

Table III. X-Ray Data for  $\text{LiInMo}_3\text{O}_8$ : *abac* Layering

<i>hkl</i>	$d_{\text{calcd}}$	$I_{\text{calcd}}$	$I_{\text{obsd}}$
002	4.991	34	64
100	4.972		
101	4.450	49	
102	3.522	45	100
110	2.871	0.1	0.5
103	2.765	17	0.8
004	2.496		
112	2.488	54	84
200	2.486		
201	2.412	34	
104	2.230	10	19
202	2.225		
203	1.992	36	
114	1.883	3	3
210	1.879		
105	1.853	15	
211	1.847		
204	1.761	13	72
212	1.759		
006	1.664	1	3
300	1.657		
213	1.636	21	
301	1.635		
106	1.578	15	21
302	1.573		
205	1.557	28	
214	1.501	3	2
303	1.483	3	
116	1.439	20	16
220	1.435		
206	1.383	3	8
304	1.381		
222	1.379		
310	1.379		

In compounds is consistent with the unit cell size of  $\text{Zn}_2\text{Mo}_3\text{O}_8$ , their observed intensities are not compatible with an *abac* layering; e.g., the 101 reflection for  $\text{LiInMo}_3\text{O}_8$  on the basis of this layering should be very strong for x rays and of moderate intensity for neutrons, but Kerner-Czesleba and Tourne did not observe it. This would seem to preclude even the possibility of their phases being a mixture of polymorphs with the *aba* type dominant.

Although the nearest-neighbor arrangements in the  $\text{Zn}_2\text{Mo}_3\text{O}_8$  and  $\text{LiRMO}_3\text{O}_8$  structures are very similar, the second nearest-neighbor arrangements are significantly different. In  $\text{Zn}_2\text{Mo}_3\text{O}_8$ , both tetrahedral and octahedral zinc atoms have nine second nearest-neighbor molybdenums. For tetrahedral zinc, three Mo's are 3.54 Å distant while six more Mo's are at 3.48 Å. In the case of octahedral zinc these distances are 3.21 and 3.27 Å, respectively. Using  $\text{LiInMo}_3\text{O}_8$  as an example for the  $\text{LiRMO}_3\text{O}_8$  type, each Li is surrounded by a trigonal prism of molybdenums, three of which are 2.97 Å distant with the remaining three at 3.26 Å. On the other hand, In is surrounded by 12 second nearest-neighbor Mo's at the corners of an irregular hexagon, resulting in two sets of In-Mo distances of 3.71 and 3.91 Å respectively. The net effect then is to make the Zn-Mo distances more nearly equal in  $\text{Zn}_2\text{Mo}_3\text{O}_8$ , while in the  $\text{LiRMO}_3\text{O}_8$  types the Li-Mo distances decrease and the R-Mo distances increase along with the change in coordination number. The differences in coordination number are qualitatively consistent with what might be expected on the basis of the electrostatic repulsions and provides a possible explanation for the observed structural differences. However, it should be noted that the best data currently available do not allow one to locate Li and O with the degree of certainty required for the calculation of electrostatic potentials in these systems.

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Registry No.  $\text{LiScMo}_3\text{O}_8$ , 12201-19-3;  $\text{LiYMo}_3\text{O}_8$ , 12201-20-6;  $\text{LiInMo}_3\text{O}_8$ , 64475-44-1;  $\text{LiSmMo}_3\text{O}_8$ , 60606-28-2;  $\text{LiGdMo}_3\text{O}_8$ , 60606-18-0;  $\text{LiYbMo}_3\text{O}_8$ , 60606-30-6;  $\text{LiLuMo}_3\text{O}_8$ , 64475-43-0.

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Contribution from the Department of Chemistry,  
University of Utah, Salt Lake City, Utah 84112

### Deuteration of Triborane(7) Adducts with Anhydrous Deuterium Chloride

Alan R. Dodds and Goji Kodama\*

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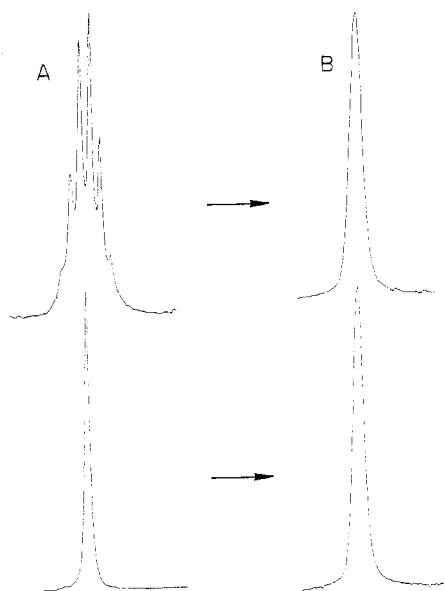
Deuterated boron hydride compounds are useful for structural and mechanistic studies in boron hydride chemistry. A number of hydrogen-deuterium exchange reactions that can be used for preparation of deuterated boron hydride compounds have been reported in the literature. Some of the reactions yield compounds which are deuterated at specific positions of the borane molecules, as represented by the reaction of pentaborane(9) with DCl in the presence of  $\text{AlCl}_3$  to give 1-deuteriopentaborane(9)<sup>1</sup> and by the reaction of decaborane(14) with  $\text{D}_2\text{O}$  to give  $\mu$ -tetradedeuteriodecaborane(14).<sup>2</sup> Some involve the exchange of all the hydrogen atoms that are bonded to boron atoms. These include the isotopic exchanges between tetraborane(10) and deuterated diborane(6)<sup>3</sup> and between  $\text{B}_{12}\text{H}_{12}^{2-}$  and  $\text{D}_2\text{O}$ .<sup>4</sup> A rapid exchange of the hydrogen atoms attached to the boron atom in trimethylamine-borane(3) with the deuterium atoms in acidified heavy water was used successfully to prepare the B-deuterated borane adduct which is useful as a research chemical.<sup>5</sup>

We now report a hydrogen-deuterium exchange reaction between triborane(7) adducts and deuterium chloride which involves all the hydrogen atoms in the  $\text{B}_3\text{H}_7$  moiety and proceeds rapidly even at low temperatures.

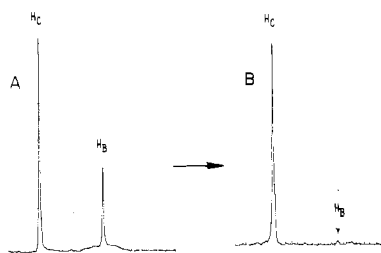
### Results and Discussion

Treatment of a dichloromethane solution of trimethylamine-triborane(7) or tetrahydrofuran-triborane(7) with anhydrous deuterium chloride (90% enrichment) at  $-80^\circ\text{C}$  for about 5 min resulted in the exchange of the borane hydrogens with deuterium in the deuterium chloride sample. Evidence for the exchange is provided by loss of the fine structure of the  $^{11}\text{B}$  NMR signal of the triborane(7) adduct and by the increased intensity of the HCl absorption band accompanied by the decreased intensity of the DCl absorption band in the infrared spectrum of the deuterium chloride sample recovered after the treatment.

The equilibrated distribution of the two isotopes in the mixture is reached rapidly. Thus, eight successive treatments of a dichloromethane solution of trimethylamine-triborane(7) with deuterium chloride (90% D), in a 1:4.2 molar ratio at each treatment, gave a sample of the triborane(7) adduct with



**Figure 1.**  $^{11}\text{B}$  NMR spectra of normal (A) and 87% B-deuterated (B) trimethylamine-triborane(7) at 25 °C in  $\text{CH}_2\text{Cl}_2$ : upper, normal spectra; lower, proton spin-decoupled spectra. Chemical shift, 18.9 ppm upfield from  $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ .



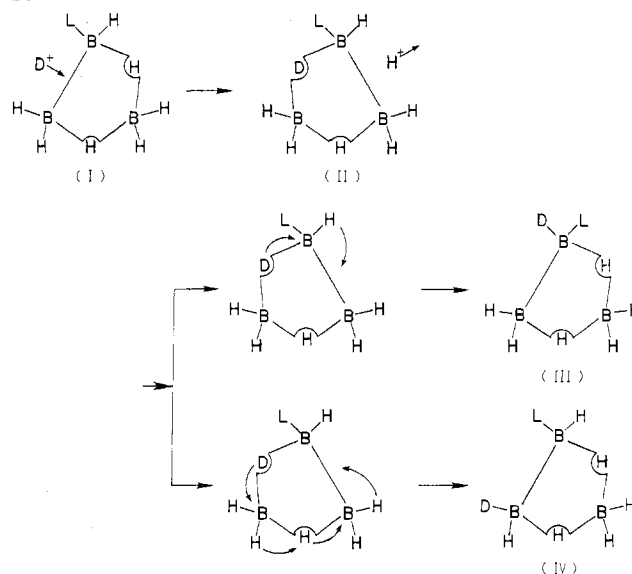
**Figure 2.**  $^{11}\text{B}$  spin-decoupled  $^1\text{H}$  NMR spectra of normal (A) and 87% B-deuterated (B) trimethylamine-triborane(7) at 25 °C in  $\text{CH}_2\text{Cl}_2$ . Chemical shifts,  $H_C \tau 7.48$  and  $H_B \tau 8.94$  (shift for  $\text{CH}_2\text{Cl}_2$  taken as  $\tau 4.72$ ).

87% deuterium enrichment. The  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectra of the sample are presented in Figures 1 and 2.

The exchange reactions also proceed, apparently at slower rates, in tetrahydrofuran solutions. However, the difficulty of separation of hydrogen-deuterium chloride from the reaction mixture would make the use of this solvent unfavorable if a successive batch process were to be employed for the deuteration of the borane adducts. Solutions of the trimethylamine adduct can be treated with deuterium chloride at room temperature without introducing a serious amount of side-reaction products. A mixture of trimethylamine-triborane(7) and hydrogen chloride in tetrahydrofuran remains unchanged at room temperature over a period of 50 h. In dichloromethane, however, the mixture evolves hydrogen gas *very slowly* at room temperature, and a substantial amount of the chlorotriborane(7) adduct<sup>6</sup> and other borane compounds are detected after 24 h.

The rapid scrambling of hydrogen may be explained by the mechanism indicated in Scheme I. The structure of the triborane(7) adduct used in this mechanism is based on the reported structure of ammonia-triborane(7).<sup>7</sup> The addition of  $\text{D}^+$  to triborane(7) adduct I, followed by the elimination of  $\text{H}^+$ , would result in a structure with deuterium in a bridge position, II. The rapid hydrogen tautomerism would transfer the deuterium to other parts of the triborane(7) moiety as indicated in III and IV. The addition of  $\text{H}^+$  to a boron-boron bond (or the basic nature of a B-B bond) has been established in the reaction of hexaborane(10) with  $\text{H}^+$  to form  $\text{B}_6\text{H}_{11}^+$ ,<sup>8</sup> and the hydrogen tautomerism that was originally suggested

**Scheme I**



by Lipscomb<sup>9</sup> has been well substantiated.<sup>10</sup>

The exchange reaction described above will be useful for the preparation of deuterated triborane(7) adducts. In cases where the direct treatment of a solution of a particular Lewis base-triborane(7) adduct with anhydrous deuterium chloride is not feasible, the simple base displacement reaction<sup>11</sup> or the acid-assisted base displacement reaction<sup>12</sup> of the deuterated triborane(7) etherate with the particular Lewis base would yield the desired deuterated triborane(7) adduct. Furthermore, knowledge of the derivative chemistry of triborane(7) adducts<sup>13</sup> gives promise that certain other deuterated borane compounds will be conveniently prepared starting from deuterated triborane(7) adducts.

### Experimental Section

**General.** Conventional vacuum line techniques were used for the handling of chemicals. Trimethylamine-triborane(7) and tetrahydrofuran-triborane(7) were prepared from tetraborane(10) by methods reported in the literature.<sup>11a,c</sup> Laboratory stock deuterium chloride, which had been prepared by the reaction of  $\text{PCl}_3$  with  $\text{D}_2\text{O}$ , was used after fractionation. The deuterium enrichment of the  $\text{DCl}$  sample was estimated to be 90% by infrared spectroscopy. Reagent grade dichloromethane was stored over molecular sieves and tetrahydrofuran over  $\text{LiAlH}_4$ . These solvents were distilled from the storage vessel into the vacuum line as needed.

The NMR spectra were recorded on a Varian XL-100-15 instrument equipped with a spin-decoupler unit (Gyrocode), operating at 32.1 MHz for  $^{11}\text{B}$  and at 100 MHz for  $^1\text{H}$ . A Beckman Model IR-20 spectrophotometer was used for the IR measurements with a 100-mm gas cell.

**Treatments of Triborane(7) Adducts with  $\text{DCl}$ .** A 0.46-mmol quantity of  $(\text{CH}_3)_3\text{N}\cdot\text{B}_3\text{H}_7$  was prepared in a 22-mm o.d. Pyrex reaction tube fitted with a 24/40 male joint. About 3 mL of dichloromethane was condensed in the tube, and a solution of the adduct was prepared by raising the temperature to near 0 °C. The tube was frozen again and a 1.95-mmol quantity of the  $\text{DCl}$  sample was condensed in the tube. The tube was then allowed to warm to -80 °C and the resulting solution was stirred for about 5 min. The stopcocks between the tube and the vacuum line fractionation system were then opened. The vapor that came out of the tube was passed through a -126 °C trap and condensed in a -196 °C trap, while the solution was constantly stirred and kept at -80 °C. The condensation of volatile material in the -196 °C trap stopped within 10 min. The volatile material was identified by its IR spectrum as a mixture of  $\text{DCl}$  and  $\text{HCl}$ , with less enrichment of  $\text{DCl}$  than that of the original  $\text{DCl}$  sample. The total amount of the gas mixture was 1.95 mmol. This gas was discarded. The tube was again cooled to -196 °C, the component in the -126 °C trap (a small amount of  $\text{CH}_2\text{Cl}_2$ ) was condensed back into the reaction tube, and a new portion (1.95 mmol) of the  $\text{DCl}$  sample was condensed in the reaction tube. The procedure

described above was repeated a total of eight times. After the eighth treatment the solvent dichloromethane was distilled out under vacuum. The solid remaining in the tube was dissolved in a fresh portion of dichloromethane, and the solution was transferred into an NMR sample tube for the NMR measurements.

When a solution of tetrahydrofuran-triborane(7) was treated with DCl in a manner similar to that described above, similar results were obtained; the recovered DCl was of lower enrichment in deuterium, and the total recovery of the DCl-HCl mixture was quantitative.

Similar runs were made using tetrahydrofuran as solvent. Since the separation of DCl-HCl gas from the reaction mixture cannot be effected by the ordinary distillation method, the reaction mixture was allowed to warm to higher temperature (not above 0 °C) and all volatile components were distilled out. The deuterated triborane adduct which remained in the tube was dissolved in dichloromethane and its  $^{11}\text{B}$  NMR spectrum was examined.

**Stability of Trimethylamine-Triborane(7) toward HCl in Tetrahydrofuran and Dichloromethane.** A solution of  $(\text{CH}_3)_3\text{N}\cdot\text{B}_3\text{H}_7$  (0.65 mmol) in about 2 mL of tetrahydrofuran was prepared in a 10-mm o.d. NMR sample tube. The tube was cooled to  $-196^\circ\text{C}$ , and a measured amount of HCl (0.62 mmol) was condensed in the tube. The tube was then allowed to slowly warm to room temperature. The  $^{11}\text{B}$  NMR spectrum of the mixture was identical with that of an authentic sample of  $(\text{CH}_3)_3\text{N}\cdot\text{B}_3\text{H}_7$ , and no evidence of any reaction between the triborane(7) adduct and HCl was observed, even after 50 h at room temperature.

A solution of  $(\text{CH}_3)_3\text{N}\cdot\text{B}_3\text{H}_7$  (0.58 mmol) in about 2 mL of dichloromethane was prepared in a 22-mm o.d. reaction tube. A 1.16-mmol quantity of HCl was condensed in the tube and the mixture was allowed to warm to room temperature and kept at this temperature for 24 h. Slow continuous evolution of hydrogen gas proceeded during this period. The solution was transferred to a 10-mm o.d. NMR sample tube and its  $^{11}\text{B}$  NMR spectrum was examined. Trimethylamine-chlorotriborane(7), trimethyl-dichloroborane(3), and minor quantities of other borane compounds were identified in the spectrum.

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**Registry No.** Trimethylamine-triborane(7), 12076-72-1; tetrahydrofuran-triborane(7), 12544-89-7; B-deuterated trimethylamine-triborane(7), 64282-97-9; B-deuterated tetrahydrofuran-triborane(7), 64282-96-8.

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Contribution from the Department of Chemistry,  
Howard University, Washington, D. C. 20059

## A Novel Metal Ion-Porphyrin Equilibrium

Adegboye Adeyemo and M. Krishnamurthy\*

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The normal metal-complex formation equilibria have not been observed for metalloporphyrins by virtue of their extreme thermodynamic stability. Though some equilibrium constants for such reactions of metalloporphyrins have been reported,<sup>1</sup> there has been no evidence of a truly labile equilibrium under the conditions of those studies. Results of our studies on an instance of a truly dynamic equilibrium observed in the case of a water-soluble porphyrin, tetrakis(*p*-sulfonatophenyl)porphine ( $\text{H}_2\text{TPPS}$ ), are reported here.

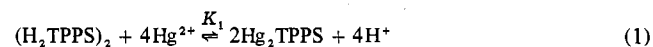
## Experimental Section

Tetraphenylporphine was synthesized by the literature methods<sup>2</sup> and sulfonated.<sup>3</sup> A stock solution of mercury(II) nitrate (J. T. Baker) was made and standardized complexometrically with EDTA. Other standard chemicals such as  $\text{NaNO}_3$  (Alfa Products), THAM (tris(hydroxymethyl)aminomethane) (Fisher Scientific), etc., were used as obtained.

A Beckman Model Acta CIII spectrophotometer with thermostated cell compartment and a Radiometer PHM 64 Research pH meter were used for titration studies. A typical titration was carried out as follows. A  $4.12 \times 10^{-5}$  M solution of  $\text{H}_2\text{TPPS}$  (500 mL), which was 0.20 M in  $\text{NaNO}_3$  and 0.02 M in THAM, was constantly stirred in a thermostated (30 °C) vessel. Initially, the pH was adjusted to 7.0, and the pH was found to remain constant by intermittent monitoring. Constant volumes of mercury(II) nitrate solution ( $1.556 \times 10^{-2}$  M) were added to the porphyrin solution using a semimicro buret at 5-min intervals. Earlier it was established that longer waiting periods do not effect any further changes in the spectrum. A visible spectrum of the porphyrin solution between 700 and 450 nm was recorded by drawing a sample just before every addition of mercury(II) nitrate solution. By returning the sample to the reaction vessel, the volume of the bulk solution remained essentially constant.

## Results

Changes in the spectrum of  $\text{H}_2\text{TPPS}$  during a titration with mercury(II) nitrate are presented in Figure 1. The initial spectrum indicates the porphyrin species in the solution to be dimeric, as expected from earlier studies.<sup>4</sup> As mercury(II) nitrate solution was added, the spectrum changed with a clear set of isosbestic points at 492 and 571 nm. The close resemblance between the spectrum of the novel mercury porphyrin reported recently<sup>5</sup> and the final spectrum of this titration suggests the composition of the complex species to be two mercury(II) ions to one porphyrin. The presence of a set of isosbestic points in the spectra would mean that either the 2:1 mercury-porphyrin is formed in a single step or the intermediate 1:1 mercury-porphyrin exists in only negligible quantities in the solution at any instance during the titration. A plot of the absorbance at 518 and 616 nm as a function of the concentration of mercury(II) ion is shown in Figure 2. Assuming an equilibrium<sup>6</sup> such as



the following equation for the equilibrium constant,  $K_1$ , can be derived as

$$K_1 = \frac{2(A - A_i)^2 C_p (\text{H}^+)^4}{(A_f - A)(A_f - A_i)(\text{Hg}^{2+})_{\text{eq}}^4}$$

$$(\text{Hg}^{2+})_{\text{eq}} = (\text{Hg}^{2+})_{\text{total}} - 2 \left( \frac{A - A_i}{A_f - A_i} \right) C_p$$

where  $A_i$ ,  $A$  and  $A_f$  are absorbances of the solution initially