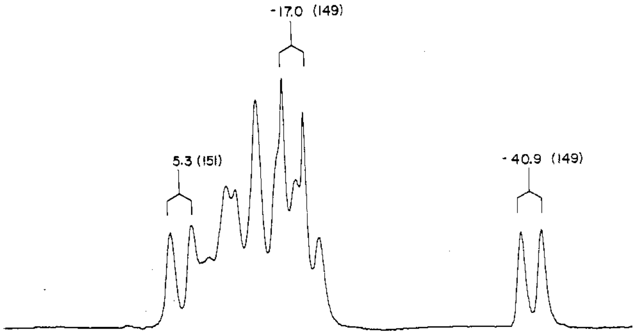

Figure 4. 70.6-MHz ^{11}B NMR spectrum of $SeB_9H_9C{\cdot}N(CH_3)_3$ (solvent = CH_3CN).

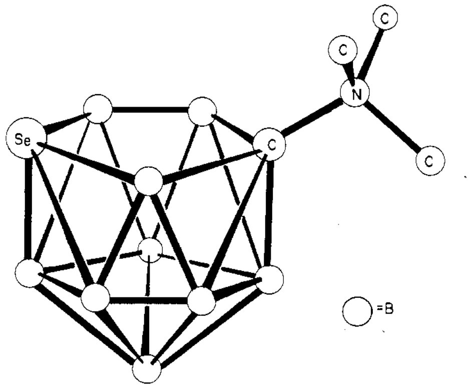

Figure 5. Proposed structure of $SeB_9H_9C{\cdot}N(CH_3)_3$ (all hydrogen atoms have been omitted for clarity).

duction in coupling would lead to a doublet with narrower line width. In addition, all of the known nido 11-member heteroboranes[22] exhibit a high-field doublet similar to the doublet observed at −40.9 ppm for $SeB_9H_9C{\cdot}N(CH_3)_3$. This doublet can be attributed to the "apical" boron atom located at the bottom of the cage. On the basis of the NMR data, we propose the structure given in Figure 5 for $SeB_9H_9C{\cdot}N(CH_3)_3$.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 78-08719.

Registry No. I, 71230-54-1; II, 71230-53-0; III, 71230-51-8; $B_9H_{11}C{\cdot}N(CH_3)_3$, 31117-20-1; $Cs_2B_{10}H_{13}CN$, 71250-00-5.

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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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Received March 20, 1979

The *nido*-carborane anion $[2,3\text{-}(CH_3)_2C_2B_4H_5]^-$ 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 °C 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.

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 $(\eta^5\text{-}C_5H_5)Co^{2+}$ 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 seven-vertex MC_2B_4 polyhedral cage system. A rather extensive chemistry has been developed in this area[1] 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

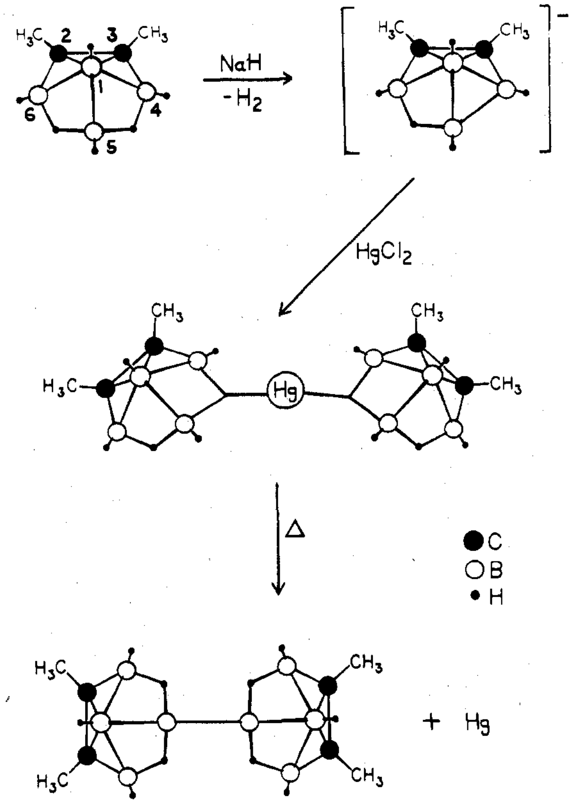

Figure 1. Scheme for the formation of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ (I) and its thermal conversion to 5,5′-$[(CH_3)_2C_2B_4H_5]_2$ (II). Only the isomer of I having C_s symmetry is shown; the product is presumably a mixture of the C_s and C_2 isomers. In both isomers, free rotation of carboranyl groups on the B_2–Hg axes is assumed.

contrast, the attack of monocoordinate units such as $(\eta^5\text{-}C_5H_5)Fe(CO)_2^+$, $[(C_6H_5)_3P]_3Rh^+$, $[(C_6H_5)_3P]Au^+$, 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.[2] In some cases these bridged species undergo thermal rearrangement to terminally η^1-substituted isomers.

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 μ,μ'-$SiH_2(C_2B_4H_7)_2$, 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 fusion[4] of $R_2C_2B_4H_4^{2-}$ ligands which generates tetracarbon 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 μ,μ'-$(B_5H_8)_2Hg$ is reported.

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

compd	solvent	δ^a (*J*, Hz)	rel areas
μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$, I	$CDCl_3$	−4.0 (117) −47.7 (181)	3 1
5,5′-$[(CH_3)_2C_2B_4H_5]_2$, II	C_6D_6	−3.33 (151),[b] (44)[c] −46.25 (166)	3[d] 1
4-C_6H_5-2,3-$(CH_3)_2$-2,3-$C_2B_4H_5$, III	$CDCl_3$	+5.89,[e] −2.18 (~180),[f] −4.92 (180),[f] −44.8 (176)	1, 1, 1, 1
μ,μ'-$(B_5H_8)_2Hg$, IV	C_6D_6	[−7.92, −9.60][g] −43.85 (176)	3 1

[a] Chemical shifts are relative to $BF_3\cdot O(C_2H_5)_2$ with a positive sign denoting a downfield shift. [b] Primary splitting (151 Hz) assigned to $H_{terminal}$–$^{11}B(4,6)$ coupling. [c] Secondary splitting (44 Hz) assigned to H_{bridge}–^{11}B coupling. [d] Area-3 peak consists of superimposed resonances arising from B(4,6) and B(5). [e] Singlet arising from $^{11}B(4)$–C_6H_5. [f] Heavily overlapped doublets which collapse to singlets in the ^1H-decoupled spectrum. [g] Nearly superimposed resonances (apparent doublets) which collapse to overlapping singlets in the ^1H-decoupled spectrum.

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

compd	δ (rel area)[a]	assignt
μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$, I	1.90 (1),[b] 1.94 (1)[b] ~−2.3[c]	CH_3, CH_3 B–H–B
5,5′-$[(CH_3)_2C_2B_4H_5]_2$, II	1.80 (6) 3.37[d] (~2) −0.70[e] (~1) ~−2.0[c]	CH_3 H_t(base) H_t(apex) B–H–B
4-C_6H_5-2,3-$(CH_3)_2C_2B_4H_5$, 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'-$(B_5H_8)_2Hg$, IV	2.39 (4)[i,j] −1.82 (1)[i,k] −2.90 (3)[i,k,l]	H_t(base) H_t(apex) B–H–B

[a] Chemical shifts relative to $(CH_3)_4Si$ with a positive sign indicating a downfield shift. [b] Satellites due to ^{199}Hg–^1H 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. [c] Broad peak, area not measurable. [d] Quartet, *J* = 158 Hz. [e] Quartet, *J* = 180 Hz. [f] Quartet, *J* = 165 Hz. [g] Quartet, *J* = 180 Hz. [h] Multiplet. [i] Singlet observed on ^{11}B decoupling. [j] Satellites due to ^{199}Hg–^1H(base) coupling are observed with *J* = 141 Hz. [k] Line narrowing produced fine structure due to H–H coupling with *J* ≈ 10 Hz. [l] Satellites due to ^{199}Hg–^1H(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, vbr, 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, 1100 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, vbr, 1330 vs, vbr, 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, vbr, 1455 s, vbr, 1375 m, br, 1190 s, 1000 w, 930 m, 880 m, 715 m, br

Results and Discussion

Synthesis of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$. 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 °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, mp 78 °C, that survives brief exposure to air and can be handled on the laboratory bench over limited periods. The compound was structurally char-

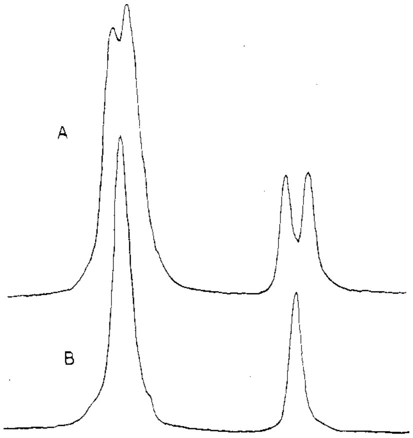

Figure 2. 32.1-MHz ^{11}B FT NMR spectra of μ,μ'-$[(CH_3)_2C_2B_4H_5]_2Hg$ (I) in $CDCl_3$: A, undecoupled; B, proton decoupled at 99.998 404 Hz. Chemical shifts and coupling constants are reported in Table I.

acterized from its unit- and high-resolution mass spectra (Experimental Section), ^{11}B, ^{1}H, and ^{13}C NMR spectra (Tables I and II), and infrared spectrum (Table III).

The 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 $[(CH_3)_2C_2B_4H_5]Hg^+$, Hg^+, and $(CH_3)_2C_2B_4H_6^+$, respectively; in each case the pattern of intensities is consistent with the composition indicated, on the basis of 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-$(CH_3)_2C_2B_4H_6$ (δ −3.7, −7.2, and −47.7).[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[17] can be inferred from the absence of a separate ^{11}B–Hg singlet in the undecoupled ^{11}B spectrum; terminal substitution on boron would be expected to produce a 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 which is exhibited by all known heteroatom-bridged $C_2B_4H_8$ 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 μ,μ'-$(C_2B_4H_7)_2SiH_2$ as discussed several years ago.[2d] In the silicon system, there was some indication, based on NMR resonances (H–Si), 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.

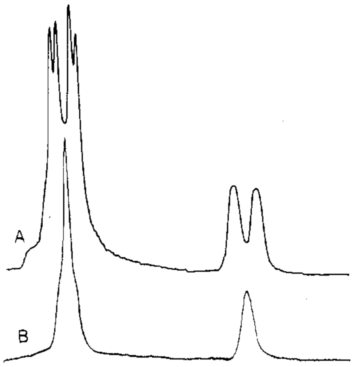

Figure 3. 32.1-MHz ^{11}B FT NMR spectra of 5,5'-$[(CH_3)_2C_2B_4H_5]_2$ (II) in C_6D_6: A, undecoupled; B, proton decoupled.

Compound I is the first confirmed example of a μ-mercury carboranyl complex, although we have reported the preparation of μ-(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-mercury carboranyl 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'-$[(CH_3)_2C_2B_4H_5]_2$. The mercury-bridged complex I at 180 °C in benzene expels mercury as the free metal and forms the bis(carborane) 5,5'-$[(CH_3)_2C_2B_4H_5]_2$ (II) in 91% yield (Figure 1). In addition to bulk experiments conducted on a 1–2-g scale, this conversion was monitored via proton NMR over an 18-h 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 °C. The ^{11}B, ^{1}H, and ^{13}C NMR spectra indicate high (C_{2v}) symmetry with only one C–CH_3 environment and two boron signals in a 3:1 area ratio. The area-3 ^{11}B 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 equivalance 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 carboranes[9]) 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 $(CH_3)_3Si$–SiH_3 from $(CH_3)_3Si$–Hg–SiH_3 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 $(1,2\text{-}C_2B_9H_{11})_2$, which consists of linked ico-

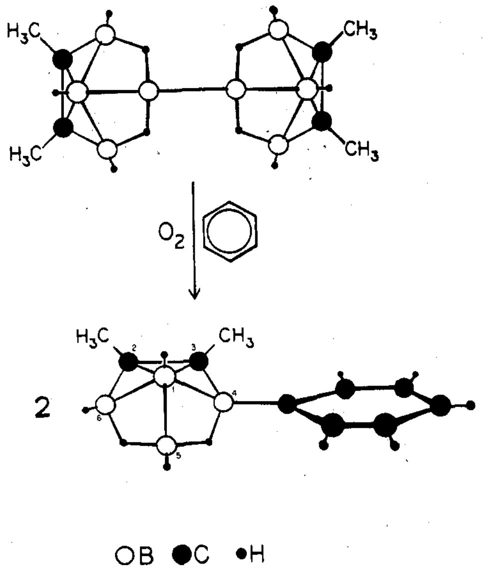

Figure 4. Scheme showing the oxidative addition of benzene to II to give 4-C_6H_5-2,3-$(CH_3)_2C_2B_4H_5$ (III). The enantiomer (6-substituted product) is not shown.

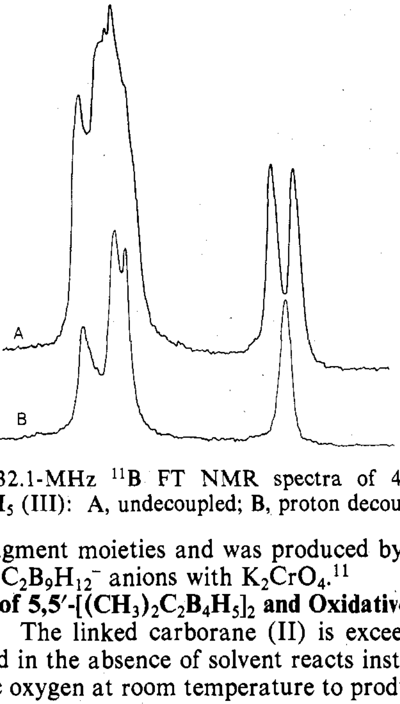

Figure 5. 32.1-MHz ^{11}B FT NMR spectra of 4-C_6H_5-2,3-$(CH_3)_2C_2B_4H_5$ (III): A, undecoupled; B, proton decoupled.

sahedral-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).

$$^1/_2(5,5\text{-}[(CH_3)_2C_2B_4H_5]_2) + C_6H_6 \xrightarrow[-H]{O_2} \underset{\text{III}}{4\text{-}C_6H_5\text{-}2,3\text{-}(CH_3)_2C_2B_4H_5}$$

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 ^{11}B NMR (Figure 5) and proton NMR indicate low symmetry. When this reaction was conducted in benzene-d_6, the mass spectrum of the product indicated a hexadeuterated species corresponding to $C_6D_5(CH_3)_2C_2B_4H_4D$, indicating that *all six hydrogens of benzene are retained* in the product. Thus we formulate the reaction as an oxidative addition of benzene to $(CH_3)_2C_2B_4H_5$–$H_5B_4C_2(CH_3)_2$ 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 phenyldimethylcarborane, 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.

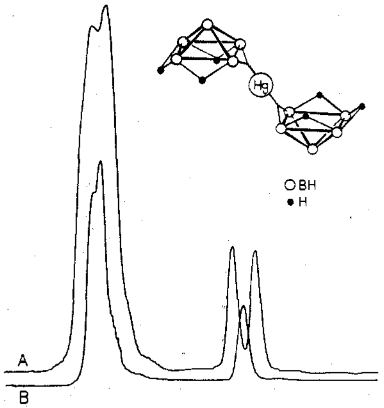

Figure 6. Proposed structure and ^{11}B FT NMR spectra of μ,μ'-$(B_5H_8)_2Hg$: A, undecoupled; B, proton decoupled.

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'-$(B_5H_8)_2Hg$ (IV). The ease with which the bis(carboranyl)mercury complex I forms from $(CH_3)_2C_2B_4H_5^-$ 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'-$(B_5H_8)_2Hg$ in nearly quantitative yield. The mass spectrum exhibits strong groupings with local cutoffs at m/e 330 (parent peak), 267, and 204, corresponding to $(B_5H_8)_2Hg^+$, $(B_5H_8)Hg^+$, 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 and not an 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 with terminal substitution; 32-MHz ^{11}B spectra of 2-metalated B_5H_9 derivatives usually exhibit clear nonequivalence of the basal borons.[12] The ^{11}B-decoupled ^1H NMR 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–$^1H_{\text{terminal}}$ coupling (Table II).

A number of bridged pentaborane complexes have been reported by Gaines and co-workers,[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 μ,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 methods[15]) was not extensively studied, but pyrolysis of IV at 70 °C for 20 h 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 bis(carborane) to generate $(CH_3)_2C_2B_4H_5\cdot$ radicals which in turn combine with the solvent. Studies of the oxidation of 5,5′-$[(CH_3)_2C_2B_4H_5]_2$ and similar linked carboranes in other solvents will be required to test this point.

Experimental Section

Materials. 2,3-Dimethyl-2,3-*nido*-dicarbahexaborane(8), 2,3-$(CH_3)_2C_2B_4H_6$, was prepared by reaction of 2-butyne with pentaborane(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 $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2Hg$ (I). $Na^+(CH_3)_2C_2B_4H_5^-$ (prepared by reaction of 5.94 mmol of 2,3-$(CH_3)_2C_2B_4H_6$ with excess sodium hydride in THF as described previously[5]) was dissolved in 30 mL of dry THF, and 3.00 mmol of anhydrous $HgCl_2$ was added on the vacuum line. After the mixture was stirred for 4 h at 25 °C, during which a white precipitate formed, 30 mL of hexane was added under a dry N_2 atomosphere. 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: calcd for $^{202}Hg^{12}C_8{}^{11}B_8{}^1H_{22}{}^+$, 408.2172; found, 408.2176. ^{13}C NMR (C_6D_6): sharp CH_3 peaks of equal area at δ 18.0 and 19.2 relative to Me_4Si.

Conversion of I to $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$ (II). A 1.31-g sample (3.21 mmol) of $[(CH_3)_2C_2B_4H_5]_2Hg$ was placed under N_2 in a 30-mL Pyrex ampule fitted with a break-seal, 5 mL of dry benzene was added, the contents were frozen in liquid nitrogen, and the ampule was sealed under vacuum. The mixture was heated at 180 °C for 18 h, 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 °C for 18 h 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 ampule was opened under vacuum, the contents were 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 °C under vacuum into a trap cooled to 0 °C to give 0.60 g (2.91 mmol, 91% yield) of the colorless liquid 5,5′-$[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$ (II). Exact mass: calcd for $^{12}C_8{}^{11}B_8{}^1H_{22}{}^+$, 206.2466; found, 206.2477. ^{13}C NMR (C_6D_6): sharp CH_3 peak at δ 21.0 relative to Me_4Si.

Oxidation of $[2,3\text{-}(CH_3)_2C_2B_4H_5]_2$ in Benzene. A 100-mg (0.48-mmol) sample of 5,5′-$[(CH_3)_2C_2B_4H_5]_2$ (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 under vacuum at 25 °C, which we continued for 2 h to remove the last traces of volatiles. The residue consisted of colorless, viscous 4-C_6H_5-2,3-$(CH_3)_2C_2B_4H_5$ (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 $^{12}C_{10}{}^{11}B_4{}^1H_{17}{}^+$ (protonated parent ion), 181.1703; found, 181.1712.

Synthesis of μ,μ'-$(B_5H_8)_2Hg$ (IV). A THF solution of $Na^+B_5H_8^-$ was prepared from 0.648 g (10.1 mmol) of B_5H_9 and 0.553 g (23.0 mmol) of NaH in 50 mL of THF and filtered in vacuo onto 1.32 g (4.84 mmol) of anhydrous $HgCl_2$ in a 250-mL round-bottom flask cooled to −78 °C. The solution was warmed to −30 °C and stirred for 2 h with little or no evolution of gas. After distillation of solvent out of the mixture at −30 °C over a 2-h period, a gray residue remained. To this residue was added 50 mL of dry hexane; the solution was filtered in vacuo, the 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 $(B_5H_8)_2Hg$, which is not highly soluble in hexane or other organic solvents. Evaporation of the solvent followed by sublimation of the product at 100 °C for 8 h gave 1.42 g (4.36 mmol, 90% yield) of pure white crystalline $(B_5H_8)_2Hg$, mp 161–162 °C (sealed capillary). The compound is moderately air stable, surviving exposure of several hours 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 °C fraction was nearly pure B_5H_9 (IR and mass spectra), 2.68 mmol. The −63 °C condensate was shown by mass spectroscopic analysis to consist of B_5H_9 and a small quantity of $(B_5H_8)_2$ (isomer not identified).

Acknowledgment. We thank Mr. David Finster and Mr. William Hutton for the ^{11}B NMR spectra. This work was supported in part by the Office of Naval Research.

Registry No. I, 70879-11-7; II, 70519-07-2; III, 70850-51-0; IV, 70850-80-5; 2,3-$(CH_3)_2C_2B_4H_6$, 20741-68-8; B_5H_9, 19624-22-7.

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(17) In a reaction similar to the formation of I, the pyramidal anion $[(\eta^5\text{-}(CH_3)_5C_5)Co(CH_3)_2C_2B_3H_4]^-$ on treatment with $HgCl_2$ in THF generates the complex $(\eta^5\text{-}(CH_3)_5C_5)Co(CH_3)_2C_2B_3H_4\text{-}\mu\text{-}HgCl$, which has been shown via X-ray crystallography to have a B–Hg–B bridge on the base of a CoC_2B_3 nido cage: Finster, D.; Sinn, E.; Grimes, R. N., to be submitted for publication.

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Complex Formation between the Aquopentacyanoferrate(II) Ion and Thiourea and Its N-Substituted Derivatives

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Received March 28, 1979

The results of a kinetic investigation of the substitution reactions of pentacyanoaquoferrate(II) with thiourea and N-substituted thioureas are presented. The substitution rate constants, measured in the pH range 2.8–9.0, show a hydrogen ion dependence $k_f = (k_{AH_2}[H^+]^2 + k_{AH_1}K_{AH_2}[H^+] + k_A K_{AH_1}K_{AH_2})/([H^+]^2 + K_{AH_2}[H^+] + K_{AH_1}K_{AH_2})$, which is consistent with the presence of three reacting species: $HFe(CN)_5OH_2^{2-}$, $Fe(CN)_5OH_2^{3-}$, and $Fe(CN)_5OH^{4-}$. The acid dissociation constant for the aquo species has been determined ($K_{AH_1} = (1.37 \pm 0.20) \times 10^{-8}$ M). The aquo species is found to be more reactive toward thiourea (k_{AH}(25 °C) = 202 $M^{-1}\ s^{-1}$) than the hydroxy species (k_A(25 °C) = 100 $M^{-1}\ s^{-1}$) while the protonated aquo species (k_{AH_2}(25 °C) = 2 $M^{-1}\ s^{-1}$) is much less reactive. The dissociation rates of the $Fe(CN)_5TU^{3-}$ (TU = thiourea) species are larger than those of complexes with N-donor ligands, indicating labile Fe–S bonds. An isokinetic plot of the activation parameters suggests different mechanisms operating in the formation (I_d mechanism) and dissociation (D mechanism) reactions of $Fe(CN)_5TU^{3-}$ species.

Introduction

The reactions of pentacyanoferrate(II), $Fe(CN)_5L^{n-}$, complexes are currently the subject of considerable interest, for several reasons. Mechanistic aspects[1-8] have been studied by using a variety of ligands and solvent systems since there is evidence for a dissociative, D, mechanism in the substitution of these complexes. In studies of complexes of this type where the volumes of activation have been measured, the data are consistent with this proposed mechanism. Also, these low-spin iron species represent models for active sites in biological systems, and reactions with imidazole have been investigated[10] in this regard. Another feature of these complexes is their use as the reducing center is the identification of precursor complexes in inner-sphere electron transfer.[11,12]

To date, most of the studies have been undertaken for N-donor ligands, and relatively few data are available for sulfur-bonded complexes. In aqueous media, complexes are formed between $Fe(CN)_5(OH_2)^{3-}$ and thiols or thioureas, the rates of formation being pH dependent. There is also a need for the study of the comparative reactivities of the pH-related forms of the pentacyanoferrate(II) ion. Davies[8] has reported a value of $\sim 2 \times 10^{-7}$ M for the aquo–hydroxo equilibrium

$$Fe(CN)_5(OH_2)^{3-} \rightleftharpoons H^+ + Fe(CN)_5OH^{4-} \quad K_{AH_1} \quad (1)$$

Malin[13] has shown that at low pH, protonation occurs (at cyanide)

$$H[Fe(CN)_5OH_2]^{2-} \rightleftharpoons H^+ + Fe(CN)_5OH_2^{3-} \quad K_{AH_2} \quad (2)$$

with a dissociation constant $K_{AH_2} = (2.35 \pm 0.6) \times 10^{-3}$ M at 25 °C. The protonated species was found to be much less reactive than the aquo form.[13] There are no rate constants available for the reaction of the hydroxo form. In this paper, we wish to report details of a kinetic study of the reaction with thiourea and several N-substituted thioureas. These ligands are particularly useful for identifying pH effects since there is no evidence for protonation[14] over a wide (1–10) pH range, and the relative reactivities of the interrelated complex ions may be determined.

Experimental Section

Reagents. Sodium pentacyanoammineferrate(II) was prepared from sodium nitroprusside by the standard procedure.[15] The product was recrystallized from aqueous ammonia at 0 °C and washed with cold methanol. The dried yellow powder was stored under nitrogen in the dark at 5 °C. Thiourea (Fisher), allylthiourea (BDH), and *N,N'*-dimethylthiourea (Ralph-Emanuel) were used after repeated recrystallization from water.

Kinetic Measurements. Studies were made by using a stopped-flow apparatus described previously.[16] The apparatus was thermostated to ±0.05 °C. Formation reactions were monitored at 440 nm and dissociation reactions at 400 nm. The pentacyanoaquoferrate(II) ion was generated in solution by dissolving solid $Na_3[Fe(CN)_5NH_3]$ in deoxygenated distilled water. Freshly prepared solutions of low concentration ($(2–4) \times 10^{-5}$ M) were used to prevent dimerization of the anion.[17,18] In order to control the reaction pH, we used phosphate, phthalate, or borax buffers, since these were observed to have no effect on the reactant solutions and have in some instances been used in other studies.[13] The ionic strength was maintained at 0.50 M by using sodium chloride.

All measurements were made under pseudo-first-order conditions with ligand in excess. Plots of ln $(A_\infty - A_t)$ against time derived from photographic traces of photomultiplier output were linear for at least 3 half-lives.

Spectra. The spectra of pentacyanoferrate(II) solutions (1.5×10^{-4} M) were measured at various pH values by using a Varian Techtron 635 spectrophotometer over the range 350–500 nm. The sample cell holder was thermostated at the appropriate temperature (between 10 and 30 ± 0.1 °C). Freshly prepared solutions of low complex concentration, adjusted to pH ~4, were deoxygenated and allowed to thermostat prior to each run. The hydrogen ion concentration was changed by addition of small volumes (0.01 mL) of 0.1 M NaOH, and after equilibration the shift in the spectrum was monitored. Measurements were made over the range pH 4–10, the pH values

0020-1669/79/1318-2891$01.00/0