In control measurements on species in equilibrium with disulfite, the Raman spectrum of a concentrated aqueous solution of sodium sulfite was recorded. While our spectrum is in general agreement with that reported by Evans and Bernstein,[23] the degenerate modes ν_3 and ν_4, at 933 and 469 cm^{-1}, respectively, each appear to be split into two components. These are measured at 950 and 930 cm^{-1} for ν_3 and 480 and 460 cm^{-1} for ν_4. The removal of these degeneracies is reminiscent of similar effects for the degenerate frequencies of the nitrate ion in concentrated solutions.[17,24,25] The detailed analysis of this perturbation in terms of contact ion pairing or solvent-separated ion pairing is not apparent, but the sulfite spectrum may be as sensitive to these effects as that of nitrate.

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A New Synthesis of 2-Chloroborazine. The Reaction of a Pyridine Complex of 2,4,6-Trichloroborazine with Lithium Borohydride[1]

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The unsymmetrically substituted 2-chloroborazine $H_2ClB_3N_3H_3$ has been prepared in approximately 50% yield from the reaction of a pyridine complex of 2,4,6-trichloroborazine with lithium borohydride in diethyl ether. Smaller yields of $HCl_2B_3N_3H_3$ (6%) and $H_3B_3N_3H_3$ (12%) were also obtained. The reaction of an analogous pyridine complex of $Br_3B_3N_3H_3$ with $LiBH_4$ gives $H_3B_3N_3H_3$ as the major product, not $H_2BrB_3N_3H_3$. The ^1H and ^{11}B nmr chemical shift data for $H_2ClB_3N_3H_3$ and $HCl_2B_3N_3H_3$ have been compared to $H_3B_3N_3H_3$. The ^1H nmr data suggest that the chlorine is a weak electron-releasing substituent. The preparation of $H_2CH_3B_3N_3H_3$ in a 25% yield from the reaction of $H_2ClB_3N_3H_3$ with CH_3MgI in diethyl ether is also discussed.

One of the most intriguing problems in borazine chemistry is the synthesis of the unsymmetrically substituted derivatives. The logical starting materials for the preparations of the B-substituted compounds are the mono- and dichloroborazines. The chlorine can react with or be exchanged for a large variety of other groups. There are two previously reported preparative routes to $H_2ClB_3N_3H_3$ and $HCl_2B_3N_3H_3$ but both methods have definite drawbacks. In the reaction[2] of $H_3B_3N_3H_3$ with $HgCl_2$, the formation of the hydrogen chloride addition compound of borazine significantly limits the percentage yields of the unsymmetrically substituted chloroborazines. The reaction[3] of $H_3B_3N_3H_3$ with BCl_3 suffers from long reaction times and the small quantities of reagents which can be used in sealed-tube experiments. In addition, both of these reactions require the prerequisite preparation of $H_3B_3N_3H_3$, a tedious step. Therefore, a reaction of the more readily available 2,4,6-trichloroborazine, which would give a good yield of an unsymmetrically substituted chloroborazine, would be a significant improvement over these existing methods. We wish to report the reaction of a pyridine complex[4] of $Cl_3B_3N_3H_3$ with $LiBH_4$ in diethyl ether as a good route to $H_2ClB_3N_3H_3$. The proton and boron-11 nmr spectra of the chloroborazines have been studied in order to monitor the effect of a chlorine atom on the borazine ring.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means. The 2,4,6-trichloroborazine[5] was prepared by allowing BCl_3 to react with NH_4Cl in a tube at 200°. The unsymmetrically substituted chloroborazines[2] were identified by their vapor pressures and mass spectra.

Preparation of 2-Chloroborazine.—In a typical experiment, 5.15 g (65.3 mmol) of dry pyridine was added, by means of a vacuum distillation, to 6.043 g (32.6 mmol) of $Cl_3B_3N_3H_3$ which was dissolved in 30 ml of dry diethyl ether. Upon warming the reaction flask from −196° to room temperature, a white insoluble solid, a pyridine complex of $Cl_3B_3N_3H_3$, formed. The suspension was then cooled to 0° and 1.43 g (65.6 mmol) of $LiBH_4$ was added by means of a side-arm addition tube. The mixture was stirred, warmed to room temperature over a period of about 30 min, and then fractionated. Trap temperatures of −46, −63, −78, and −196° separated 0.279 g of $HCl_2B_3N_3H_3$ (5.7% based on $Cl_3B_3N_3H_3$ reacted), 1.758 g of $H_2ClB_3N_3H_3$ (47%), 0.23 g of a mixture of $H_2ClB_3N_3H_3$ and diethyl ether, and a mixture of $H_3B_3N_3H_3$ (4.3 mmol by N analysis) and diethyl ether, respectively. It was very tedious[2] to remove the ether from the $H_2ClB_3N_3H_3$ in the −78° trap. The reaction flask contained a viscous white material which was a mixture of LiCl and pyridine–borane (5.2 g, 56 mmol). It was not possible to detect any unreacted $Cl_3B_3N_3H_3$ or pyridine complexes of chloroborazines but some could have

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been present. The idealized reaction may be summarized by the equation

$$Cl_3B_3N_3H_3\cdot 2C_5H_5N + 2LiBH_4 \xrightarrow{\text{diethyl ether}} H_2ClB_3N_3H_3 + 2H_3B\cdot NC_5H_5 + 2LiCl$$

Very concentrated reaction mixtures and the very slow addition of $LiBH_4$ have been observed to lead to smaller yields of $H_2ClB_3N_3H_3$.

A word of warning must be issued with this preparative reaction. A reaction mixture exploded after mixing the reagents. In this one experiment, the adduct, $Cl_3B_3N_3H_3\cdot 2C_5H_5N$, was prepared in ether, and then the ether was removed by vacuum distillation. The solid adduct was scraped down off the walls of the reaction flask in the drybox, and then the flask was reevacuated. Solid $LiBH_4$ was added to the adduct by means of a side-arm addition tube and mixed with a magnetic stirrer. An explosion, accompanied by an orange ball of fire, followed about 5 min after the addition of the $LiBH_4$. We have run this reduction many, many times now, and as long as ether is present, there is not enough heat generated to even reflux the ether. We cannot explain fully why this one experiment exploded but it is suggested that the solid reagents should not be mixed in the absence of ether.

Attempted Preparation of $H_2BrB_3N_3H_3$.—This new synthetic procedure for $H_2ClB_3N_3H_3$ suggested that we should try the same type of reaction for the preparation of $H_2BrB_3N_3H_3$. In a typical experiment 3.53 g (11.1 mmol) of $Br_3B_3N_3H_3$, 1.761 g (22.2 mol) of pyridine, and 0.488 g (22.2 mmol) of $LiBH_4$ were allowed to react in 25 ml of diethyl ether according to the previously described procedure. Traps of −46, −63, −78, and −196° were used for the fractionation. The −46° trap contained 0.081 g of a material whose vapor pressure and mass spectrum agreed closely with those of 2-ethoxyborazine[6] ($H_2C_2H_5OB_3N_3H_3$), not $HBr_2B_3N_3H_3$.[3] The −63° trap contained 0.075 g of a material whose vapor pressure and mass spectrum suggested the presence of $H_2BrB_3N_3H_3$ and $H_2C_2H_5OB_3N_3H_3$. The −78° trap was empty and the −196° trap contained $H_3B_3N_3H_3$ (5.8 mmol, estimated by N analysis) and diethyl ether. The theoretical yield of $H_3B_3N_3H_3$, if all $LiBH_4$ reacted to form $H_3B_3N_3H_3$, would be 7.40 mmol. This reaction was repeated several times but it was never possible to prepare pure $H_2BrB_3N_3H_3$. We have also attempted to prepare $H_2BrB_3N_3H_3$ from $H_3B_3N_3H_3$ and $HgBr_2$, but there is no reaction.

Preparation of $H_2CH_3B_3N_3H_3$.—An ether solution of methylmagnesium iodide (3.12 ml, 3 *M*) was slowly added to 1.00 g (8.72 mmol) of $H_2ClB_3N_3H_3$ dissolved in 15 ml of dry ether. The mixture was stirred for several hours at room temperature and then the ether was removed by distillation at atmospheric pressure. The remaining material was fractionated by a vacuum distillation using trap temperatures of −46, −63, −78, and −196°. The −78° trap separated 0.236 g (2.48 mmol) of pure $H_2CH_3B_3N_3H_3$ (vapor pressure 18.4 mm at 0°, lit.[7] value 18.6 mm). The −46 and −63° traps contained very small amounts of mixtures of $H_2CH_3B_3N_3H_3$ and $H(CH_3)_2B_3H_3N_3$. The −196° trap contained an inseparable mixture of ether and $H_2CH_3B_3N_3H_3$.

Nuclear Magnetic Resonance Spectra.—The proton nmr spectra were recorded at 100 MHz with a Varian Model HA-100 spectrometer. The boron-11 nmr spectra were recorded at 15.871 MHz with a Varian Model HR-60 spectrometer. The reference compounds were tetramethylsilane and boron trifluoride–diethyl etherate. The chemical shifts of the ^{11}B spectra were determined using the side-band technique. The compounds were run neat or as 5% solutions in CCl_4. There was no apparent dependence of the spectra on concentration.

Results and Discussion

The synthesis of 2-chloroborazine in approximately 50% yields by the lithium borohydride reduction of a pyridine complex of the readily available $Cl_3B_3N_3H_3$ represents a significant advancement toward the goal of preparing a variety of unsymmetrically substituted borazines. If $Cl_3B_3N_3H_3$ is allowed to react with a deficiency of a metal borohydride, in the absence of pyridine, the major product is $H_3B_3N_3H_3$. Therefore, pyridine has a major influence on the course of the borohydride reduction. The stoichiometry of the reaction for the formation of the pyridine complex, 2 mol of pyridine per mole of $Cl_3B_3N_3H_3$, and the mode of addition of the reagents[4] suggest that the initial complex is $Cl_3B_3N_3H_3\cdot 2C_5H_5N$. The postulated structure[4] for this compound has the two pyridine molecules bound to one boron atom of the borazine ring and the chlorine is displaced as the negative ion, $Cl_2(C_5H_5N)_2B_3N_3H_3{}^+Cl^-$. The lack of solubility of this compound has precluded a definitive structure determination. If this postulated structure, $Cl_2(C_5H_5N)_2B_3N_3H_3{}^+Cl^-$, is correct, the mechanism of the reaction with $LiBH_4$ to form $H_2ClB_3N_3H_3$ is probably very complex. There are two different types of reaction sites, the ionic and the covalently bound chlorine atoms, and either or both of these sites could react separately or simultaneously. However, as the structure of the pyridine complex of $Cl_3B_3N_3H_3$ is open to question, further discussion of the reaction mechanism would only be speculation.

The 100-MHz proton nmr spectra of $H_2ClB_3N_3H_3$ and $HCl_2B_3N_3H_3$ were comprised of triplets due to the NH protons and quartets due to the BH protons. The NH triplet is very clearly resolved in the spectrum of $H_2ClB_3N_3H_3$ but poorly resolved for $HCl_2B_3N_3H_3$. These spectra were similar in appearance to those for the corresponding B-methylborazines.[7] The chemical shift data are given in Table I. The NH and BH proton resonances are shifted upfield relative to $H_3B_3N_3H_3$ but the *ortho* and *para* NH protons are indistinguishable. Chlorine is apparently acting normally as an electron-releasing group. For comparison, the shift due to the chlorine is smaller than the shift[7] due to the methyl group in $H_2CH_3B_3N_3H_3$ or $H(CH_3)_2B_3N_3H_3$. The π bonding between boron and chlorine is apparently almost balanced by the electronegativity effect. Similar trends[8] have been observed in the spectra of aromatic organic compounds. It is interesting to note that as more chlorine atoms are bound to the ring, there is increased broadening of the proton resonances but very little change in the chemical shift. Each additional chlorine has an effect on the electric field gradient at the ^{14}N nuclei.

Table I

Nuclear Magnetic Resonance Data

	$H_2ClB_3N_3H_3$	$HCl_2B_3N_3H_3$	$H_3B_3N_3H_3$
δ, ppm	−5.33	−5.30	−5.45
J, Hz	55	(≪55)	55
δ, ppm	−4.38	Broad	−4.47
J, Hz	136		137

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The boron-11 nmr spectrum of $H_2ClB_3N_3H_3$ was an unsymmetrical doublet. The higher field resonance was twice the size of the lower field resonance, but both resonances appeared symmetrical. This spectrum was the mirror image of the spectrum[7] of $H_2CH_3B_3N_3H_3$. The ^{11}BH doublet (δ -31.7 ppm, J = 133 Hz) is shifted downfield (-2.5 ppm) whereas the ^{11}BCl resonance (δ -27.4 ppm) is shifted upfield ($+1.8$ ppm) relative to $H_3B_3N_3H_3$. The factors influencing these nmr shifts are not fully understood[7] and, therefore, no significance can be attached to their direction or magnitude.

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The Formation of 2-Carba-*nido*-hexaborane(9) and Several of Its Alkyl Derivatives

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The reactions of 2,5-$C_2B_6H_8$ and its C-methyl or C,C′-dimethyl derivatives with tetramethylammonium borohydride have been investigated. The immediately formed ionic products, when treated with HCl gas, yield CB_5H_9 and several alkyl-substituted derivatives of CB_5H_9. This appears to be the first example of the removal of a carbon atom from a closed carborane polyhedron.

In the past few years carboranes have been reported which contain only one carbon atom in the polyhedral structure. They can all be considered members of the CB_nH_{n+2} or the CB_nH_{n+4} series. The former series includes CB_5H_7[1,2] and its ion $CB_5H_6^-$[2] and the ions $CB_9H_{10}^-$,[3] $CB_{10}H_{11}^-$,[4] and $CB_{11}H_{12}^-$[3] (which are formally derived from the hypothetical carboranes CB_9H_{11}, $CB_{10}H_{12}$, and $CB_{11}H_{13}$, respectively). The latter series includes CB_5H_9[5] and the ions $CB_{10}H_{13}^-$[3] and $CB_{10}H_{11}^{3-}$[6,7] (which are formally derived from the hypothetical carborane $CB_{10}H_{14}$).

We wish to report here the preparation of the parent member of the CB_nH_{n+4} series where n = 5, 2-carba-*nido*-hexaborane(9), CB_5H_9, and some of its methyl and ethyl derivatives in addition to those reported previously.[5,8–10]

Experimental Section

Apparatus and Procedures.—All operations involving carboranes were carried out using standard high-vacuum techniques. An Aerograph Model A-350 gas chromatograph containing either a $^3/_8$ in. × 10 ft aluminum column packed with 30% Apiezon L on Chromosorb P or an 8 mm × 20 ft Pyrex column packed with 30% Apiezon L on Chromosorb P was employed. Helium was used as carrier gas at 60-cm^3/min flow rate for all separations. Injection was accomplished using an apparatus similar to that suggested by Jeffery and Kipping.[11] Samples were collected in traps cooled in Dry Ice–2-propanol. Infrared spectra of gases were obtained using a 10-cm Pyrex cell with sodium chloride windows with a Perkin-Elmer 137 sodium chloride spectrophotometer. Nuclear magnetic resonance measurements were obtained with a Varian Model A-60 for proton spectra and a Varian Model HA-100 operating at 32.1 Mc/sec for boron-11 spectra. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6D mass spectrometer.

Diglyme (diethylene glycol dimethyl ether) was obtained from the Ansul Co. and distilled from sodium followed by distillation from $LiAlH_4$ at reduced pressure. It was stored and all transfers were made in a nitrogen-filled drybox. Tetramethylammonium borohydride was obtained from Ventron, Metal Hydrides Division, and recrystallized from acetonitrile before use. Hydrogen chloride was obtained from Matheson Co. and passed through a trap cooled in pentane slush (−131°) before use. Boron trichloride and methyl chloride were obtained from Matheson Co. and were passed through traps cooled in Dry Ice–2-propanol. 2,5-Dicarba-*closo*-octaborane(8), 2,5-$C_2B_6H_8$,[12] and its C-methyl and C,C′-dimethyl derivatives were prepared and purified according to literature methods.[13]

1. **Reaction of 2,5-$C_2B_6H_8$ and Tetramethylammonium Borohydride.**—To a 500-ml cylindrical flask containing a magnetic stirring bar to which a stopcock fitted with a water jacket about the joint was fixed was added 1.3664 g (15.4 mmol) of $(CH_3)_4NBH_4$.[14] The flask was evacuated, taken into the drybox, and

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