Table III. Reaction[a,b] of SiH_4 with HCl over Surfaces from Table II

	amt, mmol			
	reactants consumed		products[c]	
surface (Table II)	SiH_4	HCl	H_2	others
1	0.2	0.3	0.39	none
	0.2[d]	0.3	0.37	0.1, $ClSiH_3$[e] 0.1, Cl_2SiH_2
2	0.15	0.4	0.38	0.1, $ClSiH_3$[e]
3	0.3	0.35		0.1, $ClSiH_3$[e]

[a] Reactions carried out for 1 h at ambient temperature. [b] Typically, 0.4 mmol of SiH_4 and 0.4 mmol of HCl were added to the reaction vessel (~200 mL). [c] Volatile products distilled from reaction vessel. [d] Second reaction over surface 1. [e] A small quantity of SiH_3OSiH_3 was also obtained.

overnight under vacuum, and then used in the same reaction vessel the next day.

The results listed in Table III demonstrate that SiH_3Cl is formed when SiH_4 and HCl react over the prepared (≡SiO-$GaCl_2$) surface at room temperature. In a control experiment, a silica surface was treated as generally described in Table II except that the TMG treatment was omitted. This surface did not catalyze the SiH_4–HCl reaction (i.e., no H_2 or SiH_3Cl was produced).

The first reaction over surface 1 presumably generated $ClSiH_3$ (H_2 was formed) which was consumed by the surface. The second reaction was then successful in generating free chlorosilanes. The much larger quantity of TMG used for surface 2 presumably destroyed the sites which "retained" the product $ClSiH_3$.

In an effort to ensure that the catalysis was due to ≡$SiOGaCl_2$ bound to silica we carried out the experiments described in section 4.

4. Catalysis with Modified (≡$SiOGaCl_2$?) Pyrex Glass. Results similar to those described in section 3 were obtained in the same reaction vessel when the 0.3 g of silica was not present.

In addition, a new reaction vessel (50 mL) was treated as follows: (i) cleaned with alcoholic KOH, HNO_3, and distilled water and dried; (ii) treated with 0.20 mmol of TMG (20 min) (the TMG was consumed with the formation of 0.09 mmol of CH_4); (iii) treated with 0.72 mmol of HCl in two doses. Methane (0.14 mmol) was produced while 0.37 mmol of HCl was consumed. Silane (0.43 mmol) and HCl (0.39 mmol) were allowed to react in this vessel for 1 h at ambient temperature, yielding 0.46 mmol of H_2 and 0.26 mmol of SiH_3Cl (with a small quantity of SiH_3OSiH_3 present). It would appear that ≡$SiOGaCl_2$ (or possibly =$BOGaCl_2$) was also generated on the Pyrex glass surface. When this vessel was exposed to laboratory air and then evacuated, the SiH_4–HCl reaction produced only a small amount of H_2 and no chlorosilanes. To our surprise, the treated Pyrex reaction vessel with a very small effective surface area compared to that of the silica (about 70 m^2) was as effective as the treated silica.

5. Catalysis with Al_2Cl_6. In an effort to compare the effectiveness of the "≡$SiOGaCl_2$" catalytic surface to that of Al_2Cl_6, we examined the HCl–SiH_4 reaction over Al_2Cl_6.

The Al_2Cl_6[9] catalysis of the HCl–SiH_4 reaction is reported to require 100 °C while it is now known that SiH_4 reacts with HI over Al_2I_6[10] at −45 °C. We have now observed that the HCl–SiH_4 reaction is catalyzed by freshly sublimed Al_2Cl_6 at 25 °C and also at −45 °C. However, it is difficult to compare these catalysts without having more carefully defined surfaces. We have also observed formation of chlorosilanes (no iodosilanes) from reaction of SiH_4 with HCl over Al_2I_6 at 25 °C. The equilibrium[11] of SiH_3I with HCl lies toward SiH_3Cl and HI so this latter result could be from either initial SiH_3I or initial SiH_3Cl formation.

Experimental Section

All experiments were carried out in standard high-vacuum Pyrex glass systems. Starting materials and products were examined for purity and identified by infrared and mass spectral analysis. Methane–H_2 mixtures were Toepler-pumped into a calibrated volume to determine their total quantity while their ratio was determined from mass spectra by using known mixtures to calibrate the mass spectrometer. Separations of products were made by trap to trap distillations.

Silica samples were preheated to 800 °C in air prior to use for bulk reactions and prior to being pressed into disks. Silica disks of 2.5-cm diameter were prepared from about 25-mg of silica pressed in a stainless steel die at 2000 lb/in^2. The infrared cell was similar in design to that described by Morrow and Ramamurthy.[12]

The infrared spectra were obtained on a Perkin-Elmer Model 625 spectrometer with the reference beam intensity decreased by a standard screen. Typical scan times to cover 600 cm^{-1} were 16 h with a very slow pen response.

Registry No. Silica, 7631-86-9; TMG, 1445-79-0; HCl, 7647-01-0; SiH_4, 7803-62-5.

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Deuterated Sodium Octahydrotriborate(1−)

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Deuterated octahydrotriborate(1−) ($B_3H_8^-$) can be obtained by the known methods for the preparation of $B_3H_8^-$ by using deuterated borane species. Some of the reactions that may be used are

$$2B_2H_6 + 2Na/Hg \rightarrow NaB_3H_8 + NaBH_4{}^{1}$$

$$B_2H_6 + NaBH_4 \rightarrow NaB_3H_8 + H_2{}^{2}$$

$$B_4H_{10} + NaBH_4 \rightarrow NaB_3H_8 + B_2H_6{}^{3}$$

$$3NaBH_4 + I_2 \rightarrow NaB_3H_8 + 2NaI + 2H_2{}^{4}$$

Alcoholyses of B_5H_9[5] and $(CH_3)_4NB_9H_{12}$[6] are also known to give $B_3H_8^-$ ion.

Recently a method using anhydrous deuterium chloride for the deuteration of tetrahydrofuran–triborane(7) (THF·B_3H_7) was reported.[7] Meanwhile, treatment of THF·B_3H_7 with sodium hydride under appropriate conditions should give NaB_3H_8. Combination of the above two processes, therefore, would

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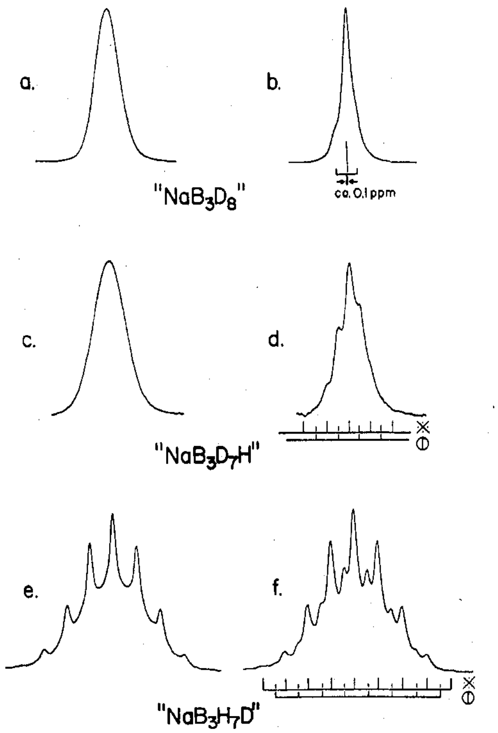


Figure 1. ^{11}B NMR spectra of deuterated NaB$_3$H$_8$ in diglyme at 25 °C: (a, c, and e) normal spectra; (b, d, and f) ^{2}H-spin-decoupled spectra. The markers ※ and ⦶ indicate the approximate peak positions of odd and even multiplets, respectively.

be a practical method for the preparation of deuterated NaB$_3$H$_8$, in which the use of B_2D_6 or B_4D_{10} is avoided. In this paper we report the preparation and the ^{11}B NMR spectra of perdeuterated and partially deuterated NaB$_3$H$_8$.

Results and Discussion

Treatment of THF·B$_3$H$_7$ with sodium hydride in diglyme gives NaB$_3$H$_8$ in a quantitative yield. The reaction proceeds smoothly at room temperature and is complete in 1 h.

$$\mathrm{NaH + THF{\cdot}B_3H_7 \xrightarrow[\text{diglyme}]{} NaB_3H_8 + THF}$$

In diethyl ether, however, in spite of the high solubility of NaB$_3$H$_8$ in the solvent, the reaction is very slow. After about 1 h at room temperature, most (over 90%) of the THF·B$_3$H$_7$ remained unchanged and small amounts of NaB$_3$H$_8$ and B_4H_{10} were found in the reaction mixture. Therefore, the preparation of deuterated NaB$_3$H$_8$ was performed by using diglyme as the solvent. Treatments of THF·B$_3$H$_7$ and THF·B$_3$D$_7$ with NaD or NaH gave differently deuterated NaB$_3$H$_8$ samples.

$$\mathrm{NaD + THF{\cdot}B_3D_7 \rightarrow \text{“}NaB_3D_8\text{”} + THF}$$

$$\mathrm{NaD + THF{\cdot}B_3H_7 \rightarrow \text{“}NaB_3H_7D\text{”} + THF}$$

$$\mathrm{NaH + THF{\cdot}B_3D_7 \rightarrow \text{“}NaB_3D_7H\text{”} + THF}$$

The ^{11}B NMR signals of the deuterated products in the normal spectra are generally broad and featureless. The fine structures due to the B–H couplings can only be seen for the samples of low deuterium content. The deuterium-spin-decoupling technique was, therefore, useful in characterizing the deuterated samples. Shown in Figure 1a,b are the spectra for the "NaB$_3$D$_8$" sample. The deuterium purity of the sample is estimated to be 97% on the basis of the deuterium purities of the NaD (98%) and the THF·B$_3$D$_7$ (97%) used. The featureless broad signal in the normal spectrum (Figure 1a) sharpens when the ^{2}H spins are decoupled. Some weak signal appears overlapping with the intense singlet signal (Figure 1b). The weak signal is probably a doublet due to the $B_3D_7H^-$ ion in the sample as indicated in the figure.

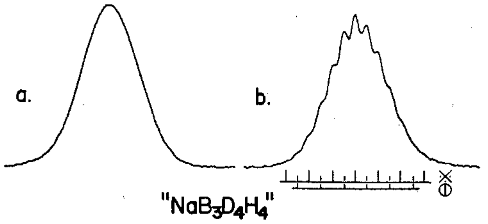


Figure 2. ^{11}B NMR spectra of a NaB$_3$H$_8$ (1.2 mmol)–THF·B$_3$D$_7$ (1.3 mmol) mixture in diglyme at 25 °C: (a) normal spectrum; (b) ^{2}H-spin-decoupled spectrum. The markers ※ and ⦶ indicate the approximate peak positions of odd and even multiplets, respectively. The resonance signals of the triborane adduct are not shown here.

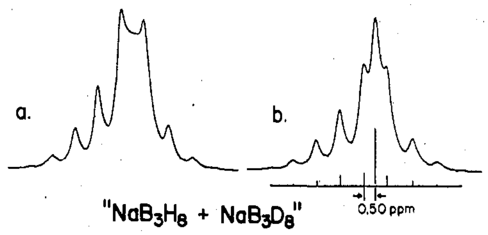
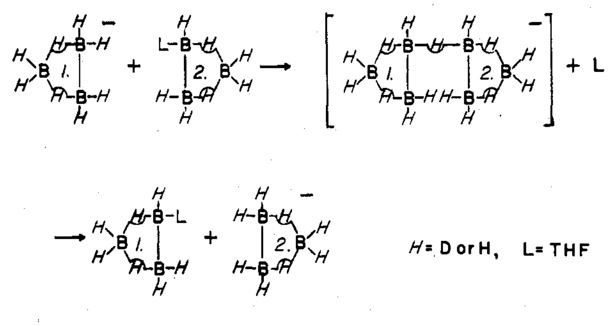


Figure 3. ^{11}B NMR spectra of a NaB$_3$H$_8$ (1.3 mmol)–NaB$_3$D$_8$ (1.4 mmol) mixture in diglyme at 25 °C: (a) normal spectrum; (b) ^{2}H-spin-decoupled spectrum.

Scheme I



The spectra of the "NaB$_3$D$_7$H" and "NaB$_3$H$_7$D" samples shown in Figure 1c–f indicate informatively the nature of these products. The simple replacement of THF in THF·B$_3$D$_7$ by H^- would yield the $B_3D_7H^-$ species. The ^{2}H-spin-decoupled signal of such a species is expected to be a simple doublet signal since the hydrogen atom would be coupled equally to the three boron atoms due to its rapid tautomeric motion within the ion.[8] Likewise, an octet signal is expected from the "NaB$_3$H$_7$D" sample if only the simple replacement should have occurred. Figure 1d,f shows that these are obviously not the case. Apparently an intermolecular H–D exchange reaction had occurred. This exchange reaction proceeds rapidly during the process of the anion formation. The tetrahydrofuran adduct of triborane(7) in the reaction mixture served as the exchange medium. In support of this hypothesis, when NaB$_3$H$_8$ and THF·B$_3$D$_7$ were mixed at −80 °C in diglyme in a 1:1 molar ratio and the mixture was examined on the NMR instrument immediately after the sample was warmed to 0 °C, the spectrum shown in Figure 2 was obtained, indicating that the H–D exchange had occurred. On the other hand, a 1:1 mixture of NaB$_3$H$_8$ and NaB$_3$D$_8$ in diglyme remained unchanged for a period of over 2 h at room temperature (Figure 3).[9] Scheme I for the H–D exchange is proposed, as that involves the formation of an intermediate "$B_6H_{15}^-$" similar to $B_2H_7^-$ in the mixture of BH_4^- and B_2H_6 in diglyme.[10]

Accordingly, the spectrum of each of the two samples represents a superposition of several multiplet signals. The shift values of the multiplet signals are slightly different from each other due to isotope effects. The upfield shift due to the substitution of D for H is visually evident in the spectra, and the difference between the shifts for NaB_3D_8 and NaB_3H_8 was measured as 0.50 ± 0.01 ppm on the spectrum in Figure 3. The peak separations of the multiplets measured on the spectra in Figures 1d,f and 2, are 1 to 2 Hz smaller than the J_{BH} value of 33.1 ± 0.1 Hz for NaB_3H_8, which was obtained in this study. While this difference may indicate the isotope effect on the coupling constants, the severe overlap of peaks in each of the spectra obscures the true coupling constant values for the partially deuterated triborate species. It was reported[11] that the ^{11}B signal of BD_4^- appears 0.54–0.58 ppm to high field of the BH_4^- resonance and that the J_{BH} value for BD_3H^- is 1 Hz lower than that for BH_4^-.

Experimental Section

Conventional vacuum line techniques were used for the handling of volatile chemicals. Deuterium chloride was prepared by treating PCl_3 with D_2O (99.8% isotopic purity) in the vacuum line. The PCl_3 sample was refluxed for 12 h under 1 atm of pressure of dry nitrogen gas before the D_2O treatment. The generated DCl was fractionated and stored in a stainless steel cylinder. The isotopic purity of the DCl sample as estimated by infrared spectroscopy was higher than 99%. Laboratory stock tetraborane(10) was treated with tetrahydrofuran to prepare the $THF \cdot B_3H_7$ sample.[12] Deuteration of $THF \cdot B_3H_7$ was performed by the method described elsewhere by using CH_2Cl_2 solvent.[7] The deuterated $THF \cdot B_3H_7$ samples were of about 97% isotopic purity. The purity was estimated by assuming complete H–D scrambling at each batch treatment of the $THF \cdot B_3H_7$ sample with the DCl. Sodium hydride (K and K Laboratories, Inc., 50% oil suspension) and NaD (Alfa Ventron, 20% in oil, 98% isotopic purity) were washed with diethyl ether in the vacuum line, and the resulting powder was handled in an atmosphere of dry nitrogen. Reagent grade diethyl ether, tetrahydrofuran, and diglyme were stored over $LiAlH_4$ and were distilled from the storage vessels into the vacuum line as needed.

The ^{11}B NMR spectra were recorded on a Varian XL-100-15 instrument equipped with a spin-decoupler unit (Gyrocode), the observed frequency being 32.1 MHz. The ^2H spin was decoupled by using the maxium decoupler power (119db or Hetero High) of the instrument. The samples were not spinned.

Reactions of $THF \cdot B_3H_7$ with NaH. A sample of $THF \cdot B_3H_7$ (1.20 mmol) was prepared in a 22-mm o.d. Pyrex reaction tube, and a diglyme solution (3 mL) of the adduct was prepared by condensing the solvent in the tube. The solution was transferred, in the vacuum line, into another similar reaction vessel which contained excess NaH (0.1 g). The reaction mixture was allowed to warm to 0 °C and stirred for 15 h. Unchanged NaH was then filtered in the vacuum line. No hydrogen gas evolved and no volatile borane compounds could be detected during this entire process. The ^{11}B NMR spectrum of the clear filtrate indicated the presence of only NaB_3H_8. The resonance signal appears at −29.7 ± 0.2 ppm (J_{BH} = 33.1 ± 0.1 Hz) ($BF_3 \cdot O(C_2H_5)_2$ standard downfield shift being taken as positive). The experiment with diethyl ether as the solvent was run similarly.

Preparation of the Deuterated NaB_3H_8. Samples of $THF \cdot B_3D_7$ were prepared in large reaction vessels (100-mL long-necked flasks for 1.0–1.5 mmol of $THF \cdot B_3H_7$) so that a high $DCl/THF \cdot B_3H_7$ ratio could be used at each DCl treatment of the batch processes.[7] Generally the reaction mixtures of the triborane adducts and excess NaD (or NaH) were stirred at 0 °C overnight and then filtered into NMR sample tubes. In an experiment a diglyme solution of $THF \cdot B_3D_7$ was poured into a 10-mm o.d. Pyrex tube which contained excess NaH, and the tube was sealed. The tube was allowed to warm to room temperature and the reaction was monitored on the NMR instrument while the mixture was agitated occasionally. The triborate signal grew steadily at the expense of the triborane adduct signal and the reaction was virtually complete in 1 h. The ^{11}B NMR spectra of this resulting solution are shown in Figure 1c,d.

The NMR Samples. "$NaB_3H_8 + NaB_3D_8$". The mixture was prepared by breaking an ampule which contained a diglyme solution of NaB_3H_8 (1.3 mmol), in sealed glassware which contained a diglyme solution of NaB_3D_8 (1.4 mmol). The resulting solution was decanted into a 10-mm o.d. tube, which had been attached to the sealed glassware, and the 10-mm tube end was then inserted in the probe of the NMR instrument for the spectral measurements.

"$NaB_3H_4D_4$". A diglyme solution of NaB_3H_8 (1.2 mmol) was placed in a 10-mm o.d. tube, cooled to −196 °C, and 1.3 mmol of $THF \cdot B_3D_7$ was sublimed into the tube and the tube sealed. The tube was then allowed to warm to −80 °C and shaken to prepare a uniform solution. The solution was examined for its ^{11}B NMR spectra starting at −80 °C. Below 0 °C the resonance signals (^2H spin decoupled) were too broad to observe the progress of the H–D exchange reaction.

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Registry No. NaB_3D_8, 71341-77-0; NaB_3H_8, 12007-46-4; $THF \cdot B_3D_7$, 71341-54-3; $THF \cdot B_3H_7$, 12544-89-7; NaD, 15780-28-6; NaH, 7646-69-7; NaB_3D_7H, 71341-74-7; NaB_3H_7D, 71341-75-8; $NaB_3H_4D_4$, 71341-76-9.

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Metal Complexes of Cyclic Triamines. 3. A Kinetic Study of the Acid Hydrolysis of (1,4,7-Triazacyclononane)nickel(II) and (1,5,9-Triazacyclododecane)nickel(II)

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The acid hydrolysis of polyamine nickel(II) chelates proceeds rapidly unless ligand stereochemistry impedes the dissociation process. Thus macrocyclic and polysubstituted amines coordinate in such a fashion that they hinder the normal stepwise unwrapping of the ligand from the metal ion, and nickel(II) complexes of these compounds hydrolyze slowly in aqueous acid solution.[1] Similar inert kinetic behavior is shown by the two triamines tris(anhydro-*o*-aminobenzaldehyde) (TRI)[2] and *cis*,*cis*-1,3,5-triaminocyclohexane (*c*-tach).[3] Both these amines form tridentate complexes which can only coordinate to the face of the coordination polyhedron of a metal ion. Once a Ni–N bond is broken, the ligand structure restricts the translational freedom of the first nitrogen donor atom so that it cannot be removed very far from the metal.