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(50) Recent pulse radiolysis experiments have detected a two-stage reduction of *Clostridium pasteurianum* 8-Fe Fd_{ox} by solvated electrons.[51] The very fast initial reduction ($k_1 = 3.4 \times 10^{10}\ M^{-1}\ s^{-1}$) is followed by a slower, apparently intramolecular process ($k_2 = 1.1 \times 10^3\ s^{-1}$). It is not clear whether the latter corresponds to electron transfer from one 4-Fe site to the other or from a reduced phenyl ring of a Phe or Tyr residue to a 4-Fe site.[51]
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Hydroboration Reactions with 6-Thia-*nido*-decaborane(11)

B. J. Meneghelli, M. Bower, N. Canter, and R. W. Rudolph*

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109.

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Abstract: Alkenes and alkynes undergo a facile hydroboration reaction with $6\text{-}SB_9H_{11}$. Alkenes give $9\text{-}R\text{-}6\text{-}SB_9H_{10}$ products where R = alkyl. Those alkenes investigated were ethylene, 1-octene, cyclohexene, cyclopentadiene, styrene, and 1-methyl-1-cyclohexene. Alkynes give $9\text{-}R'\text{-}6\text{-}SB_9H_{10}$ products where R′ = alkenyl. In the case of acetylene a double hydroboration occurs to give $9,9'\text{-}CH_3CH\text{-}(6\text{-}SB_9H_{10})_2$. Those alkynes investigated were acetylene, diphenylacetylene, phenylacetylene, and 3-hexyne. Attachment of the organic moiety to the 9 position of the $6\text{-}SB_9H_{10}$ cage was established by ^{11}B NMR. The ^{13}C and ^1H NMR spectra and mass spectra were also consistent with hydroboration. Oxidation of the organothiaboranes by alkaline peroxide gave the expected ketone or alcohol for most cases. The observation of *trans*-2-methylcyclohexanol after oxidation of the 1-methyl-1-cyclohexene hydroboration product indicates that the hydroboration is a regiospecific anti-Markownikoff syn addition. A possible mechanism is discussed. Pyrolysis (400–450 °C) of the nido $9\text{-}R\text{-}6\text{-}SB_9H_{10}$ molecules gives the corresponding closo derivative as a mixture of 2-, 6-, and $10\text{-}R\text{-}1\text{-}SB_9H_8$ isomers. The interaction of aldehydes and ketones with $6\text{-}SB_9H_{11}$ is more complex and involves degradative hydroboration.

Introduction

A facile and clean hydroboration reaction for a nonpyrophoric, polyhedral borane was not demonstrated until our recent report concerning the reactions of $6\text{-}SB_9H_{11}$.[1] For instance, it is necessary to subject a mixture of the pyrophoric pentaborane(9) and an olefin to 150 °C in order to form 2-alkyl-B_5H_8 species (alkyl = *n*-Bu, *sec*-Bu, *i*-Bu, Et).[2] Pentaborane(11) hydroborates ethylene,[3] but the reaction is not clean and B_5H_{11} is even more difficult to prepare and handle than B_4H_{10} or B_5H_9. The reactions of B_5H_{11} and B_4H_{10} with acetylenes lead to complex product mixes which include carboranes[4] (i.e., some carbon is incorporated into the cage). In contrast, the hydroboration described here involves the easily handled and readily prepared 6-thia-*nido*-decaborane(11).

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Experimental Section

General. Infrared spectra were obtained on a Perkin-Elmer 457 as thin films spread on a KBr plate. The ^{13}C and ^{11}B NMR spectra were obtained on a JEOL JNM-PS-100 with an EC-100 data system operating at 25.0 and 32.1 MHz, respectively. ^1H NMR spectra were determined on a Varian T-60, or the JEOL JNM-PS-100. The chemical-shift standards and conventions are reported in the tables. Mass spectra were obtained on an AEI MS-902. GC-MS analyses were performed on either an AE/MS-30 double beam instrument with a Pye series 104 chromatograph using a 5 ft × 1/4 in. column or a Du Pont Dimaspec Model 321 with a 5 ft × 1/8 in. column packed with OV-101 (1.5-2%), OV-17 (2%), or SE-30 (4%) on supports of Chromosorb G 100/120 or Chromosorb W 100/120.

The preparation of 6-SB_9H_{11} has been described previously.[5] The benzene or cyclohexane solvent was either vacuum distilled from Na and benzophenone prior to use or syringed under N_2 from a reservoir containing 3A molecular sieves as a drying agent. Diethyl ether was distilled from P_2O_5 or $LiAlH_4$ and stored over 3A molecular sieves prior to use. Cyclohexane was vacuum distilled from $LiAlH_4$. Reactions and purifications were run under an atmosphere of prepurified nitrogen (Linde).

[9-(6-Thia-*nido*-decaboranyl)]ethane. This preparation describes a typical procedure. Subsequent descriptions include only the essential differences; yields of sublimed products are given in Table I. To 25 mL of dry benzene or cyclohexane in a 100-mL three-necked flask was added 347.5 mg (2.45 mmol) of 6-SB_9H_{11}. Ethylene (Linde, CP grade) was bubbled through the refluxing solution for 7 h. Gradually the color of the solution turned from clear to a pale yellow. Evaporation of the solvent and sublimation of the product at 70 °C yielded 180 mg (43%) of a yellow, air-sensitive liquid. Mass spectral analysis showed a cutoff of 172 corresponding to $^{34}S^{11}B_9{}^1H_{15}{}^{12}C_2$. The ratio of the *m/e* 170 to 172 peaks was 20:1, which corresponds well with the expected ^{32}S:^{34}S ratio of 22.5:1.

1,1-[9,9′-Bis(6-thia-*nido*-decaboranyl)]ethane. Typically, 348 mg (2.45 mmol) of 6-SB_9H_{11} was used. An excess of acetylene (Linde, purified grade) was bubbled through the solution while an H_2SO_4 scrubbing apparatus similar to that described previously[6] was employed. After 8 h of reflux, the pale yellow solution was evaporated and the residue sublimed at 100°C in vacuo to yield 180 mg (47%) of off-white, air-sensitive crystals. Mass spectral analysis showed the presence of two SB_9H_{10} units indicating a double hydroboration.

1-[9-(6-Thia-*nido*-decaboranyl)]-*cis*-1,2-diphenylethene. Typically, 228 mg (1.61 mmol) of 6-SB_9H_{11} and 286 mg (1.61 mmol) of diphenylacetylene (Aldrich) were used. During 12 h of reflux the yellow color of the solution deepened. The sublimed yellow crystals had mp 93-95 °C (uncorrected). Mass spectral analysis showed the cutoff to be 322, which corresponds to a formulation $^{34}S^{11}B_9{}^1H_{21}{}^{14}C_{12}$. The product was relatively air stable for 12-24 h but slowly decomposed over a period of 2-3 weeks. Anal. Calcd: S, 10.06; B, 30.53; H, 6.64; C, 52.77. Found: S, 9.9; B, 30.23; H, 6.49; C. 52.42.

[9-(6-Thia-*nido*-decaboranyl)]cyclohexane. Typically, 316 mg (2.23 mmol) of 6-SB_9H_{11} and 0.23 mL of freshly distilled cyclohexene (dried over P_2O_5) were used. Mass spectral analysis indicates an *m/e* cutoff of 226, which corresponds to $^{34}S^{11}B_9{}^1H_{21}{}^{12}C_6$. The ratio of the *m/e* 224:226 peaks is 20:1, which corresponds well with the expected ^{32}S:^{34}S ratio of 22.5:1. This pale yellow, semisolid product decomposes to boric acid and unidentified organic compounds over a few hours in the air.

1-Methyl-2-[9-(6-thia-*nido*-decaboranyl)]cyclohexane. Typically, 224 mg (1.55 mmol) of 6-SB_9H_{11} and 0.185 mL (1.55 mmol) of 1-methylcyclohexene were used. Mass spectral analysis of this air-sensitive liquid showed a cutoff of *m/e* 240 and a correct ratio for $^{32}S/^{34}S$.

3-[9-Thia-*nido*-decaboranyl)]-*cis*-3-hexene. Typically, 401 mg (2.82 mmol) of 6-SB_9H_{11} and 0.34 mL (0.282 mmol) of 3-hexyne (Farchan) were used. Mass spectral analysis of the product gave a cutoff at *m/e* 226, corresponding to a $^{34}S_1{}^{11}B_9{}^1H_{21}{}^{12}C_6$ formulation. The foul-smelling liquid decomposes readily in air as evidenced by the growth of boric acid in the IR on successive runs (approximately 10-15 min between runs).

1-[9-(6-Thia-*nido*-decaboranyl)]octane. Typically, 319 mg (2.25 mmol) of 6-SB_9H_{11} and 0.35 mL (2.25 mmol) of 1-octene (Aldrich) were used. The color of the solution turned yellow after 4 h of reflux. Evaporation of the yellow solution after an additional 8 h of refluxing yielded a yellow, liquid residue. Sublimation of this residue at 80 °C resulted in 400 mg (69.5%). Mass spectral analysis of the light yellow, foul-smelling liquid showed an *m/e* of 256, corresponding to $^{11}B_9{}^{34}S^{10}H_1{}^{12}C_8{}^{17}H_1$.

1,3-[9,9′-Bis(6-thia-*nido*-decaboranyl)]cyclopentane. Typically, 422.8 mg (2.98 mmol) of 6-SB_9H_{11} and 0.12 mL (1.49 mmol) of freshly distilled cyclopentadiene were used. The slightly yellow product had a *m/e* cutoff at 364. Infrared analysis showed the terminal B-H stretch at ~2600 cm^{-1}, a bridge B-H-B absorption at ~2000 cm^{-1}, and no C=C bond absorptions.

1-[9-(6-Thia-*nido*-decaboranyl)]-2-phenylethane. Typically, 200 mg (1.42 mmol) of 6-SB_9H_{11} and 0.16 mL (1.41 mmol) of styrene were used. The solution did not yellow appreciably even after 22 h of reflux. Evaporation gave a slightly yellow, viscous liquid which was sublimed with a 49% yield (170 mg). Characterization is given in the tables.

Reaction of 6-SB_9H_{11} with Diphenylacetylene in THF or CH_3CN. To 25 mL of dry tetrahydrofuran in a 100-mL, three-neck, round-bottomed flask was added 150 mg (1.04 mmol) of 6-SB_9H_{11}. After the mixture was stirred for 30 min at 25 °C, 186 mg (1.04 mmol) of diphenylacetylene was added, but no change in color was observed. Evaporation of the clear solvent after 24 h of stirring and then vacuum sublimation at 75 °C yielded 175 mg (94%) of white crystals identified as diphenylacetylene. Mass spectral analysis of the white residue showed it to have a cutoff at *m/e,* 216, corresponding to SB_9H_{11}·THF. Acetonitrile as a solvent under similar conditions also gave no hydroboration of the acetylene and yielded SB_9H_{11}·CH_3CN. Some evidence for hydroboration was obtained when SB_9H_{11}·THF or SB_9H_{11}·CH_3CN[7] was used in benzene or cyclohexane at reflux.

Reaction of 6-SB_9H_{11} with Diphenylacetylene in Diethyl Ether. To 25 mL of dry diethyl ether were added 170 mg (1.18 mmol) of 6-SB_9H_{11} and 210 mg (1.18 mmol) of diphenylacetylene. The color of the solution gradually turned dark yellow over a period of 24 h. Evaporation of the solvent and sublimation of the yellow residue yielded 251 mg (66%) of yellow crystals. Infrared and mass spectral data showed the product to be identical with the hydroboration product obtained in benzene or cyclohexane.

Oxidation of Organothiaboranes. Oxidation products were identified by GC/MS, ^1H NMR, and IR.

Oxidation of 1-[9-(6-Thia-*nido*-decaboranyl)]-*cis*-1,2-diphenylethene. To 25 mL of diethyl ether in a 100-mL three-necked flask equipped with a reflux condenser and a nitrogen inlet was added 76.3 mg (0.24 mmol) of 1-[9-(6-thia-*nido*-decaboranyl)]-*cis*-1,2-diphenylethene. The yellow color remained during the addition of 0.08 mL of 3 M NaOH and 5 mL of 95% ethanol as a cosolvent. The slow addition of 1.07 mL (12 mmol) of 30% H_2O_2 produced immediate bubbling and dissipation of the yellow color with concurrent precipitation of a white solid. After 3 h of stirring at 25 °C, the colorless solution was neutralized with dilute HCl and shaken with three 20-mL portions of cold distilled water to remove the boric acid. The ether layer was finally washed with saturated NaCl and dried over $MgSO_4$. Rotary evaporation of the ether left behind 42 mg (90%) of a white solid identified as deoxybenzoin (α-phenylacetophenone).

Oxidation of 3-[9-Thia-*nido*-decaboranyl)]-3-hexene. To 25 mL of diethyl ether were added 175 mg (0.77 mmol) of 3-[9-(6-thia-*nido*-decaboranyl)]-3-hexene, 0.26 mL of 3 M NaOH, and 5 mL of 95% ethanol. The addition of 3.5 mL of 30% H_2O_2 was controlled so as to produce a gentle reflux. After 6 h of stirring at 25 °C, the ether layer was separated. The aqueous layer was neutralized with dilute HCl and extracted with three 25-mL portions of ether. The combined ether layers were dried over $MgSO_4$ and evaporated to yield 62 mg (80%) of 3-hexanone.

Oxidation of 1-[9-(6-Thia-*nido*-decaboranyl)]octane. To 25 mL of diethyl ether in a 100-mL, three-necked flask equipped with a reflux condenser and a nitrogen bubbler were added 576 mg (2.25 mmol) of 1-[9-(6-thia-*nido*-decaboranyl)]octane, 0.75 mL of 3 M NaOH, and 5 mL of 95% ethanol. The addition of 10 mL (112.5 mmol) of 30% H_2O_2 was controlled so as to produce a gentle reflux of the ether. The yellow color of the solution gradually disappeared over a period of 3 h. The clear solution was neutralized with dilute HCl and the ether layer washed with three 20-mL portions of cold distilled water. The ether layers were dried over $MgSO_4$ and evaporated to give 279 mg (95%) of a clear liquid whose IR and NMR spectra agreed with those of 1-octanol. A GC/MS of the product showed <5% of 2-octanol as a byproduct.

Oxidation of 1-[9-(6-Thia-*nido*-decaboranyl)]cyclohexane. To 25 mL of diethyl ether in a 100-mL, three-necked flask were added 150 mg (0.66 mmol) of 1-[9-(6-thia-*nido*-decaboranyl)]cyclohexane, 0.22 mL of 3 M NaOH, and 5 mL of 95% ethanol. After a gradual addition

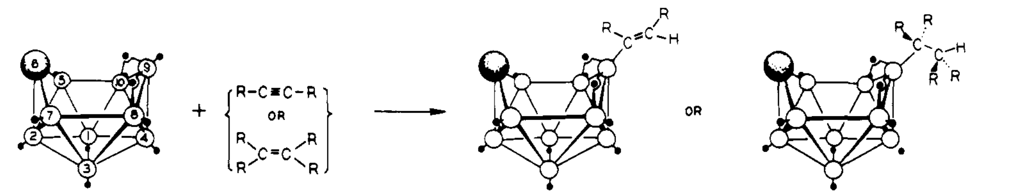

Figure 1. The hydroboration of alkenes and alkynes by $6\text{-}SB_9H_{11}$.

Table I. Organothiaboranes and Oxidation Products

substrate	% yield hydroborn product[a]	oxidn product[b]	% yield
diphenylacetylene	85	deoxybenzoin	90
3-hexyne	55	3-hexanone	80
acetylene	69[c]	*e*	
ethylene	60	*e*	
1-octene	55	1-octanol	95
cyclohexene	70	cyclohexanol	83
cyclopentadiene	67[d]	*e*	
1-methyl-1-cyclohexene	74	*trans*-2-methylcyclohexanol	75
styrene	50	2-phenylethanol	65

[a] Recovery by sublimation. [b] Oxidation with alkaline hydrogen peroxide. [c] Two moles of thiaborane consumed per mole of acetylene. [d] Molar ratio of thiaborane/cyclopentadiene = 2/1. [e] Oxidation not investigated.

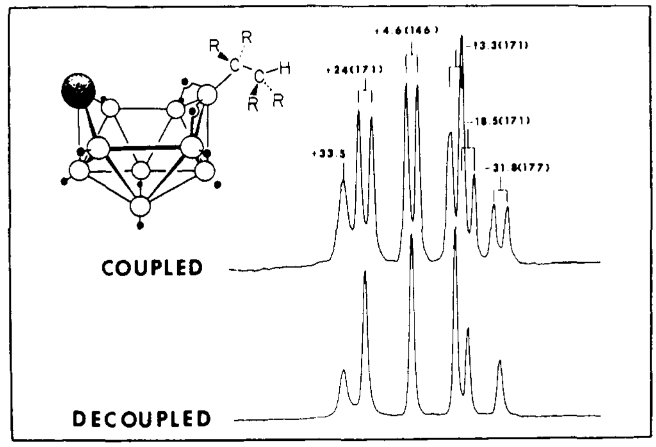

Figure 2. The 32.1-MHz ^{11}B NMR spectrum of $1\text{-}[9\text{-}(6\text{-}SB_9H_{10})]\text{-}C_2H_5$. The bottom trace is proton decoupled.

of 3 mL (33 mmol) of 30% H_2O_2 and 5 h of stirring, the ether layer was separated. The aqueous layer was neutralized with dilute HCl and extracted with three 25-mL portions of ether. The ether layers were combined and dried over $MgSO_4$. Evaporation of the ether yielded 54 mg (83%) of cyclohexanol.

Oxidation of 1-Methyl-2-[9-(6-thia-*nido*-decaboranyl)]cyclohexane. To 25 mL of diethyl ether were added 135 mg (0.56 mmol) of 1-methyl-2-[9-(6-thia-*nido*-decaboranyl)]cyclohexane, 0.19 mL of 3 M NaOH, and 5 mL of 95% ethanol. After gradual addition of 2.6 mL of 30% H_2O_2 and 6 h of stirring, the ether layer was separated. The aqueous layer was neutralized with dilute HCl and washed with three 25-mL portions of dry ether. The combined ether layers were dried over $MgSO_4$ and evaporated to yield 48 mg (75%) of *trans*-2-methylcyclohexanol.

Aldehydes and Ketones with $6\text{-}SB_9H_{11}$. To 14.1 mg (0.10 mmol) of $6\text{-}SB_9H_{11}$ dissolved in 0.4 mL of benzene-d_6 in a 5-mm o.d. NMR tube was added 5.6 μL of acetaldehyde (0.10 mmol). The ^{11}B NMR spectrum was determined within 0.5 h; then a second 5.6-μL aliquot of CH_3CHO was added and the spectrum determined again, etc., until an excess of aldehyde was present. Samples for the ^1H NMR spectra were determined in the same manner using 8–10 mg of $6\text{-}SB_9H_{11}$. Similar experiments were run with benzaldehyde and acetone. The results are summarized in the Results and Discussion section. At each reactant ratio, the $6\text{-}SB_9H_{11}$ signal was subtracted with the computer from the ^{11}B spectrum until it was evident that the SB_9H_{11} had reacted completely.

Pyrolysis of Organothiaboranes. The two organothiaboranes derived from diphenylacetylene and 3-hexyne were investigated. The pyrolysis apparatus and procedures have been described previously in detail.[5] Here, about 200 mg of the organothiaborane was placed at the bottom of a tube 60 cm long and 15 mm in diameter. Sublimation of the material through a 20-cm hot zone at 350 °C gave 90% recovery of unchanged starting material. However, at 450 °C hydrogen evolution was observed. After 4–5 h all the material had passed through the hot zone and condensed on the cooler glass walls above the furnace. After cooling to 25 °C the system was back-filled with nitrogen. The pyrolysate was dissolved in dry benzene and transferred to a sublimator for purification. Typically, about 100 mg of sublimate was recovered. GC/MS showed three peaks of the same molecular weight which were all 2 mass units lower than starting material. The infrared spectrum was much simpler than that of the starting material with no absorption in the B–H–B region and a double B–H peak at ~2500–2600 cm^{-1} which is very similar to that of $1\text{-}SB_9H_9$.[5] The ^{11}B NMR of the mixture of three products shows the presence of a downfield signal at +70 ppm from $BF_3{\cdot}OEt_2$ and a complex upfield multiplet centered at −10 ppm. Both of these signals are close to those observed for $1\text{-}SB_9H_9$.[5] Therefore, the three peaks observed in the GC/MS are most likely due to upper belt, lower belt, and axially substituted closo thiaboranes.[8,9]

Results and Discussion

Although the reactions proceed at 25 °C for most alkenes and alkynes, they usually were run in refluxing benzene for 7–12 h to ensure completion. The solution generally turns yellow quickly upon addition of the alkene or alkyne to the thiaborane. Products were recovered by rotary evaporation of the benzene and sublimation of the yellow residue. Yields of sublimed product are shown in Table I. In all cases, the mass spectrum showed the expected parent ion cutoff with the correct ^{32}S:^{34}S intensity.

Structural Characterization. Hydroboration of alkenes and alkynes by $6\text{-}SB_9H_{11}$ clearly occurs by addition of the exo BH at the 9 position across the unsaturated CC bond as shown schematically in Figure 1. The substitution site is substantiated readily by ^{11}B NMR. All of the alkene and alkyne hydroboration products discussed here gave very similar ^{11}B NMR spectra (Figure 2 and Table II). These spectra all are reminiscent of that of $6\text{-}SB_9H_{11}$ (Table II)[5a] except for the marked downfield shift for the 9 position and its collapse from a doublet to a broad singlet due to replacement of a B–H by a B–C bond. The singlet position was verified by $^{11}B\{^1H\}$ double resonance as shown in Figure 2. The IR spectra of these organothiaboranes show bridge-hydrogen adsorptions in the 2040–1940-cm^{-1} range; those for $6\text{-}SB_9H_{11}$ are at 1920–1950 cm^{-1}. The alkenylthiaboranes also have a characteristic C=C stretch at 1590–1615 cm^{-1} (Table III). Unfortunately, ^1H and ^{13}C NMR data were not as useful for characterization as might be anticipated. The ^{13}C spectra were consistent with hydroboration even though of the six investigated only two spectra [those with the $B\text{-}C_5H_8$ and $B\text{-}C_2H_5$ moieties (Table IV)] showed signals which would be attributed to carbon bound to ^{11}B. Similar difficulties have been encountered for other organoboranes.[10a] The quadrupolar ^{11}B apparently gives rise to a broadening attributable to a T_2 scalar coupling such as that

Table II. ^{11}B NMR Data[a-c]

product	assignment: B(1,3) or B(5,7)	B(4)	B(2)	B(5,7) or B(1,3)	B(8,10)	B(9)
3-[9-(6-thia-*nido*-decaboranyl)]-3-hexene	+3.4 (151)	−31.3 (181)	−16.4 (156)	+24 (161)	−16.4 (156)	+31.3
1-[9-(6-thia-*nido*-decaboranyl)]cyclohexane	+4.6 (146)	−31.7 (171)	−18.8 (151)	+24.1 (176)	−13.9 (161)	+34.2
[9-(6-thia-*nido*-decaboranyl)]ethane	+4.6 (146)	−31.8 (177)	−18.5 (171)	+24 (171)	−13.3 (171)	+33.5
1-[9-(6-thia-*nido*-decaboranyl)]octane	+4.4 (147)	−31.9 (191)	−18.6 (156)	+23.8 (176)	−13.7 (154)	+32.2
1-methyl-2-[9-(6-thia-*nido*-decaboranyl)]-cyclohexane	+3.9 (149)	−31.7 (193)	−18.6 (144)	+24.3 (169)	−14 (144)	+34.8
1-[9-(6-thia-*nido*-decaboranyl)]-*cis*-1,2-diphenylethene[d]	+3.7 (147)	−30.8 (201)	−16.6 (151)	+23.5 (156)	−16.6 (151)	+29.2
1,1-bis[9-(6-thia-*nido*-decaboranyl)]ethane	+4.25 (152)	−31.8 (175)	−18.5 (123)	+24.6 (166)	−14.2 (142)	+33.8
1,3-bis[9-(6-thia-*nido*-decaboranyl)]cyclo-pentane	+4.6 (146)	−30.1 (161)	−18.8 (156)	+24.4 (161)	−13.6 (177)	+34.1
6-thia-*nido*-decaborane(11)	+6.8 (150)	−30.7 (180)	−21.5 (160)	+24.9 (170)	−10.1 (145)	+17.3 (170)

[a] All spectra taken at 32.1 MHz. [b] All signals are reported as follows: chemical shift in parts per million from external $BF_3{\cdot}OEt_2$, coupling constants in hertz (if applicable). Positive shifts are downfield from external $BF_3{\cdot}OEt_2$. [c] All compounds were run using C_6D_6 as the solvent (unless otherwise noted). [d] Solvent used was $CDCl_3$.

seen for ^{14}N–C bonds.[10b] The ^{1}H NMR spectra were in many cases simpler than expected (Table IV) and could not be used for definitive characterization in most cases.

Analysis of the alcohol or ketone which results upon alkaline-peroxide oxidation of the organothiaboranes establishes the stereochemistry of hydroboration. Alkenes and alkynes and their oxidation products after hydroboration are given in Table I. A particularly definitive observation is that 1-methyl-1-cyclohexene gives *trans*-2-methylcyclohexanol after oxidation of the organothiaborane. This indicates that the hydroboration is a regiospecific anti-Markownikoff syn addition. The other oxidations also are consistent but not definitive for the latter stereochemistry. The boron is preferably attached to the least hindered carbon.

Organothiaboranes. Because of their thermal stability, organothiaboranes may prove superior to monoboranes[11] in multistep synthesis. The latter and other facets of synthetic organic chemistry via organothiaboranes currently are under investigation. Conversely, this hydroboration reaction allows for a wide modification of thiaborane properties through the easy formation of a multitude of organic derivatives. Thus, although thiaboranes such as *arachno*-6-$SB_9H_{12}^-$, *nido*-6-SB_9H_{11}, and *closo*-1-SB_9H_9 are readily available in good yield from $B_{10}H_{14}$,[5] there previously was no ready means for the preparation of a wide variety of organothiaboranes in good yield. Methods such as the Friedel-Crafts alkylation of 1-SB_9H_9[9] do not provide the variety demonstrated here.

Just as the pyrolysis of *nido*-6-SB_9H_{11} at 450 °C gives *closo*-1-SB_9H_9,[5] we have found that organo-substituted derivatives of *closo*-1-thiadecaborane(9) can be obtained by the 450 °C pyrolysis of the correspondingly 9-substituted *nido*-6-thiadecaborane(11). The pyrolysate typically contains a mixture of three closo isomers as shown by GC/MS analysis. None of the latter isomers was separated, but the ^{11}B NMR of the mixture was distinctly similar to that of 1-SB_9H_9[5] and is interpreted best as a mixture of the 10-, 6-, and 2-substituted isomers of 1-SB_9H_9.[8,9]

Carborane Formation. The treatment of *nido*-$B_{10}H_{14}$ with acetylene in the presence of Lewis bases such as MeCN and Me_2S produces *closo*-1,2-$C_2B_{10}H_{12}$.[12,13] Substituted acetylenes give the corresponding C-substituted icosahedral cluster molecule. In the absence of Lewis bases, no reaction occurs between acetylenes and $B_{10}H_{14}$.[12] Since *nido*-6-SB_9H_{11} has the same framework structure[5a] as *nido*-$B_{10}H_{14}$ and since 6-SB_9H_{11} is isoelectronic with $B_{10}H_{14}$, it was anticipated that treatment of 6-SB_9H_{11} with acetylenes in the presence of Lewis bases would produce a new dicarbathiaborane with a 12-atom framework. However, the results cited above demonstrate that no C atoms are substituted into the framework. The substitution is exo- rather than endopolyhedral. We have found that the exopolyhedral hydroboration proceeds slower in the presence of MeCN or THF. It is best to exclude Lewis bases from the reaction mixture for efficient hydroboration; however, a weak donor such as Et_2O can be used as a solvent. The formation of 1,2-dicarba-*closo*-dodecaborane(12) from *nido*-$B_{10}H_{14}$ proceeds as outlined in the following equations.

$$B_{10}H_{14} + 2L \rightarrow B_{10}H_{12} \cdot 2L + H_2$$

$$B_{10}H_{12} \cdot 2L + C_2H_2 \rightarrow C_2B_{10}H_{12} + H_2 + 2L$$

Kinetic investigations suggest that dissociative loss of L from *arachno*-6,9-$L_2B_{10}H_{12}$ to form *nido*-$B_{10}H_{12}{\cdot}L$ is critical to the formation of $C_2B_{10}H_{12}$.[14] The exact structure of the nido intermediate is not known, but one isolable isomer does not have the chemical reactivity necessary to be this critical intermediate.[14,15] There is, however, evidence of hydroboration side products.[14] Since *nido*-6-SB_9H_{11} is isoelectronic with *nido*-$B_{10}H_{12}{\cdot}L$, the hydroboration of acetylenes by 6-SB_9H_{11} probably models an intermediate in the insertion of C_2H_2 into *nido*-$B_{10}H_{12}{\cdot}L$ to ultimately give $C_2B_{10}H_{12}$. In addition to our results and another brief report,[14] separate evidence for the intermediacy of a "hydroborated" species is provided by 5-SMe_2-9-C_6H_{11}-*nido*-$B_{10}H_{11}$ which formed by the reaction of $B_{10}H_{12}{\cdot}(SMe_2)_2$ with cyclohexene.[15]

Based on the examples of hydroboration by SB_9H_{11} and $B_{10}H_{12}{\cdot}SMe_2$, it would appear that a low-order BH vertex attached to the remainder of the polyhedron through only three nearest-neighbor borons and two bridge hydrogens (Figure 3) is a prerequisitie for facile hydroboration. The results with simpler boranes such as B_5H_9 corroborate this observation.[4]

Aldehydes and Ketones. The interaction of aldehydes and ketones such as acetaldehyde, benzaldehyde, and acetone is more complex than with alkenes and alkynes. We have been unable to isolate pure products regardless of reaction stoichiometry. However, a good indication of the nature of the reactions was gleaned from a ^{1}H and ^{11}B NMR study as a function of the (SB_9H_{11}):(carbonyl) mole ratio. Fourier-transform "difference" techniques proved invaluable in interpreting the ^{11}B spectra since even at (SB_9H_{11}):(1–4 carbonyl) some unreacted SB_9H_{11} was evident but could be subtracted with the computer. The difference spectra indicated that at (SB_9H_{11}):(1–2 carbonyl) the primary reaction was hydroboration through the 9 position to give an alkoxy-substituted thiaborane:

$$6\text{-}SB_9H_{11} + RR'C{=}O \rightarrow 9\text{-}HRR'CO\text{-}6\text{-}SB_9H_{10} \quad (1)$$

The difference ^{11}B NMR was very reminiscent of those for

Table III. Infrared Spectra[a-c]

3-[9-(6-Thia-*nido*-decaboranyl)]-3-hexene
2966 s, 2941 s, 2876 s, 2570 vs, 2036 m, 1610 vs, 1470 sh, 1455 s, 1378 m, 1351 w, 1315 m, 1298 m, 1275 m, 1217 s, 1118 s, 1080 s, 1063 m, 1025 s, 1005 w, 980 m, 925 s, 895 w, 865 m, 832 w, 815 w, 805 w, 792 s, 738 m, 725 sh, 692 s, 650 m, 610 m, 595 w, 565 m, 435 w

1-[9-(6-Thia-*nido*-decaboranyl)]cyclohexane
2920 vs, 2900 sh, 2848 vs, 2560 vs, 2020 m, 1450 vs, 1375 w, 1358 m, 1295 m, 1285 m, 1270 m, 1258 sh, 1225 sh, 1220 m, 1190 w, 1172 w, 1155 sh, 1140 s, 1095 w, 1080 w, 1070 w, 1042 sh, 1025 s, 1005 m, 976 s, 935 w, 928 w, 906 m, 895 w, 885 m, 870 sh, 855 m, 838 m, 800 m, 773 w, 755 m, 740 m, 698 s, 668 sh, 652 m, 632 w, 625 w, 570 m, 555 sh, 513 w, 438 m

[9-(6-Thia-*nido*-decaboranyl)]ethane
2966 s, 2925 s, 2899 w, 2848 w, 2566 vs, 2000 m, 1458 m, 1418 w, 1381 w, 1294 m, 1195 w, 1130 w, 1102 s, 1132 s, 1008 s, 994 w, 970 w, 945 w, 922 w, 896 m, 864 w, 848 m, 835 sh, 792 m, 755 m, 747 sh, 730 sh, 692 s, 635 w, 615 w, 598 w, 563 m, 428 w

1-[9-(6-Thia-*nido*-decaboranyl)]octane
2955 sh, 2925 s, 2855 m, 2565 s, 2000 m, 1451 w, 1381 w, 1345 w, 1230 w, 1200 w, 1130 w, 1104 m, 1025 m, 990 m, 926 w, 900 w, 884 w, 850 sh, 840 w, 795 w, 740 w, 695 m, 645 w, 615 w, 560 w, 545 w, sh, 430 w

1-Methyl-2-[9-(6-thia-*nido*-decaboranyl)]cyclohexane
2900 s, 2840 s, 2550 s, 2000 m, 1460 sh, 1446 m, 1379 m, 1350 w, 1340 w, 1300 w, 1290 w, 1250 w, 1220 w, 1208 sh, 1138 m, 1085 w, 1072 w, 1020 m, 990 w, 970 w, 935 w, 920 sh, 895 w, 870 w, 860 w, 836 m, 795 m, 765 sh, 750 w, 740 w, 690 m, 650 w, 615 w, 565 w, 558 w

1-[9-(6-Thia-*nido*-decaboranyl)]-*cis*-1,2-diphenylethene
3070 w, 3055 m, 3020 m, 2970 sh, 2920 w, 2860 w, 2830 w, 2570 vs, 2000 m, 1960 m, 1945 m, 1890 w, 1865 w, 1800 w, 1655 w, 1600 sh, 1592 s, 1572 m, 1568 m, 1560 sh, 1525 w, 1490 s, 1480 sh, 1475 w, 1465 w, 1448 s, 1444 sh, 1370 w, 1315 w, 1290 w, 1265 w, 1215 m, 1185 w, 1155 w, 1117 m, 1100 w, 1072 m, 1025 m, 998 m, 975 w, 925 m, 905 w, 890 w, 858 w, 840 w, 795 w, 785 w, 755 s, 750 sh, 725 w, 695 s, 655 m, 637 w, 610 w, 563 m, 542 m

1,1-Bis[9-(6-thia-*nido*-decaboranyl)]ethane
2950 w, 2925 w, 2895 w, 2865 w, 2540 vs, 1990 m, 1457 sh, 1447 w, 1431 sh, 1375 w, 1290 w, 1178 m, 1118 sh, 1093 m, 1013 s, 970 s, 925 m, 900 sh, 893 w, 870 m, 853 w, 836 m, 790 m, 748 sh, 738 m, 690 s, 650 w, 610 w, 570 m, 542 w, 510 w, 475 sh, 442 w, 405 w

1,3-Bis[9-(6-thia-*nido*-decaboranyl)]cyclopentane
2931 m, 2864 m, 2530 vs, 2365 sh, 1985 m, 1445 m, 1300 m, 1260 w, 1150 sh, 1120 m, 1020 s, 990 s, 930 m, 918 w, 898 m, 868 w, 835 m, 795 m, 755 w, 740 m, 695 s, 653 m, 630 m, 572 s, 528 w, 478 w, 435 m

1-[9-(6-Thia-*nido*-decaboranyl)]-2-phenylethane
3075 w, 3055 w, 3025 m, 2915 m, 2855 m, 2560 vs, 1985 w, 1601 m, 1495 s, 1450 s, 1320 w, 1095 s, 1040 s, 985 s, 730 s, 680 s

[a] Bands are reported in cm^{-1} and intensities are described by s = strong, m = medium, w = weak, v = very, sh = shoulder. [b] Samples contain some boric acid owing to decomposition in air. [c] All samples were taken as neat films on a KBr plate.

9-(alkyl or alkenyl)-6-SB_9H_{10} (Table II). The results for acetaldehyde appear to be typical [ppm shift; d = doublet (J = 160–180 Hz), s = singlet; (intensity)]: 31.2, s (1); 23.1, d (2); −4.4, d (2); −22.1, d (1); −28.6, d (2); −32.9, d (1). There also is a small singlet at 17.7 ppm corresponding to $B(OEt)_3$.[16] The borate ester is evidenced also in the ^1H NMR by characteristic quartet and triplet signals at δ 3.87 and 1.11, respectively. Other quartets and triplets appear in these regions and are attributed to the ethoxy substituent of 9-CH_3CH_2O-6-SB_9H_{10} and the ethoxy substituents of other partial degradation products. With acetone and benzaldehyde, isopropoxy and benzyl signals, respectively, are apparent. As the amount of the carbonyl is increased, the degradation becomes more extensive as evidenced by loss of 6-SB_9H_{11} absorptions and growth of borate ester signals. At (SB_9H_{11}):(3–4 carbonyl) there appears to be evidence in the ^{11}B difference spectra for a fragment such as $SB_8H_6(OR)_2$. The ^{11}B spectrum for R = CH_2CH_3 is 29, s (~2); 4.8, d (1); −1.6, d (2); −13.4, d (2); −17.4, d (1). The partial degradation might be given by the equation

$$SB_9H_{11} + 5CH_3CHO \rightarrow SB_8H_6(OCH_2CH_3)_2 + B(OCH_2CH_3)_3 \quad (2)$$

However, this is rather speculative at this point. We previously observed that the thiaboranes $SB_{11}H_{11}$, $SB_{10}H_{12}$, and SB_9H_9 are partially degraded by alcohols to SB_8 species which appear to have enhanced kinetic stability and can be "trapped" in the presence of phosphine platinum complexes to give platinathiadecaboranes such as 9,9-$(PPh_3)_2$-6,9-$SPtB_8H_{10}$ and 8-OEt-9,9-$(PPh_3)_2$-6,9-$SPtB_8H_9$.[17] The placement of the ethoxide in the latter molecule suggests that the second region of attack during degradative hydroboration of 6-SB_9H_{11} is at the 8,10 positions [the two B atoms adjacent to the B(9) "prow" position].

Analysis of the degradative hydroboration by GC/MS has not been successful yet because the products do not come off our columns. Mixtures have been investigated on the direct

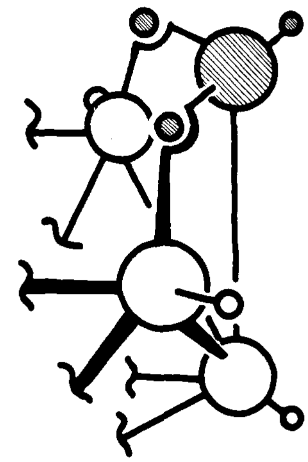

Figure 3. Structural feature which may be necessary for hydroboration by polyhedral boranes. A "coordinated" BH_3 group which is shown by the shaded atoms.

Table IV. ^{13}C and ^1H NMR Data[a-c]

$SB_9H_{10}[C_2H_5C{=}C(H)C_2H_5]$. ^{13}C: 25.0 (t) 125; 22.1 (t) 123; 14.4 (q) 123; 13.6 (q) 125; 146.7 (d) 160. ^1H: 5.93 (t) 7 (1); 2.16 (q) 8 (2); 1.90 (d of q) 7 and 7 (2); 0.93 (t) 7 (3); 0.83 (t) 7 (3)
$SB_9H_{10}[C_6H_5C{=}C(H)C_6H_5]$. ^{13}C: 141.9 (d) 154; 130.0–126.8 (d) 160;[d] ^1H: 7.08 (m) (6) 6.93 (m) (5)
$(SB_9H_{10})_2CHCH_3$. ^{13}C: 19.3 (q) 127. ^1H: 1.40 (q) 7 (1); 1.09 (d) 7 (3)
$(SB_9H_{10})CH_2CH_3$. ^{13}C: 29.7 (t) 125; 12.1 (q) 123. ^1H: 0.92 (s)
$(SB_9H_{10})C_6H_{11}$.[e] ^{13}C: 32.2 (t) 127; 27.2 (t) 126; 26.1 (t) 125. ^1H: 1.60 (d) 5 (1); 1.07 (d) 5 (1)
$(SB_9H_{10})_2C_5H_8$. ^{13}C: 38.3 (t) 128; 34.6 (t) 133; 29.4 (d, br) 140. ^1H: 1.74 (s, br) (1); 1.66 (s) (~0.7); 1.30 (s, br) (1)
$(SB_9H_{10})CH_2CH_2C_6H_5$. ^1H: 7.0 (m) (5); 2.4 (t) 3 (2); 1.2 (t, br) 3 (2)

[a] Presentation of data after each compound: NMR nucleus, chemical shift (ppm from Me_4Si), multiplet designation where observed (s = singlet, t = triplet, d = doublet, q = quartet, m = complex multiplet, br = broad), coupling constant in hertz, and relative intensity in parentheses. [b] ^{13}C and ^1H determined at 25 and 100 MHz, respectively. [c] Determined in C_6D_6 unless otherwise noted. [d] Six doublets with $J \simeq$ 160 Hz observed in this range. [e] Determined in $CDCl_3$.

probe and appear to give peak manifolds corresponding to the borate ester, multiple hydroboration, and degradation. For example, *m/e* cutoffs of 262 and 176 are consistent with $^{34}S^{11}B_8H_5(^{12}C_2H_5{}^{16}O)_3$ and $^{34}S^{11}B_8H_7(^{12}C_2H_5{}^{16}O)$, respectively. Fragments such as *m/e* 217 might correspond to CH_3 loss from $^{34}S^{11}B_9H_9(^{12}C_2H_5O)_2$ upon electron impact; however, the same envelopes appear using chemical ionization conditions.

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Distances of Electron Transfer to and from Metalloprotein Redox Sites in Reactions with Inorganic Complexes

A. Grant Mauk, Robert A. Scott, and Harry B. Gray*

Contribution No. 6090 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received August 8, 1979*

Abstract: A modified form of Hopfield's equation relating rate constants to electron-transfer distances has been applied to a series of metalloprotein redox reactions. For proteins containing redox centers with minimal inner-sphere reorganization barriers, the relationship between one-half the intersite distance (R_p, Å) and the self-exchange rate constant at infinite ionic strength (k_{11}^{∞}) is estimated to be $R_p = 6.2 - 0.35 \ln (k_{11}^{\infty})$. Calculated R_p values based on redox reactions of heme *c*, blue copper, and iron-sulfur proteins with inorganic complexes support the conclusion that hydrophobic, π-conducting ligands are able to penetrate into protein interiors, thereby reducing the distance over which electron transfer occurs. The following estimates of metalloprotein redox site-to-surface distances (ΔR_p's) have been made based on $Fe(EDTA)^{2-}$ rate data: cytochrome *c*, 3.4; cytochrome c_{551}, 4.0; plastocyanin, 2.6; azurin, 5.5; HiPIP, 5.8 Å. These kinetically determined distances accord reasonably well with estimates of metalloprotein redox site-to-surface distances based on examination of molecular models. The electron-transfer distance in the ferricytochrome *c*-$Fe(CN)_6{}^{4-}$ complex has been estimated from kinetics data to be 10 Å, which accords closely with an estimate of 7–10 Å based on spectroscopic measurements.

Introduction

A problem that has received attention in recent years is the determination of the distance over which electron transfer occurs in metalloprotein redox reactions.[1-3] The basis for this attention is seated in the implications of the distance of transfer for our understanding of metalloprotein redox mechanisms and their specificity. Owing to our continuing interest in this subject, we have undertaken an investigation with the goal of developing a method that allows conventional rate data to be used in a systematic way to estimate the distances of electron transfer to and from redox sites in blue copper, heme *c*, and iron-sulfur proteins in reactions with inorganic complexes.

Methods

General Considerations. We assume first that the electron-transfer rate constant, *k*, is related to a tunneling matrix element, T_{ab}, as given in the equation

$$k = C_0 |T_{ab}|^2 \tag{1}$$

According to standard electron-transfer theory, the magnitude of T_{ab} is dependent on the extent of donor and acceptor electronic wave function overlap.[3-9] C_0 is a complicated function whose value is dependent on a number of properties of the donor and acceptor sites.[10] In general, the matrix element T_{ab} can be expressed as an exponential function of the intersite distance R (as originally derived by Gamow[11]), as in the equation

$$k = Ce^{-2aR} \tag{2}$$

Taking $a = 0.72$ Å^{-1}, as proposed by Hopfield,[3] we have

$$R = -0.694 \ln (k/C) \tag{3}$$

Previous calculations employing estimates for the parameters that comprise C in eq 3 have enjoyed reasonable success.[12-14] However, we prefer to reduce our assumptions by appealing to experiment to obtain an acceptable value for C without attempting to estimate values for its various components. This approach will work only if it is referenced to a system where we know the rate and have a good estimate for the distance of electron transfer. The system we have chosen for the analysis is discussed in the following section.

Analytical Procedure and Rationale. The reactions of interest in this analysis are those between a metalloprotein and a substitutionally inert transition metal complex. This selection is

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