seems surprising in the light of the other systems.

For the metathetic reaction

$$[CuL^{III}]^{2+}(aq) + L^{II}(aq) \rightarrow [CuL^{II}]^{2+}(aq) + L^{III}(aq)$$

the values of ΔH and $T\Delta S$ are compared as follows (values in kJ mol^{-1}; 25 °C) with those obtained from the reaction

$$[Cu(dmen)_2]^{2+}(aq) + 2meen(aq) \rightarrow [Cu(meen)_2]^{2+}(aq) + 2dmen(aq)$$

system	ΔH	$T\Delta S$	system	ΔH	$T\Delta S$
L_{10}/L_6	−2	+6	L_{13}/L_9	−20	+6
L_{11}/L_7	−8	−4	dmen/meen	−12	−2
L_{12}/L_8	−15	−4			

It is apparent that both the L_{11}/L_7 and L_{12}/L_8 systems follow the pattern of the dmen/meen system, whereas for the smaller and larger pairs the agreement is not so good, possibly reflecting the more severe distortions from square-plane geometry present in the complexes with ligands at the extremes of the series.

The purpose of this work was to prepare a series of noncyclic ligands that would serve as more appropriate reference ligands for the cyclic ligands in series I than the hitherto used ligands in series II. Considering the parallel behavior in both protonation and metal complex formation (Figure 3), it can be reasonably concluded that the new ligands in series III are more appropriate models with which to compare the macrocyclic ligands. However, the almost identical values that we previously observed for L_{10} and L_6 are not continued for the remainder of the series, where the difference between the thermodynamic parameters steadily increases with the length of the ligand skeleton.

The important consequence of considering the macrocyclic effect in relation to the reference ligands in series III rather than series II is that not only is the magnitude of the effect increased for both free energy and enthalpy terms but it also now remains approximately constant for different pairs of ligands along the series, as evident from the more or less parallel curves for log K and ΔH in Figure 3. Thus the magnitude of the macrocyclic effect appears to be independent of the size of the macrocyclic ligand provided the appropriate reference ligand is chosen. In further work we will be considering the effects of solvation on tetraaza ligands and their metal complexes, and we again expect, because of the greater similarity in both size and chemical constitution, that the ligands in series III will be more suitable models with which to compare the macrocyclic ligands in series I.

Acknowledgment. The authors wish to thank the Italian CNR, SERC, and NATO for financial support.

Registry No. L_6, 112-24-3; L_6·4HCl, 4961-40-4; L_6, tetratosyl derivative, 4961-40-4; L_7, 4741-99-5; L_7, tetratosyl derivative, 97807-55-1; L_7, tetrakis(benzylsulfonyl) derivative, 97807-53-9; L_8, 10563-26-5; L_8·4HCl, 13493-17-9; L_8, tetratosyl derivative, 74676-47-4; L_9, 4605-14-5; L_9·4HCl, 16632-23-8; L_9, tetratosyl derivative, 67341-38-2; L_{10}, 25077-85-4; L_{10}·4HCl, 27162-57-8; L_{10}, tetratosyl derivative, 97807-48-2; L_{11}, 6809-77-4; L_{11}·4HCl, 27162-58-9; L_{11}, tetrakis(benzylsulfonyl) derivative, 97807-54-0; L_{12}, 77500-19-7; L_{12}·4HCl, 97807-51-7; L_{12}, tetratosyl derivative, 97807-49-3; L_{13}, 97807-56-2; L_{13}·4HCl, 97807-52-8; L_{13}, tetratosyl derivative, 97807-50-6; $[CuL_{10}](ClO_4)_2$, 97825-42-8; $[CuL_{11}](ClO_4)_2$, 97825-44-0; $[CuL_{12}](ClO_4)_2$, 97825-46-2; $[CuL_{13}](ClO_4)_2$, 97825-48-4; $BrCH_2CH_2Br$, 106-93-4; $BrCH_2CH_2CH_2Br$, 109-64-8; $H_2NCH_2CH_2NH_2$, 107-15-3; $H_2NCH_2CH_2CH_2NH_2$, 109-76-2; $HOCH_2CH_2NHMe$, 109-83-1; $TsOCH_2CH_2N(Ts)Me$, 3559-06-6; $TsNHCH_2CH_2CH_2NHTs$, 53364-99-1.

Contribution from the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Reactions of Halopentaboranes and Other Haloboranes with Tributyltin Hydride

DONALD F. GAINES,* JOAN C. KUNZ, and MATTHEW J. KULZICK

Received March 26, 1985

Halopentaboranes(9) are converted to the parent pentaborane(9) in high yields with tributyltin hydride as the halogen reducing agent. Tributyltin hydride also reduces several other haloboranes and halometalloboranes. Deuterium-labeled pentaboranes(9) are produced from halopentaboranes(9) and tributyltin deuteride.

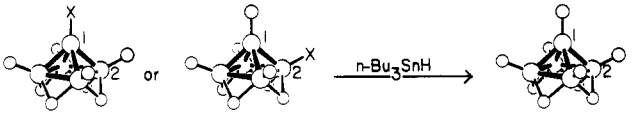
Introduction

Reactions of trialkyltin hydrides with a variety of organic functional groups have been known for nearly 40 years.[1] The first report of trialkyltin hydride reduction of boron–halogen bonds appeared in 1968.[2] In this study, chlorobis(dimethylamino)borane and 2-chloro-1,3,2-benzodioxaborole were reduced with *n*-Bu_3SnH to bis(dimethylamino)borane and 1,3,2-benzodioxaborole, respectively. Mechanistic investigations indicated a polar mechanism for these reactions. A second report of boron–halogen bond reduction by trialkyltin hydrides has recently appeared.[3] In this study, B_4Cl_4 was converted to B_4H_{10} with excess Me_3SnH.

Our interest in trialkyltin hydrides stems from a desire to replace halogens on boranes with hydrogen or deuterium atoms. We found that *n*-Bu_3SnH efficiently reduces halogens on halopentaborane(9) molecules, as well as on several other haloboranes. We report here the details of these hydrogen/halogen exchange studies along with preliminary investigations of deuterium/halogen exchange between *n*-Bu_3SnD and halopentaboranes(9) and pentaborane(9), respectively.

Results and Discussion

Halogen reduction of the several haloboranes examined by using trialkyltin hydrides or deuterides are listed in Table I. The halopentaborane(9) reductions with tributyltin hydride produce excellent yields of pentaborane(9) (eq 1), which are easily sepa-



(1)

rated from the low-volatility tin byproducts. Reaction conditions are remarkably mild when compared to the conditions frequently required for reactions of R_3SnH with alkyl or aryl halides.[1] The ease of reduction of the halopentaboranes(9) increases in the order Cl < Br < I. This trend is similar to that noted for alkyl and aryl halides.[1] A halogen position effect is also observed, in that the 2-halopentaboranes(9) produce slightly higher yields and react more rapidly than the corresponding 1-halopentaboranes(9). In view of the pseudoaromatic character associated with the chemistry of the H(1) position in pentaborane(9),[4] these observations may be construed as correlating with the organic halide analogues, in

(1) Much of this information has been reviewed. Nomenclature in this paper will be consistent with that used in the organic literature, as summarized in a review article by: Kuivila, H. G. *Adv. Organomet. Chem.* **1964**, *1*, 47.
(2) Newsome, H. C.; Woods, W. G. *Inorg. Chem.* **1968**, *7*, 177.
(3) Morrison, J. A. *J. Am. Chem. Soc.*, in press.
(4) Gaines, D. G.; Heppert, J. A.; Coons, D. E.; Jorgenson, M. W. *Inorg. Chem.* **1982**, *21*, 3662 and references therein.

0020-1669/85/1324-3336$01.50/0

Table I. Reaction Conditions and Results of Haloborane Reduction by Trialkyltin Hydrides (Deuterides)

borane	tin reagent	ratio[a]	time	temp, °C	product	yield,[b] %
1-ClB_5H_8	*n*-Bu_3SnH	1.15	2 h	0	B_5H_9	87.6
1-ClB_5H_8	*n*-Bu_3SnD	1.24	5 h	0	DB_5H_8[c]	*g*
2-ClB_5H_8	*n*-Bu_3SnH	1.09	2 h	0	B_5H_9	95.8
2-ClB_5H_8	*n*-Bu_3SnD	0.99	12 h	0	2-DB_5H_8	*g*
1-BrB_5H_8	*n*-Bu_3SnH	1.26	12 h	0	B_5H_9	97.8
1-BrB_5H_8	*n*-Bu_3SnD	1.24	12 h	0	DB_5H_8[c]	*g*
2-BrB_5H_8	*n*-Bu_3SnH	1.51	12 h	0	B_5H_9	97.4
2-BrB_5H_8	*n*-Bu_3SnD	1.57	12 h	0	2-DB_5H_8, DB_5H_8[c]	*g*
1-IB_5H_8	*n*-Bu_3SnH	1.00	2 h	0	B_5H_9	99.2
B_5H_9	*n*-Bu_3SnD	1.14	2 days	23	DB_5H_8[c]	*g*
2-ClB_5H_8	Me_3SnH	1.11	3 days	23	*d*	*g*
2-ClB_5H_8	$(C_6H_5)_3SnH$	1.12	$^1/_2$ h	23	*e*	*g*
BCl_3	*n*-Bu_3SnH	2.92	12 h	23	B_2H_6	84.8
$(CO)_4MnB_3H_7Br$	*n*-Bu_3SnH	1.13	9 h	0	$(CO)_4MnB_3H_8$	49.0
$(CO)_4MnB_3H_7Br$	*n*-Bu_3SnD	3.11	1 h	0	$(CO)_4MnB_3H_7D$	*g*
$(CO)_4MnB_3H_8$	*n*-Bu_3SnD	2.53	$1^1/_2$ h	0	*f*	*g*
$(\mu\text{-Br})Mn_2(CO)_6B_3H_8$	*n*-Bu_3SnH	1.11	4 days	23	$(\mu\text{-H})Mn_2(CO)_6B_3H_8$	*g*

[a] The ratio is moles of tin reagent per mole of starting borane. [b] The product yield is based on starting borane. [c] The deuterium label is statistically distributed between three hydrogen environments in the pentaborane cage. [d] Decomposition occurred, producing only trace B_5H_9. [e] Rapid decomposition occurred, producing a precipitate and entirely consuming the liquid phase. [f] No reaction was observed. [g] Yields not measured.

that alkyl halides generally react with *n*-Bu_3SnH under less forcing conditions than aryl halides.[1]

Reactions of Me_3SnH or $(C_6H_5)_3SnH$ with halopentaboranes(9) lead to decreased yields of pentaborane(9) and increased boron cage decomposition under the conditions employed (Table I). This altered reactivity may be related to the increased Sn–H bond polarity[5,6] in $(C_6H_5)_3SnH$ and Me_3SnH compared to *n*-Bu_3SnH. Reactions of 1-halopentaboranes(9) with Me_3SiH and GeH_4 produced no dehalogenated pentaborane(9) product, and starting materials were recovered.

Reactions of BCl_3 with 3 equiv of *n*-Bu_3SnH result in good yields of high-purity B_2H_6. This represents a convenient but expensive synthesis for B_2H_6 (or B_2D_6) and also demonstrates that multiple halogens may be removed from the same boron atom, as is the case in similar organic systems.[7]

The reactions of *n*-Bu_3SnH with other halogenated boranes illustrate the utility of this method of halogen removal. In the reduction of $(CO)_4MnB_3H_7Br$ yields of $(CO)_4MnB_3H_8$ are modest due in part to decomposition of the product at ambient temperature during the rather slow reduction reaction. A more surprising example of the *n*-Bu_3SnH halogen reduction versatility is its reaction with $(\mu\text{-Br})Mn_2(CO)_6B_3H_8$,[8] in which the halogen is not bonded to boron, to form the new metalloborane derivative $(\mu\text{-H})Mn_2(CO)_6B_3H_8$.

Reactions of halopentaboranes(9) with *n*-Bu_3SnD were prompted by desires to selectively label pentaborane with deuterium in order to study pentaborane rearrangement processes.[9] The reaction of 2-ClB_5H_8 with *n*-Bu_3SnD was investigated first, as a potentially reliable source for 2-DB_5H_8. When 2-ClB_5H_8 reacts with Bu_3SnD for several hours (Table I), the product distribution is 75% 2-DB_5H_8, 9.0% 1-DB_5H_8, and 16% μ-DB_5H_8. Thus, this experiment yields the expected 2-DB_5H_8, but it can also produce significant quantities of the μ-DB_5H_8 isomer. Reactions between 1-halopentaboranes(9) and *n*-Bu_3SnD yield monodeuterated pentaborane(9) product with the deuterium label statistically distributed between each of the three types of hydrogen environments. If an excess of *n*-Bu_3SnD is used in the reduction of halopentaboranes(9), slightly more than one deuterium atom per boron cage is detected by mass spectrometry. This observation suggested that direct H/D exchange between B_5H_9 and *n*-Bu_3SnD may occur. Experiments using B_5H_9 and *n*-Bu_3SnD showed that deuterium/hydrogen exchange does occur and that the deuterium is statistically incorporated into all hydrogen positions in B_5H_9. While *n*-Bu_3SnD/H appears to react with 2-XB_5H_8 in 15 min and with 1-XB_5H_8 in 30 min, reaction of *n*-Bu_3SnD/H continues for weeks, until significant decomposition of the tin reagent occurs. Ratios of deuterium incorporation into the three pentaborane hydrogen environments for each experiment are listed in Table II.

Table II. Percent Deuterium Incorporation[a] in Pentaborane for the Reaction $XB_5H_8 + R_3SnD \rightarrow R_3SnX + DB_5H_8$

starting borane	apex	base	bridge
statistical distribn[b]	11.2	44.4	44.4
1-ClB_5H_8	11[c]	46	43
2-ClB_5H_8	9.0	75	16
1-BrB_5H_8	11	47	42
2-BrB_5H_8	14	60	26
B_5H_9	10	43	47

[a] Approximately one deuterium atom was incorporated into each pentaborane cage, as verified by mass spectrometry. [b] Calculated. [c] The figures give relative amounts of deuterium in each hydrogen position, as measured by integration of the ^2H NMR spectrum of each product.

These complicated results from a seemingly straightforward halogen replacement by hydrogen led us to undertake a more detailed look at the mechanism(s) of the halopentaborane(9) reductions with *n*-$Bu_3SnH(D)$. The majority of organic halide reductions occur via a two-step radical mechanism.[10] AIBN, a radical initiator, and galvinoxyl, a radical inhibitor, have been successfully used to establish a radical mechanism for organic halide reductions by trialkyltin hydrides. The radical mechanistic possibility for halopentaboranes was tested by using chloropentaboranes(9) with *n*-Bu_3SnH in the presence of AIBN or in the presence of galvinoxyl. We detected no significant difference in reaction rates for 2-ClB_5H_8 or 1-ClB_5H_8 in either the presence or the absence of initiator or inhibitor, using ^{11}B NMR spectroscopy. These results suggest a nonradical mechanism for the *n*-Bu_3SnH reduction of halopentaboranes(9).

Nonradical mechanisms in some organic halide reductions by tin hydrides have been observed.[5,11,12] In addition, the boron halides previously reported[2] were shown to be unaffected by radical initiators and inhibitors. Reaction rates in these studies were found to be enhanced in polar solvents and diminished in nonpolar solvents, and polar, four-centered associative mechanisms were postulated.[2,5,11,12] We found that reductions of 1- and 2-ClB_5H_8

(5) Leusink, A. J.; Marsman, J. W. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1123.
(6) Kriegsmann, V. H.; Ulbricht, K. *Z. Anorg. Allg. Chem.* **1964**, *328*, 90.
(7) Seyferth, D.; Yamazaki, H.; Alleston, D. L. *J. Org. Chem.* **1963**, *28*, 703.
(8) $(CO)_4MnB_3H_8$: Hildebrandt, S. J.; Gaines, D. F. *Inorg. Synth.* **1979**, *19*, 227. $(CO)_4MnB_3H_7Br$: Gaines, D. F.; Hildebrandt, S. J., unpublished results. $(\mu\text{-Br})Mn_2(CO)_6B_3H_8$: Chen, M. W.; Gaines, D. F.; Hoard, L. G. *Inorg. Chem.* **1980**, *19*, 2989.
(9) Heppert, J. A.; Gaines, D. F., *Inorg. Chem.* **1983**, *22*, 3155.
(10) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(11) Leusink, A. J.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1123.
(12) Smith, P. J.; Smith, L. *Inorg. Chim. Acta, Rev.* **1973**, *7*, 11.

with tri-*n*-butyltin hydride proceed approximately twice as fast in chlorobenzene solution as in *n*-pentane solution. These increased rates of reaction in polar solvents compared to the rates in nonpolar solvents support, by analogy, a polar mechanism for the *n*-Bu_3SnH reduction of halopentaboranes(9).

While the reaction rates of halopentaborane reductions in various solvents were monitored, an intermediate was observed in the ^{11}B NMR spectra. In the case of 1-halopentaboranes, the ^{11}B NMR spectrum of the intermediate is characterized by a broad low-field resonance centered at +2.0 ppm and a high-field doublet resonance at −61 ppm. The observation of these resonances before the production of the pentaborane reduction product and the disappearance of these intermediate resonances as the reduction approaches completion is consistent with the hypothesis that this intermediate is intimately associated with the reaction process. An intermediate-type resonance is also observed in the ^{119}Sn NMR spectrum, at +45 ppm (relative to external Me_4Sn standard). Deuterium incorporation into all positions requires either a very special geometry for the intermediate or a very facile rearrangement mechanism.

In the case of 2-halopentaboranes, only minute intermediate resonances could be discerned in the ^{11}B NMR spectra of the reaction mixtures. The resonances are similar to those found in the 1-halopentaborane case except that the −61 ppm resonance is a singlet. That 2-DB_5H_8 is the primary product suggests that either the intermediate is different from that formed in the 1-halopentaborane reductions or the barrier to rearrangement of the 2-DB_5H_8 product is substantially higher than the barrier to rearrangement for the DB_5H_8 product obtained in the former case. It has also been observed that the reduction of 2-XB_5H_8 by *n*-Bu_3SnH is much faster than the reduction of 1-XB_5H_8 under identical conditions.

An interaction between B_5H_9 itself and *n*-Bu_3SnH/D has also been observed and is somewhat different from both halopentaborane/*n*-Bu_3SnH interactions. The formation of the intermediate is substantially slower than for the halopentaboranes, but the H/D exchange appears to be at equilibrium over a time period that is shorter than the time required for the intermediate concentration to reach a maximum. In addition, the high-field resonance in the ^{11}B NMR spectrum of the intermediate now appears at −45 ppm.

Further experiments are in progress to elucidate the nature of the halogen reduction mechanism for halopentaboranes and the nature of the observed intermediate.

Experimental Section

n-Bu_3SnH, *n*-Bu_3SnD, and $(C_6H_5)_3SnH$ were purchased from Alfa Chemical Co. These were stored at +5 °C and were handled in a dry N_2 atmosphere. Me_3SnH,[13] 1-ClB_5H_8, 2-ClB_5H_8, 1-BrB_5H_8, 2-BrB_5H_8, and 1-IB_5H_8[14] were synthesized by published methods. BCl_3 (technical grade) was purchased from Matheson Co. and was used without further purification. $(CO)_4MnB_3H_7Br$ was made from $(CO)_4MnB_3H_8$ and Br_2. $(\mu\text{-Br})Mn_2(CO)_6B_3H_8$ was prepared from $(CO)_3MnB_3H_8$ and Br_2.[8] AIBN, α,α'-azobis(isobutyronitrile), was obtained from Alfa Chemical Co. and galvinoxyl, also known as [2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy], was purchased from Aldrich Chemical Co. Both AIBN and galvinoxyl were stored at −30 °C and used as received. Me_3SiH was obtained from Petrarch Systems, Inc., and was used as received. GeH_4 was made by a published procedure.[15] Volatile materials were manipulated by using standard high-vacuum techniques.[16] Nonvolatile and low-volatility materials were handled in a glovebag under dry N_2.

^{11}B, ^{119}Sn, and ^1H NMR spectra were acquired on Bruker 270-MHz and IBM WP 270-MHz instruments (86.6 MHz ^{11}B, 100.6 MHz ^{119}Sn). ^2H NMR spectra were acquired at 30.6 MHz on a JEOL FX-200 instrument with a 50-s pulse repetition rate. Mass spectra were obtained on an AEI MS-9 instrument at 70 eV. Infrared spectra were recorded on a Beckman 4250 infrared spectrophotometer.

A. General Reaction Procedure. Tributyltin hydride or deuteride was measured by syringe in a dry N_2 filled glovebag and was placed in a carefully dried high-vacuum reaction vessel, which was then attached to the vacuum line, cooled to −196 °C, and evacuated. The *n*-$Bu_3SnH(D)$ was thawed, refrozen, and reevacuated. The freeze–thaw cycle was repeated twice. The halogenated borane was then condensed on top of the *n*-$Bu_3SnH(D)$ at −196 °C. These reaction mixtures were then warmed and magnetically stirred at the temperature listed in Table I. After the indicated reaction time, the volatile contents were separated by conventional low-temperature distillation on the vacuum line and were analyzed by ^{11}B, ^1H, and ^2H NMR spectroscopy, IR spectroscopy, and mass spectrometry. The mass spectral cutoff for B_5H_9 is 64 *m/e* units. The cutoff for 2-DB_5H_8 from 2-ClB_5H_8 and *n*-Bu_3SnD is 65 *m/e* units, indicating one deuterium atom incorporated per cage. For reaction of 1-ClB_5H_8 with slight excess *n*-Bu_3SnD, the cutoff for DB_5H_8 is 67 *m/e* units, with a large intensity drop at *m/e* 66. This indicates that most of the product is monodeuterated and some much smaller portion has two or three deuterium atoms per cage.

Reaction of $(\mu\text{-Br})Mn_2(CO)_6B_3H_8$ with $HSnBu_3$. $(\mu\text{-Br})Mn_2(CO)_6B_3H_8$ reacted with *n*-Bu_3SnH to produce $(\mu\text{-H})Mn_2(CO)_6B_3H_8$ in approximately 15% yield. The ^{11}B NMR spectrum showed peaks in an approximate ratio of 1:2 at +22.4 and −32.6 ppm, respectively, relative to $BF_3{\cdot}OEt_2$ external reference. The ^1H NMR spectrum revealed four types of hydrogen resonances for intensities 2:2:4:1 as follows: 3.8 (multiplet, J = 116 Hz), −1.25 (quartet, J = 68 Hz), −13.6 (quartet, J = 67 Hz), −18.3 ppm (singlet). The infrared spectrum (gas phase, ~2 torr) contained bands at 2600 (ν_{BH}, w), 2090 (ν_{CO}, m), 2065 (ν_{CO}, m), 2050 (ν_{CO}, mw), and 2010 cm^{-1} (ν_{CO}, s). In the mass spectrum, the parent ion was found at *m/e* 319.9441 (calculated for $^{12}C_6{}^{16}O_6{}^1H_9{}^{11}B_3{}^{55}Mn_2$ *m/e* 319.94403).

B. General Reaction Procedure for NMR Tube Experiments. Tributyltin hydride was measured by syringe in a dry N_2 filled glovebag and was placed in a carefully dried 5-mm-o.d. NMR tube equipped with a high-vacuum Teflon stopcock, which was attached to the vacuum line, cooled to −196 °C, and evacuated. Solvents and boranes were added at −196 °C in vacuo. Tubes were sealed and remained frozen at −196 °C until NMR time. Samples were thawed immediately before being placed in the spectrometer. Solid reagents, such as AIBN or galvinoxyl, were added in the glovebag prior to Bu_3SnH addition. Reactions were monitored by ^{11}B or ^{119}Sn NMR spectroscopy.

Radical Influence on the Reaction of 1-ClB_5H_5 with *n*-Bu_3SnH. Into each of three NMR tubes were placed 1.14 mmol of $HSnBu_3$ and 0.78 mmol of 1-ClB_5H_8. The first tube was then sealed in vacuo. ABIN (0.2 mmol) was added to the second tube, and galvinoxyl (0.2 mmol) was added to the third tube. These tubes were sealed in vacuo. The reaction rates were then monitored by ^{11}B NMR spectroscopy.

Radical Influence on the Reaction of 2-ClB_5H_8 with *n*-Bu_3SnH. Each of three NMR tubes was loaded with 1.14 mmol of *n*-Bu_3SnH and approximately 0.87 mmol of 2-ClB_5H_8. One was sealed immediately, while 0.17-mmol amounts of AIBN and galvinoxyl were added to the second and third tubes, respectively. Reaction progress was monitored by ^{11}B NMR spectroscopy.

Solvent Influence on the Reaction of 2-ClB_5H_8 with *n*-Bu_3SnH. Two NMR tubes were each loaded with 0.38 mmol of *n*-Bu_3SnH and 0.24 mmol of 2-ClB_5H_8. To one was added 0.19 mL of chlorobenzene, and to the other, 0.19 mL of *n*-pentane. Reaction rates were monitored by ^{11}B NMR spectroscopy.

^{119}Sn NMR Study of the Reaction of XB_5H_8 with *n*-Bu_3SnH. Into each of three NMR tubes was placed 0.755 mmol of *n*-Bu_3SnH. 1-ClB_5H_8 (0.69 mmol) was added to the first, 2-ClB_5H_8 (0.87 mmol) was added to the second, and 1-BrB_5H_8 (1.24 mmol) added to the third. All were sealed in vacuo, and the ^{119}Sn NMR spectra were recorded. In a separate experiment, 1.51 mmol of *n*-Bu_3SnH and 0.30 mmol of B_5H_9 were sealed in an NMR tube and the ^{119}Sn NMR spectrum was recorded.

Acknowledgment. This research was supported in part by grants from the National Science Foundation.

Registry No. $(CO)_4MnB_3H_8$, 53801-97-1; $(CO)_4MnB_3H_7D$, 97997-62-1; $(\mu\text{-H})Mn_2(CO)_6B_3H_8$, 97997-63-2; $(\mu\text{-Br})Mn_2(CO)_6B_3H_8$, 74432-08-9; $(CO)_4MnB_3H_7Br$, 65452-33-7; B_5H_9, 19624-22-7; 1-DB_5H_8, 63643-91-4; 2-DB_5H_8, 63643-93-6; B_2H_6, 19287-45-7; 1-ClB_5H_8, 19469-13-7; 2-ClB_5H_8, 19469-14-8; 1-BrB_5H_8, 23753-67-5; 2-BrB_5H_8, 23753-64-2; 1-IB_5H_8, 30624-33-0; BCl_3, 10294-34-5; *n*-Bu_3SnD, 6180-99-0; *n*-Bu_3SnH, 688-73-3.

(13) Kuivila, H. G.; Dixon, J. E. *J. Organomet. Chem.* **1975**, *86*, 89.
(14) Gaines, D. F.; Martens, J. A. *Inorg. Chem.* **1968**, *7*, 704. Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430.
(15) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970.
(16) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.