(4) and β-P_4S_4 (8) are being pursued currently in our laboratories.

Registry No. 1, 19257-89-7; 2, 34330-76-2; 3, 1314-85-8; 4, 39350-99-7; 5, 65995-90-6; 6, 65815-60-3; 7, 65815-59-0; 8, 20419-03-8; 10, 65815-62-5; $C_6H_5NH_2$, 62-53-3; P_2I_4, 13455-00-0.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

References and Notes

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$$\frac{2.0 + \sin\theta\,\cos\theta}{0.5\dfrac{\cos^2 2\theta_{mono} + \cos^2 2\theta}{1.0 + \cos^2 2\theta_{mono}} + 0.5\dfrac{\cos^2 2\theta_{mono} + \cos^2 2\theta}{1.0 + \cos^2 2\theta_{mono}}}$$

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Oxidative Cleavage of Dimethylstannaundecaborane: Preparation and Structural Characterization of 5,10-Dibromodecaborane(14)

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Reaction of $(CH_3)_2SnB_{10}H_{12}$ with halogens (X_2 = Br_2, I_2) yields $(CH_3)_2SnX_2$ and $B_{10}H_{12}X_2$ as products. The principal dibromodecaborane product has been characterized, based on spectral data and a single-crystal x-ray analysis, as 5,10-$B_{10}H_{12}Br_2$. Crystals of 5,10-$B_{10}H_{12}Br_2$ are monoclinic (space group $P2_1/c$), a = 13.323 (3) Å, b = 7.416 (3) Å, c = 24.890 (8) Å, β = 153.61 (1)°, Z = 4, and d = 1.701 g cm^{-3}. The structure was solved by the heavy-atom method and was refined by block-diagonal least squares to R_1 = 0.051 and R_2 = 0.053 for 1440 independent reflections. The 5,10-$B_{10}H_{12}Br_2$ has approximate C_s molecular symmetry in the crystal. The mean B–Br distance is 1.941 (8) Å. The B_{10}-cage unit shows only slight distortions from the cage structure seen in $B_{10}H_{14}$. The $B_{10}H_{12}I_2$ obtained is thermally unstable and consequently was not characterized structurally. Reaction of $(CH_3)_2SnB_{10}H_{12}$ with a deficiency of Br_2 yields traces of product identified as $(CH_3)_2SnBrB_{10}H_{12}Br$, providing evidence that Br_2 cleavage of $(CH_3)_2SnB_{10}H_{12}$ occurs via the stepwise cleavage of B–Sn–B three-center bonds in an oxidative cleavage reaction process.

Introduction

Dialkylstannaundecaboranes,[3] $R_2SnB_{10}H_{12}$, are a potentially useful series of *nido*-borane derivatives upon which to base syntheses of other substituted decaboranes. An x-ray structural analysis shows the R_2Sn moiety is bonded to the decaborane cage at edge boron atoms B(5)–B(6) and B(9)–B(10) by what

can be regarded formally as two three-center B–Sn–B bonds.[4,5] Thus, to the extent that the R_2Sn moiety can be selectively displaced or cleaved from the decaborane cage (or vice versa), there exists a route to facial disubstituted (boron atoms B-(5)–B(10)) *nido*-decaborane derivatives.

Recently, as part of a general study of the reactivity of $R_2SnB_{10}H_{12}$ compounds, we have examined reactions of halogens (Cl_2, Br_2, and I_2) with $(CH_3)_2SnB_{10}H_{12}$. From the Br_2–$(CH_3)_2SnB_{10}H_{12}$ reaction we have been able to isolate in high yield and characterize by single-crystal x-ray crystallography, a new *nido*-dibromodecaborane, 5,10-$B_{10}H_{12}Br_2$. A preliminary account of this work has been published earlier.[6] Although a variety of basal-[7,8] and monofacial-substituted[8,9] halodecaboranes are known, the 5,10-$B_{10}H_{12}$ represents the first example of a facial disubstituted *nido*-halodecaborane(14). The results of our work are described below.

Experimental Section

Apparatus, Techniques, and Materials. All manipulations were carried out using standard high-vacuum and Schlenk apparatus techniques.[10] All samples were handled and stored under vacuum or N_2-flushed systems.

Infrared spectra were obtained with a Perkin-Elmer Model 337G spectrometer. Proton spectra were obtained at 60.0 and 100.0 MHz, using Varian A-60A and HA-100 spectrometers, respectively. Chemical shifts were measured relative to internal $(CH_3)_4Si$. ^{11}B NMR spectra at 32.1 MHz were obtained using a Varian HA-100 equipped with standard probe and rf unit accessories. $^{11}B\{^1H\}$ spin decoupling was accomplished using "noise" decoupling techniques. The 70.6-MHz ^{11}B NMR spectra were obtained by Professor Riley Schaeffer, Indiana University. ^{11}B chemical shifts were measured relative to external BBr_3 and are given relative to $BF_3\cdot O(C_2H_5)_2$. Mass spectra were obtained using a Varian MAT CH-5 spectrometer.

$(CH_3)_2SnB_{10}H_{12}$ was prepared and purified as described previously.[3,4] Chlorine (Matheson Co.) and Br_2 (Matheson Coleman and Bell) were used without further purification. Carbon disulfide and benzene were distilled from P_4O_{10} and CaH_2, respectively.

Reactions of $(CH_3)_2SnB_{10}H_{12}$ with Halogens. (A) Cl_2. Chlorine (1.3 mmol) was condensed into a solution of 0.31 mmol of $(CH_3)_2SnB_{10}H_{12}$ in 10 mL of CS_2. The reaction mixture was allowed to warm to –78 °C. After 1 h, an aliquot of solution was removed and evaporated to dryness in vacuo. The solid which remained was shown by infrared and mass spectral analysis to be only unreacted $(CH_3)_2SnB_{10}H_{12}$. The $(CH_3)_2SnB_{10}H_{12}$–Cl_2 solution was warmed further to 25 °C. After 1 h, CS_2 and Cl_2 were removed in vacuo. An ^{11}B NMR spectrum of the remaining solid showed resonances due only to unreacted $(CH_3)_2SnB_{10}H_{12}$ and small quantities of $B_{10}H_{14}$. The mass spectrum of the solid showed traces of $B_{10}H_{13}Cl$ and possibly $B_{10}H_{12}Cl_2$.

In a separate reaction, Cl_2 (1.4 mmol), $(CH_3)_2SnB_{10}H_{12}$ (0.2 mmol), and $AlCl_3$ (0.5 mmol) in 10 mL of CS_2 were warmed slowly to –78 °C and then to 25 °C. After 1 h, CS_2, $(CH_3)_2SnCl_2$, $B_{10}H_{14}$, and $B_{10}H_{13}Cl$ (characterized by mass spectrum) were removed in vacuo. Mass spectral analysis of the remaining solid indicated the presence of unreacted $(CH_3)_2SnB_{10}H_{12}$, di- and trichlorodecaboranes, and unidentified aluminum chloride containing materials.

(B) Br_2. Typically, Br_2 (0.86 mmol) in CS_2 solvent was added dropwise to a –78 °C solution of $(CH_3)_2SnB_{10}H_{12}$ (0.43 mmol) in 5–7 mL of CS_2 and allowed to react. After 3 h, the temperature was raised slowly to 25 °C. The ^{11}B and ^1H NMR spectrum indicated that all $(CH_3)_2SnB_{10}H_{12}$ had reacted. $(CH_3)_2SnBr_2$ was the only tin-containing product present. Carbon disulfide, $(CH_3)_2SnBr_2$ (0.41 mmol), and small quantities of $B_{10}H_{14}$ were removed in vacuo. Sublimation of the remaining material in a 30-cm tube (hot zone 80 °C) separated it into three fractions: a trace fraction, A, of $B_{10}H_{13}Br$ (confirmed by mass spectrum), a major fraction, B, consisting mainly of solid along with minor quantities of liquid, and a minor fraction, C, of $B_{10}H_{11}Br_3$ (confirmed by mass spectrum). Mass spectral analysis showed that both the solid and oil of fraction B had composition $B_{10}H_{12}Br_2$. By repeated sublimation of fraction B, 70–80% yields of pure 5,10-$B_{10}H_{12}Br_2$ were obtained. Because only small quantities of fractions A ($B_{10}H_{13}Br$) and C ($B_{10}H_{11}Br_3$) were obtained, they were not studied further.

In a second series of reactions, 0.05–0.10 mmol quantities of Br_2

in 10 mL of CS_2 were allowed to react with 0.40–0.50 mmol quantities of $(CH_3)_2SnB_{10}H_{12}$ at –78 °C. As soon as reaction had occurred, as evidenced by disappearance of bromine coloration, the reaction mixture was warmed to room temperature. Carbon disulfide and $(CH_3)_2SnBr_2$ were removed in vacuo. A mass spectrum of the reaction mixture indicated the presence of mainly $(CH_3)_2SnB_{10}H_{12}$, along with a small quantity of $B_{10}H_{12}Br_2$. In addition, low-intensity envelopes centered at m/e 334, 349, and 428, attributable to $CH_3SnB_{10}BrH_x^+$, $(CH_3)_2SnB_{10}BrH_x^+$, and $(CH_3)_2SnB_{10}Br_2H_x^+$ ions, are present. Attempts to isolate the species that yield these latter envelopes by extraction, sublimation, and silica gel chromatography[11] were unsuccessful.

The 5,10-$B_{10}H_{12}Br_2$ is a colorless solid which shows partial decomposition after 10 days exposure to ambient air. Anal. Calcd for $B_{10}H_{12}Br_2$: B, 38.61; H, 4.32; Br, 57.07. Found: B, 38.51; H, 4.44; Br, 56.93. The most intense peak in the parent and four most intense mass spectral envelopes occur at m/e (relative intensity) 275 (100%, $B_{10}Br_2H_x^+$), 181 (31%), 169 (15%), 101 (17%), and 90 (15%). The mass spectral cutoff occurs at m/e 284 ($^{11}B_{10}H_{12}{}^{81}Br_2^+$). Infrared absorptions (KBr pellet) occur at 2591 (vs), 1923 (w), 1887 (w), 1538 (w, sh), 1451 (vs), 1383 (w), 1326 (w, sh), 1269 (w), 1087 (m), 1045 (s), 1010 (m), 952 (m), 917 (vs), 901 (s), 877 (s), 855 (m), 830 (s), 816 (s), 791 (m), 769 (s), 752 (w), 722 (s), 697 (s), 658 (m), 606 (m), 581 (vs), 459 (m, sh), and 452 (s) cm^{-1}. The ^{11}B NMR spectrum consists of a low-field group of overlapped resonances (doublet, δ –13 ppm, and doublet, δ –9.2 ppm, estimated; singlet, δ –5.9 ppm, total area 6), a doublet at δ 4.3 ppm (J = 165 Hz, area 2), and a doublet at δ 35.6 ppm (J = 160 Hz, area 2).

The ^{11}B NMR spectrum of the liquid portion of fraction B was obtained. The low-field region (area 8) of the spectrum appeared approximately like that of 5,10-$B_{10}H_{12}Br_2$, except that it was less well resolved. The high-field region (area 2) consisted of a broad, skewed-to-high-field doublet at δ 36 ppm.

(C) I_2. Iodine (0.90 mmol) in 10 mL of CS_2 was added dropwise to 0.45 mmol of $(CH_3)_2SnB_{10}H_{12}$ in 5 mL of CS_2 at –78 °C. During 2 h, the solution turned from dark to light brown. The solution was warmed to room temperature and the CS_2, $B_{10}H_{14}$, and $(CH_3)_2SnI_2$ (0.41 mmol) were removed in vacuo. The mass spectrum of the thermally unstable solid which remained showed a pattern of envelopes characteristic of diiododecaborane(s) (most intense peak of parent envelope occurs at m/e 370; $B_{10}I_2H_x^+$ ions). The ^{11}B NMR spectrum (benzene) exhibited a group of broad, poorly resolved low-field resonances (area 8) and a broad, high-field resonance at δ 35 ppm (area 2). However, because of the product(s) thermal instability, attempts to isolate the iododecaborane product(s) by sublimation, fractional crystallization, and silica gel chromatography[11] were unsuccessful.

Crystal Data. Crystals of 5,10-$B_{10}H_{12}Br_2$ were obtained by sublimation in a temperature gradient column (70–80 °C). The crystals were clear, colorless parallelepipeds. They showed slight oxidation during a 10-day exposure to air; however, upon irradiation with x rays, degradation was evident after 1 day. Therefore, a crystal (0.22 × 0.22 × 0.28 mm) mounted in a sealed capillary was used in the x-ray analysis.

The unit cell is monoclinic. The cell parameters, refined by least-squares fit of the parameters to 15 reflections carefully measured on the diffractometer, are a = 13.323 (3) Å, b = 7.416 (3) Å, c = 24.890 (8) Å, and β = 153.61 (1)°. The volume is 1093.2 (7) Å^3. Because of the high solubility of 5,10-$B_{10}H_{12}Br_2$ in halocarbons and its decomposition in protic solvents, its density could not be measured conveniently. Assuming four molecules of the compound (molecular weight = 280.024) per unit cell, the calculated density is 1.701 g cm^{-3}. From the absences observed in the measurement of the sphere of reflection, the space group is $P2_1/c$. The systematic absences are $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$. $F(000)$ is 528.[12] The absorption coefficient (Mo Kα) is 77.8 cm^{-1}.

Intensity measurements were made at room temperature using a Syntex PĪ diffractometer equipped with a graphite monochromator. The procedure used was the θ–2θ scanning technique as programmed at Syntex. A constant scan rate of 2°/min was used with scan ranges starting 1° below 2θ for Kα_1 and ending 1° above 2θ for Kα_2. Background measurements were made at the beginning and end of each measurement cycle for a total period equal to half the scan time. The background, collected using the stationary crystal–stationary counter technique, was assumed to be linear between the two measured points.

Table I. Final Atom Positional Parameters and Thermal Parameters[a] (Å²)

Atom	x/a	y/b	z/c	B
Br(1)	1.04618 (13)	0.22135 (11)	0.05150 (7)	
Br(2)	1.44864 (12)	0.58379 (13)	0.28637 (7)	
B(1)	1.0802 (13)	0.3941 (12)	0.1858 (7)	
B(2)	0.7949 (14)	0.3204 (13)	0.0459 (8)	
B(3)	0.8795 (14)	0.4771 (14)	0.1368 (7)	
B(4)	1.1146 (14)	0.6106 (12)	0.2326 (7)	
B(5)	0.9478 (13)	0.3829 (11)	0.0611 (7)	
B(6)	0.6518 (13)	0.4310 (13)	−0.0734 (8)	
B(7)	0.6271 (14)	0.5137 (14)	−0.0182 (7)	
B(8)	0.8368 (15)	0.7042 (14)	0.1036 (8)	
B(9)	1.0407 (16)	0.7801 (14)	0.1535 (8)	
B(10)	1.1611 (13)	0.5772 (11)	0.1858 (7)	
H(1)	1.201 (16)	0.294 (12)	0.249 (8)	4.4
H(2)	0.771 (15)	0.180 (13)	0.040 (8)	4.7
H(3)	0.861 (15)	0.444 (12)	0.165 (8)	4.6
H(4)	1.285 (16)	0.636 (12)	0.342 (9)	4.7
H(5,6)	0.820 (15)	0.491 (12)	−0.018 (8)	4.3
H(6)	0.524 (16)	0.382 (12)	−0.159 (9)	4.3
H(6,7)	0.602 (15)	0.574 (12)	−0.072 (8)	4.6
H(7)	0.477 (16)	0.510 (12)	−0.071 (8)	4.7
H(8)	0.772 (17)	0.814 (13)	0.100 (9)	5.4
H(8,9)	0.849 (18)	0.773 (13)	0.067 (10)	5.3
H(9)	1.098 (15)	0.921 (13)	0.173 (8)	5.2
H(9,10)	1.053 (15)	0.695 (13)	0.114 (8)	4.7

[a] Standard deviations of the least significant figures are given in parentheses in this and in all following tables.

Some 3300 independent reciprocal lattice points were surveyed within a single quadrant to $2\theta \le 60°$. The data were monitored every 60 measurement cycles and were corrected for a decline of 3.3% in F_o and 6.9% in I_o. Data were corrected for Lorentz and polarization effects. No correction was made for absorption, owing to the near equidimensions of the crystal.

Of the 3300 independent points measured, 1440 were determined to have intensity significantly above background and were used in the refinement. A reflection was considered significant when

$$F_o{}^2 > 3.0 \times \sigma(F_o{}^2)$$

and

$$\sigma(F_o{}^2) = RLP \times \{TSC + BACK + [p(TSC - BACK)]^2\}^{1/2}$$

RLP is the reciprocal of the Lp correction, TSC is the total counts collected during the measurement scan, and BACK is twice the number of counts accumulated during the background measurement. The factor of 2 is included in BACK because, as mentioned previously, the background was counted for only half the scan time. For p, a damping factor to downweight stronger intensities, a value of 0.04 was used.[13]

Solution and Refinement of the Structure. The positions of the two independent bromine atoms were determined from a three-dimensional Patterson map ($R_1 = \sum \|F_o| - |F_c\|/\sum|F_o| = 0.38$) and were refined with six cycles of block-diagonal least-squares refinement ($R = 0.29$). The block-diagonal approximation assigned 3 × 3 blocks to the

positional coordinates and 1 × 1 blocks to the isotropic thermal parameters. The positions of all boron atoms were located from the first electron-density synthesis ($R = 0.23$). After three cycles of isotropic full-matrix refinement, $R_1 = 0.13$ and $R_2 = |\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2|^{1/2} = 0.14$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, w, calculated from counting statistics as $4 \times F_o{}^2/\sigma^2(F_o{}^2)$. The standard deviations, $\sigma(F_o{}^2)$, were determined as described previously. With the two bromine atoms assigned anisotropic temperature factors, the full-matrix least-squares calculation converged with $R_1 = 0.063$ and $R_2 = 0.070$. With all atoms anisotropic, convergence was reached after five cycles, $R_1 = 0.061$ and $R_2 = 0.068$. From a difference map, calculated using the results of this refinement, the positions of all 12 hydrogens were located. When these were included in full-matrix least-squares calculations with positional parameters and allowed to refine and isotropic temperature[14] parameters held constant, convergence was reached with $R_1 = 0.051$ and $R_2 = 0.053$. The standard deviation of an observation of unit weight was 1.706. The ratio of observations to parameters was 10 to 1. Final positional and thermal parameters and their errors are listed in Tables I and II.

In the calculations the scattering functions used were those for neutral atoms.[15] The curve for bromine was corrected for the effects of anomalous dispersion.[16] The data were reduced and all nonhydrogen atoms located using programs written in this laboratory for a Data General Nova 1200 computer. The full-matrix refinement was carried out and other final calculations were done using programs supplied by Dr. James Ibers of Northwestern University.

Results and Discussion

Halogen Cleavage Reactions. Reactions of Cl_2, Br_2, and I_2 with $(CH_3)_2SnB_{10}H_{12}$ were carried out in carbon disulfide solvent at temperatures from −78 to 25 °C. Reaction of 2 equiv of Br_2 or I_2 with $(CH_3)_2SnB_{10}H_{12}$ yields $(CH_3)_2SnX_2$ and $B_{10}H_{12}X_2$ (X = Br, I) as principal products according to

$$(CH_3)_2SnB_{10}H_{12} + 2X_2 \rightarrow (CH_3)_2SnX_2 + B_{10}H_{12}X_2 \qquad (1)$$
$$X = Br, I$$
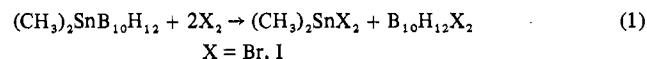
The Br_2–$(CH_3)_2SnB_{10}H_{12}$ reaction proceeds smoothly at −78 °C and typically only minor quantities (<10%, based on initial $(CH_3)_2SnB_{10}H_{12}$) of $B_{10}H_{14}$, $B_{10}H_{13}Br$, and $B_{10}H_{11}Br_3$ are formed along with the major product, $B_{10}H_{12}Br_2$. Above −78 °C, relatively less $B_{10}H_{12}Br_2$ is formed. The I_2–$(CH_3)_2Sn$-$B_{10}H_{12}$ reaction is less clean, yielding larger quantities of $B_{10}H_{14}$, $B_{10}H_{13}I$, and $B_{10}H_{11}I_3$ products along with small quantities of nonvolatile, intractable solid residue. Under conditions considerably more vigorous than required for the Br_2–$(CH_3)_2SnB_{10}H_{12}$ or I_2–$(CH_3)_2SnB_{10}H_{12}$ reactions, i.e., temperatures to 25 °C and Cl_2:$(CH_3)_2SnB_{10}H_{12}$ reactant ratios in excess of 10:1, reaction between Cl_2 and $(CH_3)_2SnB_{10}H_{12}$ occurs slowly and leads to $B_{10}H_{14}$ and traces of chlorodecaboranes as products. Upon the addition of small quantities of $AlCl_3$, reaction occurs to yield a complex mixture of products. Some cleavage of $(CH_3)_2Sn$ moieties from $(CH_3)_2SnB_{10}H_{12}$ occurs, since $(CH_3)_2SnCl_2$ is observed among the products. However, the mixture of borane products is

Table II. Anisotropic Thermal Parameters[a]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	571 (5)	610 (5)	559 (5)	74 (4)	514 (5)	−3 (4)
Br(2)	389 (4)	876 (7)	534 (5)	−128 (4)	400 (4)	−144 (5)
B(1)	427 (44)	474 (54)	449 (46)	69 (41)	395 (43)	102 (42)
B(2)	399 (44)	566 (61)	479 (49)	68 (42)	393 (45)	101 (44)
B(3)	443 (46)	737 (64)	439 (48)	99 (45)	410 (45)	110 (46)
B(4)	462 (45)	581 (54)	395 (46)	86 (43)	386 (44)	50 (42)
B(5)	338 (39)	387 (48)	381 (42)	47 (36)	308 (39)	44 (37)
B(6)	327 (40)	533 (56)	379 (44)	−22 (41)	305 (40)	−18 (40)
B(7)	357 (44)	619 (59)	387 (46)	86 (43)	321 (43)	79 (44)
B(8)	505 (52)	633 (61)	482 (51)	121 (49)	436 (49)	21 (49)
B(9)	503 (54)	500 (56)	446 (50)	66 (47)	406 (50)	−8 (45)
B(10)	370 (39)	488 (51)	344 (40)	8 (39)	316 (38)	−1 (40)

[a] Anisotropic thermal parameters (×10^4) are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

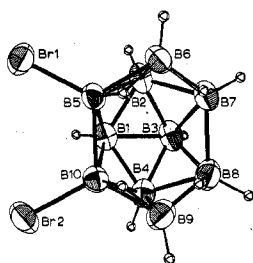**Figure 1.** Molecular structure and atom numbering of $5,10\text{-}B_{10}H_{12}Br_2$.

Figure 2. Schematic representation of R_2Sn-moiety cleavage from the $R_2SnB_{10}H_{12}$ molecule.

Table III. Interatomic Distances for $5,10\text{-}B_{10}H_{12}Br_2$ (Å)

Br(1)–B(5)	1.942 (8)	B(4)–H(4)	1.23 (9)
Br(2)–B(10)	1.940 (8)	B(5)–B(6)	1.80 (1)
B(1)–B(2)	1.78 (1)	B(5)–B(10)	2.00 (1)
B(1)–B(3)	1.78 (1)	B(5)–H(5,6)	1.19 (9)
B(1)–B(4)	1.79 (1)	B(6)–B(7)	1.78 (1)
B(1)–B(5)	1.72 (1)	B(6)–H(6)	1.03 (10)
B(1)–B(10)	1.73 (1)	B(6)–H(5,6)	1.25 (9)
B(1)–H(1)	1.04 (9)	B(6)–H(6,7)	1.27 (9)
B(2)–B(3)	1.78 (1)	B(7)–B(8)	1.95 (1)
B(2)–B(5)	1.77 (1)	B(7)–H(7)	1.01 (9)
B(2)–B(6)	1.73 (1)	B(7)–H(6,7)	1.14 (9)
B(2)–B(7)	1.79 (1)	B(8)–B(9)	1.79 (1)
B(2)–H(2)	1.06 (9)	B(8)–H(8)	1.13 (10)
B(3)–B(4)	1.76 (1)	B(8)–H(8,9)	1.17 (10)
B(3)–B(7)	1.74 (1)	B(9)–B(10)	1.78 (1)
B(3)–B(8)	1.73 (1)	B(9)–H(9)	1.12 (9)
B(3)–H(3)	0.96 (9)	B(9)–H(8,9)	1.14 (10)
B(4)–B(8)	1.79 (1)	B(9)–H(9,10)	1.29 (9)
B(4)–B(9)	1.72 (1)	B(10)–H(9,10)	1.19 (9)
B(4)–B(10)	1.76 (1)		

sufficiently complex that further investigation was deemed not desirable.

The Br_2–$(CH_3)_2SnB_{10}H_{12}$ reaction yields $5,10\text{-}B_{10}H_{12}Br_2$ as the major product (Figure 1) along the minor quantities of other isomeric dibromodecaboranes. However, the minor $B_{10}H_{12}Br_2$ isomer(s) were not obtained in sufficient quantity or sufficiently free of $5,10\text{-}B_{10}H_{12}Br_2$ to allow their structural characterization. The $5,10\text{-}B_{10}H_{12}Br_2$ can be obtained pure by repeated fractional sublimation. It exhibits a sharp mass spectral cutoff at m/e 284 which can be assigned to $^{11}B_{10}H_{12}{}^{81}Br_2{}^+$ ions. By analogy with what has been reported for monohalodecarboranes,[17,18] the tentative assignment of characteristic infrared absorptions can be made: 2591 cm^{-1}, terminal B–H stretch; 1923–1887 cm^{-1}, bridge B–H–B stretch (in phase); 1451 cm^{-1}, bridge B–H–B stretch (out-of-phase); 1045 cm^{-1}, terminal B–H asymmetric bend; 877 and 830 cm^{-1}, B–Br stretch. The ^{11}B NMR spectrum at 32.1 and 70.6 MHz or at 32.1 MHz with heteronuclear spin decoupling could not be resolved completely into its component resonances. However, the resonances at δ −5.9, 4.3, and 35.8 ppm, which can be resolved, are readily assigned to boron atoms B(5,10), B(7,8), and B(2,4), respectively, by comparison with assignments made previously for facial and basal monosubstituted bromide–caboranes.[19]

Sprecher and Aufderheide[8] have shown that the changes in chemical shift for a particular boron atom of a monohalodecaborane[19] relative to the equivalent boron in unsubstituted decaborane (Δ shift) are additive and can be used directly to predict the chemical shifts for a variety of basal disubstituted and facial monosubstituted dihalodecaboranes. Their empirically derived equation, from which the shifts for boron atoms in dihalodecaboranes ($\Delta\sigma_C$) can be calculated is

$$\Delta\sigma_C = (0.92 \pm 0.019)[\Delta\sigma_A + \Delta\sigma_B] - (0.047 \pm 0.049) \quad (2)$$

where $\Delta\sigma_A$ and $\Delta\sigma_B$ are the Δ shifts obtained from the monohaloboranes.[19] Since no facial disubstituted haloboranes were available previously, it is of interest to examine how well for $5,10\text{-}B_{10}H_{12}Br_2$ the calculated chemical shifts agree with the measured values. Of the five boron resonance types of interest B(1), B(3), B(6,9), B(2,4), and B(7,8), chemical shifts for only B(2,4) and B(7,8) could be measured accurately enough to be compared. However, using $\Delta\sigma_C$ values calculated from eq 2, chemical shift values of δ 3.7 ppm [B(7,8)] and δ 34.6 ppm [B(2,4)] are obtained, agreeing within experimental error with the values of δ 4.3 and 35.6 ppm measured experimentally. Based on this limited analysis, it appears that the generalization that ^{11}B NMR chemical shifts in dihalodecaboranes are additive and can be predicted is valid also for facial disubstituted halodecaboranes.

The principal products of the I_2–$(CH_3)_2SnB_{10}H_{12}$ reaction are $(CH_3)_2SnI_2$ and diiododecaborane(s); however, the thermal instability of the latter makes it difficult to separate completely from minor monoiodo- and triiododecaboranes which form also. The mass spectrum of the $B_{10}H_{12}I_2$ fraction shows small quantities (estimated 5%) of $B_{10}H_{11}I_3$ material as a result of initial sample impurity and/or also some thermal decomposition of $B_{10}H_{12}I_2$ in the heated source of the mass spec-
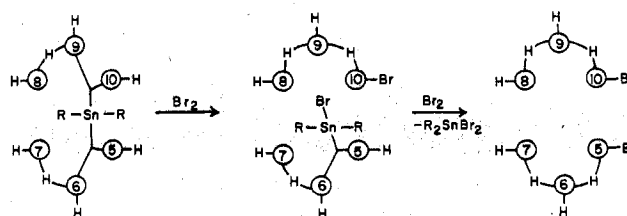
trometer. Because of the uncertain purity of samples and poor resolution obtained in the ^{11}B NMR spectra, assignment of structure to the $B_{10}H_{12}I_2$ product was not attempted.

The reaction of Br_2 (or I_2) with $(CH_3)_2SnB_{10}H_{12}$ can be classed as an oxidative cleavage reaction in which the two three-center B–Sn–B bonds undergo stepwise cleavage to the formation of $(CH_3)_2SnX_2$ and $B_{10}H_{12}X_2$ (X = Br, I) products. Mass spectral examination of the products obtained from reactions of $(CH_3)_2SnB_{10}H_{12}$ with a substantial deficiency of Br_2, after $(CH_3)_2SnBr_2$ and unreacted $(CH_3)_2SnB_{10}H_{12}$ have been removed in vacuo, show the presence of a small quantity of material exhibiting mass spectral envelopes at m/e 334, 349, and 428. These envelopes are attributable to $CH_3SnB_{10}BrH_x{}^+$, $(CH_3)_2SnB_{10}H_{12}Br^+$, and $(CH_3)_2SnB_{10}Br_2H_x{}^+$ ions, respectively. $Br(CH_3)_2SnB_{10}H_{12}Br$ may form in the first (Figure 2) of an overall two-step process. In the second reaction, the second B–Sn–B three-center bond is cleaved, with removal of the $(CH_3)_2Sn$ moiety as $(CH_3)_2SnBr_2$ and the formation of $B_{10}H_{12}Br_2$.

It is of interest of note that Br_2 and I_2 react readily with $(CH_3)_2SnB_{10}H_{12}$ under conditions in which Cl_2 does not. This appears to be inconsistent with an electrophilic reaction mechanism since in such reactions the expected order of reactivity is $Cl_2 > Br_2 > I_2$.[21,22] However, until additional experiments bearing on the question of mechanism are carried out, further speculation is unwarranted.

Description of Structure

The structure of the major product of the Br_2–$(CH_3)_2$-$SnB_{10}H_{12}$ reaction, $5,10\text{-}B_{10}H_{12}Br_2$, has been established by a single-crystal x-ray analysis. The $5,10\text{-}B_{10}H_{12}Br_2$ contains four molecules per unit cell. The molecular structure is shown in Figure 1. Interatomic bond distances and bond angles are listed in Tables III and IV, respectively. The structure of $5,10\text{-}B_{10}H_{12}Br_2$ consists of the ten boron atom fragment of an icosahedron, characteristic of a *nido*-decaborane system, to which bromine atoms are bonded in adjacent B(5) and B(10) positions. The molecule has approximate C_s molecular symmetry in the crystal.

Table IV. Interatomic Bond Angles for 5,10-$B_{10}H_{12}Br_2$ (deg)

B(2)-B(1)-B(3)	60.1 (5)	B(9)-B(4)-B(10)	61.7 (5)
B(2)-B(1)-B(4)	113.8 (6)	Br(1)-B(5)-B(1)	122.6 (5)
B(2)-B(1)-B(5)	60.8 (5)	Br(1)-B(5)-B(2)	125.9 (5)
B(2)-B(1)-B(10)	118.6 (6)	Br(1)-B(5)-B(6)	119.3 (5)
B(3)-B(1)-B(4)	59.1 (5)	Br(1)-B(5)-B(10)	117.3 (4)
B(3)-B(1)-B(5)	107.3 (6)	B(1)-B(5)-B(2)	61.3 (5)
B(3)-B(1)-B(10)	106.3 (6)	B(1)-B(5)-B(6)	110.2 (6)
B(4)-B(1)-B(5)	118.1 (6)	B(1)-B(5)-B(10)	55.0 (4)
B(4)-B(1)-B(10)	60.0 (5)	B(2)-B(5)-B(6)	57.9 (4)
B(5)-B(1)-B(10)	70.7 (5)	B(2)-B(5)-B(10)	106.5 (6)
B(1)-B(2)-B(3)	60.1 (5)	B(6)-B(5)-B(10)	116.4 (6)
B(1)-B(2)-B(5)	57.9 (5)	B(2)-B(6)-B(5)	60.2 (5)
B(1)-B(2)-B(6)	110.6 (6)	B(2)-B(6)-B(7)	61.3 (5)
B(1)-B(2)-B(7)	105.7 (7)	B(5)-B(6)-B(7)	104.1 (6)
B(3)-B(2)-B(5)	105.1 (6)	B(2)-B(7)-B(3)	60.6 (5)
B(3)-B(2)-B(6)	110.0 (7)	B(2)-B(7)-B(6)	57.8 (5)
B(3)-B(2)-B(7)	58.3 (5)	B(2)-B(7)-B(8)	106.7 (6)
B(5)-B(2)-B(6)	61.9 (5)	B(3)-B(7)-B(6)	109.4 (6)
B(5)-B(2)-B(7)	105.1 (6)	B(3)-B(7)-B(8)	55.6 (5)
B(6)-B(2)-B(7)	60.9 (5)	B(6)-B(7)-B(8)	116.7 (6)
B(1)-B(3)-B(2)	59.9 (5)	B(3)-B(8)-B(4)	59.9 (5)
B(1)-B(3)-B(4)	60.6 (5)	B(3)-B(8)-B(7)	55.9 (5)
B(1)-B(3)-B(7)	107.8 (6)	B(3)-B(8)-B(9)	109.3 (6)
B(1)-B(3)-B(8)	108.2 (6)	B(4)-B(8)-B(7)	106.7 (6)
B(2)-B(3)-B(4)	114.9 (6)	B(4)-B(8)-B(9)	57.5 (5)
B(2)-B(3)-B(7)	61.1 (5)	B(7)-B(8)-B(9)	118.5 (6)
B(2)-B(3)-B(8)	117.7 (6)	B(4)-B(9)-B(8)	61.3 (6)
B(4)-B(3)-B(7)	118.4 (7)	B(4)-B(9)-B(10)	60.3 (5)
B(4)-B(3)-B(8)	61.6 (5)	B(8)-B(9)-B(10)	104.0 (7)
B(7)-B(3)-B(8)	68.5 (5)	Br(2)-B(10)-B(1)	121.9 (5)
B(1)-B(4)-B(3)	60.3 (5)	Br(2)-B(10)-B(4)	127.0 (5)
B(1)-B(4)-B(8)	105.6 (6)	Br(2)-B(10)-B(5)	116.1 (5)
B(1)-B(4)-B(9)	111.2 (6)	Br(2)-B(10)-B(9)	120.0 (6)
B(1)-B(4)-B(10)	58.6 (4)	B(1)-B(10)-B(4)	61.5 (5)
B(3)-B(4)-B(8)	58.4 (6)	B(1)-B(10)-B(5)	54.3 (4)
B(3)-B(4)-B(9)	111.2 (6)	B(1)-B(10)-B(9)	110.6 (6)
B(3)-B(4)-B(10)	106.2 (6)	B(4)-B(10)-B(5)	106.0 (5)
B(8)-B(4)-B(9)	61.2 (6)	B(4)-B(10)-B(9)	58.0 (5)
B(8)-B(4)-B(10)	104.8 (6)	B(5)-B(10)-B(9)	117.1 (5)

Table V. Deviation of Atoms from Selected Planes[a]

Plane	Atom	Deviation of atom from plane, Å
B(1), B(3), B(5), B(6), B(7)	B(1)	-0.035 (9)
	B(3)	-0.020 (10)
	B(5)	0.055 (8)
	B(6)	-0.079 (9)
	B(7)	0.071 (10)
B(1), B(3), B(8), B(9), B(10)	B(1)	0.020 (8)
	B(3)	0.035 (9)
	B(8)	-0.086 (9)
	B(9)	0.095 (9)
	B(10)	-0.051 (8)
Br(1), Br(2), B(5), B(10)	Br(1)	0.000 (1)
	Br(2)	0.000 (1)
	B(5)	0.000 (8)
	B(10)	-0.003 (8)

[a] Coefficients of the equations of the planes in the form $ax + by + cz - d = 0$; $a = 4.2431$, $b = 6.9794$, $c = -5.8484$, and $d = 6.2822$. Least-squares planes calculated according to W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961). Equations given in monoclinic coordinates.

2.00 (1) Å (1.97 Å in $B_{10}H_{14}$).

The bromine–boron bonding parameters compare quite favorably with what has been observed in other bromoborane systems, 1-Br-μ-$(CH_3)_3SiB_5H_7$,[23] o-$B_{10}Br_2H_8C_2H_2$,[24] o-$B_{10}Br_3H_7C_2H_2$,[25] and o-$B_{10}Br_4H_6C_2H_2$.[26] The Br(1)-B(5) and Br(2)-B(10) bond distances of 1.942 (8) and 1.940 (8) Å, respectively, lie at the short end of the 1.96–1.99 Å range observed for borane B–Br bonds. The Br(1)–Br(2) nonbonded distance is 3.95 Å, close to the minimum van der Waals distance of 3.9 Å calculated for two bromine atoms in adjacent positions on an icosahedron.[24] The average B–B–Br angles in the system differ only slightly from the analogous B–B–H angles found in $B_{10}H_{14}$[27] (B–B–H analogue angle in parentheses): B(10)-B(5)-Br(1) and B(10)-B(5)-Br(2), 116.7° (116.9°); B(2)-B(5)-Br(1) and B(4)-B(10)-Br(2), 126.5° (125.3°); B(6)-B(5)-Br(1) and B(9)-B(10)-Br(2), 119.7° (120.3°); B(1)-B(5)-Br(1) and B(1)-B(10)-Br(2), 122.3° (121.4°). This, along with the fact that Br(1), Br(2), B(5), and B(10) remain coplanar (Table V), indicates that interaction between bromine atoms of 5,10-$B_{10}H_{12}Br_2$ must be relatively small.

Furthermore, bromine atom substitution at the B(5) and B(1) positions causes relatively little distortion of the decaborane cage. Only small deviations from pentagonal coplanarity are shown by the boron atoms of the B(1), B(3), B(5), B(6), B(7) and B(1), B(3), B(8), B(9), B(10) atom groups (Table V). Within the limits of our data, all B–B distances in the 5,10-$B_{10}H_{12}Br_2$ cage are equivalent to the distances between corresponding boron atoms in $B_{10}H_{14}$[27] except for the shorter B(1)–B(5) and B(1)–B(10) distances of 1.73 (1) and 1.72 (1) Å (1.77 Å in $B_{10}H_{14}$), the shorter B(3)–B(7) and B(3)–B(8) distances of 1.73 (1) and 1.74 (1) Å (1.78 Å in $B_{10}H_{14}$), the shorter B(7)–B(8) distance of 1.95 (1) Å (1.97 Å in $B_{10}H_{14}$), and the slightly longer B(5)–B(10) distance of

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Synthesis, Structure, and Properties of Trichloro- and Tribromo(2-(2'-pyridyl)quinoline)gold(III)

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The title complexes Au(pq)Cl$_3$ and Au(pq)Br$_3$ (pq = 2-(2'-pyridyl)quinoline) have been synthesized and their crystal and molecular structures determined from X-ray data obtained by counter methods. The compounds are isomorphous and crystallize in the space group $P2_12_12_1$, with $Z = 4$ in unit cells of dimensions $a = 7.711$ (7), $b = 10.04$ (1), and $c = 19.34$ (4) Å (Au(pq)Cl$_3$) and $a = 8.050$ (4), $b = 10.13$ (2), and $c = 19.52$ (1) Å (Au(pq)Br$_3$). The structures were solved by the heavy-atom method and refined by full-matrix least squares to $R = 6.5\%$ (Au(pq)Cl$_3$, 1511 reflections) and $R = 5.1\%$ (Au(pq)Br$_3$, 907 reflections). The compounds consist of discrete diamagnetic five-coordinated molecules. The distribution of the ligands about the metal is approximately square pyramidal with the axial ligand displaced from the vertical and at a relatively great distance from the metal, so that they may also be described as strongly distorted square planar. The direction of the distortion is such as to reduce the energy of the high-spin (triplet) state but not enough to produce a high-spin ground state.

Introduction

Gold compounds have been of long-standing biological interest for use as drugs and catalysts in biological systems.[1] The observation of five-coordinated complexes is important in the understanding of gold(III) chemistry. Many reactions of gold(III) are proposed to proceed via a five-coordinated intermediate. The slow kinetics[2] of ligand exchange and substitution with gold(III) compounds may be explained by the relative instability of the five-coordinated intermediates compared with the square-planar compounds. Five-coordinated intermediates are also important in the action of gold(III) on certain amino acids. Gold(III) has been shown to stereospecifically drive the oxidation of (S)-methionine to (S)-methionine S-sulfoxide,[3] a reaction which presumably proceeds via a five-coordinate intermediate with the amino acid chelated to the gold(III). The oxidative attack is then confined to an approach that is sterically limited by the other ligands (chlorine) on the gold.

Ring-substituted dipyridyl, phenanthroline, and terpyridyl ligands induce a variety of unusual structures with transition metals, including pseudotetrahedral, five-coordinated monomeric, or dimeric compounds of manganese(II), nickel(II), and copper(II).[4-8] Stable five-coordinated gold complexes have been obtained with two such ligands,[9,10] (I) 2,2'-biquinolyl and (II) 2,9-dimethylphenanthroline, due to extreme ligand–ligand

I
biq

II
dmp

III
pq

steric crowding caused by the ring substituents. An exami-

nation of these structures leads us to postulate that five-coordinated complexes could be formed with the much less sterically hindered ligand (III) 2-(2'-pyridyl)quinoline. We report here on the synthesis and crystal structures of the five-coordinated gold(III) complexes trichloro- and tribromo(2-(2'-pyridyl)quinoline)gold(III), Au(pq)X$_3$, X = Cl, Br.

Experimental Section

Preparation of Compounds. Au(pq)Cl$_3$. Sodium tetrachloroaurate(III) in absolute ethanol was added to a stoichiometric amount of pq in benzene. The orange-yellow crystals precipitated slowly and were filtered, washed with benzene and ethanol, and dried. Crystals suitable for X-ray study were obtained by slow evaporation of a saturated solution of the compound in nitrobenzene.

Au(pq)Br$_3$. The preparation of the compound is as above using NaAuBr$_4$. The product is formed as orange-red crystals. Sodium tetrabromoaurate(III) was prepared by repeatedly dissolving NaAuCl$_4$ in concentrated HBr and then heating to dryness.
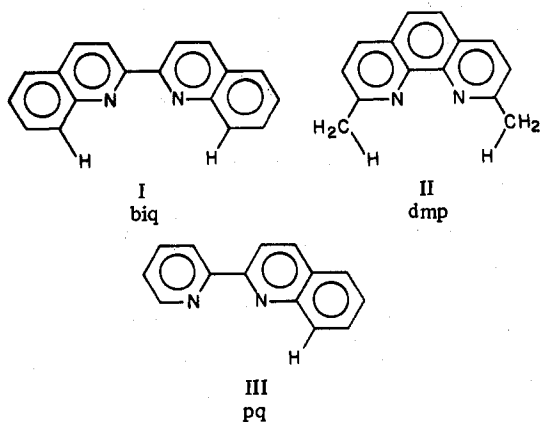
2-(2'-Pyridyl)quinoline. This ligand was prepared by the method of Smirnoff.[11] o-Aminobenzaldehyde, freshly prepared by steam distillation,[12] in ethanol is mixed with a stoichiometric amount of 2-acetylpyridine. After a stoichiometric amount of NaOH was added as 1 N NaOH, the mixture was refluxed for 1 h on a steam bath. The mixture was decolorized with charcoal, filtered, and diluted with hot water until turbid. The compound crystallized on cooling in ice, was filtered, and recrystallized twice from methanol.

Magnetic Susceptibility. Measurements were made on a superconducting susceptometer and the complexes were found to be diamagnetic.

Crystal Data for Au(pq)Cl$_3$. AuCl$_3$N$_2$C$_{14}$H$_{10}$: mol wt 510; space group $P2_12_12_1$; $Z = 4$; $a = 7.711$ (7), $b = 10.04$ (1), $c = 19.34$ (4) Å; $V = 1498$ Å^3; $\rho_{calcd} = 2.13$ g cm^{-3}, $\rho_{obsd} = 2.2$ g cm^{-3}; μ(Mo Kα) = 100 cm^{-1}; crystal dimensions (mm from centroid) (100) 0.32, ($\bar{1}$00) 0.32, (010) 0.40, (0$\bar{1}$0) 0.40, (001) 0.038, (00$\bar{1}$) 0.038, (110) 0.30, ($\bar{1}\bar{1}$0) 0.30, (1$\bar{1}$0) 0.295, ($\bar{1}$10) 0.295; maximum and minimum transmission coefficients 0.58 and 0.26.

Crystal Data for Au(pq)Br$_3$. AuBr$_3$N$_2$C$_{14}$H$_{10}$, mol wt 643; space group $P2_12_12_1$; $Z = 4$; $a = 8.050$ (4), $b = 10.13$ (2), $c = 19.52$ (1) Å; $V = 1592$ Å^3; $\rho_{calcd} = 2.68$ g cm^{-3}, $\rho_{obsd} = 2.7$ g cm^{-3}; μ(Mo Kα) = 175 cm^{-1}, crystal dimensions ($2\bar{1}$0) 0.07, ($\bar{2}$10) 0.07, (011) 0.05, (0$\bar{1}\bar{1}$) 0.05, (01$\bar{1}$) 0.05, (0$\bar{1}$1) 0.05; maximum and minimum transmission coefficients 0.32 and 0.18.

For each crystal, the Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an ori-