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Technical Report No. 8

Reactions Of Hydrogen Chloride and Boron
Trichloride With Trimethylsilylamino Groups

by

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Accepted for Publication

in the

Inorganic Chemistry

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16775 Von Karman Avenue
Irvine, California 92714

April 4, 1989

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AD-A209 006

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release distribution unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S) Technical Report No. 8	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 8		7a. NAME OF MONITORING ORGANIZATION Office Of Naval Research	
6a. NAME OF PERFORMING ORGANIZATION Ultrasystems Defense Inc.	6b. OFFICE SYMBOL (if applicable)	7b. ADDRESS (City, State, and ZIP Code) Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	
6c. ADDRESS (City, State, and ZIP Code) 16775 Von Karman Avenue Irvine, California 92714	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-C-0713		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code)		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) REACTIONS OF HYDROGEN CHLORIDE AND BORON TRICHLORIDE WITH TRIMETHYLSILYLAMINO GROUPS			
12. PERSONAL AUTHOR(S) K. J. L. Paciorek, R. H. Kratzer, J. H. Nakahara and W. Krone-Schmidt			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) April 4, 1989	15. PAGE COUNT 11
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Hydrogen Chloride, Boron Trichloride, <i>Chemical reaction</i> , Borazine, Tris(trimethylsilyl)amine. (JES)	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Reactions of hydrogen chloride and triethylamine hydrochloride with the novel B-tris[bis-(trimethylsilyl)amino]borazine failed to give B-tris[trimethylsilylamino]borazine, but following liberation of Me ₃ SiCl resulted in condensations. At lower temperatures ammonia was eliminated; at higher temperatures hexamethyldisilazane. The possible mechanisms are postulated. Boron trichloride action on tris(trimethylsilyl)amine and 1,3-trimethylsilyl-2,4-bis-(trimethylsilyl)amino-1,3-diaza-diborethane was investigated. In the first instance the cleavage of the Si-N bond occurred to a very low degree, the major process was the replacement of the methyl groups on silicon by chlorine atoms. In the case of diborethane only the second reaction took place.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynne		22b. TELEPHONE (Include Area Code) (202) 696-4410	22c. OFFICE SYMBOL ONR

REACTIONS OF HYDROGEN CHLORIDE AND BORON TRICHLORIDE WITH TRI-METHYLSILYLAMINO GROUPS

K. J. L. Paciorek*, R. H. Kratzer, J. H. Nakahara and W. Krone-Schmidt

ABSTRACT

Reactions of hydrogen chloride and triethylamine hydrochloride with the novel B-tris[bis(trimethylsilyl)amino]borazine failed to give the expected B-tris[trimethylsilylamino]borazine, but following the liberation of trimethylchlorosilane resulted in condensations. At lower temperatures ammonia was eliminated, at higher temperatures hexamethyldisilazane was the condensation product. The possible mechanisms are postulated. Boron trichloride action on tris(trimethylsilyl)amine and 1,3-trimethylsilyl-2,4-bis(trimethylsilyl)amino-1,3-diaza-diboretane was investigated. In the first instance the cleavage of the Si-N bond occurred to a very low degree, the major process was the replacement of the methyl groups on silicon by chlorine atoms. Only the latter reaction was found to occur in the case of 1,3-trimethylsilyl-2,4-bis(trimethylsilyl)amino-1,3-diaza-diboretane.



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REACTIONS OF HYDROGEN CHLORIDE AND BORON TRICHLORIDE WITH TRI-METHYLSILYLAMINO GROUPS

K. J. L. Paciorek*, R. H. Kratzer, J. H. Nakahara and W. Krone-Schmidt

B-tris(amino)-N-tris(trimethylsilyl)borazine and its telomers^{1,2} provide precursors for boron nitride preceramic polymers. Due to the low yield multistage synthesis, alternate routes to isomeric compositions and intermediates needed to be developed. The reactions of silylamines with hydrogen chloride are well established³, as well as the Si-N bond cleavage by boron halides⁴⁻⁶. Thus one attempt was based on the partial replacement of trimethylsilyl groups by protons in B-tris[bis(trimethylsilyl)amino]borazine using hydrogen chloride, the other attempt was to form bis(trimethylsilyl)aminodichloroborane from tris(trimethylsilyl)amine and boron trichloride. We now report that the reaction of hydrogen chloride with B-tris[bis(trimethylsilyl)amino]borazine led to condensed products, whereas the major action of boron trichloride was the exchange of one of its chlorines for a methyl group on silicon instead of the expected Si-N bond cleavage.

Experimental Section

General Procedures and Materials. Operations were carried out either in an inert atmosphere enclosure (Vacuum/Atmo-

spheres Model HE-93B), under nitrogen bypass, or in vacuo. Infrared spectra of solids were recorded as double mulls (Kel-F oil No. 10 and Nujol); of gases in 10 cm cells, using a Perkin-Elmer Infrared Spectrophotometer Model 1330. The mass spectrometric analyses were obtained employing a DuPont Model 21-491B spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph, equipped with a flame ionization detector. Gas chromatography was performed employing a 10' x 1/8" stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G using a programming rate of 8°C/min from 50-300°C. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The reactions summarized in Tables I and II, were performed employing vacuum line techniques, volatile products were separated by fractional condensations quantitated and identified by combinations of the use of calibrated traps, quantitative infrared spectral analysis and GC/MS. Room temperature nonvolatile, organic solvent soluble, residues were analyzed by GC/MS.

B-trichloroborazine⁷ and 1,3-trimethylsilyl-2,4-bis(trimethylsilyl)amino-1,3-diaza-diboretane⁸ were prepared by known procedures. Tris(trimethylsilyl)amine was purchased from Strem Chemicals and was purified by sublimation, hexamethyldisilazane was obtained from Aldrich Chemical, Co.. Boron trichloride and hydrogen chloride were obtained from Matheson Gas Products and were purified by vacuum line fractional condensations.

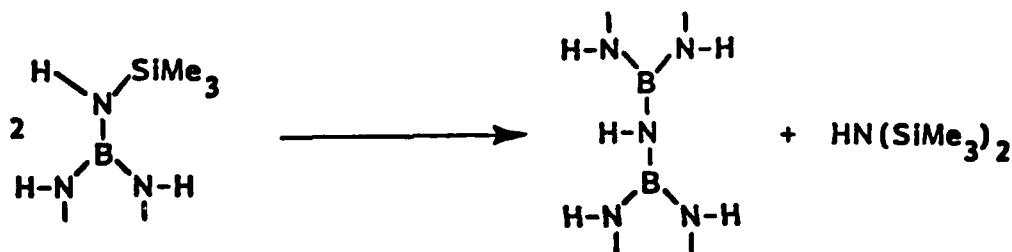
Preparation of B-tris[bis(trimethylsilyl)amino]borazine

To a stirred solution of B-trichloroborazine (10.7 g, 58.2 mmol) in benzene (200 mL) was added, at room temperature, a mixture of hexamethyldisilazane (56.46 g, 349.2 mmol) and triethylamine (35.34 g, 349.2 mmol); stirring at room temperature was continued for a total of 115 h. Filtration gave 96% yield (23.0 g) of triethylamine hydrochloride; from the filtrate 29.2 g (90%) of the borazine were obtained. B-tris[bis(trimethylsilyl)amino]borazine was purified by crystallization from hexane resulting in 71% yield of pure product, mp 131.5-132°C. Anal. Calcd. for $C_{18}H_{57}Si_6N_6B_3$: C, 38.70; H, 10.28; N, 15.04; Si, 30.17; B, 5.81; MW, 558.64. Found: C, 38.89; H, 10.38; N, 14.64; Si, 31.42; B, 6.02; MW, 563 (by osmometry, in benzene). Mass spectral data: $M^+(m/e\ 558; 46\%)$, $[M-CH_3]^+(m/e\ 543, 100\%)$.

Results and Discussion

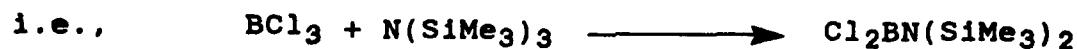
Interaction of B-tris[bis(trimethylsilyl)amino]borazine utilizing three moles of hydrogen chloride at 131°C resulted in 13.6% recovery of the starting material, and the formation of an insoluble and infusible product accompanied by a loss of 91.5% of the available trimethylsilyl groups (54.0% as Me_3SiCl ; 37.5% as $HN(SiMe_3)_2$). Similar results as above were obtained employing triethylamine hydrochloride as the hydrogen chloride source. With hydrogen chloride under milder conditions, in benzene at room temperature, 36.1% of the starting material was left unreacted; the product lost 69.8% of the available trimethylsilyl

groups as trimethylchlorosilane. The by-product of condensation in this case was ammonium chloride. Based on the above data it can be postulated that at the higher temperature the initially formed trimethylsilylamino substituents condense with elimination of hexamethyldisilazane and the establishment of -B-NH-B-bridges i.e.:



At the lower temperature no condensation of the trimethylsilylamino groups occurs. Instead the HNSiMe_3 groups, which apparently present a lesser steric hindrance to the attack of hydrogen chloride than the $\text{N(SiMe}_3)_2$ moiety, are transformed into amino groups. The latter subsequently condense and the liberated ammonia reacts with hydrogen chloride giving the isolated ammonium chloride. The identification of a borazine, wherein one of the trimethylsilyl groups was replaced by a proton, supports this argument. It should be noted that the mole ratio of borazine consumed to ammonium chloride formed was found to be 1:1.06.

Interaction of boron trichloride at room temperature with tris(trimethylsilyl)amine (Table II) gave the expected trimethylchlorosilane and bis(trimethylsilyl)aminodichloroborane⁹



But the yield was very low. Increasing the temperature failed to

promote the desired process, instead resulted in the production of methylboron dichloride accompanied by replacement of methyl groups on silicon by chlorine atoms i.e.:



It has been established from the mass spectral data, that only one methyl on a given silicon atom was replaced by chlorine (m/e 93, 95; SiMe_2Cl^+) proving the formation of $\text{N}(\text{SiMe}_2\text{Cl})_2\text{SiMe}_3$ not $\text{NSiMeCl}_2(\text{SiMe}_3)_2$. This type of compound was obtained¹⁰ from low temperature reactions of trisilylamines, containing one or two SiH bonds, with boron trichloride. Under these conditions no methyl-chlorine exchange was observed. The reaction of boron tribromide with tris(trimethylsilyl)amine was reported¹¹ to give methylboron dibromide at low temperatures, however, at elevated temperatures the formation of bis(trimethylsilyl)aminodibromoborane was claimed to be occurring. Our studies using boron trichloride, as evident from the results in Table II, show an opposite behavior, namely, a 78% yield of methylboron dichloride and 9.5% boron trichloride recovery at 150°C. On the other hand boron trifluoride with tris(trimethylsilyl)amine was found to afford the expected bis(trimethylsilyl)aminodifluoroborane¹². These results show clearly the differences in the behavior of the different boron halides.

In view of the above findings it became of interest to determine whether the methyl-chlorine exchange on silicon is specific to tris(trimethylsilyl)amine or whether other systems

show a related behavior. Boron trichloride failed to react with 1,3-trimethylsilyl-2,4-bis(trimethylsilyl)amino-1,3-diaza-dibor-
etane up to 70°C. However at 150°C the replacement of methyl groups on silicon by chlorine atoms accompanied by methylboron dichloride formation was essentially quantitative. Only a trace of trimethylchlorosilane was detected pointing to a virtual absence of Si-N cleavage. The products listed in Table II were identified by mass spectroscopy; each of the materials exhibited a high intensity molecular ion. No deductions could be made whether these were single compounds or mixtures of isomers.

Acknowledgment Support of this research from the Strategic Defense Sciences Office through Contract N-00014-87-C-0713 from the Office of Naval Research is gratefully acknowledged.

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- * To whom correspondence should be addressed at Ultrasystems Defense and Space Inc.
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TABLE I

REACTIONS OF $[(\text{Me}_3\text{Si})_2\text{NBH}]_3$ WITH
HYDROGEN CHLORIDE AND TRIETHYLAMINE HYDROCHLORIDE^a

Test No.	Reactants		Conditions		Products			
	$[(\text{Me}_3\text{Si})_2\text{NBH}]_3$ mmol	HCl ($\text{NEt}_3 \cdot \text{HCl}$) mmol	Time h	Temp °C	Start. Mat'l %	ClSiMe_3 mmol	$\text{HN}(\text{SiMe}_3)_2$ mmol	% ^b
1	0.525	1.58	17	131	13.6	1.47	0.510	37.5
2 ^c	0.546	1.83	17	RT	36.1	1.46 ^d	0	0
3 ^e	1.86	(5.58)	120	120(N ₂) ^f	25.2 ^g	n.d. ^h	n.d.	n.d.
4 ^e	0.553	(4.86)	46	135-150	0	1.86	0.622	37.5

^a All the reactions with the exception of Test 3 were performed in evacuated, sealed ampoules. ^b The percent is given with respect to the total Me_3Si groups present. ^c Benzene employed, 1.494 g. ^d 0.410 mmol of NH_4Cl produced. ^e Triethylamine hydrochloride reagent. ^f Nitrogen bypass. ^g 6.4% of $[(\text{Me}_3\text{Si})_2\text{NBH}]_2[\text{Me}_3\text{SiNBH}]$ together with 3.3% of unidentified compound formed; bulk insoluble polymer. ^h Not determined.

TABLE II

REACTIONS OF BORON TRICHLORIDE^a

Reagents, mmol NR ₃	BCl ₃	Conditions		Volatiles, mmol			Nonvolatiles, % ^d		
		Temp °C	Time h	BCl ₃	Me ₃ SiCl	MeBCl ₂	BCl ₂ - mmol Incorp	NR ₃	NR ₂ R' NR ₂
B ₂ N ₄ R ₆ ^c									
2.79 ^b	2.82	RT	20	2.46	0.28	none	0.36	n.d. ^e	n.d.
3.35 ^b	7.74	100	6	5.07	0.53	1.97	0.70	30.9	43.5
2.31 ^b	4.72	150	16	0.45	0.52	3.72	0.36	0.0	32.3
0.36 ^c	1.07	150	16	0.0	0.03	1.11	0.0	na ^f	na

^a All reactions were performed in evacuated, sealed ampoules. ^b Tris(trimethylsilyl)amine. ^c 1,3-trimethylsilyl-2,4-bis(trimethylsilyl)amino-1,3-diaza-diborethane. ^d R=SiMe₃; R'=SiMe₂Cl. ^e Not determined. ^f The products formed were of the general formula, B₂N₄R₃R' : B₂N₄R₆ (starting material) 5.2%; B₂N₄R₅R', 14.8%; B₂N₄R₄R'², 32.8%; B₂N₄R₃R'³, 41.0%; B₂N₄R₂R'⁴, 6.1%.