) Greenwood, N.N.; Hails, M.J.; Kennedy, J.D.; McDonald, W.S. *J. Chem. Soc., Chem. Commun*. **1980**, 37. (g) Greenwood, N.N.; McGinnety, J.A.; Owen, J.D. *J. Chem. Soc., Dalton Trans*., **1972**, 989; (h) Guggenberger, L.J. *J. Am. Chem. Soc*. **1972**, *94*, 114.

(5) In the known mercury complexes of the nido-$B_{10}H_{12}^{2-}$ ligand,[6] Hg is evidently η^4-coordinated to the cage, and in the complexes of nido-$C_2B_9H_{11}^{2-}$ and closo-$C_2B_{10}H_{11}^{-}$ it is η^1-coordinate (σ-bonded).[7,8] A partially characterized complex formulated as μ-$[C_6H_5Hg]$-2,3-$C_2B_4H_7$ was reported several years ago.[9]

(6) (a) Greenwood, N.N.; Thomas, B.S.; Waite, D.W. J. Chem. Soc., Dalton Trans. 1975, 299; (b) Greenwood, N.N., Sharrocks, D.N. J. Chem. Soc. A. 1969, 2334; (c) Greenwood, N.N. Pure Appl. Chem. 1977, 49, 791.

(7) (a) Colquhoun, H.M.; Greenhough, T.J.; Wallbridge, M.G.H. J. Chem. Soc., Chem. Commun. 1977, 737; (b) Colquhoun, H.M.; Greenhough, T.J.; Wallbridge, M.G.H. J. Chem. Soc., Dalton Trans. 1979, 619.

(8) See reference 2, footnote 8.

(9) Magee, C.P.; Sneddon, L.G.; Beer, D.C.; Grimes, R.N. J. Organometal. Chem. 1975, 86, 159.

(10) Grimes, R.N.; Beer, D.C.; Sneddon, L.G.; Miller, V.R.; Weiss,R. Inorg. Chem. 1974, 13, 1138.

(11) Finster, D.C.; Sinn, E.; Grimes, R.N., submitted for publication.

(12) Onak, T.; Dunks, G.B. Inorg. Chem. 1966, 5, 439.

(13) See papers cited in ref. 2, footnote 2.

(14) Adducts of $HgCl_2$ with organic sulfides and with organometallics such as $(\eta^5\text{-}C_5H_5)(CO)_2Co$ are known: see Cotton, F.A.; Wilkinson, G. "Advanced Inorganic Chemistry, Fourth Edition"; Wiley: New York, 1980, pp. 607-608, and references cited therein.

(15) (a) Seyferth, D.J. Organomet. Chem. 1973, 62, 33; 1974, 75, 13; 1975, 98, 133; and 1977, 143, 153.

(16) (a) Braekken, H.; Scholten, W. Z. Krist., 1934, 89, 448; (b) Grdenić, D. Arkiv Kemi, 1950, 2, 14.

(17) Mangion, M.; Ragaini, J.D.; Schmitkons, T.A.; Shore, S.G. J. Am. Chem. Soc. 1979, 101, 754.

(18) Elian, M.; Chen, M.M.L.; Mingos, D.P.M.; Hoffmann, R. Inorg. Chem. 1976, 15, 1148.

(19) Silveira, A.D., Jr.; Bretherick, H.D., Jr.; Negishi, E. J. Chem. Ed. 1979, 56, 569.

(20) Wong, K-S.; Bowser, J.R.; Pipal, J.R.; Grimes, R.N. J. Am. Chem. Soc., 1978, 100, 5045.

(21) Corfield, P.W.R.; Doedens, R.J.; Ibers, J.A., Inorg. Chem. 1967, 6, 197.

(22) Cromer, D.T.; Waber, J.T., "International Tables for X-ray Crystallography," Vol. IV, the Kynoch Press, Birmingham, England, 1974.

(23) Stewart, R.F.; Davidson, E.R.; Simpson, W.T.; J. Chem. Phys., 1965, 42, 3175.

(24) Cromer, D.T.; Ibers, J.A., ref. 22.

(25) Freyberg, D.P.; Mockler, G.M.; Sinn, E., J. Chem. Soc., Dalton Trans. 1976, 447.

Table I. Yields of Mercury-Bridged Cobaltacarboranes[a]

$Na^{+}[\mu\text{-}(\eta^{5}\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4\cdot HgCl_2]^{-}$ VA, R = H; VB, R = CH_3

$\mu\text{-}[(\eta^{5}\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$ VIA, R = H; VIB, R = CH_3

$\mu,\mu'\text{-}[(\eta^{5}\text{-}C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ VIIA, R = H; VIIB, R = CH_3

R	Reaction time	V	VI	VII
H	10 min	t	t	66
H	4 days	t	t	t
CH_3	10 min	19	4	t
CH_3	2 days	t	31	27

[a] Yields given as percent of theoretical based on starting cobaltacarborane consumed; t = trace.

Table II. 32.1 MHz ^{11}B NMR Data

Compound	Solvent	Chemical shifts (rel area)[a]
VIIA	$CDCl_3$	8.8 (2)
		2.8 (1)
VIB	$CDCl_3$	12.2 (1)
		7.5 (2)
VIB	C_6D_6	10.2 (2)
		5.0 (1)
VIIB	$CDCl_3$	13.6 (2)
		8.5 (1)

[a] vs. $BF_3 \cdot O(C_2H_5)_2$, positive shifts downfield. J_{BH} coupling constants not readily determined due to peak overlap.

Table III. 100 MHz ^{1}NMR Data

Compound (solvent	Chemical Shift[a] (rel area)	Assignment[b]
VII A ($CDCl_3$)	4.68 (5)	C_5H_5
	3.60 (1)	BH
	3.44 (1)	BH
	3.03 (1)	BH
	1.89 (3)	CH_3
	1.75 (3)	CH_3
	-6.37 (1)[b]	BHB
VI B (C_6D_6)	3.21 (2)	BH
	2.65 (1)	BH
	1.38[c]	CH_3(cage and ring)
	-5.58 (1)[d]	BHB
VII B (C_6D_6)	3.68 (1)	BH
	3.26 (1)	BH
	2.94 (1)	BH
	1.60 (6)	CH_3 (cage)
	1.56 (15)	CH_3 (ring)
	-5.51 (1)	BHB
V B (C_6D_6)	3.5 (2)	BH
	3.3 (1)	BH
	1.93 (3)	CH_3 (cage)
	1.62 (15)	CH_3 (ring)
	1.59 (3)	CH_3 (cage)
	-5.1 (1)	BHB

[a] Ppm vs. TMS = 0. [b] ^{199}Hg satellites at $^2J_{HgH}$ = 113 Hz. [c] Integration not clear due to impurities. [d] ^{199}Hg satellites at $^2J_{HgH}$ = 67 Hz.

Table IV. Ir absorptions (cm^{-1}, KBr pellets)

μ-$[\eta^5$-$C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4HgCl$ (VIB)

2950sh, 2910s, 2860s, 2540sh, 2515s, 1850m, 1730m, 1585m, 1560sbr, 1360s, 1265w, 1075m, 1025s, 1015s, 1000s, 990w, 950w, 910s, 785s, 735s, 650m.

μ-$[(\eta^5$-$C_5H_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ (VIIA)

2930m, 2900m, 2850m, 2510s, 2435s, 1830sh, 1815m, 1580s, 1415m, 1360m, 1350m, 1110m, 1000s, 950s, 890w, 840m, 820s, 780w, 760w, 695s.

μ-$\{\eta^5$-$[C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4\}_2Hg$ (VIIB)

2950sh, 2900s, 2860sh, 2485s, 2415s, 1815m, 1555m, 1460sbr, 1375s, 1360sh, 1260w, 1070m, 1025s, 1000s, 945s, 885w, 840s, 800m, 755m, 695s.

---

s = strong, m = medium, w = weak, br = broad, sh = shoulder

TABLE V. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR μ-[$C_5(CH_3)_5$ $Co(CH_3)_2C_2B_3H_4$]HgCl.[a]

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
HG	0.14758(7)	0.10274(5)	-0.01295(5)	0.0744(3)	0.0859(4)	0.0944(4)	-0.0181(4)	-0.0163(3)	0.0462(3)
CO	0.1475(2)	0.3113(1)	-0.1975(1)	0.060(1)	0.056(1)	0.053(1)	-0.006(1)	0.0011(9)	0.0115(9)
CL	0.1442(5)	-0.0201(3)	0.1018(3)	0.115(3)	0.113(3)	0.127(3)	-0.046(3)	-0.045(3)	0.078(2)
C(P1)	0.225(2)	0.443(1)	-0.155(1)	0.082(10)	0.07(1)	0.104(13)	-0.017(9)	0.023(9)	0.005(10)
C(P2)	0.120(2)	0.456(1)	-0.225(1)	0.077(10)	0.06(1)	0.140(14)	0.001(9)	0.025(10)	0.041(10)
C(F3)	0.149(2)	0.407(1)	-0.310(1)	0.096(11)	0.11(1)	0.080(10)	-0.028(10)	-0.023(9)	0.057(9)
C(F4)	0.184(2)	0.362(1)	-0.285(1)	0.124(11)	0.09(1)	0.079(10)	-0.007(10)	0.061(8)	0.009(9)
C(P5)	0.326(1)	0.391(1)	-0.189(1)	0.051(8)	0.08(1)	0.099(10)	-0.010(8)	0.007(7)	0.042(9)
C(M1)	0.234(3)	0.489(1)	-0.051(2)	0.260(22)	0.11(1)	0.137(16)	-0.092(15)	0.077(15)	-0.050(13)
C(M2)	-0.011(2)	0.516(2)	-0.224(2)	0.097(12)	0.11(2)	0.325(29)	0.044(11)	0.078(14)	0.070(18)
C(M3)	0.663(3)	0.410(2)	-0.408(2)	0.219(24)	0.25(3)	0.104(15)	-0.063(22)	-0.067(15)	0.055(19)
C(M4)	0.365(2)	0.307(2)	-0.351(2)	0.229(18)	0.18(2)	0.152(15)	0.010(18)	0.126(12)	-0.043(16)
C(M5)	0.471(2)	0.366(2)	-0.125(2)	0.077(12)	0.19(2)	0.264(26)	-0.039(13)	-0.055(14)	0.104(19)
C(2)	-0.013(2)	0.217(1)	-0.228(1)	0.183(15)	0.10(1)	0.042(9)	-0.079(10)	-0.020(10)	0.015(8)
C(3)	-0.025(1)	0.260(1)	-0.142(1)	0.071(9)	0.10(1)	0.105(11)	0.005(9)	0.034(8)	0.046(10)
C(B2)	-0.150(2)	0.236(2)	-0.309(2)	0.191(15)	0.20(2)	0.189(18)	-0.107(14)	-0.131(12)	0.054(18)
C(B3)	-0.146(2)	0.316(2)	-0.116(2)	0.126(13)	0.12(2)	0.228(21)	0.040(13)	0.094(12)	0.050(17)
B(4)	0.120(2)	0.249(1)	-0.069(1)	0.09(1)	0.07(1)	0.08(1)	-0.01(1)	0.02(1)	0.01(1)
B(5)	0.222(2)	0.186(1)	-0.139(2)	0.12(1)	0.06(1)	0.12(2)	0.03(1)	0.03(1)	0.05(1)
B(6)	0.116(3)	0.174(2)	-0.254(3)	0.24(3)	0.10(2)	0.33(3)	0.03(2)	0.15(2)	0.09(2)
H(56)	0.19(2)	0.10(1)	-0.21(1)	3.(5)					

---

[a] THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS $EXP\left[-2\pi^2(U_{11}h^2a*^2 + U_{22}k^2b*^2 + U_{33}\ell^2c*^2 + 2U_{12}hka*b* + 2U_{13}h\ell a*c* + 2U_{23}k\ell b*c*)\right]$. For hydrogen atoms, standard isotropic B values are given.

TABLE VI. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR μ,μ'-$[C_5H_5Co(CH_3)_2C_2B_3H_4]_2Hg$ [a]

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
HG	0.0000(0)	0.0000(0)	0.0000(0)	0.0546(5)	0.0464(4)	0.0415(4)	0.0078(5)	-0.0095(4)	-0.0081(5)
CO	0.0110(2)	0.1926(2)	0.2838(2)	0.040(1)	0.035(1)	0.046(1)	0.002(1)	0.0001(8)	-0.006(1)
C(2)	0.175(2)	0.058(1)	0.315(1)	0.038(8)	0.038(8)	0.050(8)	0.007(7)	0.003(7)	-0.001(8)
C(3)	0.212(2)	0.133(1)	0.226(1)	0.036(8)	0.041(9)	0.064(9)	0.002(7)	0.007(7)	-0.008(8)
C(M2)	0.294(2)	0.045(2)	0.429(2)	0.048(10)	0.096(13)	0.060(10)	0.013(10)	-0.020(9)	0.022(10)
C(M3)	0.371(2)	0.194(2)	0.237(2)	0.050(9)	0.072(12)	0.082(11)	-0.023(10)	0.017(8)	-0.019(10)
C(P1)	0.060(2)	0.361(2)	0.341(2)	0.063(12)	0.053(11)	0.134(17)	-0.012(10)	0.015(11)	-0.035(11)
C(P2)	-0.077(2)	0.361(2)	0.263(2)	0.091(13)	0.047(10)	0.080(12)	0.028(10)	0.012(10)	-0.012(9)
C(P3)	-0.185(2)	0.288(2)	0.303(2)	0.054(11)	0.073(14)	0.150(19)	0.002(11)	0.019(12)	-0.027(14)
C(P4)	-0.172(3)	0.246(2)	0.403(2)	0.163(14)	0.066(13)	0.123(11)	-0.007(12)	0.113(9)	-0.066(11)
C(P5)	0.035(3)	0.288(2)	0.434(2)	0.166(22)	0.082(15)	0.043(10)	0.039(15)	-0.001(12)	-0.008(11)
B(4)	0.063(2)	0.153(2)	0.126(1)	0.070(12)	0.04(1)	0.030(8)	-0.005(9)	0.001(8)	-0.003(7)
B(5)	-0.094(2)	0.073(2)	0.163(2)	0.054(11)	0.04(1)	0.053(10)	-0.004(10)	-0.007(9)	-0.009(9)
B(6)	0.005(2)	0.011(2)	0.303(2)	0.046(9)	0.05(1)	0.048(9)	0.000(10)	0.003(8)	-0.010(9)
H(56)	-0.06(2)	-0.06(2)	0.18(1)	6.(5)					
H(4)	0.05(2)	0.21(1)	0.05(1)	5.(4)					
H(5)	-0.22(2)	0.05(2)	0.11(1)	6.(4)					
H(6)	-0.03(2)	-0.03(1)	0.36(1)	5.(4)					
H(P1)	0.14(2)	0.39(1)	0.34(1)	5.(4)					
H(P2)	-0.09(2)	0.39(2)	0.17(1)	6.(5)					
H(P3)	-0.31(2)	0.29(2)	0.30(2)	8.(5)					
H(P4)	-0.15(2)	0.21(2)	0.46(1)	7.(5)					
H(P5)	0.09(3)	0.26(3)	0.51(2)	9.(7)					

[a] THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS $EXP\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}h\ell a^*c^* + 2U_{23}k\ell b^*c^*)\right]$. For hydrogen atoms, standard isotropic B values are given.

Table VII. Interatomic Distances (Å)
for $[\eta^5-C_5(CH_3)_5]Co(CH_3)_2C_2B_3H_4HgCl$ (VIB)
and $[(\eta^5-C_5H_5)Co(CH_3)_2C_2B_3H_4]_2Hg$ (VIIA)

	VIB	VIIA
Hg-Cl	2.349 (3)	
Hg-Cl*	3.155 (3)	
Hg-Hg*	4.10	
Hg-B(4)	2.207(13)	2.277 (8)
Hg-B(5)	2.289(15)	2.355 (9)
Hg-H(56)	2.793	2.416
Co-C(P1)	2.059(12)	2.047 (9)
Co-C(P2)	2.080(11)	2.050 (9)
Co-C(P3)	2.068(10)	2.024(11)
Co-C(P4)	2.023(11)	2.037(10)
Co-C(P5)	2.039 (9)	2.052(10)
<Co-C(P)>	2.05	2.05
Co-C(2)	2.045(11)	2.047 (8)
Co-C(3)	2.043(10)	2.059(10)
Co-B(4)	2.093(28)	2.037 (8)
Co-B(5)	2.036(13)	2.045 (8)
Co-B(6)	2.025(13)	2.075(10)
C(2)-C(3)	1.347(16)	1.428(12)
C(3)-B(4)	1.632(17)	1.586(12)
B(4)-B(5)	1.717(20)	1.723(12)
B(5)-B(6)	1.786(37)	1.848(12)
B(6)-C(2)	1.486(25)	1.521(11)

(continued)

(Table VII continued)

C(2)-C(B2,M2)	1.652(18)	1.535(11)
C(3)-C(B3,M3)	1.494(16)	1.499(16)
B(5)-H(56)	1.531(18)	1.549 (9)
B(6)-H(56)	1.362(26)	1.629 (9)
C(P1)-C(P2)	1.332(16)	1.349(14)
C(P2)-C(P3)	1.421(17)	1.373(15)
C(P3)-C(P4)	1.455(17)	1.298(17)
C(P4)-C(P5)	1.415(16)	1.394(17)
C(P5)-C(P1)	1.346(15)	1.424(16)
<C(P)-C(P)>	1.39	1.37
C(P1)-C(M1)	1.569(18)	
C(P2)-C(M2)	1.518(16)	
C(P3)-C(M3)	1.506(18)	
C(P4)-C(M4)	1.477(17)	
C(P5)-C(M5)	1.598(16)	
<C(P)-C(M)>	1.53	

*Intermolecular interaction

Table VIII. Bond Angles (deg) for VIB and VIIA

	VIB	VIIA
B(4)-Hg-B(5)	44.9 (5)	43.6(3)
Cl-Hg-B(4)	156.0 (4)	
Cl-Hg-B(5)	157.3 (4)	
Cl-Hg-Cl*	84.9 (3)	
Cl*-Hg-B(4)	98.0 (3)	
Cl*-Hg-B(5)	103.5 (4)	
Hg-Cl-Hg*	95.1 (3)	
C(2)-Co-C(3)	38.5 (5)	40.7 (3)
C(3)-Co-B(4)	47.3 (5)	45.6 (3)
B(4)-Co-B(5)	50.0 (6)	49.9 (3)
B(5)-Co-B(6)	51.3 (9)	53.3 (4)
B(6)-Co-C(2)	41.5 (7)	43.3 (3)
C(2)-C(3)-B(4)	110.7(10)	112.5 (7)
C(3)-B(4)-B(5)	101.6(10)	106.3 (6)
B(4)-B(5)-B(6)	104.1(12)	100.6 (6)
B(5)-B(6)-C(2)	99.2(19)	102.7 (7)
B(6)-C(2)-C(3)	124.0(18)	117.9 (7)
C(3)-C(2)-C(B2,M2)	112.5(16)	120.4 (8)
B(6)-C(2)-C(B2,M2)	122.5(19)	120.9 (8)
C(2)-C(3)-C(B3,M3)	127.3(14)	121.2 (8)
B(4)-C(3)-C(B3,M3)	121.9(14)	125.8 (8)
B(5)-H(56)-B(6)	76.0(15)	71.1 (5)
Hg-B(4)-C(3)	111.3.(8)	115.9 (5)
Hg-B(4)-B(5)	70.1 (7)	70.6 (4)
Hg-B(5)-B(4)	65.1 (7)	65.8 (4)

(continued)

(Table VIII continued)

Hg-B(5)-B(6)	115.7(11)	115.3 (5)
C(P1)-C(P2)-C(P3)	109.7(11)	108.4(11)
C(P2)-C(P3)-C(P4)	105.9(95)	109.9(11)
C(P3)-C(P4)-C(P5)	104.0(11)	109.3(10)
C(P4)-C(P5)-C(P1)	110.8(10)	105.4(10)
C(P5)-C(P1)-C(P2)	109.5(12)	106.8(10)
<C(P)-C(P)-C(P)>	108	108
C(P5)-C(P1)-C(M1)	125.1(14)	
C(P2)-C(P1)-C(M1)	125.2(15)	
C(P1)-C(P2)-C(M2)	128.7(17)	
C(P3)-C(P2)-C(M2)	121.5(16)	
C(P2)-C(P3)-C(M3)	126.2(17)	
C(P4)-C(P3)-C(M3)	127.7(18)	
C(P3)-C(P4)-C(M4)	127.3(16)	
C(P5)-C(P4)-C(M4)	128.3(16)	
C(P4)-C(P5)-C(M5)	126.1(15)	
C(P1)-C(P5)-C(M5)	123.1(15)	
<C(P)-C(P)-C(M)>	126	

*Intermolecular Hg-Cl interaction

Table IX. Least squares planes for VIB and VIIA with deviations of selected atoms (Å)

$[(\eta^5\text{-}C_5(CH_3)_5)Co(CH_3)_2C_2B_3H_4]HgCl$ (VIB)

Plane 1(VIB): C(P1), C(P2), C(P3), C(P4), C(P5)

$$0.4809x + 0.8193y - 0.3123z - 6.9441 = 0$$

C(P1)	-0.0148	C(P5)	0.0208	C(M3)	0.1421
C(P2)	0.0023	Co	-1.6760	C(M4)	0.0603
C(P3)	0.0097	C(M1)	0.0239	C(M5)	0.0884
C(P4)	-0.0180	C(M2)	0.0859		

Plane 2(VIB): C(2), C(3), B(4), B(5), B(6)

$$0.3703x + 0.8678y - 0.3314z - 3.8037 = 0$$

C(2)	-0.0306	B(5)	-0.0297	Co	1.5358
C(3)	0.0054	B(6)	0.0360	C(B2)	0.1329
B(4)	0.0189	Hg	-1.9580	C(B3)	0.1241

Plane 3(VIB): Hg, B(4), B(5)

$$-0.7530x - 0.2881y - 0.5915z + 1.3967 = 0$$

Cl	-0.2730

Plane 4(VIB): Co, B(4), B(5)

$$-0.7663x - 0.4695y - 0.4386z + 2.1944 = 0$$

Hg	0.4896

Plane 5(VIB): B(5), B(6), H(56)

$$0.8420x + 0.2565y - 0.4745z - 3.5713 = 0$$

Plane 6(VIB): Co, B(5), B(6)

$$0.8750x + 0.0947y + 0.4747z - 3.2279 = 0$$

H(56)	0.1864

Plane 7(VIB): Hg, Cl, Cl*

$$0.5341x - 0.6067y - 0.5888z = 0$$

(continued)

(Table IX, continued)

$\{[\eta^5\text{-}C_5(CH_3)_5]\,Co(CH_3)_2C_2B_3H_4\}_2Hg$ (VIIA)

Plane 1(VIIA): C(P1), C(P2), C(P3), CP(4), C(P5)

$$0.4260x - 0.7830y - 0.4532z + 5.0877 = 0$$

C(P1)	0.0078	C(P3)	0.0082	C(P5)	-0.0029
C(P2)	-0.0099	C(P4)	-0.0032	Co	1.6784

Plane 2(VIIA): C(2), C(3), B(4), B(5), B(6)

$$0.3585x - 0.8022y - 0.4774z - 1.9800 = 0$$

C(2)	0.0011	B(6)	-0.0043	C(M2)	-0.2250
C(3)	0.0034	Hg	1.9800	C(M3)	-0.1504
B(4)	-0.0058	Co	-1.5174		
B(5)	0.0056	H(56)	1.1856		

Plane 3(VIIA): Hg, B(4), B(5)

$$0.5589x + 0.5828y - 0.5899z = 0$$

Plane 4(VIIA): Co, B(4), B(5)

$$-0.5802x + 0.7009y - 0.4148z - 0.4533 = 0$$

Hg	-0.4533

Plane 5(VIIA): B(5), B(6), H(56)

$$0.9556x + 0.0956y - 0.2788z + 1.5284 = 0$$

Plane 6(VIIA): Co, B(5), B(6)

$$0.9339x - 0.0801y - 0.3484z + 1.7815 = 0$$

H(56)	0.2446

Dihedral Angles (deg)

Compound VIB		Compound VIIA	
Planes	Angle	Planes	Angle
1,2	7.01	1,2	4.25
2,3	70.56	2,3	67.27
3,4	13.65	3,4	12.19
5,6	9.47	5,6	10.92
2,5	46.24	2,5	66.49
3,7	83.06		

Figure Captions

Figure 1. Reaction sequence for complexation of cobaltacarborane anions with $HgCl_2$. Product yields are given in Table I.

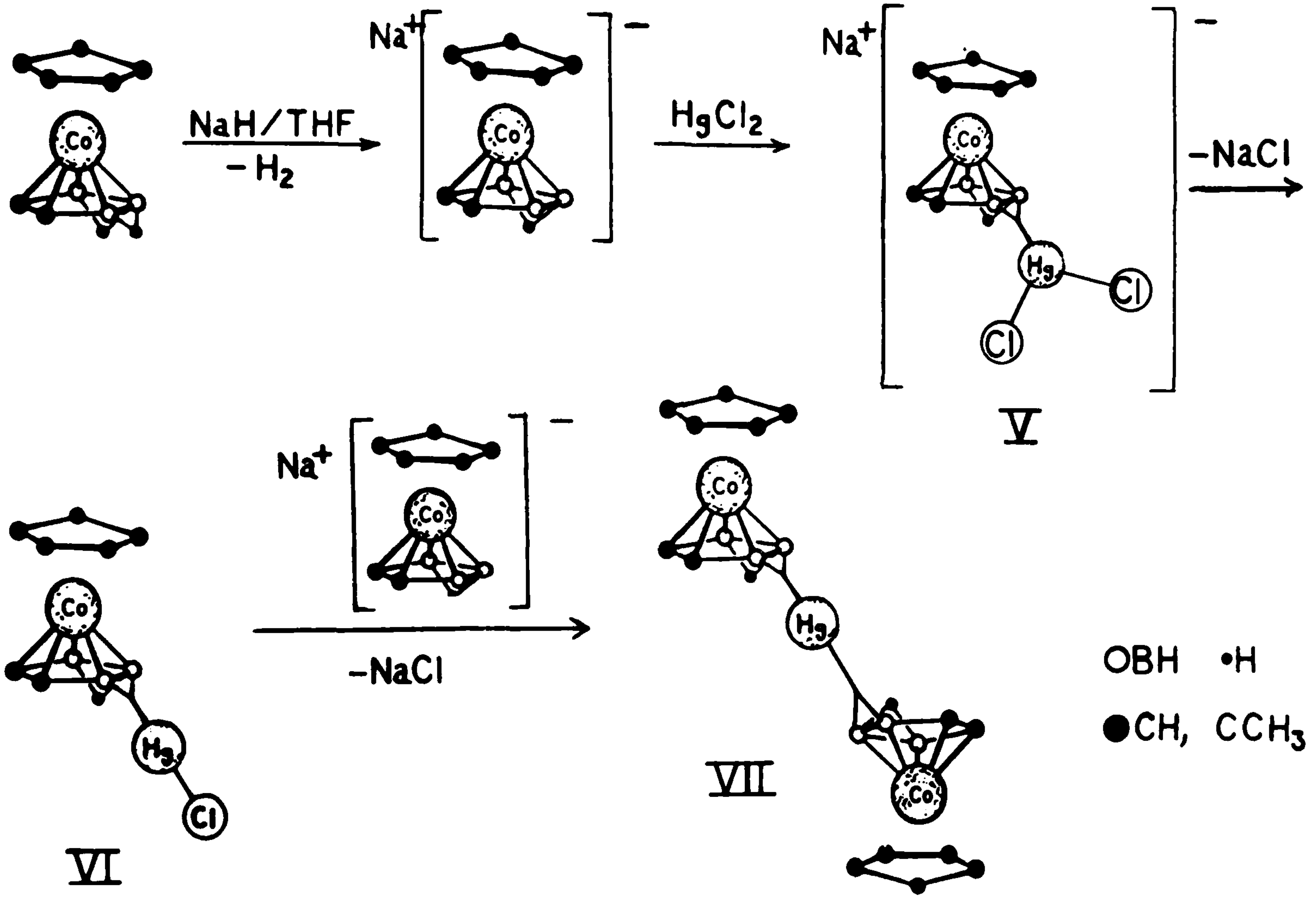
Figure 2. Stereoview of the molecular structure of VI B, with atoms shown as spheres of arbitrary radius. The weak intermolecular Hg···Cl interactions are represented by dashed lines.

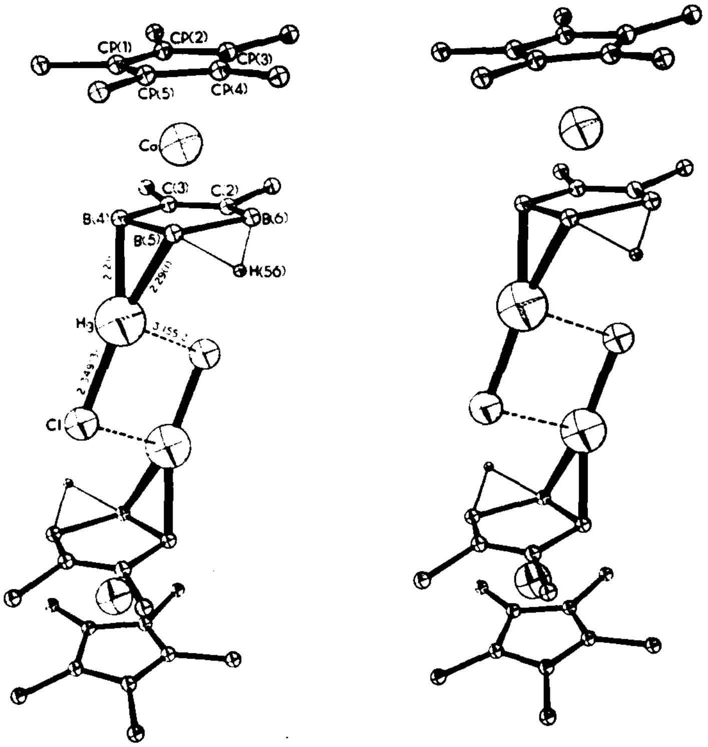
Figure 3. Stereoviewsof the molecular structure of VII A, with atoms shown as spheres of arbitrary radius.

Figure 4. Unit cell packing in VI B.

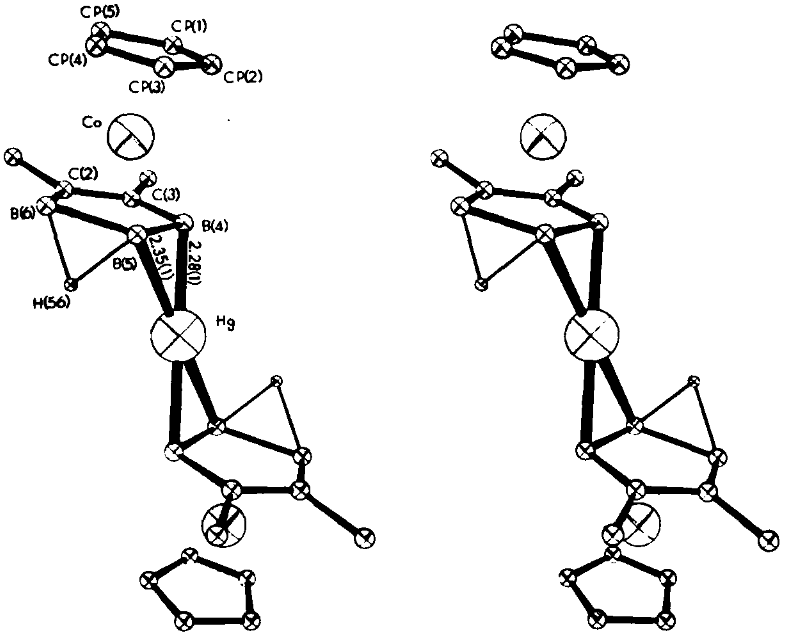
Figure 5. Unit cell packing in VII A.

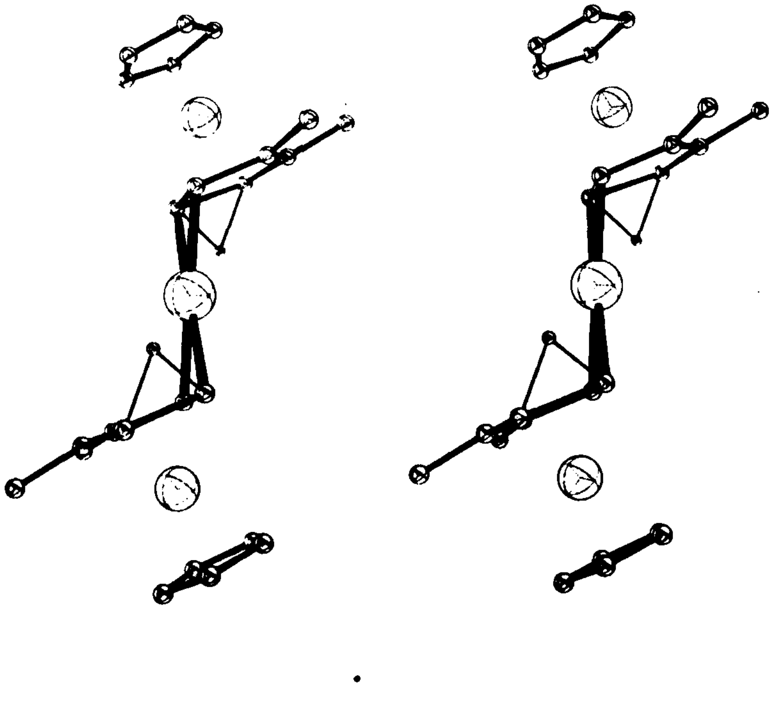
Figure 6. Displacement of the bridging hydrogen atom H(56) out of the Co-B(5)-B(6) plane in VI B and VII A.

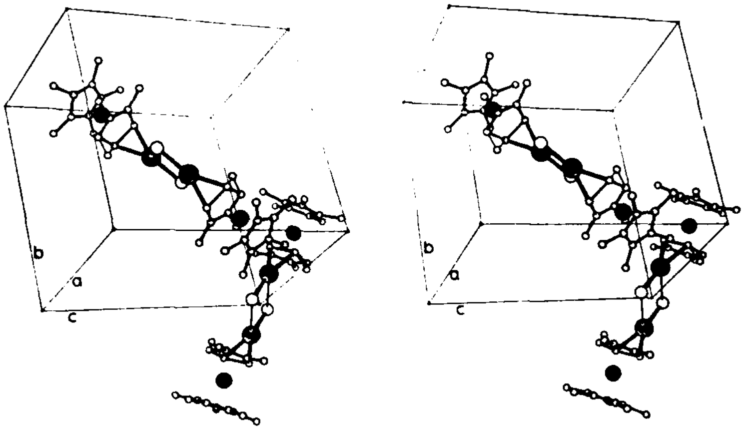

Co
NaH/THF
−H₂
Na⁺
−
HgCl₂
Hg
Cl
−NaCl
V
VI
VII
○BH •H
●CH, CCH₃

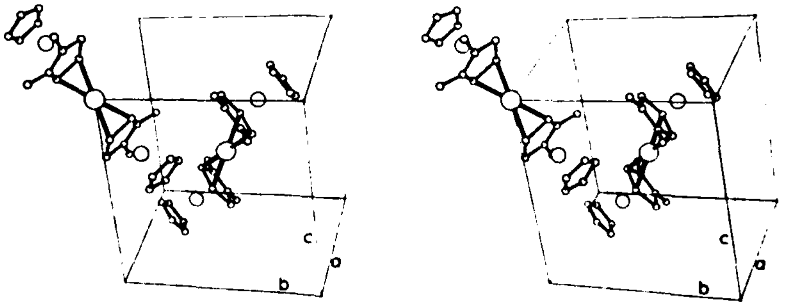

CP(1)
CP(2)
CP(3)
CP(5)
CP(4)
Co
C(3)
C(2)
B(4)
B(5)
B(6)
H(56)
2.29(1)
Hg
3.155
2.349(3)
Cl

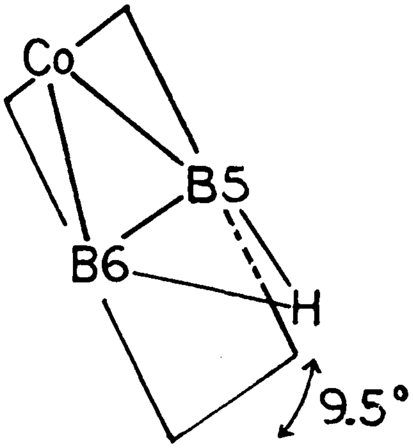
μ,μ'-$(CpCoMe_2C_2B_3H_4)_2Hg$



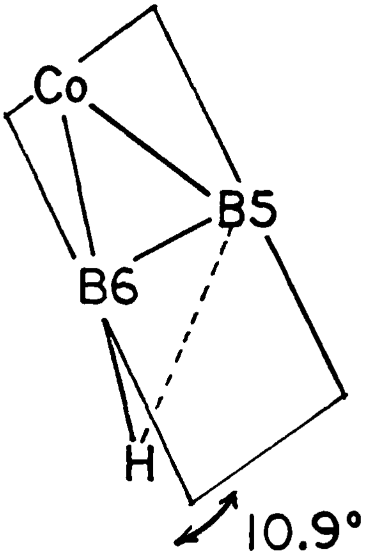



b
a
c
b
a
c


c
a
b
c
a
b



VI B



VII A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 36	2. GOVT ACCESSION NO. AD A092270	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Mercury-Bridged Cobaltacarborane Complexes Containing B-Hg-B Three-Center Bonds. Synthesis and Structure of μ,μ'-$[(C_5R_5)Co(CH_3)_2C_2B_3H_4]_2Hg$, μ-$[(C_5R_5)Co(CH_3)_2C_2B_3H_4]HgCl$ (R = H, CH_3) and Related Compounds		5. TYPE OF REPORT & PERIOD COVERED Interim 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) David C. Finster and Russell N. Grimes		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0305
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Virginia Department of Chemistry Charlottesville, Va. 22901		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-569
11. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Branch, Office of Naval Research Arlington, Va. 22217		12. REPORT DATE November, 1980 13. NUMBER OF PAGES 39
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

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

Cobaltacarborane
Mercury-bridged metallacarboranes
Boron-mercury-boron three-center bonds

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

See title page

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1
Professor M. Newcomb Texas A&M University Department of Chemistry College Station, Texas 77843	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Professor Richard Eisenberg Department of Chemistry University of Rochester Rochester, New York 14627	1

TECHNICAL REPORT DISTRIBUTION LIST, 053

No. Copies

Dr. M. F. Hawthorne
Department of Chemistry
University of California
Los Angeles, California 90024 1

Dr. D. B. Brown
Department of Chemistry
University of Vermont
Burlington, Vermont 05401 1

Dr. W. B. Fox
Chemistry Division
Naval Research Laboratory
Code 6130
Washington, D.C. 20375 1

Dr. J. Adcock
Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37916 1

Dr. A. Cowley
Department of Chemistry
University of Texas
Austin, Texas 78712 1

Dr. W. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514 1

Dr. D. Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 1

Professor Ralph Rudolph
Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48109 1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402 1

No. Copies

Professor H. Abrahamson
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019 1

Dr. M. H. Chisholm
Department of Chemistry
Indiana University
Bloomington, Indiana 47401 1

Dr. B. Foxman
Department of Chemistry
Brandeis University
Waltham, Massachusetts 02154 1

Dr. T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201 1

Dr. G. Geoffrey
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania 16802 1

Dr. J. Zuckerman
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019 1

Professor O. T. Beachley
Department of Chemistry
State University of New York
Buffalo, New York 14214 1

Professor P. S. Skell
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802 1

Professor K. M. Nicholas
Department of Chemistry
Boston College
Chestnut Hill, Massachusetts 02167 1

Professor R. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, Texas 76129 1

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503 1

DATE
FILMED

— 8