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Comparison of Some Properties of Amine-Boranes and Borazines[1]

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A series of B-monosubstituted amine-boranes and borazines have been compared according to their chemical reactivity and ^1H nmr spectral properties. No previous direct comparisons between these classes of compounds have been made. Mercury(II) halides have been observed to be more reactive toward $H_3B{\cdot}N(CH_3)_3$ than $H_3B_3N_3H_3$. This decreased reactivity of $H_3B_3N_3H_3$ is considered to be related to π bonding in the borazine ring which leads to a decreased hydridic character of the hydrogen bound to boron and partial positive charge on boron compared to $H_3B{\cdot}N(CH_3)_3$. Steric effects would have enhanced the reactivity of $H_3B_3N_3H_3$ compared to $H_3B{\cdot}N(CH_3)_3$. The comparison of the ^1H nmr data for $H_2XB{\cdot}N(CH_3)_3$, $H_2XB{\cdot}N(CH_3)_2H$, $H_2XB_3N_3(CH_3)_3$ and $H_2XB_3N_3H_3$ (X = Cl, Br, CH_3, CN) supports the hypothesis that a resonance interaction between a substituent and the borazine ring is responsible for the changes in the relative chemical shifts of the ortho and para protons in $H_2XB_3N_3H_3$. Field effects might be important in accounting for the substituent effects on the CH resonance in $H_2XB_3N_3(CH_3)_3$.

The elucidation of the nature of bonding in the borazine ring through the investigation of the effects of substituents on the chemical and spectral properties of unsymmetrically substituted borazines is of current interest. The data for B-monosubstituted borazines ($H_2XB_3N_3H_3$) are consistent with the hypothesis that the π electrons are delocalized, at least partially, and substituents interact with the π system by means of a resonance effect. Chemical reactivity studies[2,3] have clearly demonstrated that a single substituent on one boron of the borazine ring in a $H_2XB_3N_3H_3$ derivative has a definite influence on the reactivity of the substituents bound to the other boron atoms. Correlations between the ^1H chemical shift of the para protons of B-monosubstituted borazines[4,5] with ^{11}B chemical shift for the boron atom to which the substituent is bound are also consistent with π-electron delocalization. However, the nmr data could also be interpreted in terms of anisotropic effects and through-space field effects.

In this paper, we report the preparation and chemical and spectral properties of a series of B-monosubstituted amine-boranes. These types of compounds have been studied in order to understand more fully the differences between the chemical and spectral properties of borazines and other boron-nitrogen compounds. There has been no previous comparison between these classes of compounds. Amine-boranes are coordinately saturated. Both boron and nitrogen are four-coordinate. Since π bonding is unlikely, resonance interactions will be prevented and changes in the ^1H nmr data will result from field effects. A comparative study of the effects of boron substituents in $H_2XB{\cdot}N(CH_3)_2H$, $H_2XB{\cdot}N(CH_3)_3$, $H_2XB_3N_3H_3$, and $H_2XB_3N_3(CH_3)_3$ requires a variety of types of substituents. The substituents were selected on the basis of the availability of spectral data for the B-monosubstituted borazine. Very little data on B-monosubstituted amine-boranes were previously available.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means.

Preparation of $H_2XB{\cdot}N(CH_3)_3$ and $H_2XB{\cdot}N(CH_3)_2H$ (X = Cl, Br). The compounds $H_2ClB{\cdot}N(CH_3)_3$, $H_2BrB{\cdot}N(CH_3)_3$, $H_2ClB{\cdot}N(CH_3)_2H$, and $H_2BrB{\cdot}N(CH_3)_2H$ were prepared by means of the reaction between $H_3B{\cdot}N(CH_3)_3$ or $H_3B{\cdot}N(CH_3)_2H$ with $HgCl_2$ or $HgBr_2$ in diethyl ether at room temperature. The trimethylamine-borane adducts were isolated, after solvent removal, by sublimation at 25° to a 0° cold finger. The average yields (based on the quantity of $H_3B{\cdot}N(CH_3)_3$ used) of $H_2ClB{\cdot}N(CH_3)_3$, mp 84-85° (lit.[6] mp 85°) and $H_2BrB{\cdot}N(CH_3)_3$, mp 68-69° (lit.[6] mp 67°), were 87 and 76%, respectively. The compounds were further identified by elemental analysis and their spectral properties.

In the case of the synthetic procedure for $H_2XB{\cdot}N(CH_3)_2H$ (X = Cl, Br), the reaction mixture was filtered, after hydrogen evolution was complete. The diethyl ether was removed from the filtrate by vacuum distillation to leave a colorless liquid. The product $H_2ClB{\cdot}N(CH_3)_2H$ was then purified by a vacuum distillation at 59° using a short-path still. The average yield of $H_2ClB{\cdot}N(CH_3)_2H$, fp 16° (lit.[6] 18°), was 65% based on the quantity of $H_3B{\cdot}N(CH_3)_2H$ used. The compound was further identified by elemental analysis and its spectral properties. For $H_2BrB{\cdot}N(CH_3)_2H$, a viscous, thermally unstable liquid was obtained after filtration and removal of ether. Upon standing, H_2 and $B_2H_5N(CH_3)_2$ were evolved at room temperature. Reaction at 0° and keeping the product cool failed to yield a sufficiently pure product which could be adequately characterized.

Preparation of $H_2(CH_3)B{\cdot}N(CH_3)_3$ and $H_2(CH_3)B{\cdot}N(CH_3)_2H$. The compound $H_2(CH_3)B{\cdot}N(CH_3)_3$ was readily prepared by means of the reaction between $LiB(CH_3)H_3$ and $N(CH_3)_3HCl$. The derivative, $H_2(CH_3)B{\cdot}N(CH_3)_2H$, was obtained from $H_2(CH_3)B{\cdot}N(CH_3)_3$ by means of an amine exchange reaction. A variety of other potential preparative routes to $H_2(CH_3)B{\cdot}N(CH_3)_3$ and $H_2(CH_3)B{\cdot}N(CH_3)_2H$ were attempted but they did not give the desired compounds.

In a typical reaction, 0.981 g (27.6 mmol) $LiB(CH_3)H_3$[7] was allowed to react with 2.57 g (27.0 mmol) of $N(CH_3)_3{\cdot}HCl$ in diethyl ether. When hydrogen evolution was complete (about 1 hr), the volatile components were removed and separated by means of a fractional vacuum distillation using -78 and -196° traps. The product $H_2(CH_3)B{\cdot}N(CH_3)_3$, which was stopped by the -78° trap, had a melting point of 0° and a vapor pressure of 3 mm at 20° (lit.[8] mp 0.8°, vp 3 mm (20°)). The average yield of $H_2(CH_3)B{\cdot}N(CH_3)_3$ was 24% based on the quantity of $LiB(CH_3)H_3$ used. The compound $H_2(CH_3)B{\cdot}N(CH_3)_2H$ was prepared from $H_2(CH_3)B{\cdot}N(CH_3)_3$ by means of an amine-exchange reaction. A large excess of $N(CH_3)_2H$ was combined with $H_2(CH_3)B{\cdot}N(CH_3)_3$ and allowed to stand for 18 hr at room temperature. After the amine mixture was removed by vacuum distillation, a colorless liquid, nonvolatile at room temperature, remained. These characteristics were previously observed for $H_2(CH_3)B{\cdot}N(CH_3)_2H$.[9] This product was further identified by its spectral properties. The reaction between $LiB(CH_3)H_3$ and $N(CH_3)_2H_2Cl$ did not give the desired product. Instead, mixtures of $[H_2B{\cdot}N(CH_3)_2]_2$, $(CH_3)_2B{\cdot}N(CH_3)_2$, and other unidentified products were observed.

The reaction between $H_2ClB{\cdot}N(CH_3)_3$ and $(CH_3)MgI$ in diethyl ether was also studied as a route to $H_2(CH_3)B{\cdot}N(CH_3)_3$. The only product which could be isolated was $H_3B{\cdot}N(CH_3)_3$ (approximately 25% yield based on the quantity of $H_2ClB{\cdot}N(CH_3)_3$ reacted). The origin of this product is unknown. Analysis of the starting material ($H_2ClB{\cdot}N(CH_3)_3$) conclusively proved that $H_3B{\cdot}N(CH_3)_3$ was not an impurity.

Preparation of $H_2(CN)B{\cdot}N(CH_3)_3$ and $H_2(CN)B{\cdot}N(CH_3)_2H$. The compound $H_2(CN)B{\cdot}N(CH_3)_3$ was prepared from $H_3B{\cdot}N(CH_3)_3$ and AgCN. Subsequent transamination produced $H_2(CN)B{\cdot}N(CH_3)_2H$.

In a typical reaction 0.218 g (3.00 mmol) of $H_3B{\cdot}N(CH_3)_3$ and 0.403 g (3.00 mmol) of AgCN were heated in a sealed, evacuated

Table I. ^1H Nuclear Magnetic Resonance Data[a]

Compd	Solvent	Concn, *m*	*N*-CH_3	J_{C-H}[c]	*N*-H	*B*-CH_3
$H_3B\cdot N(CH_3)_3$	$CDCl_3$	*b*	−2.64			
$H_2ClB\cdot N(CH_3)_3$	$CDCl_3$	*b*	−2.67			
$H_2BrB\cdot N(CH_3)_3$	$CDCl_3$	*b*	−2.71			
$H_2BrB\cdot N(CH_3)_3$	C_6H_6	*b*	−2.11			
$H_2BrB\cdot N(CH_3)_3$	CH_3CN	*b*	−2.71			
$H_2CH_3B\cdot N(CH_3)_3$	$CDCl_3$	*b*	−2.54			−0.25
$H_2CH_3B\cdot N(CH_3)_3$	C_5H_{10}	*b*	−2.44			−0.23
$H_2CNB\cdot N(CH_3)_3$	$CDCl_3$	*b*	−2.74			
$H_2CN\cdot BN(CH_3)_3$	C_6H_6	*b*	−2.08			
$H_3B\cdot N(CH_3)_2H$	$CDCl_3$	1.64	−2.51[d]	6	−4.47	
$H_3B\cdot N(CH_3)_2H$	$CDCl_3$	1.12	−2.51[d]	6	−4.41	
$H_3B\cdot N(CH_3)_2H$	$CDCl_3$	0.721	−2.51[d]	6	−4.33	
$H_3B\cdot N(CH_3)_2H$	$CDCl_3$	*e*	−2.51[d]	6	−4.24	
$H_2ClB\cdot N(CH_3)_2H$	$CDCl_3$	24.7	−2.61[d]	6	−4.98	
$H_2ClB\cdot N(CH_3)_2H$	$CDCl_3$	11.1	−2.61[d]	6	−4.93	
$H_2ClB\cdot N(CH_3)_2H$	$CDCl_3$	3.18	−2.61[d]	6	−4.84	
$H_2ClB\cdot N(CH_3)_2H$	$CDCl_3$	2.12	−2.61[d]	6	−4.80	
$H_2ClB\cdot N(CH_3)_2H$	$CDCl_3$	*e*	−2.61[d]	6	−4.75	
$H_2CNB\cdot N(CH_3)_2H$	$CDCl_3$	0.819	−2.62[d]	7	−5.55	
$H_2CNB\cdot N(CH_3)_2H$	$CDCl_3$	0.494	−2.62[d]	7	−5.52	
$H_2CNB\cdot N(CH_3)_2H$	$CDCl_3$	0.295	−2.62[d]	7	−5.44	
$H_2CN\cdot BN(CH_3)_2H$	$CDCl_3$	*e*	−2.62[d]	7	−5.38	
$H_2CH_3B\cdot N(CH_3)_2H$	$CDCl_3$	3.77	−2.49[d]	5	−4.10	−0.17
$H_2CH_3B\cdot N(CH_3)_2H$	$CDCl_3$	1.94	−2.49[d]	5	−4.05	−0.17
$H_2CH_3B\cdot N(CH_3)_2H$	$CDCl_3$	1.21	−2.49[d]	5	−4.03	−0.17
$H_2CH_3B\cdot N(CH_3)_2H$	$CDCl_3$	0.774	−2.49[d]	5	−3.98	−0.17
$H_2CH_3B\cdot N(CH_3)_2H$	$CDCl_3$	*e*	−2.49[d]	5	−3.95	−0.17

[a] Shifts measured in ppm from TMS, + (applied) downfield from TMS. [b] Typically at 10% by weight solution of a sample in the solvent. [c] Coupling constants measured in Hz. [d] Doublet. [e] The chemical shift at infinite dilution was determined by plotting known concentrations *vs.* chemical shift and extrapolating to infinite dilution.

Pyrex tube at 130° for 24 hr. Elemental silver and 1.44 mmol of H_2 were formed. The product was isolated and purified by sublimation at 25° to a −78° cold finger. The sublimate was identified as $H_2(CN)B\cdot N(CH_3)_3$ by its melting point, 62–63° (lit.[10] mp 63°), and spectral properties.

The compound $H_2(CN)B\cdot N(CH_3)_2H$ was prepared from $H_2(CN)B\cdot N(CH_3)_3$ by means of an amine-exchange reaction. The product $H_2(CN)B\cdot N(CH_3)_2H$ was purified by sublimation at 50° to a −78° cold finger. There was no sublimation at 25°, indicating all $H_2(CN)B\cdot N(CH_3)_3$ had reacted with $N(CH_3)_2H$. The compound $H_2(CN)B\cdot N(CH_3)_2H$ has a melting point of 56–57° and was further characterized by its spectral properties.

It should be noted that $H_3B\cdot N(CH_3)_3$ does not react with $Hg(CN)_2$ or AgCN in refluxing acetonitrile. In both cases, 98% of the $H_3B\cdot N(CH_3)_3$ was recovered unchanged. In addition, AgCN does not react with $H_2ClB\cdot N(CH_3)_3$ in CH_3CN.

Attempted Preparative Routes to Other Compounds. $H_2(OCN)B\cdot N(CH_3)_3$. A variety of routes were investigated in an attempt to prepare $H_2(OCN)B\cdot N(CH_3)_3$. After $H_2ClB\cdot N(CH_3)_3$ or $H_2BrB\cdot N(CH_3)_3$ and AgOCN were combined in acetonitrile at 25° or at reflux, the starting materials were recovered. The reaction of $H_3B\cdot N(CH_3)_3$ (3.00 mmol) with Ag(OCN) (3.01 mmol) at 110° in a sealed tube led to decomposition. Only H_2 (2.33 mmol) and $N(CH_3)_3$ (2.33 mmol) could be identified as products.

$H_2(SCN)B\cdot N(CH_3)_3$. The combination of the reagents $H_2(Cl)B\cdot N(CH_3)_3$ and KSCN in dimethoxyethane at reflux did not yield the desired product. The starting materials were recovered.

Infrared Spectra. The infrared spectra were recorded in the range 4000 to 400 cm^{-1} by means of a Perkin-Elmer 457 spectrometer. The spectra were recorded as $CHCl_3$ solutions or Nujol mulls.

The following gives the spectral frequencies in cm^{-1}. Band intensities are reported according to the method of Durkin, DeHayes, and Glore.[11]

$H_2ClB\cdot N(CH_3)_3$: 3018 (m), 2998 (m), 2920 (s), 2460 (s), 2420 (s), 1485 (s), 1465 (s), 1405 (w), 1134 (m), 1095 (m), 1010 (w), 985 (w), and 845 (w).

$H_2BrB\cdot N(CH_3)_3$: 3018 (m), 2998 (m), 2920 (s), 2480 (s), 2438 (m), 1485 (s), 1462 (s), 1405 (w), 1120 (m), 1080 (m), 1010 (w), 980 (w), and 847 (m).

$H_2CH_3B\cdot N(CH_3)_3$: 3018 (m), 2998 (m), 2920 (s), 2833 (m), 2320 (s), 2278 (s), 2240 (s), 1485 (s), 1465 (s), 1405 (w), 1308 (s), 1187 (m), 1153 (s), 1100 (m), 1000 (s), 840 (s), and 595 (w).

$H_2CNB\cdot N(CH_3)_3$: 2990 (m), 2955 (s), 2920 (w), 2411 (s), 2275 (w), 2240 (w), 2185 (w sh), 1475 (s), 1465 (s), 1410 (m), 1253 (m), 1171 (w), 1159 (s), 1096 (s), 1012 (m), 981 (m), 962 (m), and 860 (s).

$H_2ClB\cdot N(CH_3)_2H$: 3210 (s), 3010 (m), 2960 (m), 2440 (s), 2360 (m), 1475 (m), 1465 (m), 1407 (w), 1310 (m), 1190 (m), 1152 (s), 1095 (s), 1063 (m), 1027 (m), 1007 (w), 955 (w), 909 (s), 836 (m), 745 (m), and 687 (m).

$H_2CNB\cdot N(CH_3)_2H$: 3120 (s), 3010 (m), 2998 (m), 2955 (s), 2700 (m), 2415 (s), 2330 (w), 2229 (w), 2201 (w), 1410 (w), 1368 (m), 1196 (m), 1187 (m), 1172 (m), 1076 (s), 1033 (m), 967 (w), 927 (s), 778 (m), and 563 (m).

Nuclear Magnetic Resonance Spectra. The ^1H nmr spectra of the B-monosubstituted amine–boranes were recorded at 100 MHz by means of a Jeolco Model MH-100 spectrometer. Tetramethylsilane was used as the internal reference. The chemical shifts are given in Table I.

Results and Discussion

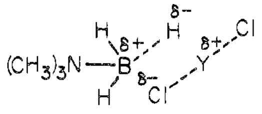
Metal salts, such as mercury(II) and silver(I) compounds, are important reagents for the synthesis of B-monosubstituted amine–boranes and borazines. As these metal salts react with both classes of boron compounds to give analogous products, it is possible to compare the reactivity of an amine–borane to that of a borazine. The following equations summarize the reactions of these types of metal salts with boron–hydrogen

$$-B-H + HgX_2 \rightarrow -B-X + Hg_2X_2 + HX \quad (X = Cl, Br) \tag{1}$$

$$-B-H + AgCN \rightarrow -B-CN + Ag + {}^1/_2H_2 \tag{2}$$

bonds. Amine–boranes are more reactive than borazines toward mercury (II) salts. For example, at 25° $HgCl_2$ reacts with both $H_3B\cdot N(CH_3)_3$ and $H_3B_3N_3H_3$[12] or $H_3B_3N_3(CH_3)_3$,[12] but $HgBr_2$ reacts with only $H_3B\cdot N(CH_3)_3$. The reagent $HgBr_2$ does not react with $H_3B_3N_3H_3$ under the conditions of our experiments. In contrast silver(I) salts are more reactive toward borazines than amine–boranes. The reagent AgCN reacts with $H_3B_3N_3H_3$ at 0° whereas $H_3B\cdot N(CH_3)_3$ requires temperatures of 130°. These differences in chemical reactivity between amine–boranes and borazines toward a given metal salt could be related to differences in bonding as well as differences in mechanisms of reactions.

All of the available data are consistent with the hypothesis that mercury(II) halides react with borazines[12,13] and amine–boranes by a polar mechanism which involves hydride transfer with a transition state[14] similar to I. Thus, the relative



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reactivity of a boron–hydrogen compound toward a given mercury(II) halide should depend on the magnitude of the partial negative charge on the hydrogen bound to boron, the partial positive charge on boron, and possibly steric effects. The less hydridic the hydrogen bound to boron, the less reactivity, if all other aspects are equivalent. Therefore, the available data on relative reactivity would suggest that $H_3B_3N_3H_3$ has less partial negative charge on the hydrogen bound to boron and/or less partial positive charge on boron than does $H_3B{\cdot}N(CH_3)_3$. The observation that acidic reagents,[15] such as HCl, initially add across the B–N bond in borazine rather than cleave the B–H bond, which occurs for amine–boranes, is also consistent but does not prove a decreased hydridic character of the hydrogen bound to boron in borazines. If a steric effect were the predominant factor affecting the reactivity of borazine toward HgX_2, borazine should have been much more reactive than the amine–borane. It is of interest to consider why the hydrogen bound to boron in $H_3B_3N_3H_3$ has a smaller partial negative charge and the boron a smaller partial positive charge compared to the corresponding atoms in an amine–borane. Both factors can be related to the partial π-electron delocalization[16,17] in the ring. π bonding *initially* gives the boron atoms a partial negative charge. However, the nitrogen atoms compensate for their donation of π-electron density by withdrawing electron density through the σ system and the B–H σ bond. Thus, a small positive charge is maintained on boron and the hydrogen bound to boron has less negative charge than a normal *B*-H. An alternative explanation for the decreased negative charge on hydrogen bound to boron in borazine compared to the same case in the amine–borane might be the differences in orbital hybridization and electronegativity.

The compounds $H_3B{\cdot}N(CH_3)_3$ and $H_3B_3N_3H_3$ exhibit very distinct differences in reactivity toward AgCN; $H_3B_3N_3H_3$ reacts at 0° whereas $H_3B{\cdot}N(CH_3)_3$ requires temperatures of 130°. This difference in reactivity could indicate a difference in mechanism. The ease of reaction of $H_3B_3N_3H_3$ might suggest that a π complex between the silver salt and the borazine is involved. In the case of amine–borane, the high reaction temperature and coordination saturation of the amine–borane might indicate that a free-radical mechanism or the dissociation of the adduct is required for reaction. However, as there are insufficient data on the mechanisms of these reactions, further discussion is not warranted at this time. It should be noted that the relative reactivity of silver(I) salts with $H_2ClB{\cdot}N(CH_3)_3$ and $H_2ClB_3N_3H_3$ to replace the chlorine is the same relative reactivity as that observed for the hydrogen bound to boron.

Table II. Relative ^1H Nmr Chemical Shifts[a]

Compd	Substituent			
	Cl	Br	CH_3	CN
	C-H Shifts			
$H_2XB{\cdot}N(CH_3)_3$	−0.03	−0.07	+0.10	−0.10
$H_2XB{\cdot}N(CH_3)_2H$	−0.10		+0.03	−0.11
$H_2XB_3N_3H_2(CH_3)$ (ortho CH_3)	+0.03	−0.05		−0.10[b]
$H_2XB_3N_3H_2(CH_3)$ (para CH_3)	+0.03	−0.02		−0.03[b]
	N-H Shifts			
$H_2XB{\cdot}N(CH_3)_2H$	−0.51		+0.29	−1.14
$H_2XB_3N_3H_3$ (ortho NH)	+0.12	−0.07	+0.35	−0.55
$H_2XB_3N_3$ (para NH)	+0.12	−0.07	+0.35	−0.55

[a] Relative chemical shift = parent − B-monosubstituted derivative: +, shift upfield; −, shift downfield from parent. [b] Data are for $H_2(CN)B_3N_3(CH_3)_3$.

The comparison of the ^1H nmr data (Table II) for the compounds $H_2XB{\cdot}N(CH_3)_3$, $H_2XB{\cdot}N(CH_3)_2H$, $H_2XB_3N_3(CH_3)_3$, and $H_2XB_3N_3H_3$ aids our understanding of substituent effects and the factors influencing the ^1H chemical shifts in boron–nitrogen compounds. The most important conclusion from these data is that a resonance effect between the substituent and the π-electron system of the borazine ring is responsible for the changes in the ^1H nmr chemical shift of the para NH proton in B-monosubstituted borazines ($H_2XB_3N_3H_3$). The substituent effect in $H_2XB_3N_3H_3$ is not, apparently, related to a field effect. Field effects are dependent on the distances between the substituent and the particular proton. If field effects were solely responsible for the relative chemical shifts in $H_2XB_3N_3H_3$ and amine–boranes, the chemical shift of the para NH in $H_2XB_3N_3H_3$ should be smaller than the ortho NH and smaller than the relative CH chemical shift of $H_2XB{\cdot}N(CH_3)_3$. The para NH in $H_2XB_3N_3H_3$ is at a greater distance from the substituent with more intervening bonds[5] than the ortho NH or the CH of the methyl group is from the substituent in $H_2XB{\cdot}N(CH_3)_3$. The relative shift of the para NH in $H_2XB_3N_3H_3$ is greater than the relative shift of the CH in $H_2XB{\cdot}N(CH_3)_3$. Furthermore, the para and ortho NH protons in these B-monosubstituted borazine derivatives have the same chemical shift. In contrast to the relative chemical shifts of NH protons in $H_2XB_3N_3H_3$, the relative chemical shifts of the CH protons in $H_2XB_3N_3(CH_3)_3$ might be due primarily to field effects. There is a correlation in both magnitude and direction between the ortho CH in $H_2XB_3N_3(CH_3)_3$ and the CH in $H_2XB{\cdot}N(CH_3)_3$ for Br and CN but not for Cl. Furthermore, the ortho and para *N*-methyl groups are distinguished in the spectra of $H_2XB_3N_3(CH_3)_3$. It should be noted that the substituent, chlorine, has been previously observed to influence the ^1H nmr of borazines in unusual ways. Correlations[3] were not observed when the ^1H nmr data of $H_{3-x}Cl_xB_3N_3H_3$ (x = 1–3) were compared. It is disappointing that a greater variety of substituents could not have been compared. The appropriate substituted amine–borane could not be prepared. More examples would help to clarify the situation further.

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Registry No. $H_2ClB{\cdot}N(CH_3)_3$, 5353-44-6; $H_2BrB{\cdot}N(CH_3)_3$, 5275-42-3; $H_2ClB{\cdot}N(CH_3)_2H$, 52920-74-8; $H_2BrB{\cdot}N(CH_3)_2H$, 52920-75-9; $H_2(CH_3)B{\cdot}N(CH_3)_3$, 52920-77-1; $H_2(CH_3)B{\cdot}N(CH_3)_2H$, 52920-78-2; $H_2(CN)B{\cdot}N(CH_3)_3$, 30353-61-8; $H_2(CN)B{\cdot}N(CH_3)_2H$, 51329-61-4; $H_3B{\cdot}N(CH_3)_3$, 75-22-9; $H_3B{\cdot}N(CH_3)_2H$, 74-94-2; *o*-$H_2ClB_3N_3H_2(CH_3)$, 37053-90-0; *o*-$H_2BrB_3N_3H_2(CH_3)$, 52920-79-3; $H_2(CN)B_3N_3(CH_3)_3$, 52920-80-6; *p*-$H_2ClB_3N_3H_2(CH_3)$, 36953-63-6; *p*-$H_2BrB_3N_3H_2(CH_3)$, 52920-81-7; $H_2ClB_3N_3H_3$, 15061-65-1; $H_2BrB_3N_3H_3$, 28019-98-9; $H_2(CH_3)B_3N_3H_3$, 21127-95-7; $H_2(CN)B_3N_3H_3$, 33926-69-1; $LiB(CH_3)H_3$, 52950-75-1; $N(CH_3)_3HCl$, 593-81-7.

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Gas-Phase Calorimetry of Trimethyl Group Va Bases with Boron Lewis Acids[1]

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The reaction between the group Va Lewis bases trimethylphosphine, trimethylarsine, and trimethylstibine and the boron Lewis acids boron trifluoride, boron trichloride, boron tribromide, diborane, and trimethylborane has been studied using gas-phase calorimetry. The heat of reaction, ΔH_{rxn}, at 25°, is reported for the reactions $(CH_3)_3M(g) + BX_3(g) \rightarrow (CH_3)_3M{\cdot}BX_3(s)$ for 11 of the 15 possible adducts. Trimethylborane underwent no reaction with either trimethylarsine or trimethylstibine, and trimethylstibine reacted anomalously with diborane and boron trifluoride. In general, the relative base strengths were in the order trimethylphosphine > trimethylarsine > trimethylstibine and the relative acid strengths were in the order boron tribromide > boron trichloride ≈ borane > boron trifluoride > trimethylborane.

Introduction

It is a generally accepted tenet that the Lewis basicity of trivalent group Va compounds decreases with the heavier congeners. Numerous studies have been concerned with the Lewis base interaction of amines and phosphines with boron Lewis acids;[2,3] however, few data are available for the arsines and stibines. We have used gas-phase calorimetry to evaluate the magnitude of the interaction between a set of boron Lewis acids and trimethylarsine and trimethylstibine. As a reference point, we have also examined by the same technique the adducts of trimethylphosphine.

Experimental Section

Preparations. (a) Trimethylphosphine. Trimethylphosphine[4] was prepared by the dropwise addition of 13.75 g (0.1 mol) of phosphorus trichloride to an ethereal solution containing a slight excess of methylmagnesium iodide under inert atmosphere. The trimethylphosphine and ether were distilled onto an aqueous solution containing 47.0 g (0.2 mol) of silver iodide, and the trimethylphosphine was isolated as the trimethylphosphine–silver iodide complex.[5] The complex was decomposed by mild heating under vacuum and the trimethylphosphine was purified *via* trap-to-trap distillation using an ethyl acetate (−83.6°) slush bath to trap the trimethylphosphine. The purity of the trimethylphosphine was confirmed by its vapor pressure[6] and gas-phase ir[7] and ^1H nmr[8] spectra.

(b) Trimethylarsine. Trimethylarsine[9] was prepared by the dropwise addition of a solution of 18.15 g (0.1 mol) of arsenic trichloride in 125 ml of xylene to a solution containing a slight excess of methylmagnesium iodide in *n*-butyl ether under an inert atmosphere. The temperature of the reaction was kept well below 50°. The trimethylarsine was distilled into a three-necked flask fitted with suitable stopcocks to allow direct transfer to a high-vacuum system. The trimethylarsine was purified using standard trap-to-trap distillation procedures with an ethyl acetate (−83.6°) slush bath used to trap the purified product. The purity of the product was verified by its vapor pressure[6] and gas-phase ir[10] and ^1H nmr spectra.[8]

(c) Trimethylstibine. Trimethylstibine[11] was prepared by the dropwise addition of an ethereal solution of 22.8 g (0.1 mol) of antimony trichloride to a solution containing excess methylmagnesium iodide in diethyl ether under inert atmosphere. The ether and trimethylstibine were distilled into a three-necked flask with maintenance of the inert atmosphere. The trimethylstibine was converted to trimethylantimony dibromide[12] by the addition of a solution of elemental bromine in carbon tetrachloride to the ethereal solution of trimethylstibine until the brown color of the bromine solution persisted. The trimethylantimony dibromide which resulted was air stable and was readily purified by filtration. The trimethylantimony dibromide was reduced by the action of granular zinc and water to yield trimethylstibine which was collected on a vacuum line and purified by trap-to-trap distillation. A chloroform slush bath (−63°) was used to collect the trimethylstibine. Vapor pressure measurements[6] and gas-phase ir[13] and ^1H nmr[8] spectra were used to verify the purity of the trimethylstibine.

(d) Trimethylborane. Trimethylborane[14] was prepared by the slow dropwise addition of a solution of 26 ml (0.1 mol) of BF_3 etherate in 200 ml of ether to excess methylmagnesium iodide in ether at 0°. The trimethylborane was collected in a trap at liquid nitrogen temperature (−196°) using a dry nitrogen carrier gas system. A Dry Ice–acetone slush bath (−78°) was used to trap out the diethyl ether in the product stream. The trimethylborane was transferred to a high-vacuum system and purified by conventional trap-to-trap distillation techniques, using a carbon disulfide slush bath (−112°) to trap the trimethylborane. Purity of the trimethylborane was confirmed by vapor pressure measurements.[15]

(e) Diborane. Diborane[16] was produced by the action of 1.6 g (0.029 mol) of potassium borohydride on 30 ml of 85% phosphoric acid (orthophosphoric acid) in an apparatus attached to a high-vacuum system. Diborane was trapped in a liquid nitrogen trap (−196°) and was purified by repeated passage through a trap held at −112° (carbon disulfide slush) to remove any less volatile materials. Purity of the diborane was verified *via* gas-phase ir spectroscopy[17] and vapor pressure measurements.[16]

(f) Boron Tribromide. Boron tribromide was obtained commercially (Alfa) and was purified on a high-vacuum system by trap-to-trap distillation using a chlorobenzene (−45°) slush bath to trap the boron tribromide. The purity of the boron tribromide was confirmed by vapor pressure measurements[18] and gas-phase ir spectroscopy.[19]

(g) Boron Trichloride. Boron trichloride was obtained commercially (Matheson Gas Products) and purified on a high-vacuum system by trap-to-trap distillation using a carbon disulfide (−112°) slush bath to trap the pure boron trichloride. The purity of the boron trichloride was checked by vapor pressure measurements[20] and ir spectroscopy.[21]

(h) Boron Trifluoride. Boron trifluoride was obtained commercially (Matheson Gas Products) and purified on a high-vacuum system by trap-to-trap distillation using a trap at liquid nitrogen (−196°) temperature to hold the purified boron trifluoride. The purity of the boron trifluoride was confirmed by vapor pressure measurements[22] and gas-phase ir spectroscopy.[23]

Calorimetry. (a) Calorimeter. The calorimeter used in these experiments was of the constant-temperature environment type.[24] All reactions were run at 25.00°. The temperature of the bath surrounding