Table I. Positions of the Dinitrogen Infrared Bands in $[Ru(NH_3)_5N_2]Br_2$[a]

	δ_{Ru-N_2} ($\pm 1\ cm^{-1}$)			ν_{N_2} ($\pm 5\ cm^{-1}$)	
Ru-N-N	Obsd (low temp)	Obsd (room temp)	Calcd[b] (room temp)	Obsd (room temp)	Calcd[b] (room temp)
$Ru-^{14}N-^{14}N$	511	508	507.7	2105	2106.7
$Ru-^{14}N-^{15}N$	505	501	502.7	2070	2071.4
$Ru-^{15}N-^{14}N$	499	496	495.9	2070	2071.4
$Ru-^{15}N-^{15}N$	495	492	490.7	2040	2035.5

[a] Nujol mulls. [b] The force constants obtained from the calculation are $k_{NN} = 18.298 \pm 0.061$ mdyn/Å and $H_\delta = 0.788 \pm 0.008$ mdyn/Å.

splitting of the band at $2075 \pm 0.5\ cm^{-1}$. The maximum separation of possible, unresolved bands under this envelope at $2075\ cm^{-1}$ is $\pm 3\ cm^{-1}$.

Our observations have recently been confirmed by Quinby and Feltham.[6] In addition, they reported only a small splitting of ν_{N_2} in only one salt (SbF_6^-) of *trans*-$[RuCl(^{15}N-^{14}N)(das)_2]^+$ (2094 and 2089 cm^{-1}). In all other salts only a single ν_{N_2} frequency was observed, and in no case was a splitting in ν_{RuN_2} at 446.5 cm^{-1} observed. However there was a splitting of the degenerate bending frequency δ_{RuN_2} near 490 cm^{-1} for almost every salt. They concluded that shifts for $\nu_{Ru^{14}N^{15}N}$ and $\nu_{Ru^{15}N^{14}N}$ could only be $\sim 1\ cm^{-1}$; however, in order to explain the shifts of $\sim 9\ cm^{-1}$ which we observed for the band at 508 cm^{-1} in $[Ru(NH_3)_5N_2]Br_2$, they suggested that the band at 508 cm^{-1}, previously assigned[1,2] as ν_{RuN_2}, be reassigned as δ_{RuN_2}. More importantly, they concluded that the assignment of the 508-cm^{-1} band to ν_{RuN_2} would require an observed shift of $\sim 9\ cm^{-1}$ for this band and should demand a corresponding shift of $\sim 35\ cm^{-1}$ for ν_{N_2}. No bands of significant intensity were observed for $[Ru(NH_3)_5N_2]Br_2$ which could be assigned to ν_{RuN_2}. In addition, they reported that they were unable to see any splitting of the 2070-cm^{-1} $[Ru(NH_3)_5N_2]Br_2$ bands (to better than 5 cm^{-1}).

No bands of significant intensity were observed for the Br^- salt that could be attributed to ν_{RuN_2}. (The I^- salt has been reported[2] to display a band at 516 cm^{-1}.) Examination of the infrared (at a readout of 1 cm^{-1}/division) spectrum to 400 cm^{-1} indicated no change in any of the other band positions (at 466, 448, 440, and 430 cm^{-1}) upon ^{15}N substitution. To confirm the assignments of the δ_{RuN_2} bands near 500 cm^{-1} and the ν_{N-N} bands in the 2100-cm^{-1} region, a simple normal-coordinate calculation was made (using the programs of Schachtschneider[14] as modified by Mann[15]) involving the linear triatomic system Ru-N-N. The bond distances were obtained from the work of Bottomley and Nyburg.[16] Since no data were available for ν_{Ru-N}, it was impossible to obtain a complete set (k_{N-N}, N-N stretch; k_{Ru-N}, Ru-N stretch; H_δ, Ru-N-N bend; $k_{Ru-N,N-N}$, the stretch-stretch interaction term) of force constants for this model. However, by performing a preliminary calculation, using as starting guesses the force constants obtained in the work of Feltham,[6] the assignment of the bands for the four isomers became readily apparent: three bands were predicted for the ν_{N-N} region, two for the ν_{Ru-N} region, and four for δ_{Ru-N-N}. The force constants k_{N-N} and H_δ were then allowed to refine, and the results obtained are displayed in Table I. It can be seen that regardless of the value of the bending force constant H_δ, the δ_{Ru-N_2} frequencies will always be in the following order: $Ru-^{14}N-^{14}N > Ru-^{14}N-^{15}N > Ru-^{15}N-^{14}N > Ru-^{15}N-^{15}N$. By using the central atom as a point of reference, one might have anticipated the bending mode for $Ru-^{15}N-^{14}N$ to be more like that for $Ru-^{14}N-^{14}N$ than that for $Ru-^{15}N-^{15}N$. Since this would have given rise to a set of frequencies different from those observed, this assumption is not correct. It is further seen that, to the extent to which the triatomic model is valid, only two bands will occur in the ν_{Ru-N} region (one for the two $Ru-^{14}N$ isomers and one for the two $Ru-^{15}N$ molecules) and three in the ν_{N-N} region, with coincident frequencies for the two $Ru-^{29}N_2$ ν_{NN} stretches. In order to validate this assignment, the value of the stretch-stretch interaction term $k_{Ru-N,N-N}$ was arbitrarily assigned inordinately large values. The resulting calculation yielded no further splitting of the bands.

In conclusion we have presented the complete description of the observed bending and stretching modes for the four isomers of $[Ru(NH_3)_5{}^{28,29,30}N_2]Br_2$. No splitting is observed for ν_{N_2} in the $^{29}N_2$ isomer, while a significant splitting is observed for δ_{Ru-N_2} in the same isomer. The latter is very useful in identifying[5,8,17] the products of dinitrogen formation reactions. The relative energies of the observed bands for δ_{Ru-N_2} can be correctly assigned by considering the isotopic shifts expected for a stretching mode of Ru-N. Using the data presented, the conclusions of Feltham regarding the reassignment of ν_{Ru-N_2} and δ_{Ru-N_2} have been confirmed.

Acknowledgment. We wish to express our thanks for the sample of nitrous oxide ($^{15}N-^{15}N-O$) provided by Professor Roberts. The work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $[Ru(NH_3)_5-^{14}N-^{14}N]Br_2$, 15246-25-0; $[Ru(NH_3)_5-^{14}N-^{15}N]Br_2$, 42402-14-2; $[Ru(NH_3)_5-^{15}N-^{14}N]Br_2$, 42402-15-3; $[Ru(NH_3)_5-^{15}N-^{15}N]Br_2$, 42402-16-4.

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Reactions of Some Lithium Alkyltrimethylsilylamides with Dichlorophenylborane and Chlorodimethylaminophenylborane[1]

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Reactions of alkali metal derivatives of bis(trimethylsilyl)amine with haloboranes (eq 1) have been used for the prepara-

$$(Me_3Si)_2NM + XB< \rightarrow (Me_3Si)_2NB< + MX \qquad (1)$$

$$M = Li, Na; X = F, Cl$$

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(1) Taken from the Ph.D. dissertation of R. H. Neilson, Duke University, Durham, N. C., 1973.

Table I. Boiling Points, Yields, and Analytical Data for the Silylaminoboranes, $Me_3Si(R)NB(Ph)X$

					Elemental analyses[a]		
No.	R	X	Bp, °C (Torr)	Yield, %	% C	% H	% N
II	*i*-Pr	NMe_2	50–53 (0.01)	82	64.42 (64.11)	10.39 (10.34)	11.13 (10.68)
III	Et	NMe_2	57–59 (0.02)	83	63.22 (62.89)	10.15 (10.15)	10.62 (11.28)
IV	Me	NMe_2	40–43 (0.01)	45	61.56 (61.52)	9.79 (9.89)	12.15 (11.96)
V[b]	*t*-Bu	Cl	75–76 (0.01)	74	58.09 (58.33)	8.84 (8.67)	
VI[c]	*i*-Pr	Cl	60–64 (0.05)	70	56.52 (56.82)	8.49 (8.34)	

[a] Calculated values in parentheses. [b] Mp 40–41°; 13.05% (13.25%) Cl. [c] Mp *ca.* 30°; 13.25% (13.95%) Cl.

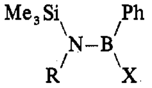
Table II. Proton Nmr and Mass Spectral Data for the Silylaminoboranes, $Me_3Si(R)NB(Ph)X$

				Proton nmr[b]			
No.	R	X	Mass spectra,[a] *m/e* (molecular ion)	$\delta(Me_3Si)$	$\delta(R)$	$\delta(X)$	$\delta(Ph)$
II	*i*-Pr	NMe_2	262.2033 (262.2037)	0.07	0.78 (CH_3)[c] 3.17 (CH)[d]	2.67	7.2
III	Et	NMe_2	248.1880 (248.1884)	0.03	0.85 (CH_3)[e] 2.75 (CH_2)[f]	2.68	7.2
IV	Me	NMe_2	234.1718 (234.1723)	−0.12	2.59	2.73	7.3
V	*t*-Bu	Cl	267.1386 (267.1381)	0.05	1.48		7.4
VI	*i*-Pr	Cl	253.1220 (253.1225)	0.03	1.26 (CH_3)[c] 3.71 (CH)[d]		7.2

[a] Values in parentheses calculated using the masses of the most abundant isotopes of all atoms. [b] In 20% (v/v) solutions in CCl_4; δ values are in ppm relative to δ(TMS) 0.00, by the tube-interchange method. [c] Doublet. [d] Septet. [e] Triplet. [f] Quartet.

tion of several bis(trimethylsilyl)amino-substituted boranes.[2-7]

Recent studies[7] in this laboratory have shown that the scope of this "metalation" reaction can be extended to allow the preparation of two germylaminoboranes, $Me_3Ge(R)NB(Ph)NMe_2$ (R = Me_3Ge, *t*-Bu), as well as the first member of the following series of silylaminoboranes



I, R = *t*-Bu, X = NMe_2
II, R = *i*-Pr, X = NMe_2
III, R = Et, X = NMe_2
IV, R = Me, X = NMe_2
V, R = *t*-Bu, X = Cl
VI, R = *i*-Pr, X = Cl
VII, R = Et, X = Cl
VIII, R = Me, X = Cl

This paper concerns attempts to prepare the remaining compounds in this series since they are of interest in relation to our studies of boron–nitrogen rotational barriers in compounds containing the silicon–nitrogen–boron linkage.[1,8,9] The determination of selected boron–nitrogen rotational barriers in these and some related compounds will be reported in the future.

Experimental Section

Materials. Chlorotrimethylsilane, isopropylamine, and *tert*-butylamine were purchased from Eastman Organic Chemicals, Rochester, N. Y., and distilled prior to use. Trichloroborane, methylamine, dimethylamine, and ethylamine were obtained as compressed gases from the Matheson Co., East Rutherford, N. J., and used without further purification. *n*-Butyllithium (*ca.* 2 *M* in hexane; Alfa Inorganics, Beverly, Mass.) and tetraphenyltin (Matheson Coleman and Bell, Norwood, Ohio) were commercial reagents used as received.

Dichlorophenylborane, obtained from the reaction of tetraphenyltin with trichloroborane,[10] was converted to bis(dimethylamino)phenylborane by its reaction with an excess of dimethylamine.[11] Chlorodimethylaminophenylborane was then obtained from the equilibration reaction of dichlorophenylborane with bis(dimethylamino)phenylborane.[11] The alkyltrimethylsilylamines[12] were prepared in high yields by the addition of chlorotrimethylsilane to a threefold excess of the alkylamine in pentane solution.

All experiments were performed under an atmosphere of dry nitrogen. Solvents were distilled from calcium hydride just prior to use. Melting and boiling points are uncorrected.

Spectra and Analyses. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The mass spectral data were obtained on an MS-902 spectrometer. Proton nmr spectra were obtained on Varian A-60 and T-60 spectrometers. A Perkin-Elmer 137 spectrophotometer was used for routine infrared spectra. Boiling points, yields, and results of elemental analyses obtained for the new compounds prepared in this study are summarized in Table I. Proton nmr and mass spectral data for these compounds are collected in Table II.

Alkyltrimethylsilylaminophenylboranes (II–VI). Except for the minor differences noted below, compounds II–VI were all prepared using the following procedure which details the synthesis of isopropyltrimethylsilylaminodimethylaminophenylborane (II). *n*-Butyllithium (2.2 *M*, 0.052 mol, 23.6 ml) was added with stirring to a cooled (0°) solution of isopropyltrimethylsilylamine (0.050 mol, 6.56 g) in ether (100 ml). The mixture was allowed to warm to room temperature and then stirred 15 min during which time a gas (presumably butane) was evolved. After recooling the solution to 0°, chlorodimethylaminophenylborane (0.050 mol, 8.38 g) was added with stirring. A white solid (presumably lithium chloride) was formed during the addition. The mixture was allowed to warm to room temperature and stirred for an additional 3 hr. The solid was removed by filtration and the solvents were removed from the filtrate leaving a yellow liquid residue from which compound II distilled as a colorless liquid.

In the synthesis of the chlorine-containing compounds V and VI, solutions of the lithium alkyltrimethylsilylamides were cooled to −80° before dichlorophenylborane was added. After removing the solvents in the preparation of compound V, the residue was an orange liquid–solid mixture instead of the usual yellow-orange liquid; nevertheless, distillation afforded V as a colorless liquid. When freshly

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distilled, compounds V and VI crystallized to low-melting white solids.

Decomposition of the Chloroboranes (V-VIII). A neat sample (4.43 g) of V was heated at 200° for 24 hr. After cooling to room temperature, distillation afforded pure starting material (4.09 g, 94% recovery, bp 76-77° (0.01 Torr)). A neat sample (2.50 g) of VI was heated at 150° for 1 hr. After cooling, chlorotrimethylsilane was removed under vacuum and identified by comparison of its infrared spectrum to that of an authentic sample. The residual brown solid was recrystallized from carbon tetrachloride (20 ml) giving white crystals of *B*-triphenyl-*N*-triisopropylborazine (0.85 g, 58% yield, mp 208-209°, lit.[13] mp 206-207°). The mass spectrum contained a molecular ion at *m/e* 435.3184 (calcd 435.3189).

Attempts to prepare the chloroboranes (VII and VIII) by the metalation procedure described for compounds II-VI were unsuccessful. In these cases when the solvents were removed from the reaction mixture, the residue was a yellow solid and chlorotrimethylsilane could be identified in the solvent fraction by its proton nmr spectrum. Recrystallization of the solid afforded crystals of the appropriate *B*-triphenyl-*N*-trialkylborazine: $(EtNBPh)_3$, mp 214-215° (lit.[14] mp 209.5-211°), 58% yield, *m/e* (molecular ion) 393.2724 (calcd 393.2719); $(MeNBPh)_3$, mp 270-274° (lit.[14] mp 275-276°), 74% yield, *m/e* (molecular ion) 351.2245 (calcd 351.2250).

Results and Discussion

The alkyltrimethylsilylaminodimethylaminophenylboranes (II-IV) have been prepared by the addition of chlorodimethylaminophenylborane to an ether solution of the corresponding lithium alkyltrimethylsilylamide (eq 2).

$$\mathrm{Me_3SiNRLi + ClB(Ph)NMe_2 \rightarrow Me_3Si(R)NB(Ph)NMe_2 + LiCl} \qquad (2)$$

$$\begin{array}{c}\text{II, R} = i\text{-Pr}\\ \text{III, R} = \text{Et}\\ \text{IV, R} = \text{Me}\end{array}$$

When similar reactions of lithium alkyltrimethylsilylamides with dichlorophenylborane were carried out, however, the products isolated were found to depend upon the nature of the alkyl substitutent. Thus, with the *tert*-butyl- and isopropyl-substituted amides, the corresponding alkyltrimethylsilylaminochlorophenylboranes (V and VI) were obtained (eq 3) but the compounds containing the smaller alkyl groups (VII and VIII) were thermally unstable and only their decomposition products, the *B*-triphenyl-*N*-trialkylborazines (IX and X), were isolated (eq 4).

$$\mathrm{Me_3SiNRLi + Cl_2BPh \rightarrow Me_3Si(R)NB(Ph)Cl + LiCl} \qquad (3)$$

$$\begin{array}{c}\text{V, R} = t\text{-Bu}\\ \text{VI, R} = i\text{-Pr}\\ \text{VII, R} = \text{Et}\\ \text{VIII, R} = \text{Me}\end{array}$$

$$\mathrm{Me_3Si(R)NB(Ph)Cl \rightarrow {}^1/_3(RNBPh)_3 + Me_3SiCl} \qquad (4)$$

$$\begin{array}{cc}\text{VII, R} = \text{Et} & \text{IX, R} = \text{Et}\\ \text{VIII, R} = \text{Me} & \text{X, R} = \text{Me}\end{array}$$

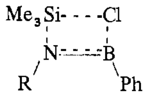
The bis(amino)boranes (II-IV) were colorless, rather viscous liquids that distilled without decomposition at moderate temperatures (Table I) under reduced pressure and were relatively stable toward hydrolysis by atmospheric moisture. The chlorine-containing compounds V and VI which hydrolyzed readily upon exposure to moist air were low-melting crystalline solids when freshly purified. They distilled as colorless liquids but crystallization occurred if the bottom of the flask was scratched with a glass rod. The new silylaminoboranes were fully characterized by elemental analyses (Table I) and high-resolution mass spectral and proton nmr results (Table II). The mass spectral fragmentation patterns as well as the integrated peak areas in the nmr spectra were consistent with the assigned structures.

The thermal stability of the alkyltrimethylsilylaminochlorophenylboranes (V-VIII) varied with the size of the alkyl substituent. Below room temperature (*ca.* 22°) the methyl- and ethyl-substituted compounds underwent condensation with elimination of chlorotrimethylsilane and formation of the borazines (eq 4), thus precluding their isolation. Borazine formation is a common mode of decomposition of compounds containing the Si-N-B-X (X = F, Cl) linkage,[2,3,15-17] although a recent study in this laboratory has shown a novel case in which an eight-membered borazocine ring was obtained.[18]

The isopropyl compound VI could be isolated but it also decomposed slowly on standing at room temperature or rapidly on heating according to eq 5. The *tert*-butyl derivative V, however, could be heated to at least 200° without decomposition and thus its stability is comparable to that of the previously reported bis(trimethylsilyl)aminodialkylaminochloroboranes, $(Me_3Si)_2NB(NR_2)Cl$.[5,6]

$$\underset{\text{VI}}{\mathrm{Me_3Si(\mathit{i}\text{-}Pr)NB(Ph)Cl}} \xrightarrow[\text{1 hr}]{150°} \mathrm{Me_3SiCl} + \underset{\text{XI}}{{}^1/_3(\mathit{i}\text{-}\mathrm{PrNBPh})_3} \qquad (5)$$

Such a sterically related trend in the thermal stability of compounds V-VIII probably indicates that the mechanism of chlorotrimethylsilane elimination is not a simple unimolecular process involving a four-center transition state (XII).



XII

The attainment of such a transition state would be expected to be favored by increasing the steric bulk of the alkyl group (R), in opposition to the trend that is observed. A bimolecular process, on the other hand, is consistent with the results reported here since cleavage of the Si-N bond of one molecule by the B-Cl bond of another should become more difficult as the size of the alkyl group increases.

Mooney and coworkers[14] have observed a similar order in the relative thermal stabilities of the bis(alkylamino)phenylboranes, $PhB(NHR)_2$. These compounds eliminate the primary amine, RNH_2, and condense to the borazines, $(RNBPh)_3$ (R = Me, Et), or to noncyclic polymers (R = *i*-Pr, *t*-Bu). The relative ease of condensation decreased in the order Me ~ Et > *i*-Pr > *t*-Bu.

Acknowledgments. The mass spectral data were obtained at the RTI Center for Mass Spectrometry supported by the National Institutes of Health under Grant PR-330. Financial assistance from the Duke University Research Council, the National Aeronautics and Space Administration, and E. I. du Pont de Nemours and Co. is gratefully acknowledged.

Registry No. $ClB(Ph)NMe_2$, 1196-44-7; $Me_3SiN(\mathit{i}\text{-}Pr)Li$, 42423-10-9; $Me_3SiN(Et)Li$, 42423-11-0; $Me_3SiN(Me)Li$, 10568-44-2; Cl_2B-Ph, 873-51-8; $Me_3SiN(\mathit{t}\text{-}Bu)Li$, 18270-42-3; $Me_3Si(\mathit{i}\text{-}Pr)NB(Ph)NMe_2$, 42561-78-4; $Me_3Si(Et)NB(Ph)NMe_2$, 42423-14-3; $Me_3Si(Me)NB(Ph)$-NMe_2, 42423-15-4; $Me_3Si(\mathit{t}\text{-}Bu)NB(Ph)Cl$, 42423-16-5; $Me_3Si(\mathit{i}\text{-}Pr)$-NB(Ph)Cl, 42423-17-6.

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