of AlCl in solution at room temperature by IR and ^{27}Al NMR spectroscopy. First results concerning the reactivity of AlCl in solution are reported as well.

The synthesis of AlCl(g) is carried out in the following way:

$$Al(l) + HCl(g) \xrightarrow[\text{yield} > 90\%]{1200\ K,\ p < 0.2\ \text{mbar}} AlCl(g) + \tfrac{1}{2}H_2(g)$$

Condensation of about 1 mg of AlCl(g) on the cold surface (77 K) of an optical cryostat gives dark red, solid AlCl. The IR spectrum shows a broad absorption with a maximum at 320 cm^{-1} and a half-width of about 100 cm^{-1}. The significant decrease of the frequency compared with the gas-phase value of 477 cm^{-1} [7] and the broad shape of the band agree with the vitreous structure of this compound. When the vitreous film of AlCl is allowed to warm up, its color changes to black at about 180 K, since disproportionation occurs according to[8]

$$3AlCl(s) \xrightarrow{180\ K} AlCl_3(s) + 2Al(s)$$

Therefore, AlCl(s) can be kept for a long time only below 77 K. Under these conditions the disproportionation reaction, which is thermodynamically favored, is prevented.

In a previous paper, we demonstrated that the synthesis described is also useful for the preparation of AlCl(s) on a larger scale.[9] The cryochemical reaction of AlCl with butyne-2, cocondensed in a pentane matrix at 77 K, leads to dimeric 1,4-dialuminacyclohexadiene via a carbene analogue [2 + 1]-cycloaddition. The product obtained is the first example of a compound containing aluminum-olefin π-bonds, as determined by X-ray structure analysis.

If AlCl is condensed into a matrix of a nonpolar and noncoordinating solvent, like pentane, disproportionation occurs also at temperatures higher than 180 K. But if AlCl (0.04 mol) is cocondensed at 77 K with Et_2O (0.2 mol) and toluene (0.6 mol), a dark red solution of AlCl is formed by warming the mixture up to 160 K. From this solution metallic aluminum precipitates at room temperature within a few hours. Visible light[10] and heat as well as concentrating the solution accelerate this process:

$$3AlCl{\cdot}xEt_2O \text{ in toluene} \rightarrow AlCl_3{\cdot}Et_2O + 2Al$$

If the solvent is removed in vacuo and the residue is hydrolyzed, only ether and $Al(OH)_3$, but no ethanol, are formed. Therefore, oxidation of AlCl by an insertion reaction into the CO bond of the ether can be excluded.

The disproportionation process has also been investigated by IR spectroscopy of the solution. In order to eliminate noncoordinated ether, the solution was carefully concentrated at 250 K to 70% of its initial volume. The resulting solution is extremely sensitive to moisture and air. Its IR spectrum was obtained in a special cell under dry nitrogen. It shows a strong, broad band at 450 cm^{-1} that is superimposed by toluene absorptions. We assign this band to ν(AlCl) of a adduct with the formula $AlCl{\cdot}xEt_2O$. When disproportionation sets in, its intensity decreases, and two new absorptions at 545 and 415 cm^{-1} arise. They have to be attributed to ν(as, AlCl) and ν(s, AlCl) of $AlCl_3{\cdot}Et_2O$. This assignment is confirmed by the spectrum of a toluene solution of pure $AlCl_3{\cdot}Et_2O$ scanned under identical conditions.

The presence of Al^{I} was proved by hydrolysis of the solution and measuring the amount of hydrogen evolved:

$$AlCl{\cdot}xEt_2O \xrightarrow{H_2O} [Al(H_2O)_6]^{3+} + H_2$$

The quantitative hydrolysis and the analytical determination of aluminum and chloride are in accordance with the formula $Al^{I}Cl{\cdot}xEt_2O$.

Evidence for the structure of the dissolved Al^{I} species could be obtained from the ^{27}Al NMR spectra: At approximately 190 K, a broad signal at 15 ppm (relative to $Al(H_2O)_6^{3+}$ as standard) is observed. This precludes monomeric Al^{I} species to be present. Resonances of monomeric AlCl are expected at significantly higher fields.[11] Consequently, we interpret our results with the presence of ether-coordinated Al species that contain metal-metal bonds.[13] When the sample is warmed up for a few minutes to approximately 380 K, a mirrorlike layer of metallic aluminum is formed on the walls of the NMR tube. If an ^{27}Al NMR spectrum of this sample is scanned at room temperature, the resonance at 15 ppm is replaced by a new sharp signal at 101 ppm. It has to be attributed to $AlCl_3{\cdot}Et_2O$.[16]

These solutions of AlCl promise to be a source of interesting chemical reactions. The following two reactions have already been studied:[17]

$$AlCl{\cdot}xEt_2O \xrightarrow[-H_2]{MeOH} (MeO)_2AlCl$$

IR in Nujol: ν(C-O) = 1050 cm^{-1} (st, br); ν(Al-Cl) = 600 cm^{-1} (st, br). Anal. Calcd: Al, 22.7; Cl, 28.5; C, 19.3; H, 4.9. Found: Al, 21.5; Cl, 28.3; C, 18.7; H, 5.1.

$$AlCl{\cdot}xEt_2O \xrightarrow{PhCH_2Cl} AlCl_3{\cdot}Et_2O + \text{polybenzyl}$$

Polybenzyl, $(C_7H_6)_n$, is isolated as an red oil with a molecular weight of 585 au in $CHCl_3$. Anal. Calcd: C, 93.3; H, 6.7; Found: C, 92.1; H, 7.9. Further work is in progress.

Our results give no evidence for $AlCl_2$. The preparation of this compound has been claimed recently.[18]

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(10) Therefore, we have not been successful in obtaining Raman spectra of these solutions (excitation at 1064 nm/647 nm). So it was not possible to detect Al-Al vibrations directly (vide infra).

(11) This is concluded from the Ga and Si NMR spectra of monomeric Ga^{I} (δ = - 800 ppm) (relative to $Ga(H_2O)_6^{3+}$)[2] and Si^{II} species(δ = -577 ppm) (relative to TMS as standard).[12]

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(13) Only a single molecular species containing Al-Al bonds has been characterized by X-ray structure analysis until now,[14] but no ^{27}Al NMR data are reported. Similar Si^{I}I species containing Si-Si bonds exhibit shifts of $\approx$0/ppm in their ^{29}Si NMR spectra (e.g. $[SiMe_2]_6$: δ = -41.86 ppm[15]). Therefore, our ^{27}Al data are in accordance with a polymeric structure of AlCl.

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Reactions of Hydrogen Chloride and Boron Trichloride with (Trimethylsilyl)amino Groups

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B,B',B''-Triamino-*N,N',N''*-tris(trimethylsilyl)borazine and its telomers[1,2] provide precursors for boron nitride preceramic polymers. Due to the low-yield multistage synthesis, alternate

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Table I. Reactions of $[(Me_3Si)_2NBNH]_3$ with Hydrogen Chloride and Triethylamine Hydrochloride[a]

test no.	mmol of reactants		conditions		products				
	$[(Me_3Si)_2NBNH]_3$	HCl ($NEt_3 \cdot HCl$)	time, h	temp., °C	% start matl	$ClSiMe_3$ mmol	$ClSiMe_3$ %[b]	$HN(SiMe_3)_2$ mmol	$HN(SiMe_3)_2$ %[b]
1	0.525	1.58	17	131	13.6	1.47	54.0	0.510	37.5
2[c]	0.546	1.83	17	*i*	36.1	1.46[d]	69.8	0	0
3[e]	1.86	(5.58)	120	120 (N_2)[f]	25.2[g]	*h*	*h*	*h*	*h*
4[e]	0.553	(4.86)	46	135–150	0	1.86	56.1	0.622	37.5

[a] All the reactions with the exception of test 3 were performed in evacuated, sealed ampules. [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 $[(Me_3Si)_2NBNH]_2[Me_3SiNHBNH]$ together with 3.3% of unidentified compound formed; bulk insoluble polymer. [h] Not determined. [i] Room temperature.

Table II. Reactions of Boron Trichloride[a]

mmol of reagents		conditions		mmol of volatiles			mmol of	% nonvolatiles[d]		
NR_3[b] or $B_2N_4R_6$[c]	BCl_3	temp., °C	time, h	BCl_3	Me_3SiCl	$MeBCl_2$	BCl_2 incorp	NR_3	NR_2R'	NRR'_2
2.79[b]	2.82	*g*	20	2.46	0.28	none	0.36	*e*	*e*	*e*
3.35[b]	7.74	100	6	5.07	0.53	1.97	0.70	30.9	43.5	0.5
2.31[b]	4.72	150	16	0.45	0.52	3.72	0.36	0.0	32.3	55.1
0.36[c]	1.07	150	16	0.0	0.03	1.11	0.0	na[f]	na	na

[a] All reactions were performed in evacuated, sealed ampules. [b] Tris(trimethylsilyl)amine. [c] 1,3-Bis(trimethylsilyl)-2,4-bis[bis(trimethylsilyl)-amino]-1,3-diazadiboretane. [d] $R = SiMe_3$; $R' = SiMe_2Cl$. [e] Not determined. [f] The products formed were of the general formula $B_2N_4R_{6-x}R'_x$: $B_2N_4R_6$ (starting material), 5.2%; $B_2N_4R_5R'$, 14.8%; $B_2N_4R_4R'_2$, 32.8%; $B_2N_4R_3R'_3$, 41.0%; $B_2N_4R_2R'_4$, 6.1%. [g] Room temperature.

routes to isomeric compositions and intermediates needed to be developed. The reactions of silylamines with hydrogen chloride are well established,[3] as well as the Si–N bond cleavage by boron halides.[4-6] Thus one attempt was based on the partial replacement of trimethylsilyl groups by protons in *B,B′,B″*-tris[bis(trimethylsilyl)amino]borazine using hydrogen chloride, the other attempt was to form [bis(trimethylsilyl)amino]dichloroborane from tris(trimethylsilyl)amine and boron trichloride. We now report that the reaction of hydrogen chloride with *B,B′,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/Atmospheres 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); IR spectra of gases were recorded in 10-cm cells, on a Perkin-Elmer Model 1330 infrared spectrophotometer. The mass spectrometric analyses were obtained by 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 by employing a 10 ft × $^1/_8$ in. stainless-steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G and using a programming rate of 8 °C/min from 50–300 °C. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

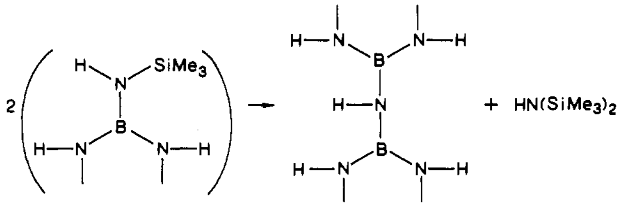
The reactions summarized in Tables I and II were performed by employing vacuum-line techniques; volatile products were separated by fractional condensations and quantitated and identified by combinations of the use of calibrated traps, quantitative infrared spectral analysis, and GC/MS. Room-temperature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

B,B′,B″-trichloroborazine[7] and 1,3-bis(trimethylsilyl)-2,4-bis[bis(trimethylsilyl)amino]-1,3-diazadiboretane[8] 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,B′,B″*-Tris[bis(trimethylsilyl)amino]borazine. To a stirred solution of *B,B′,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 a 96% yield (23.0 g) of triethylamine hydrochloride; from the filtrate 29.2 g (90%) of the borazine was obtained. *B,B′,B″*-Tris[bis(trimethylsilyl)amino]borazine was purified by crystallization from hexane, resulting in a 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,B′,B″*-tris[bis(trimethylsilyl)amino]borazine with 3 mol 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 by 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 byproduct of condensation in this case was ammonium chloride. On the basis of the above data, it can be postulated that at the higher temperature the initially formed (trimethylsilyl)amino substituents condense with elimination of hexamethyldisilazane and the establishment of –B–NH–B– bridges, i.e.:



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At the lower temperature, no condensation of the (trimethylsilyl)amino groups occurs. Instead the $HNSiMe_3$ groups, which apparently present a lesser steric hindrance to the attack of hydrogen chloride than the $N(SiMe_3)_2$ 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)amino]dichloroborane,[9] i.e.:

$$BCl_3 + N(SiMe_3)_3 \rightarrow Cl_2BN(SiMe_3)_2$$

However, the yield was very low. Increasing the temperature failed to promote the desired process; it instead resulted in the production of methylboron dichloride accompanied by replacement of methyl groups on silicon by chlorine atoms, i.e.:

$$BCl_3 + N(SiMe_3)_3 \rightarrow MeBCl_2 + N(SiMe_2Cl)_x(SiMe_3)_{3-x}$$

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 $N(SiMe_2Cl)_2SiMe_3$ not $NSiMeCl_2(SiMe_3)_2$. This type of compound was obtained[10] 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 reported[11] to give methylboron dibromide at low temperatures; however, at elevated temperatures, the formation of [bis(trimethylsilyl)amino]dibromoborane 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)amino]difluoroborane.[12] 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-bis(trimethylsilyl)-2,4-bis[bis(trimethylsilyl)amino]-1,3-diazadiboretane 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 peaks were due to single compounds or mixtures of isomers.

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