such as cage-opening *via* $C_2B_5H_7^{2-}$ attack as suggested above or intermolecular exchange of $Co(C_5H_5)^+$ moieties in solution. Evidence that the latter process may be significant has been obtained in preliminary studies of the chemistry of $(\pi\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$, which readily forms dicobalt complexes in the presence of sodium naphthalide without the addition of metal ions.[18] Direct formation of the dicobalt complexes from tetranegative anions of the $C_2B_{n-2}H_n^{4-}$ type (*e.g.*, $C_2B_6H_8^{4-}$) is improbable since such highly charged small ions are unlikely to have a stable existence, and indeed none has been characterized.

Neither of the proposed schemes adequately accounts for the preponderance of the $(\pi\text{-}C_2B_4H_6)Co(\pi\text{-}C_5H_5)$ species and its σ-bonded derivatives. A current study of the immediate products of the reaction of $C_2B_5H_7$ with sodium naphthalide is expected to provide some additional insight into the problem.

Experimental Section

Materials. Dicarba-*closo*-heptaborane(7) ($C_2B_5H_7$) was obtained from Chemical Systems, Inc. and purified by glpc (30% Apiezon L on Chromosorb W at 35°). Cobalt(II) chloride was obtained from $CoCl_2 \cdot 6H_2O$ (Baker Reagent) by dehydration *in vacuo* at 160°. Cyclopentadiene was distilled from dicyclopentadiene (Aldrich). All solvents were reagent grade, and tetrahydrofuran (THF) was dried over lithium aluminum hydride before use. Naphthalene (Fisher) was used as received.

Spectra. Boron-11 nmr spectra at 32.1 MHz and proton nmr spectra at 100 MHz were obtained on a Varian HA-100 nmr spectrometer. Infrared spectra were run in solution (*vs.* pure solvent) on a Beckman IR-8 instrument. Unit resolution mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6E mass spectrometer. High-resolution mass spectra were recorded on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source and interfaced to a PDP-8I computer. All high-resolution spectra were obtained under chemical ionizing conditions using an argon-water matrix, which characteristically produced intense P + 1 peaks due to protonation of parent ions. Each significant ion mass was accompanied by a computer printout indicating all possible compositions for the given mass within preset limits and based on selected isotopic masses which included ^{59}Co, ^{12}C, ^{11}B, ^{10}B, ^{1}H, and ^{16}O. In virtually every instance (each peak of each spectrum), only one chemically significant composition was found within acceptable limts of error.

Procedure. Sodium cyclopentadienide (NaC_5H_5) was prepared by distilling *in vacuo* approximately 170 mmol of C_5H_6 into 120 mg-atoms of divided sodium in 40 ml of THF and allowing the reaction to proceed until all the sodium was consumed. The sodium naphthalide was prepared *in vacuo* by allowing 53 mg-atoms of divided sodium to react with 53 mmol of naphthalene in 70 ml of THF overnight. To this dark green solution was added by vacuum distillation 26 mmol of $C_2B_5H_7$. After standing overnight at 25° this solution was dark orange in color with no formation of noncondensables. The carborane and NaC_5H_5 solutions were taken into a drybox, mixed (with slight gas evolution), and added dropwise over 30 min to a stirred mixture of 145 mmol anhydrous $CoCl_2$ in 500 ml of THF. The dark blue solution turned very dark brown. After stirring for 20 hr at 25°, most of the THF was distilled off under reduced pressure. The residue was suspended in a solution of 500 ml of H_2O and 50 ml of acetone and stirred for 4 hr under a stream of air. After distilling off most of the acetone and remaining THF, the solution was filtered and the solid extracted with several portions of acetone. The combined acetone fraction was reduced in volume by evaporation at reduced pressure and diluted with hexanes, after which the solution was decanted off and the solvent removed at reduced pressure. The compounds I–VIII reported herein were obtained from this residue by a combination of column and thin layer chromatography. The order of elution from a silica gel column with hexanes is II, III, VII, I, IV, V, VIII, and VI. On the plates hexanes was used to separate I, II, III, and VII while 5% THF in hexanes was used to separate IV, V, VI, and VIII. Compounds I, III, and VII were crystallized by cooling the hexane solution at −78° while IV and VIII were crystallized from heptane using slight warming and then cooling at 0°.

Approximate yields of the isolated compounds were the following: I, 1000 mg (20% of theory); II, 20 (0.5); III, 90 (2); IV, 20 (0.2); V, 20 (0.2); VI, 20 (0.2); VII, 100 (2); VIII, 150 (2).

Acknowledgment. We are grateful for a gift of mixed lower carboranes from Chemical Systems, Inc., through the courtesy of Drs. J. F. Ditter and R. E. Williams. This work was supported by the Office of Naval Research.

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[18] R. Weiss and R. N. Grimes, unpublished results.

Polar and Free-Radical Halogenation of Amine–Boranes with Halocarbons

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Abstract: Amine–boranes will react cleanly with halocarbons to give amine–haloboranes and an alkane. Polar reactions are observed with organic halides, such as chlorotriphenylmethane, which form carbonium ions readily, with reactivity increasing with the stability of the carbonium ion. Free-radical reactions are observed with CCl_4 or CCl_3Br; they can be initiated with benzoyl peroxide. 4-Methylpyridine–monochloroborane and –dichloroborane have been synthesized.

In a recent paper[1] evidence was presented which suggested that substitution of halogen for hydrogen in amine–boranes may proceed either by a polar or by a free-radical pathway, depending on the nature of the chlorinating agent. During a subsequent investigation of the reaction between dimethylchloramine and amine–boranes,[2] it was observed that the solvent, CCl_4, could become involved in the reaction and act as a chlorinat-

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[1] J. W. Wiggins and G. E. Ryschkewitsch, *Inorg. Chim. Acta*, 4, 33 (1970).

[2] V. R. Miller, G. E. Ryschkewitsch, and S. Chandra, *Inorg. Chem.*, 9, 1427 (1970).

ing agent. This study also suggested that CCl_4 could chlorinate amine–boranes even in the absence of dimethylchloramine.

In the present paper we attempted to probe the usefulness and the limitations of the reaction of amine–boranes with halocarbons in general for the synthesis of halogenated borane adducts. We have found that in certain cases halogenation proceeds by a polar mechanism and, in other cases, by a free-radical chain mechanism.

Results and Discussion

The general equation for the reaction of amine–boranes with alkyl halides is shown in eq 1. It has been

$$\text{(amine)}BH_3 + RX \longrightarrow \text{(amine)}BH_2X + RH \qquad (1)$$

shown to be applicable when the amine is trimethylamine or 4-methylpyridine and when RX is $(C_6H_5)_3CCl$, CCl_4, CCl_3Br, or $C_6H_5CH_2Cl$. In the presence of benzoyl peroxide, 1,2-dichloroethane will also chlorinate trimethylamine–borane.

The ease with which these reactions proceed depends upon both the amine–borane and the halide used. Thus, 4-methylpyridine–borane will react completely with 1 equiv of chlorotriphenylmethane in less than 1 min, while heating it in pure benzyl chloride at 73° for 20 hr will convert only about 50% of the amine–borane to the amine–chloroborane. In refluxing CCl_4 better than 90% of 4-methylpyridine–borane is converted to the chloroborane in 1 hr, while trimethylamine–borane requires 24 hr for conversion to the chloroborane adduct.

Most of the above halocarbons will react further with the monohalogenated amine–borane to give the dihalogenated compound. The difference in reactivity between the starting BH_3 compound and the monohalogenated derivative depends upon the halocarbon. With chlorotriphenylmethane the difference is large enough so that essentially all of the BH_3 compound reacts before any of the BH_2Cl compound reacts. In reactions in refluxing CCl_4 the difference is not so large and a small amount of dichloro compound is produced before all the starting borane has been used up.

As a synthetic tool, the reaction of pyridine–boranes with $(C_6H_5)_3CCl$ is quite useful. Thus, equivalent amounts of 4-methylpyridine–borane and chlorotriphenylmethane reacted quantitatively, as shown by the nmr spectrum of the reaction mixture, to give the monochloroborane adduct. Handling losses in the separation from triphenylmethane and hydrolysis losses reduced the yield of isolated pure product to 69%. In contrast, a 74% yield of 4-methylpyridine–monochloroborane containing 9% dichloro derivative was isolated from the reaction of 4-methylpyridine–borane in refluxing CCl_4. The reaction of 4-methylpyridine–borane with 2 equiv of chlorotriphenylmethane gave a 63% yield of $4\text{-}CH_3C_5H_4NBHCl_2$.

Although the stoichiometries of the reactions of various alkyl halides with amine–boranes are the same, there apparently are two distinctly different mechanisms. The first reaction mechanism is a polar one and operates in the halogenations with chlorotriphenylmethane. It is proposed that the reaction is a hydride abstraction from the borane adduct by a carbonium ion paired with chloride ion, followed by formation of the boron–chlorine bond to yield the neutral chlorinated borane adduct.

$$R_3NBH_3 + (C_6H_5)_3C^+Cl^- \longrightarrow R_3NBH_2^+ + (C_6H_5)_3CH + Cl^- \longrightarrow R_3NBH_2Cl + (C_6H_5)_3CH \qquad (2)$$

This notion is supported by the way the solvent or the structure of the reactants influences the reaction rate and by the isolation of intermediates. Thus, in CH_2Cl_2 or $C_2H_4Cl_2$ the reaction of trimethylamine–borane with $(C_6H_5)CCl$ is very rapid, whereas in C_6H_6, a less polar solvent, only about 6% reacts in 20 min under otherwise the same conditions. A similar difference is observed for the reaction with 4-methylpyridine–borane.

These results parallel those of Corey and West[3] who found that chlorotriphenylmethane will react with triphenylsilane to give triphenylmethane and chlorotriphenylsilane. They also found that solvents such as CH_2Cl_2 and 1,2-$C_2H_4Cl_2$ in which chlorotriphenylmethane forms ion pairs[4] are the solvents in which the alkyl halide is reduced the fastest. Based on this evidence and on preliminary kinetic studies they postulate a polar mechanism in which the chlorotriphenylmethane ion pair is involved in a hydride abstraction.

Structural changes also affect the reaction rate. Malachite Green (4,4′-bisdimethylaminotriphenylmethyl chloride) is substantially more reactive than is triphenylmethyl chloride, which in turn reacts much faster than benzyl chloride. This reactivity order is consistent with the proposed reaction path since it parallels the tendency of the halocarbons to form carbonium ions.[5] In further agreement with this view is our observation that the free triphenylmethyl carbonium ion in the form of the PF_6^- salt in CH_2Cl_2 is indeed very reactive as a hydride abstractor. Similar results have been reported recently for $(C_6H_5)_3C^+BF_4^-$ in acetonitrile or pyridine.[6] Finally, the greater reactivity of 4-methylpyridine–borane when compared to trimethylamine–borane also is consistent with the postulate that positive charge is developed on the borane portion of the reacting system; the charge could be more readily delocalized in the pyridine derivative *via* transfer of electronic charge from the π system to boron. The reactivity order here thus follows the expected stability order of three-coordinate boronium ions.[7]

The most direct evidence for the existence of ionic intermediates, however, comes from observations on the system $(CH_3)_3NBH_3$–$(C_6H_5)_3CCl$ in acetonitrile. The proton nmr spectrum revealed among other products the formation of a cation in which CH_3CN was coordinated to a $(CH_3)_3NBH_2^+$ unit. This cation was isolated as the chloride salt and identified after conversion to the known PF_6^- salt.[8] The cation reacted slowly with chloride ion to give $(CH_3)_3NBH_2Cl$; there was no evidence for the reverse reaction, displacement of chloride by acetonitrile, when $(CH_3)_3NBH_2Cl$ was kept in acetonitrile for several hours. This demonstrates conclusively that the chlorinated borane adduct is the thermodynamically more stable product and that, therefore, the solvent-coordinated cation must be a kinetic percursor.

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(3) J. Y. Corey and R. West, *J. Amer. Chem. Soc.*, **85**, 2430 (1963).

(4) A. G. Evans, A. Price, and J. H. Thomas, *Trans. Faraday Soc.*, **52**, 332 (1956).

(5) S. Matsumura and N. Tokura, *Tetrahedron Lett.*, 4703 (1968).

(6) L. E. Benjamin, *et al.*, *Inorg. Chem.*, 9, 1844 (1970).

(7) G. E. Ryschkewitsch and J. W. Wiggins, *J. Amer. Chem. Soc.*, **92**, 1790 (1970).

(8) G. E. Ryschkewitsch and K. Zutshi, *Inorg. Chem.*, 9, 411 (1970).

With 4-methylpyridine–borane the chlorinated derivative was the only product found; the acetonitrile-containing ionic intermediate was not observed. This is not surprising, since, in view of the vastly enhanced reactivity of pyridine-substituted cations toward nucleophilic stubstitutions, displacement of acetonitrile by chloride should occur rapidly in this instance.[9,10]

In contrast to the reaction with chlorotriphenylmethane, amine–boranes may react with alkyl halides such as 1,2-$C_2H_4Cl_2$, CCl_4, or CCl_3Br by a free-radical chain mechanism

$$R\cdot + (\text{amine})BH_3 \longrightarrow RH + (\text{amine})BH_2\cdot \qquad (3)$$

$$(\text{amine})BH_2\cdot + RCl \longrightarrow (\text{amine})BH_2Cl + R\cdot \qquad (4)$$

where R· is a radical derived by abstraction of halogen from the halocarbon. In the presence of benzoyl peroxide, a common free-radical initiator, there can be little doubt that the reaction proceeds by such a path. In the absence of the initiator, only 8% of the trimethylamine–borane will react with refluxing carbon tetrachloride in 40 min. In contrast to this, if a small amount (6%) of benzoyl peroxide is added, 64% of the amine–borane will react in this time.

Rate constants for the decomposition of benzoyl peroxide have been accurately determined by Bartlett.[11] The value of 2×10^{-5} sec^{-1} applicable to our experimental condition leads to the conclusion that the decomposition of one molecule of peroxide leads to the chlorination of nearly 200 molecules of amine–borane. In a similar experiment with free-radical initiation 1,2-dichloroethane was also shown to halogenate $(CH_3)_3NBH_3$, but at a slower rate than does CCl_4.

While this evidence shows that amine–boranes are capable of reacting by a free-radical chain mechanism, it does not rule out the possibility that in the absence of an added free-radical source the reaction proceeds by a polar mechanism. This latter possibility is less likely considering the fact that the reaction can be inhibited by purification of CCl_4 in the vacuum line, or that addition of very small quantities of water can produce an induction period of several hours before chlorination of 4-methylpyridine–borane commences. This behavior would be difficult to explain in terms of a polar mechanism, but suggests that impurities in the solvent are responsible for initiation of the radical chain, at least in CCl_4.

The most convincing evidence for a radical mechanism comes from reactions with bromotrichloromethane. This halocarbon reacts much more rapidly than CCl_4 with either 4-methylpyridine–borane or with trimethylamine–borane. The former borane adduct yields exclusively the monobromoborane and an equivalent amount of chloroform whereas the latter produces a 60:40 mixture of $(CH_3)_3NBH_2Br$ and $(CH_3)_3NBH_2Cl$ together with a 60:40 mixture of $CHCl_3$ and $CHCl_2Br$. As in the case of CCl_4 the reaction can be markedly accelerated with small amounts of benzoyl peroxide. The proportions of chlorinated and brominated borane and of reduction products of CCl_3Br remain the same as in the uninitiated reaction when the amount of initiator, the extent of reaction, or the temperature are changed. The invariance of product distribution between the uninitiated and the peroxide-initiated reaction leads to the only plausible conclusion that, except for initiation, both reactions proceed through the same path. We propose this is the kind of reaction chain cited above (eq 3 and 4), with the modification that the second step allows for competitive abstraction of bromine or chlorine, removal of the former being favored, after correction for statistics, by a factor of 4.5. All steps are feasible thermodynamically, as determined from bond dissociation energies.[12]

The fact that CCl_3Br is more reactive than CCl_4 can now be understood in terms of the lowering of bond dissociation energy when a C–Br bond is broken instead of a C–Cl bond. The higher reactivity of 4-methylpyridine–borane can also be explained by the expected weakening of the B–H bond caused by the stabilization of the resulting radical.[13] The more stable radical also should be more selective in the abstraction of halogen from the weaker bond, so that the exclusive formation of $CH_3C_5H_4NBH_2Br$ is not unexpected.

Experimental Section

Reaction of Trimethylamine–Borane with Chlorotriphenylmethane. To 10 ml of a cooled and stirred solution of 10.0 mmol of $(C_6H_5)_3CCl$ in CH_2Cl_2 was added 10.0 mmol of solid $(CH_3)_3NBH_3$. On warming an exothermic reaction occurred. After 30 min at autogenous temperature the mixture was concentrated until saturated and added to 75 ml of petroleum ether (bp 65–110°). The resulting white precipitate weighed 0.638 g and proved to be $(CH_3)_3NBH_2Cl$, free of the starting borane but containing 3 mol % $(C_6H_5)_3CH$. A second fraction of the same purity (0.160 g) was isolated from the filtrate on concentrating. A second purification yielded a product melting at 83.5–84° (lit., 85°),[14] total yield 72%. The solid recovered from the filtrate yielded, after boiling in methanol and precipitation with water, 2.220 g of $(C_6H_5)_3CH$, mp (recrystallized) 92.5–93° (lit.,[15] 92.6°), total yield 93%.

Under similar conditions, but using benzene as the solvent only, 7% reduction of $(C_6H_5)_3CCl$ occurred within 30 min. In acetonitrile with about half the above concentration, the reaction went to 50% in 30 min.

The Reaction of 4-Methylpyridine–Borane with Chlorotriphenylmethane. To a weight of 1.07 g (10.0 mmol) of 4-$CH_3C_5H_4NBH_3$ in 20 ml of CH_2Cl_2 was added, with stirring, 2.79 g (10.0 mmol) of $(C_6H_5)_3CCl$. The heat of the reaction was sufficient to bring the solution to reflux. After stirring for 10 min, 200 ml of petroleum ether (30–60°) was added and the precipitate was filtered with a minimum exposure to the atmosphere to give a 63% yield of 4-methylpyridine–monochloroborane, mp 88.0–88.5°. An analytical sample was prepared by precipitation from CH_2Cl_2 with petroleum ether (30–60°). *Anal.* Calcd for $C_6H_7NBH_2Cl$: C, 50.96; H, 6.42; Cl, 25.07; N, 9.90. Found: C, 51.31; H, 6.24; Cl, 25.03; N, 9.79. The nmr spectrum of the solid, 0.53 g, obtained after reduction of the volume of the solution showed it to be 82% 4-methylpyridine–monochloroborane and 18% triphenylmethane. Complete evaporation of the filtrate gave a 93% yield of impure triphenylmethane, mp 87–90°. The identity of the hydrocarbon was confirmed by the nmr spectrum and the melting point (93–94°) of a sample crystallized from methanol.

In a similar experiment in CH_3CN a 72% yield of 4-$CH_3C_5H_4NBH_2Cl$ melting at 84.5–86.0° was isolated.

Reaction of 4-Methylpyridine–Borane with Chlorotriphenylmethane in Benzene. A solution of 1.08 g (10.0 mmol) of 4-$CH_3C_5H_4NBH_3$ and 2.79 g (10.0 mmol) of $(C_6H_5)_3CCl$ in 20 ml of benzene was heated for 2.5 hr at 70°. The nmr spectrum showed that

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[9] K. C. Nainan and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, 91, 330 (1969).

[10] G. E. Ryschkewitsch and T. E. Sullivan, *Inorg. Chem.*, 9, 899 (1970).

[11] K. Nozake and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1686 (1946).

[12] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1938.

[13] The pyridine–diphenylboryl radical has been isolated as a stable solid. R. Koster, G. Benedikt, and H. W. Schroter, *Angew. Chem., Int. Ed. Engl.*, 3, 514 (1964).

[14] *Inorg. Syn.*, 12, 121 (1970).

[15] Gustav Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold, New York, N. Y., 1946, p 481.

43% of the $(C_6H_5)_3CCl$ had been converted into $(C_6H_5)_3CH$. After heating for a total of 140 hr the solution was allowed to cool then filtered to give 2.22 g of solid. This was crystallized from dichloromethane–petroleum ether (bp 30–60°) by evaporation to give 1.28 g, a 52% yield, of $(C_6H_5)_3CH$, mp 92.5–93.5° (lit.,[12] 92.6°). To the original filtrate was added 12 mmol of 4-methylpyridine, and the solution was stirred for 3 hr. The mixture was filtered and the solid rinsed with benzene to give 1.61 g, a 69% yield of crude $(4\text{-}CH_3C_5H_4N)_2BH_2^+Cl^-$. Treatment of a water solution of this compound with NH_4PF_6 gave a 93% conversion to $(4\text{-}CH_3C_5H_4N)_2BH_2^+PF_6^-$, mp 130–132° (lit.,[16] 132.5–133°). During the work-up there was evidence that a small amount of unreacted $4\text{-}CH_3C_5H_4NBH_3$ was present.

In a similar experiment the reaction of a solution that was 0.50 M in $4\text{-}CH_3C_5H_4NBH_3$ and 0.48 M in $(C_6H_5)_3CCl$ was allowed to proceed at 25° and the nmr spectrum recorded at various intervals. After 1.2 hr the reaction had gone to 43% and after 10 hr to 60%. After 100 hr there was a solid present and the reaction had gone to about 90%.

Preparation of 4-Methylpyridine–Dichloroborane with Chlorotriphenylmethane. A sample of 5.21 g (18.6 mmol) of $(C_6H_5)_3CCl$ was added to a stirred solution of 0.99 g (9.2 mmol) of $4\text{-}CH_3C_5H_4NBH_3$ in 20 ml of $1,2\text{-}C_2H_4Cl_2$. After the initial exothermic reaction had subsided the solution was heated for 22 hr at 60°. The product was precipitated with petroleum ether (30–60°) to give 1.40 g of solid. This was purified in a drybox by precipitation from benzene with petroleum ether (30–60°) to give 0.91 g, a 63% yield, of 4-methylpyridine–dichloroborane, mp 122–126°. The nmr spectrum showed several impurities in small amounts. An analytical sample with mp 131–132° was prepared by allowing the sample to stand for 5 min in about 20 ml of methylene chloride containing several drops of water, evaporating off the CH_2Cl_2 under reduced pressure, and, in a drybox, fractionally precipitating from benzene with petroleum ether. *Anal.* Calcd for $C_6H_7NBHCl_2$: C, 40.98; H, 4.58; N, 7.96; Cl, 40.32. Found: C, 40.76; H, 4.31; N, 7.92; Cl, 40.52.

Reaction of Trimethylamine–Borane with Chlorotriphenylmethane in Acetonitrile. In a preliminary experiment the nmr spectra of an equimolar solution of $(CH_3)_3NBH_3$ and $(C_6H_5)_3CCl$ in CH_3CN showed that the peak at 154 Hz, attributed to starting borane, decreased in area and a new peak appeared at 166 Hz at the same initial rate as the appearance of the aliphatic proton of $(C_6H_5)_3CH$. In another experiment benzene was added to the CH_3CN solution to give a precipitate. This was converted to the PF_6^- salt in water to give a 6% yield of $[(CH_3)_3N][CH_3CN]BH_2^+PF_6^-$. Crystallization by slow removal of CH_2Cl_2 gave a sample melting of 117.5–118.0° dec (lit.[8] 110–111°). The ir and nmr spectra were identical with an authentic sample. *Anal.* Calcd for $[(CH_3)_3N][CH_3CN]BH_2^+PF_6^-$: C, 23.28; H, 5.45; N, 10.86. Found: C, 23.66; H, 5.57; N, 10.61.

Trimethylamine–monochloroborane in CH_3CN gives a single peak at 157 Hz which does not change over 2.5 hr.

Reaction of Trimethylamine–Borane with Carbon Tetrachloride. A saturated solution of $(CH_3)_3NBH_3$ in CCl_4 showed no evidence (nmr spectra) of reaction after 21 days at 25° in the presence and absence of laboratory light. After refluxing for 24 hr, over 80% of the starting borane had reacted to give $(CH_3)_3NBH_2Cl$ and a small amount of dichloro derivative.

In another experiment 25 ml of a 0.404 M solution of $(CH_3)_3NBH_3$ in CCl_4 was prepared. Shortly after mixing, a sample was withdrawn and heated for 40 min at 76°. The nmr spectrum showed no evidence of reaction. Twenty hours later another sample was withdrawn from the closed container and again heated for 40 min at 76°. This time the nmr spectrum showed 8% reaction. At the same time a 1 ml aliquot of this borane solution was heated with 6.0 mg of (0.40 M) benzoyl peroxide. The nmr spectrum of this solution showed that 64% of the starting borane had reacted. A chain length of 90 was calculated for this sample. In a duplicate experiment with a different solution a chain length of 100 was calculated.

Reaction of 4-Methylpyridine–Borane with Carbon Tetrachloride. A solution of 1.00 g (9.3 mmol) of $4\text{-}CH_3C_5H_4NBH_3$ in 25 ml of CCl_4 was refluxed for 45 min. The nmr spectrum showed the mixture to be better than 80% $4\text{-}CH_3C_5H_4NBH_2Cl$ with some dichloro compound present. The solution was cooled and filtered to give 0.97 g of solid, mp 86.0–87.5°. Recrystallization from CCl_4 gave a sample melting of 89.5–90.0°. The nmr spectrum showed several per cent of the dichloro derivative.

Reaction of Trimethylamine–Borane with 1,2-Dichloroethane in the Presence of Benzoyl Peroxide. A solution of 1.09 g (14.9 mmol) of $(CH_3)_3NBH_3$ and 0.26 g (1.1 mmol) of benzoyl peroxide in 20 ml of $1,2\text{-}C_2H_4Cl_2$ was refluxed under nitrogen. The nmr spectra after 5.7 and 8.5 hr were essentially identical, showing about a 25% reaction. Another 0.66 g (2.7 mmol) of benzoyl peroxide was added, and the solution was refluxed for another 15 hr. The nmr spectrum of this solution showed that between 60 and 70% of the amine–borane had reacted to give the amine–monochloroborane. Work-up of this solution gave 0.32 g (3.0 mmol) of $(CH_3)_3NBH_2Cl$, mp 80.5–82.0 (lit.,[14] 84–85°). The identity was confirmed by the ir and nmr spectra. In a control experiment 0.71 g (9.8 mmol) of $(CH_3)_3NBH_3$ was refluxed under N_2 in 15 ml of $1,2\text{-}C_2H_4Cl_2$. The nmr spectra taken after 24 and 160 hr showed no evidence of any reaction. There was a very small amount of insoluble material formed after 160 hr.

Reaction of 4-Methylpyridine–Borane with Bromotrichloromethane. In a preliminary experiment the nmr spectrum of a solution of $4\text{-}CH_3C_5H_4NBH_3$ in CCl_3Br was observed at various intervals. After 20 min at 25° the spectrum showed two sets of 4-methylpyridine peaks in equal concentrations. These were interpreted as being starting borane and $4\text{-}CH_3C_5H_4NBH_2Br$. There was also a peak assigned to $CHCl_3$. After 140 min the 4-methylpyridine peaks showed that 95% of the starting borane had been converted to the monobromo derivative. A comparison of the areas under the pyridine and $CHCl_3$ areas confirmed this idea. The spectrum after 67 hr showed that the monobromo derivative was reacting further (about 30%) to give the dibromo compound. There was no evidence for $CHCl_2Br$.

In another experiment 1.04 g (9.7 mmol) of $4\text{-}CH_3C_5H_4NBH_3$ was stirred in 10 ml of CCl_3Br for 3 hr. When 13.2 mmol of $4\text{-}CH_3C_5H_4N$ was then added the solution became warm and a solid formed. The solution was diluted with petroleum ether (30–60°), filtered, and rinsed with petroleum ether to give 2.83 g of a hydroscopic solid. This was converted to the hexafluorophosphate salt by treatment with aqueous NH_4PF_6 and crystallized from hot water to give 1.75 g, a 52% yield, of $(4\text{-}CH_3C_5H_4N)_2BH_2^+PF_6^-$, mp 131.5–133.0° (lit.,[16] 132.5–133°).

Reagents. Trimethylamine- and pyridine-borane were obtained from Callery Chemical Co. and were purified by vacuum sublimation. 4-Methylpyridine–borane was prepared by transamination from trimethylamine–borane and purified by vacuum sublimation, mp 74.5–75.5° (lit.,[17] 72–73°). Solvents were reagent grade and stored over molecular sieves. Chlorotriphenylmethane was used as received from Matheson Coleman and Bell. Halogenated amine-boranes, if not isolated and analyzed, were identified by comparison of their ir and/or nmr spectra with those of authentic samples.[18]

Measurements. The ^1H nmr spectra were recorded on a Varian A-60A instrument using tetramethylsilane (TMS) as an internal standard. Elemental analysis were performed by Peninsular Chem-Research Inc., Gainesville, Fla. Melting points are uncorrected.

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(16) K. C. Nainan and G. E. Ryschkewitsch, *Inorg. Chem.*, 7, 1316 (1968).

(17) J. A. Bigot, T. J. DeBoar, and F. L. J. Sixma, *Recl. Trav. Chim. Pays-Bas*, 76, 996 (1957).

(18) M. A. Mathur, Doctoral Dissertation, University of Florida, 1970.