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LINKED AND MERCURY-BRIDGED NIDO-CARBORANES. HIGH-YIELD SYNTHESIS--ETC(U)

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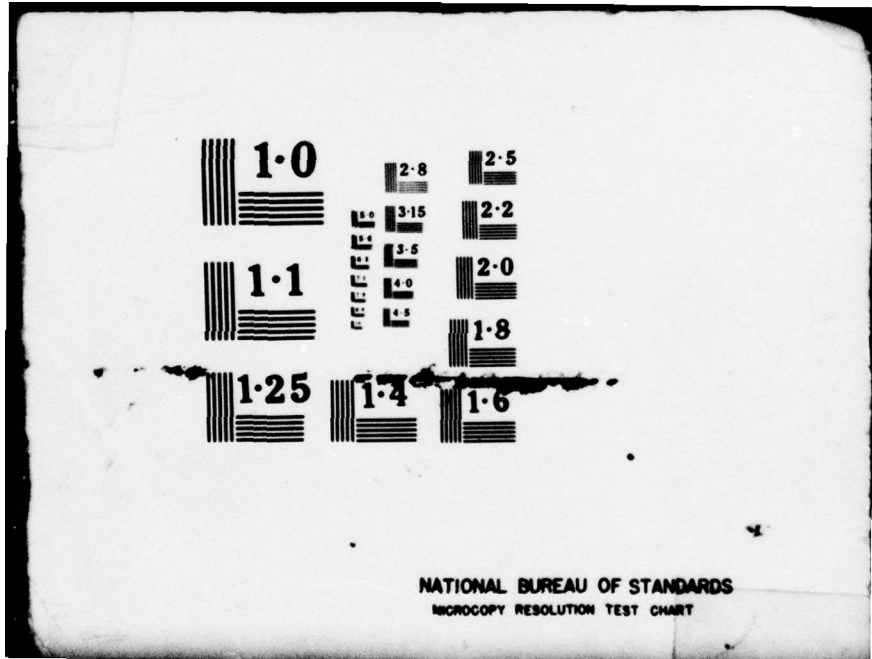
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6 Linked and Mercury-Bridged Nido-Carboranes. High-Yield Synthesis of μ, μ' - $[(CH_3)_2C_2B_4H_5]_2Hg$, Conversion to $5,5'$ - $[(CH_3)_2C_2B_4H_5]_2$, Cleavage, and Oxidative Addition of Benzene. Synthesis of μ, μ' - $(B_5H_8)_2Hg$.

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Benzene. Synthesis of μ, μ' - $(B_5H_8)_2Hg$

Narayan S. Hosmane and Russell N. Grimes*

Abstract. The nido-carborane anion $[2,3-(CH_3)_2C_2B_4H_5]^-$ reacts readily with anhydrous $HgCl_2$ in THF at room temperature, producing the bis (carboranyl) mercury(II) complex μ, μ' - $[(CH_3)_2C_2B_4H_5]_2Hg$ in which the metal is bound to two carborane ligands via B-Hg-B three-center, two-electron bridge bonds. On heating at 180° in benzene, this compound quantitatively expels free mercury and forms the B-B linked nido-carborane 5,5'- $[(CH_3)_2C_2B_4H_5]_2$ as a single pure isomer. Air oxidation of the linked carborane in benzene solution results in cleavage of the carborane-carborane B-B bond and oxidative addition of benzene to give 4- C_6H_5 -2,3- $(CH_3)_2C_2B_4H_5$, an apparently air-stable derivative of nido-2,3- $C_2B_4H_8$. Similar treatment of the linked carborane in C_6D_6 gives the corresponding hexadeuterated carborane product. The reaction of $B_5H_8^-$ ion with $HgCl_2$ in THF produces μ, μ' - $(B_5H_8)_2Hg$, a stable solid in which mercury is evidently bridge-bonded to two pentaborane ligands.

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Introduction

The small nido-carborane 2,3- $C_2B_4H_8$ and its substituted derivatives are exceedingly versatile ligands which readily form η^1 , η^2 , and η^5 complexes with metal and metalloid groups. Insertion of units such as $(CO)_3Fe$ or $(\eta^5-C_5H_5)Co^{2+}$ into the open face of the pyramidal species $R_2C_2B_4H_6$ ($R = H, CH_3$) or their anions ($R_2C_2B_4H_5^-$) yields closo-metallocarboranes in which the metal is η^5 -bonded to the carborane and completes a 7-vertex MC_2B_4 polyhedral cage system. A rather extensive chemistry has been developed in this area¹ including the oxidative fusion of face-bonded C_2B_4 ligands coordinated to the same metal ion to give tetracarbon C_4B_8 cages. In contrast, the attack of mono-coordinate units such as $(\eta^5-C_5H_5)Fe(CO)_2^+$, $[(C_6H_5)_3P]_3Rh^+$, $[(C_6H_5)_3P]Au^+$, and $R_3M_{IV}^+$ ($R = H, CH_3$; $M_{IV} = Si, Ge, Sn, Pb$) on the $R_2C_2B_4H_5^-$ ion generates bridge-substituted complexes in which the metal is η^2 -linked to the edge of the carborane cage by a three-center B-M-B bond.^{2f} In some cases these bridged species undergo thermal rearrangement to terminally (η^1)-substituted isomers.²

If an $R_2C_2B_4H_5^-$ substrate is allowed to interact with a di-coordinate metal or metalloid group, one expects to form bis-carborane complexes in which the metal participates in B-M-B three-center bonds on two different cages. The only reported example is $\mu, \mu'-SiH_2(C_2B_4H_7)_2$, prepared in this laboratory several years ago.^{2d} We are currently interested in doubly bridged complexes, in part because of their potential utility as precursors to linked nido-carboranes. These, in turn, open new

areas for exploration in metallocarborane synthesis and structure (for example, Sneddon, et al.,³ have recently obtained a mixture of $[(CH_3)_2C_2B_4H_5]_2$ isomers in the mercury-sensitized photolysis of 2,3- $(CH_3)_2C_2B_4H_6$, and from this mixture prepared a number of linked cobaltacarborane complexes). In addition, it is likely that doubly bridged metal complexes are related to intermediates in the metal-promoted oxidative fusion⁴ of $R_2C_2B_4H_4^{2-}$ ligands which generates tetra-carbon carboranes such as $R_4C_4B_8H_8$.

We report here a simple and direct route for conversion of the $(CH_3)_2C_2B_4H_5^-$ ion to neutral, boron-boron bonded 5,5'-($(CH_3)_2C_2B_4H_5^-$ $H_5B_4C_2(CH_3)_2$, via a stable, isolable mercury-linked bis(carboranyl) complex. In addition, some novel chemistry of the linked carborane is described and the closely related synthesis of $\mu, \mu'-(B_5H_8)_2Hg$ is reported.

Results and Discussion

Synthesis of $\mu, \mu'-[(CH_3)_2C_2B_4H_5]_2Hg$. The sodium salt of the 2,3- $(CH_3)_2C_2B_4H_5^-$ ion (obtained from the neutral carborane by deprotonation with NaH in tetrahydrofuran (THF)⁵) was found to react easily at room temperature (even at $-30^\circ C$) with anhydrous mercuric chloride, forming the μ, μ' -bis(carboranyl)mercury(II) complex, I, in 87% yield (Figure 1). The product I was obtained by sublimation in vacuo as a white crystalline solid, m.p. $78^\circ C$, that survives brief exposure to air and can be handled on the laboratory bench over limited periods. The compound was structurally characterized from its unit- and high-resolution mass spectra (Experimental Section), ^{11}B , 1H , and ^{13}C NMR spectra (Tables I and II), and infrared spectrum (Table III).

mass spectrum displays an intense parent grouping (cutoff at m/e 410) and strong groups with local cutoffs at m/e 307, 204, and 104 which correspond to the fragments $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]\text{Hg}^+$, Hg^+ , and $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6^+$, respectively; in each case the pattern of intensities is consistent with the composition indicated, based on natural isotope distributions of boron and mercury.

The 32.1-MHz ^{11}B NMR spectrum (Figure 2) exhibits a high field symmetric doublet corresponding to the apex B-H, and an unsymmetric doublet at lower field assigned to overlapping B(4)-H, B(5)-H, and B(6)-H resonances; the chemical shifts (Table I) correspond closely to those of 2,3- $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$ (δ -3.7, -7.2, and -47.7 ppm).⁶ The proton NMR spectrum (Table II) reveals two nonequivalent methyl environments and confirms the presence of bridging hydrogens, as shown by a broad, weak peak in the B-H-B region.

The location of mercury in a bridging, rather than a terminal position, on the cage can be inferred from the absence of a separate ^{11}B -Hg singlet in the uncoupled ^{11}B spectrum; terminal substitution on boron would be expected to produce collapse of the ^{11}B -H doublet to a singlet, and a shift with respect to the unsubstituted boron resonance. Further support for the bridged structure is found in the infrared spectrum (Table III) which contains a split B-H stretching band near 2500 cm^{-1} , a feature exhibited by all known heteroatom-bridged $\text{C}_2\text{B}_4\text{H}_8$ derivatives, but which is absent in terminally-substituted species.²

Two isomeric arrangements are possible in I, one having C_s symmetry and the other C_2 . The NMR spectra give no indication of the presence of more than one isomer (which is not surprising since one

would expect any differences in chemical shifts to be minute) and it is not possible to distinguish between the C_s and C_2 structures from available data. Indeed, it is probable that both isomers form in the reaction, since with the presumed linear (sp) hybridization of mercury the stereochemical preference for one arrangement over the other would be small. This problem is reminiscent of the question of structure in $\mu, \mu'-(C_2B_4H_7)_2SiH_2$ as discussed several years ago.^{2d} In the silicon system, there was some indication, based on 1H -Si NMR resonances, that the formation of the C_s isomer was favored (though both the C_s and the C_2 isomers form) in the reaction of $C_2B_4H_7^-$ ion with SiH_2Cl_2 . Evidently the tetrahedral hybridization on silicon, and the presence of silyl hydrogens, produce significant steric interaction between the carborane ligands and thereby lead to inequality in the amounts of the two isomers formed. This is unlikely to be the case in I.

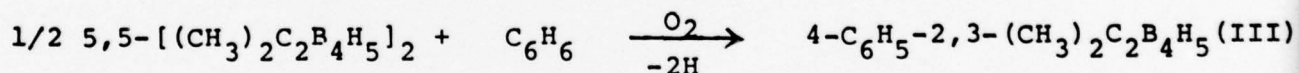
Compound I is the first confirmed example of a μ -carboranyl mercury complex, although we have reported the preparation of $\mu-(C_6H_5Hg)-C_2B_4H_7$ as a partially characterized species which decomposed in air to release elemental mercury.^{2f} Several mercury complexes of the $B_{10}H_{12}^{2-}$ ligand are known in which the metal is coordinated to one or two of the decaborane units; the mercury-borane linkages are probably η^4 , but bridged (η^2) structures have not been eliminated.⁷ A number of σ -carboranyl mercury complexes are known, all of them derived from the icosahedral 1,2-, 1,7-, or 1,12- $C_2B_{10}H_{12}$ carboranes.⁸ Most of these species involve Hg-C links, although a few examples of mercury substitution at boron in $C_2B_{10}H_{12}$ species have been reported.^{8b-d}

Synthesis of 5,5'-[(CH₃)₂C₂B₄H₅]₂. The mercury-bridged complex I at 180° in benzene expels mercury as the free metal and forms the biscarborane 5,5'-[(CH₃)₂C₂B₄H₅]₂ (II) in 91% yield (Figure 1). In addition to bulk experiments conducted on a 1-2 gram scale, this conversion was monitored via proton NMR over an 18-hr period, and was observed to occur cleanly and quantitatively with no indications of the presence of intermediate species. Moreover, only one isomer (II) is formed insofar as can be detected.

The product II is a colorless liquid that can be distilled in vacuo at 70°. The ¹¹B, ¹H, and ¹³C NMR spectra indicate high (C_{2v}) symmetry with only one C-CH₃ environment and two boron signals in a 3:1 area ratio. The area-3 ¹¹B resonance (Figure 3) consists of a doublet of doublets arising from the equivalent B(4,6)-H groups in each cage, superimposed on the B(5)-B(5') singlet. The secondary splitting of the large doublet is due to coupling between the terminal protons on B(4,6) and B(4',6') and adjacent B-H-B bridging protons. The presence of the B(5)-B(5') singlet can be deduced from the slight asymmetry of the superimposed doublet and of the proton-decoupled (collapsed) peak in Figure 3B. Although equivalence of the four methyl groups could be produced by linkage either at B(5)-B(5') or at B(1)-B(1'), the latter possibility is eliminated by the fact that the apical boron resonance (which characteristically appears at high field in pyramidal boranes and carboranes⁹) is a doublet, showing that the apex borons retain their terminal hydrogens. In addition, of course, B(5)-B(5') linkage is much more easily reconciled with the synthesis from the bridged complex. The conversion of I to II with elimination of mercury is reminiscent of the formation of (CH₃)₃Si-SiH₃ from (CH₃)₃Si-Hg-SiH₃ at room temperature.¹⁰

Compound II is the first pure isomer of a small linked nido-carborane to be isolated, although as mentioned above a mixture of $[(CH_3)_2C_2B_4H_5]_2$ isomers has been obtained by photolysis of $(CH_3)_2C_2B_4H_6$ in the presence of mercury. The only other example of a bis (nido-carborane) system to our knowledge is $(1,2-C_2B_9H_{11})_2$, which consists of linked icosahedral-fragment moieties and was produced by oxidative coupling of $C_2B_9H_{12}^-$ anions with K_2CrO_4 .¹¹

Cleavage of 5,5'- $[(CH_3)_2C_2B_4H_5]_2$ and Oxidative Addition of Benzene. The linked carborane (II) is exceedingly air-sensitive, and in the absence of solvent reacts instantly with atmospheric oxygen at room temperature to produce a nonvolatile white solid that is insoluble in organic solvents. However, exposure to air of a solution of II in benzene gave remarkably different results, rapidly generating the 4-phenyl derivative of the monomeric carborane in nearly quantitative yield (Figure 4).



The oxygenated product may be water, although this was not established.

Structural characterization of III, a colorless oil, was straightforward (Tables I-III); phenyl substitution obviously occurs at B(4), since the ¹¹B NMR (Figure 5) and proton NMR indicate low symmetry. When this reaction was conducted in benzene-d₆, the mass spectrum of the product indicated a hexadeuterated species corresponding to $C_6D_5\text{-}(CH_3)_2C_2B_4H_4D$, indicating that all six hydrogens of benzene are retained in the product. Thus we formulate the reaction as an oxidative

addition of benzene to $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5-\text{H}_5\text{B}_4\text{C}_2(\text{CH}_3)_2$ with concomitant cleavage of the central B-B link. As shown, one hydrogen from benzene is proposed to enter a bridging position, replacing a bridge hydrogen which moves to a terminal location on B(5). The phenyl dimethyl carborane, III, appears to be reasonably air-stable and does not decompose noticeably on handling in air over periods of a few hours. This property, combined with its low volatility and ready availability via the sequence described here, makes III a good candidate for extensive bench chemistry including the synthesis of metallocarborane derivatives.

As a control experiment, a solution of II in cyclohexane was exposed to the atmosphere and was found to undergo only slow decomposition to insoluble white solids; in contrast to the oxidation in benzene, no substituted carboranes were detected.

Synthesis of μ, μ' - $(\text{B}_5\text{H}_8)_2\text{Hg}$ (IV). The ease with which the bis(carboranyl)mercury complex I forms from $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ and HgCl_2 , led us to examine the analogous reaction of the B_5H_8^- ion. The -30°C addition of HgCl_2 to a THF solution of NaB_5H_8 gave white, crystalline, sublimable μ, μ' - $[\text{B}_5\text{H}_8]_2\text{Hg}$ in nearly quantitative yield. The mass spectrum exhibits strong groupings with local cutoffs at m/e 330 (parent peak), 267, and 204, corresponding to $(\text{B}_5\text{H}_8)_2\text{Hg}^+$, $(\text{B}_5\text{H}_8)\text{Hg}^+$, and Hg^+ , respectively. The ^{11}B NMR spectrum (Figure 6) contains an apex B-H doublet which collapses to a singlet on proton decoupling, indicating that mercury attachment to the boron cage occurs at a basal, not apical position; moreover, the presence of only one apex B-H resonance implies a symmetrical structure in which both B_5H_8

ligands are bound to the metal in identical fashion. The only such arrangements are μ, μ' - and $2, 2'$ - $(B_5H_8)_2Hg$, and from NMR data the μ, μ' -structure can be assigned. The near-superposition of the ^{11}B resonances of the basal boron atoms is more consistent with bridge than terminal substitution; 32-MHz ^{11}B spectra of 2-metallated B_5H_9 derivatives usually exhibit clear nonequivalence of the basal borons.¹² The ^{11}B -decoupled 1H spectrum has superimposed basal $H_{terminal}$ peaks, but the base-apex-bridge area ratio of 4:1:3 conforms with the bridged structure, as does the observation of strong ^{199}Hg - $^1H_{terminal}$ coupling (Table II).

A number of bridged pentaborane complexes have been reported by Gaines and coworkers,^{12a,c} notably the μ - $(R_3M)B_5H_8$ series in which M is Si, Ge, Sn, or Pb and R is H or alkyl. The compound $[C_6H_5)_3P]_2CuB_5H_8$, prepared by Brice and Shore,¹³ has been shown to have a B-Cu-B bridge, as confirmed in an X-ray diffraction study.¹⁴ Several bis(pentaboranyl) species of the type $(B_5H_8)_2MRR'$ [M = Si, Ge; R = H, CH_3] are also known,^{12c} and these have been assigned $\mu, 2'$ or $2, 2'$ structures. However, bis(pentaboranyl) complexes of the μ, μ' type have not, to our knowledge, been described prior to this work, nor have mercury-substituted pentaborane derivatives of any structural class been reported previously.

The possibility that IV may serve as an efficient precursor to a linked $(B_5H_8)_2$ species (whose three possible isomers have been obtained by other methods¹⁵), was not extensively studied, but pyrolysis of IV at 70° for 20 hr gave B_5H_9 , a small quantity of $(B_5H_8)_2$ (detected mass spectroscopically), elemental mercury, and nonvolatile solids.

Summary

The development of a simple high-yield route to linked nido-carboranes is of practical significance, since the linked compounds can serve as precursors to a variety of novel heterocarboranes, metallocarboranes, and tetracarbon carboranes. Indeed, this was the main rationale for initiation of this work. However, the unexpected observation of oxidative addition of benzene to the linked carborane opens up additional synthetic possibilities, particularly if such reactions prove to be general. We know of no precedent for oxidative addition of arenes to carboranes, and it is tempting to speculate that this process initially involves oxygen-promoted homolytic cleavage of the biscarborane to generate $(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5\cdot$ radicals which in turn combine with the solvent. Studies of the oxidation of $5,5'-[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2$ and similar linked carboranes in other solvents will be required to test this point.

Experimental Section

Materials. 2,3-dimethyl-2,3-nido-dicarba-hexaborane (8), $2,3-(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$, was prepared by reaction of 2-butyne with penta-borane (9) in the presence of triethylamine as described elsewhere.¹⁶ All other reagents were commercially obtained and used as received.

Spectra. Boron-11 and proton pulse Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were recorded on a JEOL PS-100P spectrometer interfaced to a JEOL-Texas Instruments EC-100 computer system. Unit-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer, while high-resolution mass measurements were conducted on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high-resolution spectra were recorded under chemical ionizing conditions in methane or argon-water. Infrared spectra were obtained on a Beckman IR-8 instrument.

Preparation of $[2,3-(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2\text{Hg}$ (I). $\text{Na}^+(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5^-$ (prepared by reaction of 5.94 mmol of $2,3-(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_6$ with excess sodium hydride in THF as described previously⁵) was dissolved in 30 ml of dry THF and 3.00 mmol of anhydrous HgCl_2 was added on the vacuum line. After stirring the mixture for 4 hr at 25°C, during which a white precipitate formed, 30 ml hexane was added under a dry N_2 atmosphere. The solution was filtered through sintered glass and the solvent was removed by vacuum distillation. The residue was heated at 70°C in a sublimator under vacuum, and white crystalline I condensed on the cold finger which was maintained at -78°C. The yield of I was 1.050 g (2.58 mmol, 87% based on starting carborane). Exact mass measurement: calcd. for $^{202}\text{Hg}^{12}\text{C}_8^{11}\text{B}_8^1\text{H}_{22}^+$ 408.2172, found 480.2176.
¹³C NMR in C_6D_6 : sharp CH_3 peaks of equal area at δ 18.0 and 19.2 ppm rel. to TMS.

Conversion of I to [2,3-(CH₃)₂C₂B₄H₅]₂ (II). A 1.31-g sample (3.21 mmol) of [(CH₃)₂C₂B₄H₅]₂Hg was placed under N₂ in a 30-ml Pyrex ampoule fitted with a break-seal, 5 ml of dry benzene was added, the contents were frozen in liquid nitrogen, and the ampoule was sealed under vacuum. The mixture was heated at 180° for 18 hr, during which the originally colorless solution acquired a pale brown color and mercury globules collected at the bottom. During this period a parallel experiment was conducted on a smaller sample in a sealed Pyrex 5 mm NMR tube which was heated at 180° for 18 hr with periodic monitoring of the 100-MHz ¹H NMR spectrum; in this way it was ascertained that the reaction reached completion with complete disappearance of the original spectrum.

The ampoule was opened under vacuum, filtered under vacuum into a 50 ml flask, and the mercury which remained on the filter was washed with hexane, dried, and weighed; the yield was 0.66 g (3.26 mmol), corresponding to slightly greater than theoretical yield. The filtrate was stripped of solvent and the liquid residue was distilled at 70° under vacuum into a trap cooled to 0°C, to give 0.60 g (2.91 mmol, 91% yield) of colorless liquid 5,5'-[2,3-(CH₃)₂C₂B₄H₅]₂ (II). Exact mass: calcd for ¹²C₈¹¹B₈¹H₂₂ + 206.2466, found 206.2477.

¹³C NMR in C₆D₆: sharp CH₃ peak at δ 21.0 ppm rel. to TMS.

Oxidation of [2,3-(CH₃)₂C₂B₄H₅]₂ in Benzene. A 100-mg (0.48 mmol) sample of 5,5'-[2,3-(CH₃)₂C₂B₄H₅]₂ (II) was dissolved in 5.0 ml of dry benzene and this solution was shaken in air for 5 min, during which a small amount of white precipitate formed. The solution was filtered in air and the solvent was removed by distillation in vacuum at 25°, which was continued for 2 hr to remove the last traces of volatiles.

The residue consisted of colorless, viscous 4-C₆H₅-2,3-(CH₃)₂C₂B₄H₅ (III) which was purified by distillation at 78 °C into a U-trap at 0 °C;

yield 0.163 g (0.905 mmol, 94 %). Exact mass: calcd for

¹²C₁₀ ¹¹B₄ ¹H₁₇⁺ (protonated parent ion) 181.1703, found 181.1712.

Synthesis of μ,μ' -(B₅H₈)₂Hg (IV). A THF solution of Na⁺B₅H₈⁻ was prepared from 0.648 g (10.1 mmol) of B₅H₉ and 0.553 g (23.0 mmol) NaH in 50 ml THF, and filtered in vacuo onto 1.32 g (4.82 mmol) of anhydrous HgCl₂ in a 250-mL round-bottom flask cooled to -78 °C. The solution was warmed to -30 °C and stirred for 2 hr with little or no evolution of gas. After distillation of solvent out of the mixture at -30 °C over a 2-hr period a gray residue remained. To this residue 50 mL of dry hexane was added, the solution was filtered in vacuo, solvent was returned to the flask containing the reaction residue, and the solution was filtered again. This process was repeated several times in order to extract most of the (B₅H₈)₂Hg, which is not highly soluble in hexane or other organic solvents. Evaporation of the solvent followed by sublimation of the product at 100 ° for 8 hr gave 1.67 g (5.08 mmol, 90% yield) of pure white crystalline (B₅H₈)₂Hg, mp. 161-162 ° (sealed capillary). The compound is moderately air-stable, surviving exposure of several hr in the solid state without noticeable decomposition.

Pyrolysis of IV.A 0.656 g (2.0 mmol) sample of IV was placed in an evacuated Pyrex tube and heated for 20 h at 70 °C, after which the volatile products were fractionated through traps at -63 and -196 °C. The -196 ° fraction was nearly pure B₅H₉ (ir and mass spectra), 2.68 mmol. The -63 ° condensate was shown by mass spectroscopic analysis to consist of B₅H₉ and a small quantity of (B₅H₈)₂, isomer not identified.

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Table I. 32.1-MHz ^{11}B FT NMR Data

Compound	Solvent	δ , ppm ^a (J, Hz)	Relative areas
μ, μ' -[(CH ₃) ₂ C ₂ B ₄ H ₅] ₂ Hg (I)	CDCl ₃	-4.0(117) -47.7(181)	3 1
5,5'-[(CH ₃) ₂ C ₂ B ₄ H ₅] ₂ (II)	C ₆ D ₆	-3.33(151) ^b , (44) ^c -46.25(166)	3 ^d 1
4-C ₆ H ₅ -2,3-(CH ₃) ₂ -2,3-C ₂ B ₄ H ₅ (III)	CDCl ₃	+5.89 ^e , -2.18(\sim 180) ^f , -4.92(180) ^f , -44.8(176)	1,1,1,1
μ, μ' -(B ₅ H ₈) ₂ Hg (IV)	C ₆ D ₆	[-7.92, -9.60] ^g , -43.85(176)	3 1

^aChemical shifts relative to BF₃·O(C₂H₅)₂ with positive sign denoting down-field shift. ^bPrimary splitting (151 Hz) assigned to H_{terminal} (4,6)- ^{11}B coupling. ^cSecondary splitting (44 Hz) assigned to H_{bridge}- ^{11}B coupling. ^dArea-3 peak consists of superimposed resonances arising from B(4,6) and B(5). ^eSinglet arising from ^{11}B (4)-C₆H₅. ^fHeavily overlapped doublets which collapse to singlets in the ^1H -decoupled spectrum. ^gNearly superimposed resonances (apparent doublets) which collapse to overlapping singlets in the ^1H -decoupled spectrum.

Table II. 100-MHz ^1H FT NMR Data (C_6D_6 Solution)

Compound	δ , ppm (rel area) ^a	Assignment
μ, μ' - $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2\text{Hg}$ (I)	1.90(1) ^b , 1.94(1) ^b $\sim -2.3^c$	CH_3 , CH_3 B-H-B
$5, 5'$ - $[(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5]_2$ (II)	1.80(6) 3.37 ^d (~ 2) -0.70^e (~ 1) $\sim -2.0^c$	CH_3 H_t (base) H_t (apex) B-H-B
$4\text{-C}_6\text{H}_5\text{-}2, 3\text{-}(\text{CH}_3)_2\text{C}_2\text{B}_4\text{H}_5$ (III)	2.10(1), 2.00(1) 4.90 ^f -0.60^g -1.70^c 7.25 ^h	CH_3 , CH_3 H_t (base) H_t (apex) B-H-B C_6H_5
μ, μ' - $(\text{B}_5\text{H}_8)_2\text{Hg}$ (IV)	2.39(4) ^{j,k} $-1.82(1)^{j,m}$ $-2.90(3)^{j,m,n}$	H_t (base) H_t (apex) B-H-B

^aChemical shifts relative to $(\text{CH}_3)_4\text{Si}$ with positive sign indicating downfield shift. ^bSatellites due to $^{199}\text{Hg}\text{-}^1\text{H}$ coupling ($J = 39$ Hz) are visible near the methyl resonances; these peaks are unaffected by sample spinning, and disappear on conversion of I to II.

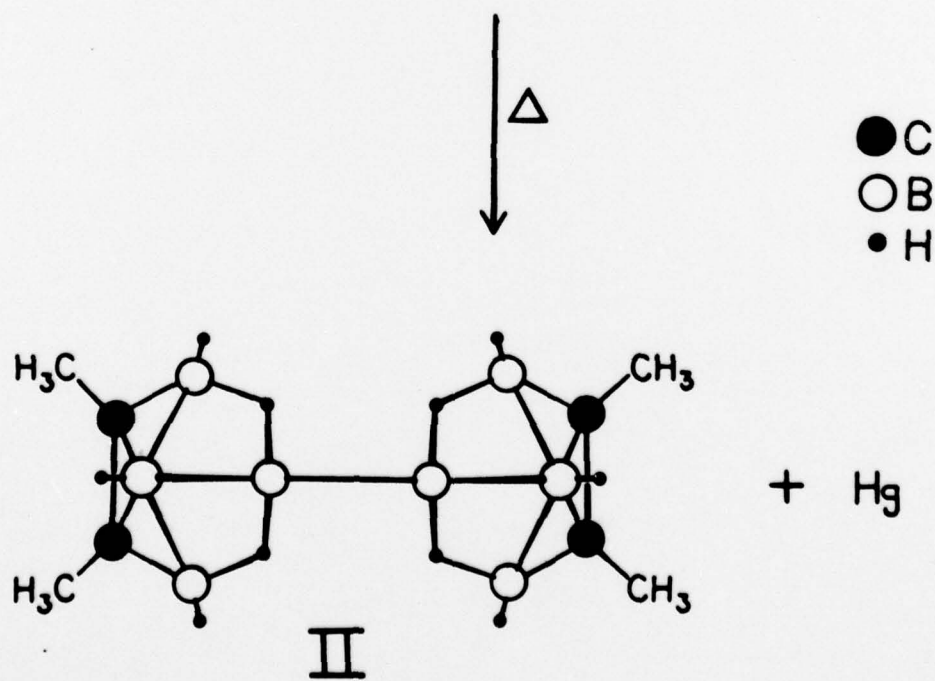
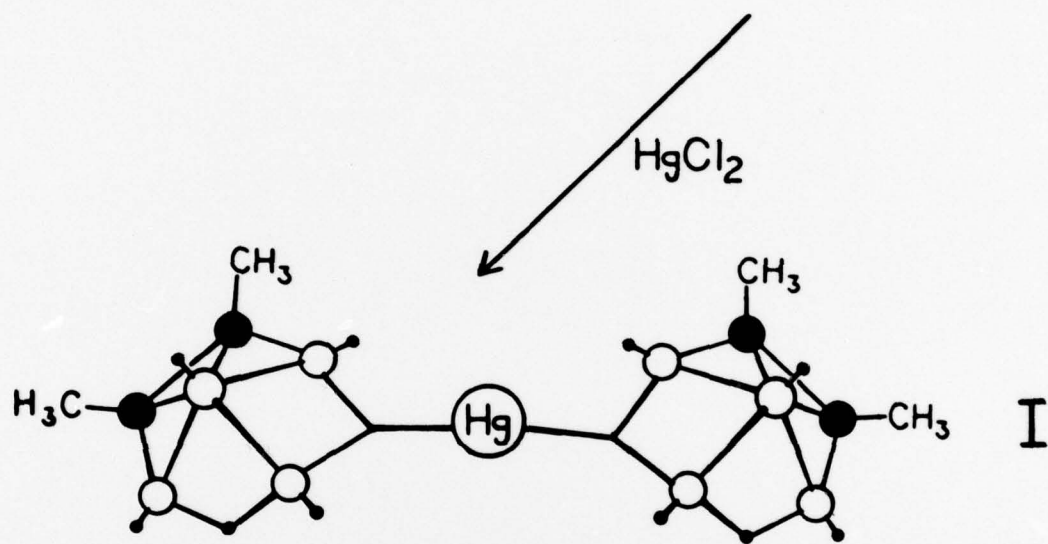
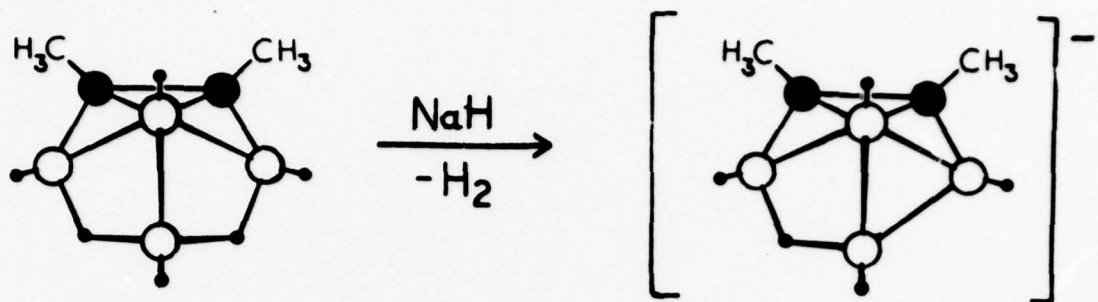
^cBroad peak, area not measurable. ^dQuartet, $J = 158$ Hz. ^eQuartet, $J = 180$ Hz. ^fQuartet, $J = 165$ Hz. ^gQuartet, $J = 180$ Hz. ^hMultiplet. ^jSinglet observed on ^{11}B -decoupling. ^kSatellites due to $^{199}\text{Hg}\text{-}^1\text{H}$ (base) coupling are observed with $J = 141$ Hz. ^mLine-narrowing produced fine structure due to H-H coupling with $J \approx 10$ Hz. ⁿSatellites due to $^{199}\text{Hg}\text{-}^1\text{H}$ (bridge) coupling are observed with $J = 96$ Hz.

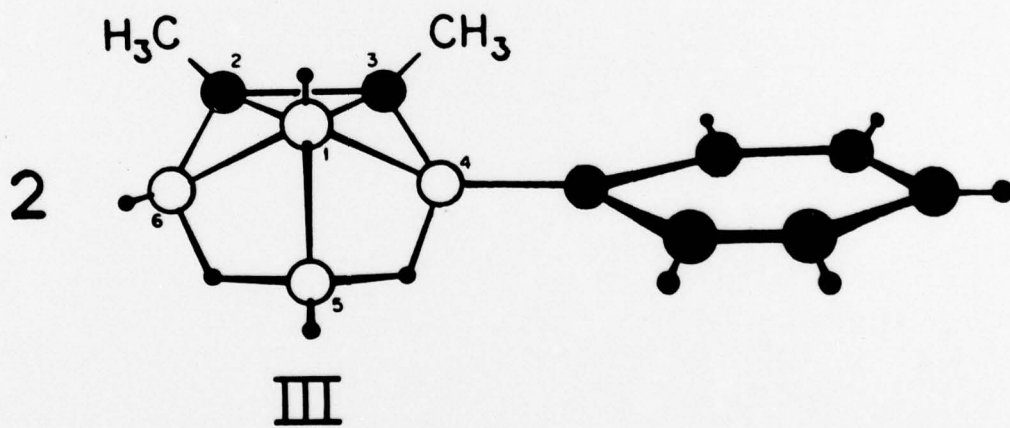
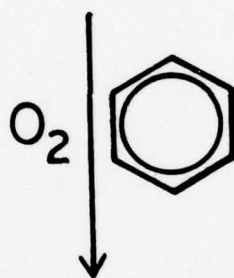
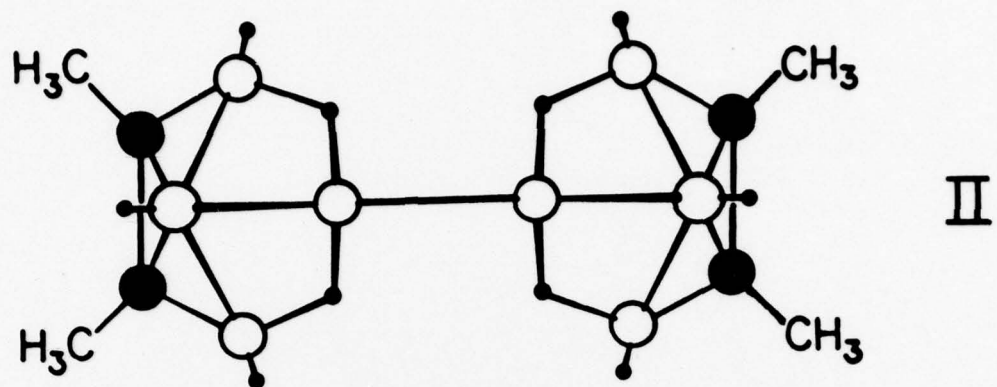
Table III. Infrared Absorptions, cm^{-1} (CCl_4 vs. CCl_4).

I	2970 m, 2942 m, 2915 s, 2855 s, 2570 vs, br, 2490 s, 1900 m,br, 1810 m, 1540 sh, 1495 s, 1435 s, 1365 s, 1330 sh, 1250 m, 1210 w, 1150 s, 1090 m, 1000 sh, 985 s, 960 s, 910 m, 895 w, 860 s, 800 s, v br, 720 s, 675 s, 625 s.
II	3070 m, 3050 m, 3000 w, 2980 sh, 2950 vs, 2920 vs, 2860 s, 2580 vs, 1930 m,br, 1885 m,br, 1435 vs,br, 1370 m, 1320 m,br, 1250 m,br, 1200 m, 110 m, 1060 m, 995 m, 933 m, 695 vs, 650 m.
III	3070 m, 3050 m, 2930 vs,br, 2860 sh, 2590 vs, 1930 m,br, 1890 m,br, 1410 vs, v br, 1330 vs,v br, 1205 m,br, 1110 w, 1055 s, 1000 w, 960 w, 935 w, 697 s, 650 s.
IV	2600 s, 2550 m, 1805 m,br, 1600 w, v br, 1455 s, v br, 1375 m, br, 1190 s, 1000 w, 930 m, 880 m, 715 m, br.

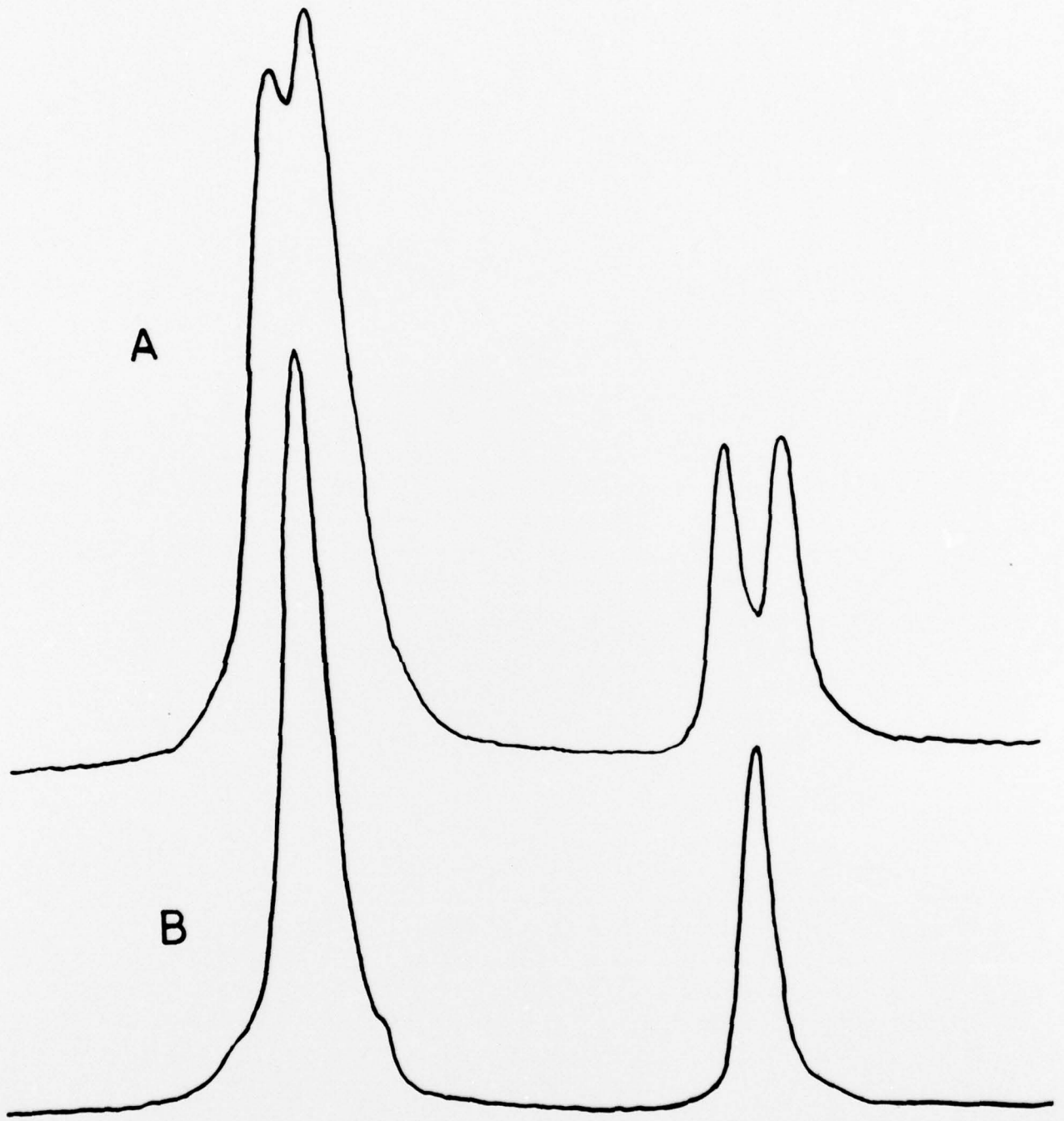
Figure Captions

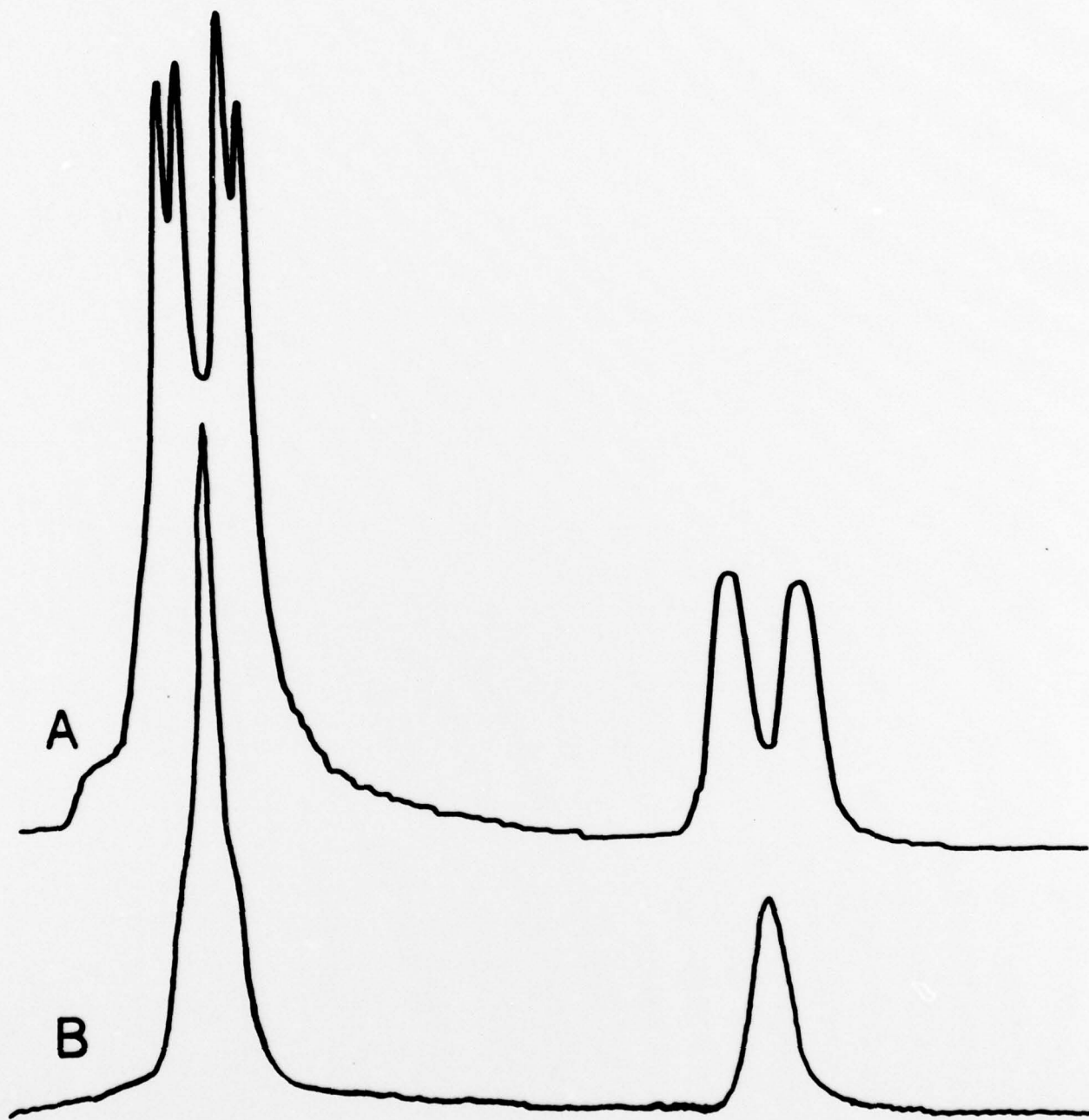
- Figure 1. Scheme for the formation of μ, μ' - $[(CH_3)_2C_2B_4H_5]_2Hg$ (I) and its thermal conversion to $5,5'$ - $[(CH_3)_2C_2B_4H_5]_2$ (II). Only the isomer of I having C_s symmetry is shown; the product is presumably a mixture of the C_s and C_2 isomers. In both isomers, free rotation of carboranyl groups around the Hg-B₂ axis is assumed.
- Figure 2. 32.1-MHz ^{11}B FT NMR spectra of μ, μ' - $[(CH_3)_2C_2B_4H_5]_2Hg$ (I) in $CDCl_3$. A, uncoupled; B, proton-decoupled at 99.998404 Hz. Chemical shifts and coupling constants are reported in Table I.
- Figure 3. 32.1-MHz ^{11}B FT NMR spectra of $5,5'$ - $[(CH_3)_2C_2B_4H_5]_2$ (II) in C_6D_6 . A, uncoupled; B, proton-decoupled.
- Figure 4. Scheme showing the oxidative addition of benzene to II to give $4-C_6H_5-2,3-(CH_3)_2C_2B_4H_5$ (III).
- Figure 5. 32.1-MHz ^{11}B FT NMR spectra of $4-C_6H_5-2,3-(CH_3)_2C_2B_4H_5$ (III). A, uncoupled; B, proton-decoupled.
- Figure 6. Proposed structure and ^{11}B FT NMR spectra of μ, μ' - $(B_5H_8)_2Hg$. A, uncoupled; B, proton-decoupled.

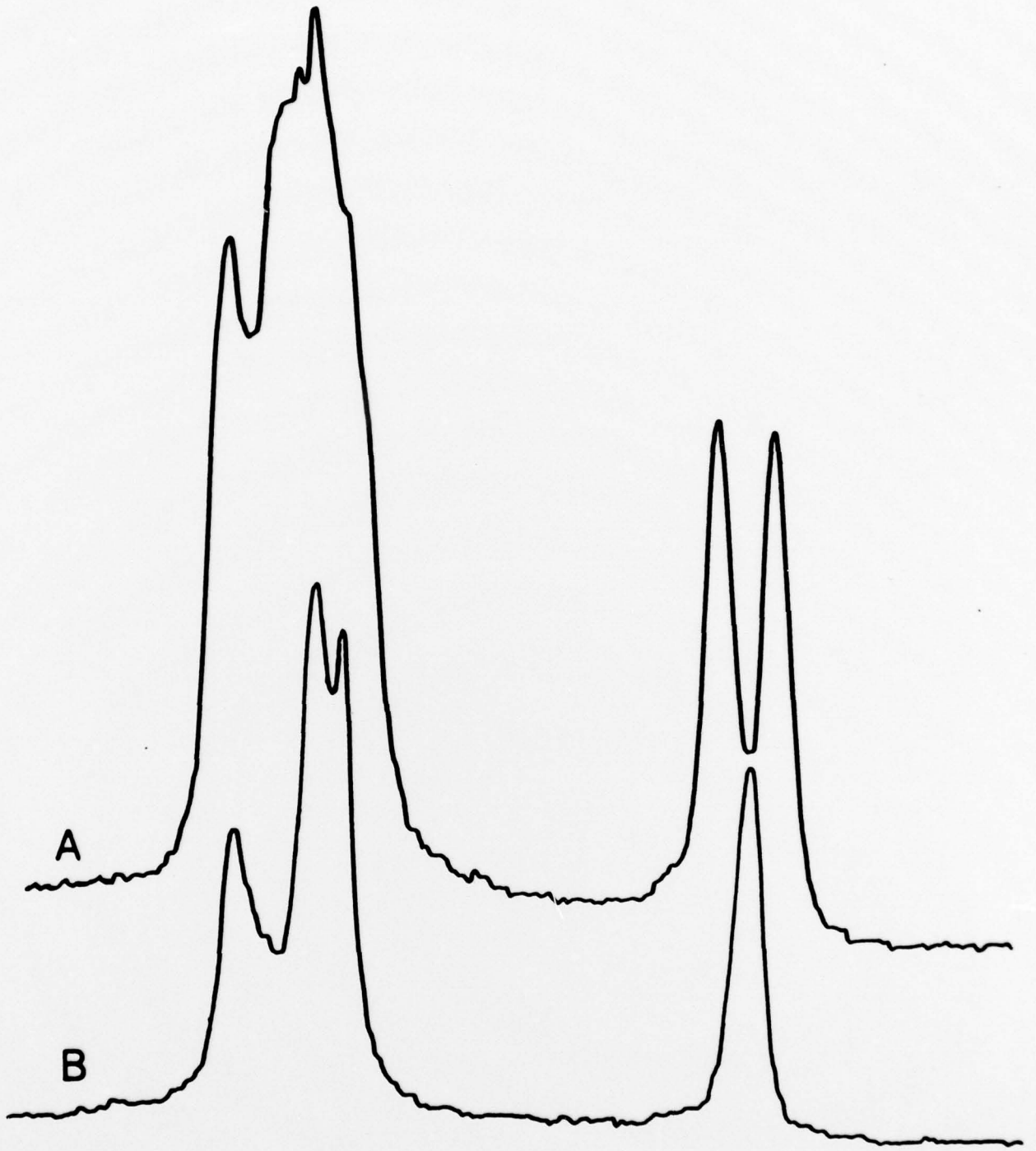


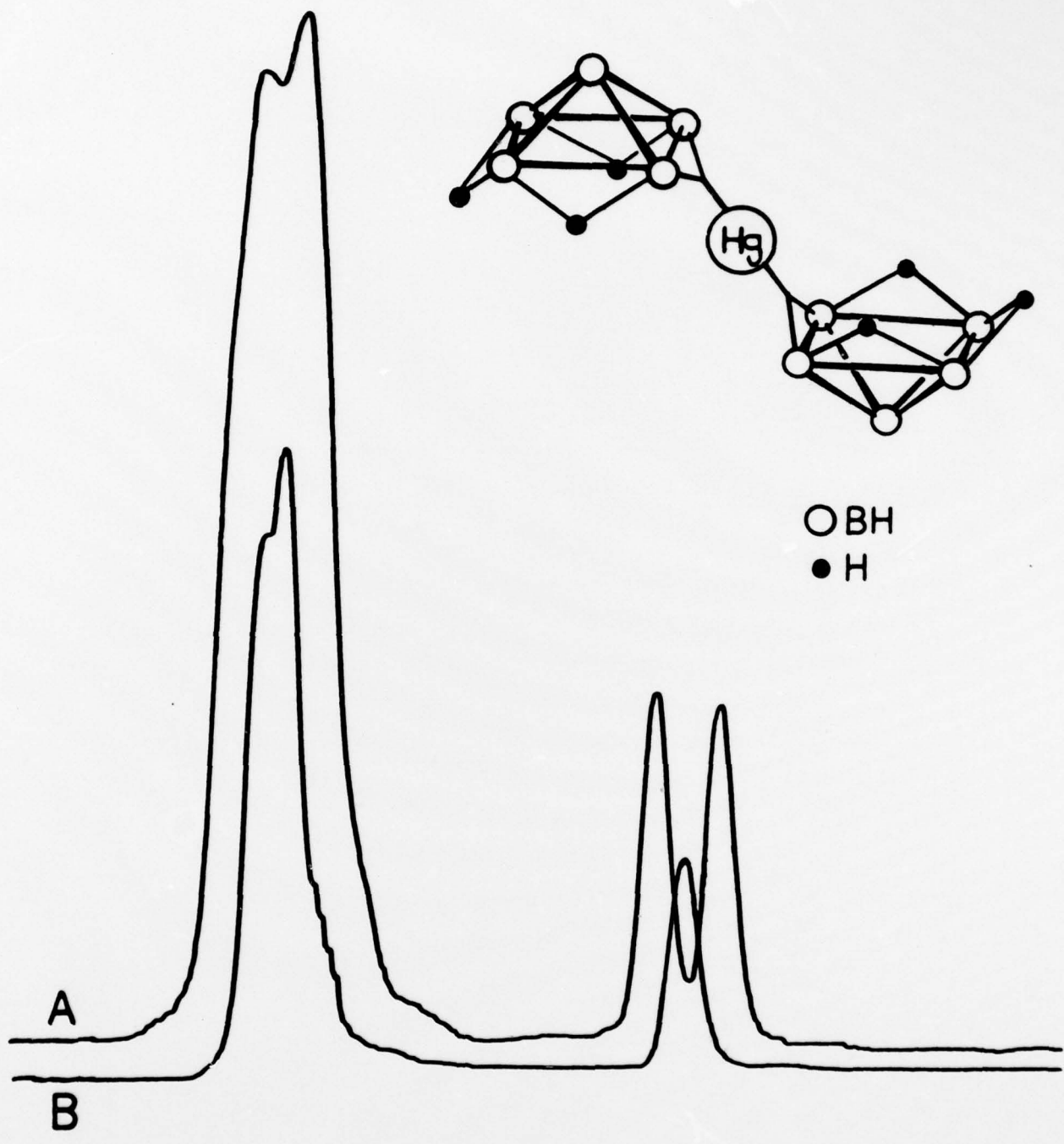


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