TABLE III
THE VIBRATIONAL SPECTRA OF SOME CRYSTALLINE INDIUM(III) HALIDE COMPLEXES (IN cm^{-1})

	R	Ir
$((CH_3)_3NH)_3[InCl_6]$	268	245 vs, vbr, 182 vs, vbr, 150 s
$((CH_3)_2NH_2)_4InCl_7$	270	290 sh, 250 vs, 214 sh, 170 sh, 151 vs
$(CH_3NH_3)_4InCl_7$	278	262 vs, 216 sh, ~182,[a] ~164[a]
$(CH_3NH_3)_4InBr_7$	172	179 vs, vbr, 146 m, 106 w
$((CH_3)_2NH_2)_3InBr_7$	169	274 w, br, 186 vs, 170 vs, 142 w, 112 m, br

[a] Not clearly resolved.

that the results for $InCl_4^-$, $InCl_5^{2-}$, and $InCl_6^{3-}$ show a smooth decrease in the ν(In–Cl) frequency as the coordination number increases from 4 (ν_1 325 cm^{-1}) to 6 (268 cm^{-1}).

The highest ν(In–Cl) absorption in both C_4InCl_7 species is at ~270 cm^{-1} (Table III), close to that for $InCl_6^{3-}$, suggesting that this anion is the indium(III) species present in these compounds. The lattice is believed to contain four cations, an InX_6^{3-} anion, and a halide ion. Such species are known for other salts; an example involving a neighboring element is $(NH_4)_3SiF_7$, studied by Hoard and Williams.[23,24] The vibrational spectrum of $(CH_3NH_3)_4InCl_7$ is then that of $InCl_6^{3-}$, plus a broad lattice mode at approximately 170 cm^{-1}, which combines with ν_4 to give a very broad absorption band. The appearance of three bands at 290, 250, and 214 cm^{-1} is very similar to the splitting of ν_3 in the pseudooctahedral crystalline $InCl_3$ (290, 235, and 210 cm^{-1}) reported by Greenwood, Prince, and Straughan.[20] There are some differences in the ir spectrum of $((CH_3)_2NH_2)_4InCl_7$, notably in the presence of a doublet at 262 and 216 cm^{-1} in place of the triplet discussed above and in the higher energy region of the badly resolved low-frequency bands. The spectra of $(CH_3NH_3)_4InBr_7$ and $(CH_3NH_2)_4InBr_7$ can be understood on a similar basis, with the ~170-cm^{-1} Raman-active band assigned to ν_1 of $InBr_6^{3-}$. No other species containing this anion were obtained in our preparative studies. The breadth of the ν_3 absorption at 179 cm^{-1} in $(CH_3NH_3)_4InBr_7$ and the series of bands in $((CH_3)_2NH_2)_4InBr_7$ are similar to those found for the corresponding chlorides and to the splitting noted in the spectrum of $InBr_3$.[20] It is believed that in all cases this broadening is a consequence of a low site symmetry in the anion.

Relative Stabilities of Anionic Indium Complexes.—The preparative and spectroscopic work, together with X-ray structure investigations,[7,8] shows that differences in reaction conditions, such as change of solvent or change of cation, result in the precipitation of different solid phases from given reactants. We conclude that for these anionic species, as for other indium(III) complexes, the energy balance of those factors involved in stabilizing the species in solution and in the solid state is a delicate one.

Two general statements can be made about the stoichiometries of the species obtained in this work. *First*, for a given cation, or for cations of similar size, the coordination number of indium(III) decreases with increasing halogen size. A similar general conclusion applies to cationic indium(III) complexes[21] and to the neutral adducts of the indium(III) halides,[25] and possible reasons for this effect have been discussed earlier.[21] The *second* generality is that, for a given halide ligand, the coordination number of indium(III) decreases with increasing cation size. This is presumably a solid-state effect in the main, since the nature of the cation should have only a small influence on equilibria in nonaqueous solution. It is hoped to investigate these matters further in subsequent experiments.

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[23] J. L. Hoard and M. B. Williams, *J. Amer. Chem. Soc.*, **64**, 633 (1942).

[24] A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 684.

[25] A. J. Carty and D. G. Tuck, *J. Chem. Soc.*, 1081 (1966).

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Exchange Reactions of Borazines with Heavy Metal Halides

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N-Trimethylborazine reacts with metal halides to yield partially halogenated derivatives of *N*-trimethylborazine as well as other reaction products: titanium tetrachloride and titanium tetrafluoride yield hydrogen and titanium trihalides; mercuric and mercurous chlorides yield hydrogen chloride and/or hydrogen and mercury; stannic chloride and stannic bromide yield hydrogen halides, hydrogen, and stannous halides; and stannic iodide does not react. Under the same conditions, stannic chloride does not react with hexamethylborazine nor does tetramethyltin react with *N*-trimethyl-*B*-trichloroborazine. Trans halogenation of *N*-trimethyl-*B*-dichloroborazine can be effected with titanium tetrafluoride.

Introduction

A number of reactions have been reported for borazines in which substitution occurs at the boron positions.[1] While the reagents in these reactions have been predominantly other boron-containing compounds, the trans halogenation of *B*-trichloroborazines with titanium tetrafluoride[2] suggests that an exchange reaction using heavy metal halides as halogen sources is also possible. Indeed, preliminary results from this laboratory[3] on *N*-trimethylborazine as well as similar

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[1] H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Amer. Chem. Soc.*, **58**, 409 (1936); H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 1296 (1938); G. W. Schaeffer, R. Schaeffer, and H. I. Schlesinger, *ibid.*, **73**, 1612 (1951); G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *ibid.*, **80**, 4515 (1958); R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 99 (1962); H. C. Newson, W. G. Woods, and A. L. McCloskey, *ibid.*, **2**, 36 (1963).

[2] K. Neidenzu, *ibid.*, **1**, 943 (1962).

[3] G. A. Anderson and J. J. Lagowski, *Chem. Commun.*, 649 (1966).

reactions of the parent compound[4] are in agreement with this suggestion; such reactions form the basis of a feasible approach to the synthesis of partially substituted *B*-halogen derivatives. In this investigation, the reactions of a variety of metal halides with B–H and B–X (X = halogen) substituted borazines have been examined.

Experimental Section

Standard methods of synthesis were employed for the preparation of *N*-trimethylborazine,[5] *N*-trimethyl-*B*-trichloroborazine,[6] hexamethylborazine,[7] stannic bromide,[8] and tetramethyltin.[9] The liquid products were purified by distillation through an annular Teflon spinning-band column (Nester/Faust); the solid products were zone refined after two sublimations *in vacuo*. Samples to be zone refined were placed in 3-ft lengths of 6-mm glass tubing in an inert-atmosphere box and degassed by standard freeze–thaw techniques; the tube was then sealed under an atmosphere of dry nitrogen. The multipass zone refiner simultaneously advanced up to 10 zones of melt at a constant rate of 2.4 cm/hr. The total number of passes always exceeded the number of zones.

Mercuric chloride and anhydrous stannic chloride (J. T. Baker), mercuric bromide (Matheson Coleman and Bell), stannic iodide and titanium tetrafluoride (Alfa Inorganics), and titanium tetrachloride (Fisher) were used without further purification. The solvents were freshly distilled after refluxing over sodium.

A greaseless vacuum manifold was used in these experiments because the reactants and/or products attacked hydrocarbon grease; in general, the halogenated greases or silicon-based substitutes were no better than the hydrocarbon greases. A basic vacuum system design[10] was altered to utilize stainless steel bellows valves (Hoke, Inc.) adapted with Ultra-Torr connectors (Cajon Co.) to form vacuum seals to the glass portions of the systems.

Reactions at elevated temperatures were conducted in a one-piece reaction vessel with a reflux condenser attached directly to the reaction bulb. Reactions which involved filtration and/or sublimation *in vacuo* were conducted in special filter flasks[11] modified from an early design.[12]

Fractional sublimations were performed in a gradient furnace which was constructed from a 48-in. length of 2-in. diameter iron rod with a 0.5-in. diameter hole along the axis. Samples were sealed in evacuated 48-in. lengths of 10-mm diameter glass tubing which were heated in the furnace. A temperature gradient was established in the iron rod by electrically heating one end and cooling the other with circulating tap water. The furnace was insulated with a 2.5-in. layer of asbestos. All transfers of solids were conducted in a drybox, the helium atmosphere of which was equilibrated with the Na–K eutectic mixture that is liquid at room temperature.

The *N*-trimethyl-*B*-haloborazines which were isolated in the reactions described below were identified by their melting points,[4] infrared spectra,[13] and mass spectra as determined on highly purified (*i.e.*, zone refined and/or multiply vacuum sublimed) samples with constant melting points. The mass spectra were consistent with the presence of a single compound undergoing a characteristic fragmentation. A detailed analysis of the mass spectral data is forthcoming.[14] The presence of small amounts of other borazines could be readily detected in the mass spectrum because of their characteristically different fragmentation pattern. Indeed, the mass spectrum of a sample proved to be the most reliable indication of its purity. When corrected for peak contributions arising from fragments formed by the loss of a hydrogen atom, all of the *N*-trimethyl-*B*-haloborazines exhibited parent peaks having the correct theoretically calculated intensity ratios based upon the normal isotopic distributions of the elements.

The Reaction of *N*-Trimethylborazine with Stannic Halides.—The addition of stannic chloride (13.2 g, 50.5 mmol) to a solution of *N*-trimethylborazine (6.29 g, 51.0 mmol) in benzene (*ca.* 25 ml) yielded an immediate white precipitate; hydrogen chloride was evolved also. The precipitate (11.46 g) was a mixture of $SnCl_2$ (78.5%) and $(CH_3)_3B_3N_3H_3 \cdot 3HCl$ (21.5%) as determined by elemental analysis (Cl, B, Sn, N). The presence of the borazine adduct was confirmed by the infrared spectrum of the precipitate which was identical with that of an authentic sample of this substance. Removal of the solvent from the filtrate yielded a white solid (2.66 g, 20%) consisting primarily of *N*-trimethyl-*B*-dichloroborazine as determined by its mass spectrum.

N-Trimethylborazine (6.38 g, 52.5 mmol) reacted immediately with stannic chloride (22.67 g, 87.0 mmol) at −23°, with copious evolution of HCl. The solid product was fractionally sublimed *in vacuo* directly from the reaction flask yielding *N*-trimethyl-*B*-dichloroborazine (3.1 g, 16.2 mmol, 30.8%) at 45°. Although both *N*-trimethyl-*B*-chloroborazine and *N*-trimethyl-*B*-trichloroborazine were present in the original reaction mixture as shown by mass spectral analysis, these substances were not isolated in pure form because the sublimates isolated above 55° were contaminated by $(CH_3)_3N_3B_3H_3 \cdot 3HCl$, identified by its infrared spectrum. Apparently the borazine undergoes dissociation at this temperature and recombines on the cold finger.

N-Trimethylborazine (5.79 g, 47.5 mmol) and stannic bromide (18.89 g, 43.5 mmol) were heated at 110° for 18 hr; hydrogen bromide was evolved during this time. Fractional sublimation of the solid product *in vacuo* yielded *N*-trimethyl-*B*-dibromoborazine (4.98 g, 17.4 mmol, 36.6%) at 35° and *N*-trimethyl-*B*-tribromoborazine (1.76 g, 4.9 mmol, 10.1%) at 55°. Fractions collected at 25° (1.56 g) and 45° (2.54 g) were mainly *N*-trimethyl-*B*-dibromoborazine containing the monobromo and tribromo species, respectively. The remaining orange residue was identified as stannous bromide by qualitative analysis, its thermochromic properties, and mass spectroscopy. $(CH_3)_3N_3B_3H_3 \cdot 3HBr$ was not detected among the solid products of the reaction.

An attempt to effect separation of the reaction products by conventional vacuum-line fractionation techniques indicated that the solid product continued to evolve hydrogen over a period of time and that an unidentified volatile tin species was also present which deposited $SnBr_2$, apparently indiscriminately throughout the vacuum system. Because of this behavior, the crude product obtained from the reaction of *N*-trimethylborazine (4.34 g, 35.1 mmol) and stannic bromide (15.67 g, 35.7 mmol) at 145° for 4 hr was refluxed in 20 ml of benzene for 2.5 hr in an attempt to decompose tin intermediates which might be formed and to expel hydrogen. The solution was filtered and fractionated through traps at −5, −23, and −196°. Although hydrogen was still evolved in the initial phases of the 60-hr fractionation, *N*-trimethyl-*B*-bromoborazine (0.4 g, 5.6%, mp 31–32°) was isolated at −23°. When vented to air the inner surfaces of the vacuum manifold again turned bright red, suggesting the presence of $SnBr_2$.

Reactions of Borazines with Other Tin Compounds.—*N*-Trimethylborazine (3.80 g, 31 mmol) and stannic iodide (20.0 g, 31.9 mmol) did not react when heated at 155° for 2 hr. Hexamethylborazine (1.0 g, 6.1 mmol) and stannic chloride (1.61 g, 6.2 mmol) did not react in a sealed tube maintained at 100° for 22 hr. Similarly, no reaction occurred after the reactants had been refluxed in benzene solution for 22 hr. *N*-Trimethyl-*B*-trichloroborazine (1.68 g, 7.45 mmol) did not react with tetramethyltin (4.82 g, 26.9 mmol) in a sealed tube maintained at 110° for 24 hr. A reaction between these compounds did not occur in refluxing benzene solution. Unreacted starting materials were recovered in 95% yield or better from each of these reactions.

The Reaction of *N*-Trimethylborazine with Mercury Salts.—*N*-Trimethylborazine (2.91 g, 23.6 mmol) and mercuric chloride (6.4 g, 23.6 mmol) were heated at 155° for 40 min yielding elemental mercury; a mixture of hydrogen and hydrogen chloride was liberated during the course of the reaction. Fractionation of the reaction product through traps maintained at 10, −10, −23, and −196° over an 18-hr period yielded *N*-trimethyl-*B*-dichloroborazine (0.47 g, 2.5 mmol, 3.4%) at −23°. The residue from sublimation was dissolved in 20 ml of pentane and filtered to remove mercury; the solid obtained upon removal of the solvent

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[4] R. Maruca, O. T. Beachly, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).

[5] D. T. Haworth and L. F. Hohnstedt, *Chem. Ind.* (*London*), 599 (1960).

[6] L. F. Hohnstedt and D. T. Haworth, *J. Amer. Chem. Soc.*, **82**, 89 (1960).

[7] E. M. Fedneva, I. V. Kryukova, and V. I. Alpatova, *Russ. J. Inorg. Chem.*, **11**, 1101 (1966).

[8] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Academic Press, New York, N. Y., 1965, p 733.

[9] See ref 8, p 744.

[10] R. T. Sanderson, "Vacuum Manipulations of Volatile Compounds," Wiley, New York, N. Y., 1948, pp 90, 110–113.

[11] R. D. Compton, Ph.D. Dissertation, The University of Texas, 1965; J. W. Fitch, Ph.D. Dissertation, The University of Texas, 1965.

[12] E. Schwartz-Berkampf, *Z. Anal. Chem.*, **69**, 337 (1926).

[13] G. A. Anderson and J. J. Lagowski, *Spectrochim. Acta, Sect. A*, **26**, 2013 (1970).

[14] L. A. Melcher, J. L. Adcock, G. A. Anderson, and J. J. Lagowski, in preparation.

sublimed *in vacuo* at 50°; *N*-trimethyl-*B*-dichloroborazine (2.38 g, 12.4 mmol, 52.5%) was recovered, mp 97–98.5°.

N-Trimethylborazine (4.24 g, 34.4 mmol) and mercurous chloride (8.36 g, 17.7 mmol) when heated at 162° for 1.5 hr yielded mercury (6.96 g, 98%) and hydrogen; no hydrogen chloride was detected during the course of this reaction. Fractionation of the solid residue through traps at 10, −10, −23, and −196° yielded a fraction at −10° which was predominantly *N*-trimethyl-*B*-chloroborazine (2.96 g, 19.0 mmol, 55.3%).

In a similar reaction using a 1:1 mole ratio of reactants, *N*-trimethylborazine (4.37 g, 36 mmol) and mercurous chloride (16.68 g, 35.4 mmol) yielded elemental mercury (13.9 g, 98%) and *N*-trimethyl-*B*-dichloroborazine (2.79 g, 14.5 mmoles, 40.4%) as the sublimation product of the solid residue at 38°.

N-Trimethylborazine (1.75 g, 14.2 mmol) and mercuric bromide (7.64 g, 21.2 mmol) were heated at 174° for 4 hr; hydrogen, but not hydrogen bromide, was liberated in the course of the reaction. Slow fractionation (18 hr) of the volatile products in the vacuum system gave *N*-trimethyl-*B*-bromoborazine (0.21 g, 1.6 mmol, 11.2%; mp 32.5–33.5°) at −10°. A mixture of elemental mercury and mercurous bromide was identified in the unsublimed residue by qualitative analysis.

The Reaction of Borazines with Titanium Tetrahalides.—*N*-Trimethylborazine (4.49 g, 34.0 mmol) and titanium tetrachloride (6.88 g, 35.5 mmol) were refluxed at 130° for 18 hr to give a chocolate brown mixture. Although a small amount of *N*-trimethyl-*B*-chloroborazine (∼0.1 g) was recovered from the residue, about 80% of the starting borazine was recovered unreacted. The presence of $TiCl_3$ in the reaction residue was confirmed by the appearance of the characteristic purple color it forms in aqueous solution.

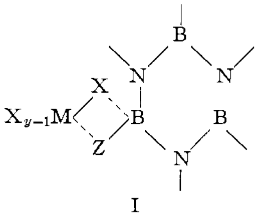
N-Trimethylborazine (1.74 g, 14.2 mmol) and titanium tetrafluoride (1.76 g, 14.2 mmol) were heated in a sealed evacuated tube at 167° for 36 hr; hydrogen was formed in the reaction. The volatile products were fractionated in the vacuum system yielding *N*-trimethyl-*B*-fluoroborazine (0.30 g, 2.1 mmol, 15.0%; mp 25–28°) in the −30° trap. Mass spectral analysis indicated that the sample contained a small amount of *N*-trimethylborazine.

N-Trimethyl-*B*-dichloroborazine (2.79 g, 14.2 mmol) and titanium tetrafluoride (1.0 g, 8.1 mmol) were heated at 200° for 10 min. The reaction mixture was fractionated on the vacuum system to yield *N*-trimethyl-*B*-difluoroborazine (0.16 g, 1.0 mmol, 6.8%; mp 62–65°) at −23°. The mass spectrum of this product indicated that the major impurity in the product was about 5% *N*-trimethyl-*B*-trifluoroborazine.

Discussion

The products observed in the reactions of borazines with heavy metal halides can be best understood in terms of a common reaction scheme. In view of the fact that most of the reported substitution reactions occur at the electron-deficient boron sites in the borazine ring, the most tempting pathway involves a four-centered bridged complex intermediate.[15] Such transition states are readily attained if both species contain atoms that can expand their coordination number and if the substituting group can act as a bridging group.[16] Thus, a possible intermediate (I) in the formation of the substituted borazines using heavy metal halides (eq 1) could involve the B–Z moiety in the borazine ring and one of the MX bonded pairs of atoms in the heavy metal halide.

$$MX_y + R_3N_3B_3Z_3 \longrightarrow MX_{y-1}X + R_3N_3B_3Z_2X' \qquad (1)$$



I

Such an intermediate would be favored by boron substituents that could act as bridging groups to metal atoms acting as acceptors. The electronic structure of the halogen atoms is admirably constituted to form bridged intermediates. Stable species incorporating halogen bridges are known among the group III elements as well as the heavy metal halides; hydrogen-bridged species are also well known. This type of exchange would be expected to give a random distribution of products if there were no barrier to the process or if there were no other factor biasing its course. However, the initial products could undergo further reactions to form other products, the properties of which essentially dictate the course of the reaction. For example, if a *B*-hydrogen atom is involved in exchange, the resulting metal hydride could be unstable with respect to disproportion to a lower oxidation state which could be attained by the evolution of hydrogen and/or hydrogen halide. The formation of hydrogen halide could affect the course of the reaction by effectively removing unreacted borazine as the very stable hydrogen halide adduct $R_3N_3B_3H_3 \cdot 3HX$.

Species of the type shown in I seem logical intermediates in the reactions of titanium halides with either the B–H or B–Cl moiety in *N*-trimethylborazines. The exchange of *B*-chlorine atoms by fluorine using TiF_4 presumably can be driven to completion by mass action yielding mixed titanium chlorofluorides ($TiCl_3F$, etc.) in the process, but the reaction of the B–H moiety with TiX_4 (X = Cl, F) should lead to species of the type TiX_3H which are unstable with respect to TiX_3.[17] The presence of reduced titanium halides was confirmed in the reactions where a *B*-hydrogen atom was available for exchange.

The general exchange scheme can also be used to understand the course of the reactions between tin(IV) compounds and borazines containing a *B*-hydrogen atom. Both $SnCl_4$ and $SnBr_4$ react with *N*-trimethylborazine to give a mixture of *N*-trimethyl-*B*-monohalo-, *N*-trimethyl-*B*-dihalo-, and *N*-trimethyl-*B*-trihaloborazines; the relative proportion of the products depends upon the ratio of borazine to SnX_4 taken initially (see eq 2). In the presence of excess *N*-trimethylborazine

$$SnX_4 + (CH_3)_3N_3B_3H_3 \longrightarrow \left\{\begin{matrix}(CH_3)_3N_3B_3H_2X \\ (CH_3)_3N_3B_3HX_2 \\ (CH_3)_3N_3B_3X_3\end{matrix}\right\} + HX + SnX_2 \qquad (2)$$

the hydrogen halide appears as the adduct $H_3B_3N_3(CH_3)_3 \cdot 3HX$ which, together with the corresponding stannous halide, is insoluble in benzene. The latter may be the driving force for the low-temperature reaction occurring in benzene.

If the reaction proceeds *via* the proposed bridged-complex intermediate, trihalostanne is the expected product (eq 3). Although species of this type have not

$$SnX_4 + (CH_3)_3N_3B_3H_3 \longrightarrow (CH_3)_3N_3B_3H_2X + HSnX_3 \qquad (3)$$

been characterized, $SnCl_3H \cdot 2(C_2H_5)_2O$, prepared by the action of anhydrous HCl on an ether suspension of $SnCl_2$, has been reported.[18] If $HSnCl_3$ were an intermediate in the reaction of the borazine with $SnCl_4$ (eq

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(15) (a) E. K. Mellon, Jr., and J. J. Lagowski, *Advan. Inorg. Chem. Radiochem.*, **5**, 259 (1963); (b) J. C. Sheldon and B. C. Smith, *Quart. Rev., Chem. Soc.*, **14**, 200 (1960).

(16) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

(17) R. J. H. Clark, "The Chemistry of Titanium and Vanadium," American Elsevier, New York, N. Y., 1968; P. Breisacher and B. Siegel, *J. Amer. Chem. Soc.*, **85**, 1705 (1963).

(18) O. M. Nefedov and S. F. Kolesnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 201 (1966); *Chem. Abstr.*, **65**, 743*h* (1966).

3) conducted in a solvent which did not stabilize the stannane, the latter might be expected to eliminate hydrogen halide to yield stannous halide (eq 4). At

$$\mathrm{HSnX_3} \longrightarrow \mathrm{HX} + \mathrm{SnX_2} \qquad (4)$$

low temperatures in the presence of excess borazine, reaction 4 would be driven to completion by the formation of the very stable adduct $(CH_3)_3N_3B_3H_3 \cdot 3HX$ which is insoluble in most common solvents. Reactions conducted with a deficiency of the borazine in a vented system at high temperatures give gaseous hydrogen halide. In the presence of excess borazine at reaction temperatures above the dissociation temperature of the hydrogen halide adduct, the predominant gaseous product is hydrogen, which can arise from either the reaction of HX with the borazine

$$\mathrm{(CH_3)_3N_3B_3H_3} + \mathrm{HX} \longrightarrow \mathrm{(CH_3)_3N_3B_3H_2X} + \mathrm{H_2} \qquad (5)$$

or the continued reaction of trihalostanne with another B–H moiety to give dihalostannane

$$>\mathrm{B{-}H} + \mathrm{H_3SnX_3} \longrightarrow\ >\mathrm{B{-}H} + \mathrm{H_2SnX_2} \qquad (6)$$

which then decomposes to stannous halide and hydrogen. Neither of these possible routes for the formation of hydrogen has been unambiguously established although there is some indirect evidence available.[19] The process described in eq 5 occurs when the adduct is heated above its decomposition temperature in a sealed tube.[20] In addition, unidentified volatile tin-containing species which decompose to stannous halides and/or liberate hydrogen were detected in our experiments as well as in the reaction of borazine with stannic chloride.[4]

Attempts to effect halogen–methyl exchange reactions between other tin compounds and borazines were unsuccessful even though (a) alkyl–aryl, aryl–alkyl,[21] and hydrogen–alkyl[22] exchanges have been observed between borazines and Grignard reagents and (b) halogen–methyl exchange reactions between tetramethyltin and boron trihalides are standard methods of preparing methylhaloboranes.[23] Tetramethyltin did not react with *N*-trimethyl-*B*-trichloroborazine and the attempted reverse reaction between stannic chloride and hexamethylborazine was also unsuccessful. These results are in accord with the reduced acceptor character of the boron atoms in borazines and the low reactivity of the methyl group in mechanisms involving bridged-complex intermediates.[16]

The reaction of mercuric chloride with *N*-trimethylborazine appears to proceed in two stages, each involving a halogen–hydrogen exchange reaction. The first stage, which terminates when the reaction is conducted in hydrocarbon solvents at room temperature,[4] gives mercurous chloride and hydrogen chloride (isolated as $(CH_3)_3N_3B_3H_3 \cdot 3HCl$) as products. At elevated temperatures, both mercuric and mercurous chlorides react with *N*-trimethylborazine to form mercury and hydrogen. These observations lend themselves to several interpretations. It has been suggested[4] that the low-temperature reaction proceeds through the formation of an intermediate mercury chlorohydride (eq 7) which

$$\mathrm{HgCl_2} + \mathrm{(CH_3)_3N_3B_3H_3} \longrightarrow \mathrm{HgClH} + \mathrm{(CH_3)_3H_3B_3H_2Cl} \qquad (7)$$

then reacts with excess mercuric chloride to yield the observed products (eq 8). The mercury chlorohydride

$$\mathrm{HgHCl} + \mathrm{Hg_2Cl_2} \longrightarrow \mathrm{Hg_2Cl_2} + \mathrm{HCl} \qquad (8)$$

proposed[4] as an intermediate in this reaction is consistent with the general exchange process described previously (1). If the high-temperature reaction follows in the same course, the halogen–hydrogen exchange would yield a mercurous chlorohydride (eq 9)

$$\mathrm{(CH_3)_3N_3B_3H_3} + \mathrm{Hg_2Cl_2} \longrightarrow \mathrm{(CH_3)_3N_3B_3H_2Cl} + \mathrm{Hg_2ClH} \qquad (9)$$

which would be expected to decompose rapidly to mercury and HCl (eq 10). Since the gas produced from

$$\mathrm{Hg_2ClH} \longrightarrow 2\mathrm{Hg} + \mathrm{HCl} \qquad (10)$$

the higher temperature reaction of mercurous chloride and *N*-trimethylborazine (1:2 mole ratio) was pure hydrogen, either the processes described by eq 9 and 10 do not occur or there is an additional reaction occurring which produces hydrogen. In an independent experiment, it was demonstrated that under the conditions necessary to effect the reaction between Hg_2Cl_2 and *N*-trimethylborazine, the latter compound undergoes a reaction with hydrogen chloride to yield hydrogen (eq 11).

$$\mathrm{(CH_3)_3N_3B_3H_3} + \mathrm{HCl} \longrightarrow \mathrm{(CH_3)_3N_3B_3H_2Cl} + \mathrm{H_2} \qquad (11)$$

Elemental mercury is formed when either $HgCl_2$ or Hg_2Cl_2 reacts with *N*-trimethylborazine at high temperatures. The fact that HCl is found among the gaseous products and that the dichloroborazine is the predominant substitution product when the reacting ratio of $HgCl/(CH_3)_3N_3B_3H_3$ is unity suggests that the reaction of HCl with a *B*-chloro-substituted borazine occurs less readily than with *N*-trimethylborazine. This suggestion is supported by the fact that HCl is not found among the gaseous products when Hg_2Cl_2 (1 mol) reacts with *N*-trimethylborazine (2 mol); under these conditions the monochloro-substituted borazine predominates.

Of the mercury–halogen compounds, the chlorides are the most reactive with *N*-trimethylborazine. Under the same reaction conditions, mercuric bromide can only be reduced to Hg_2Br_2 which does not undergo further reaction, and mercuric iodide is inert.

Exchange reactions with heavy metal halides potentially represent a good method for synthesizing unsymmetrically substituted *B*-haloborazines if reagents are employed which yield readily separable products. Titanium tetrafluoride offers little difficulty in this respect but the stannic halides form volatile tin-containing intermediates which are difficult to separate from the substituted borazines. For this reason, the reactions of the borazines with stannic halides are relatively poor methods for preparing partially halogenated borazines. By contrast, the reactions of borazines with mercuric and mercurous halides yield hydrogen and elemental mercury which are easily separated from the borazine derivatives.

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[19] W. Vaubel, *Ber.*, **57**, 515 (1924).

[20] G. A. Anderson, Ph.D. Dissertation, The University of Texas, 1969.

[21] L. J. Adcock and J. J. Lagowski, *Inorg. Nucl. Chem. Lett.*, in press.

[22] J. H. Smalley and S. F. Staffiej, *J. Amer. Chem. Soc.*, **81**, 582 (1959).

[23] W. Gerrard, E. F. Mooney, and R. G. Rees, *J. Chem. Soc.*, 740 (1964).