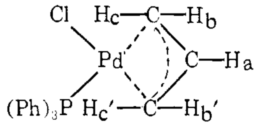
of the terminal protons first broadens; then the *cis* protons and the *trans* protons converge into two broad bands at about 30°. This change is attributed to the exchange of the Cl and $(Ph)_3As$ ligands which occurs at a higher temperature than that for the Cl–DMSO-d_6 exchange. As the temperature is further increased the two broad bands coalesce into a sharp doublet, and this is attributed to the π to σ equilibration which may be followed by a head-over-tail equilibration.

Further evidence for the proposed equilibrations was obtained from the $(Ph)_3P$ adduct of allylpalladium(II) chloride, and the temperature dependence of the nmr spectrum of the product is shown in Figure 4. Again the spectrum of the low-temperatue species shows five resonances. An assignment of the resonances to the four terminal b,c and b′,c′ protons, as depicted in the following structure, was made on the basis that the *trans* couplings $J_{P-H_b \text{ or } P-H_c}$ are expected to be larger than the *cis* couplings $J_{P-H_{b'} \text{ or } P-H_{c'}}$.[12] As the temperature is increased, the resonances for the terminal protons broaden, but the two *cis* protons and the two *trans* protons do not converge at 60°, which is about the upper limit for the system. The spectrum of the complex in solution in $o\text{-}C_6H_4Cl_2$, as obtained at 90 and 140°, shows that the complex is undergoing similar transitions as was observed for the DMSO-d_6 and $(Ph)_3As$ adducts.



Further proof for the ligand-exchange process was obtained by the addition of the allylpalladium(II) chloride dimer to a solution of the triphenylphosphine–allylpalladium(II) chloride adduct in $CDCl_3$. The spectrum of the mixture at 30° yielded sharp resonances for the dimer which was superimposed upon the broad bands of the triphenylphosphine adducts' resonances. Upon heating to 70°, the spectrum indicated that the species interact. The sharp resonances of the dimer first broaden and then converge with the broader bands for the adduct. Upon cooling to 30°, the sharp resonances reappear and the spectrum corresponds to the original mixture. The spectrum of the allylpalladium(II) chloride dimer in $CDCl_3$ did not change significantly over the corresponding temperature range 30–70°.

Although nmr spectra are sensitive to exchange processes, the mechanisms deduced from the spectra are certainly not unambiguous. A second mechanism which could explain, at least in part, the temperature dependence of the nmr spectra of the DMSO-d_6, $(Ph)_3As$, and $(Ph)_3P$ adducts of allylpalladium(II) chloride is that of a rotational process which has been postulated for the temperature dependence of the nmr spectrum of $\pi\text{-}C_6H_5CH_2Mo(CO)_2C_5H_5$.[13] Rotation of the allyl group by 180° seems somewhat improbable primarily because of the steric interaction of proton a (Table I). Furthermore, a detailed analysis of the systems involved, particularly that for the DMSO-d_6 adduct, shows that the sharp doublet as observed at the higher temperatures does not fall midway between that of the *cis* and the *trans* resonances as observed at the lower temperatures.

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(12) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

(13) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

Boron Heterocycles. III. The Effect of Borane Lewis Acid on Apparent Base Strength. New Examples of Base Strength Reversal[1,2]

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Abstract: A study of adducts of several Lewis acids including boron heterocycles containing terminal B–H bonds has led to the conclusion that the relative base strength with respect to a reference acid depends, principally, upon the strength of the acid and not necessarily upon supplementary π-type bonding involving d orbitals on phosphorus or sulfur ligand atoms. Homogeneous displacement reactions, vapor density studies, and qualitative kinetic observations suggest the apparent relative base strengths with respect to acid strength as shown in sequence 3. Results from the BH_3 system fully confirm earlier work.[3] It is believed that the order of base strength depends upon the strength of the σ bond formed between boron and the donor atom, and, as the acid becomes increasingly stronger, the tendency to reverse the normal order of base strength increases so that P > N and S > O. Nmr spectroscopy has proved to be useful in examining equilibrium distributions of adducts in solution.

Earlier work in this laboratory has shown that $\underline{SCH_2CH_2SB}HN(CH_3)_3$ is much more stable with respect to dissociation than $\underline{OCH_2CH_2OB}HN(CH_3)_3$.[2] This is consistent with observations made on the boron halides, that as one proceeds from BF_3 to BCl_3 to BBr_3

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(1) Presented before the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) Part I: S. H. Rose and S. G. Shore, *Inorg. Chem.*, **1**, 744 (1962); part II: B. Z. Egan, S. G. Shore, and J. E. Bonnell, *ibid.*, **3**, 1024 (1964).

(3) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

the effect of substituent halogen on boron is to increase the apparent acceptor character of boron.[4] This order of acceptor character has been rationalized by means of an argument which considers the relative ability of halogen to back-bond or π bond as one proceeds down the group.[4]

It has been found, using BF_3 as a reference acid, that nitrogen bases are stronger than phosphorus bases, and oxygen bases are stronger than sulfur bases.[3,5,6] Thus, for example, the following orders of stability have been observed: $BF_3N(CH_3)_3 > BF_3P(CH_3)_3$; $BF_3O(CH_3)_2 > BF_3S(CH_3)_2$. The ordering of base strength cited above has been referred to as a "normal order," being generally expected for Lewis bases reacting with a reference acid.[7] However, exceptions to this order have been observed, the most notable ones involving BH_3 as the reference acid:[3,6] $BH_3P(CH_3)_3 > BH_3N(CH_3)_3$; $BH_3S(CH_3)_2 > BH_3O(CH_3)_2$. Attempts to explain or account for reverse order of base strength have in general assumed that the electron densities of the B–H bonds can in some way interact with the d orbitals on phosphorus and sulfur, thereby adding an additional increment of stability, increasing the apparent base strength over that base which does not have d orbitals available.[7,8] It has been assumed, tacitly, that this property to interact with the d orbitals of phosphorus and sulfur is unique to the hydrogen of the B–H bond for boron Lewis acids.

The possibility that our oxygen- and sulfur-containing heterocycles might produce a reverse order of base strength was of considerable interest to us since it would represent the first information concerning the effect of substituent groups on boron with respect to relative base strength when there is but one hydrogen on boron. It was decided, therefore, to examine the relative stabilities of the trimethylamine and trimethylphosphine adducts of these compounds and several other selected Lewis acids.

Results

Observed relative stabilities of the adducts of the heterocycles prepared in this investigation are reported in Table I. Before considering the relative order of base strength, the appreciable difference in apparent acceptor character between the sulfur-containing and oxygen-containing heterocycles should be noted. The data above not only follow the boron halide case where $BF_3 < BCl_3$ with respect to acceptor character, but differences in acceptor character are much more marked.

Table I. Relative Stabilities of Adducts

Adduct	State	Temp, °C	Equilibrium pressure above solid
$\underline{\mathrm{SCH_2CH_2SB}}\mathrm{HN(CH_3)_3}$	Solid	70	*Ca.* 2 mm, no apparent dissociation
$\underline{\mathrm{SCH_2CH_2SB}}\mathrm{HP(CH_3)_3}$	Solid	70	*Ca.* 2 mm, no apparent dissociation
$\underline{\mathrm{OCH_2CH_2OB}}\mathrm{HN(CH_3)_3}$	Solid	25	*Ca.* 10 mm, completely dissociated
$\underline{\mathrm{OCH_2CH_2OB}}\mathrm{HP(CH_3)_3}$	Solid		Above −45°, existence of adduct could not be detected

The amine and phosphine adducts of $\underline{\mathrm{SCH_2CH_2SB}}\mathrm{H}$ sublime quantitatively. No indication of dissociation in the vapor phase is observed. On the other hand, infrared and vapor density studies clearly show that the corresponding adducts of the oxygen-containing heterocycles are completely dissociated in the vapor phase.[9] Whereas the adducts of $\underline{\mathrm{SCH_2CH_2SB}}\mathrm{H}$ appear to be of comparable order of stability on the basis of the qualitative observations given above,[2] the amine adducts of the oxygen-containing heterocycles are significantly more stable than the phosphine adducts.[9] Thus, in the case of the oxygen-containing heterocycles, the normal order of base strength N > P appears to be maintained.

To determine the order of base strength for those adducts of comparable stability, homogeneous displacement reactions in glyme and in tetrahydrofuran at 25° were carried out.[10] The following reactions were studied in the forward and reverse directions and the equilibrium distributions were determined through chemical analyses. Only when the systems were allowed to react for several days were reproducible distributions obtained for both the forward and reverse reactions, indicating that the attainment of equilibrium required a period of at least several days.

$$BH_3N(CH_3)_3 + P(CH_3)_3 \rightleftharpoons BH_3P(CH_3)_3 + N(CH_3)_3 \quad (1)$$

Initial conditions	% distribution of BH_3 in equilibrium mixture	
Forward and reverse reactions were started with equimolar mixtures of adduct plus base	$BH_3P(CH_3)_3$	80 ± 3
	$BH_3N(CH_3)_3$	20 ± 3

$$\underline{\mathrm{SCH_2CH_2SB}}\mathrm{HN(CH_3)_3} + \mathrm{P(CH_3)_3} \rightleftharpoons \underline{\mathrm{SCH_2CH_2SB}}\mathrm{HP(CH_3)_3} + \mathrm{N(CH_3)_3} \quad (2)$$

Initial conditions	% distribution of BH_3 in equilibrium mixture	
Forward and reverse reactions were started with equimolar mixtures of adduct plus base	$\underline{\mathrm{SCH_2CH_2SB}}\mathrm{HP(CH_3)_3}$	66 ± 2
	$\underline{\mathrm{SCH_2CH_2SB}}\mathrm{HN(CH_3)_3}$	34 ± 2

The results from system 1 fully confirm earlier work;[3] reverse order of apparent base strength P > N is observed. From system 2 it is clear that this same order is maintained when the reference acid is $\underline{\mathrm{SCH_2CH_2SB}}\mathrm{H}$; however, the apparent difference in base strength is slightly diminished.

Table II presents B^{11} nmr data obtained in this laboratory.

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(4) H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

(5) T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *ibid.*, **81**, 2989 (1959).

(6) W. A. G. Graham and F. G. A. Stone, *Chem. Ind.* (London), 319 (1956).

(7) (a) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958); (b) T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).

(8) A. B. Burg, *J. Chem. Educ.*, 37, 482 (1960).

(9) G. E. McAchran and S. G. Shore, *Inorg. Chem.*, in press.

(10) The adducts studied in this investigation were either so stable or so unstable that vapor phase dissociation studies were precluded. Calorimetric determination of heats of formation of the adducts were also precluded because of the difficulty of handling trimethylphosphine and because the heterocycle $\underline{\mathrm{SCH_2CH_2SB}}\mathrm{H}$ is associated in the solid state and dissolves only slowly in coordinating solvents such as tetrahydrofuran.

Table II. Nmr Data

Compound	δ,[d] ppm (with respect to $(CH_3O)_3B$)	J_{BH}, cps	J_{PB}, cps	Solvent
$\underline{SCH_2CH_2SB}ClN(CH_3)_3$	+ 1.1			$C_6H_5NO_2$
$\underline{SCH_2CH_2SB}ClP(CH_3)_3$	+14.5		144	$C_6H_5NO_2$
$\underline{SCH_2CH_2SB}HP(CH_3)_3$	+12.4	128		THF
$\underline{SCH_2CH_2SB}HP(CH_3)_3$	+29.6	115	84	THF
$\underline{OCH_2CH_2OB}HN(CH_3)_3$[c]	+10.6	127		CH_2Cl_2
$(CH_3)_3NBH_3$	+26.4[a]	98[a]		Glyme
$(CH_3)_3PBH_3$	+56.5[a]	95[a]	62[a]	Glyme
$(CH_3)_3NBF_3$	+17.7[a]			CH_2Cl_2
$(CH_3)_3PBF_3$	+17.3[a]		174[a]	CH_2Cl_2
$(CH_3)_3NBCl_3$	+ 8.5			Glyme
$(CH_3)_3PBCl_3$	+15.3		166	Glyme
$(CH_3)_3NBBr_3$	+22.6			$CHCl_3$
$(CH_3)_3PBBr_3$	+32.8		165	$CHCl_3$
$(CH_3)_2OBH_3$[c]	+15.8	106		$(CH_3)_2O$
$(CH_3)_2SBH_3$	+38.4	104		CH_2Cl_2
$(CH_2)_4OBH_3$[b]	+19.0	103		...
$(CH_2)_4SBH_2$	+38.4	104		CH_2Cl_2
$(CH_3)_2OBF_3$	+21.2			CH_2Cl_2
$(CH_3)_2SBF_3$	+15.5			CH_2Cl_2
$(CH_3)_2OBCl_3$	+ 6.8			$C_6H_5NO_2$
$(CH_3)_2SBCl_3$	+10.8			$C_6H_5NO_2$
$(CH_2)_4OBF_3$[b]	+19.0			...
$(CH_2)_4SBF_3$	+14.8			CH_2Cl_2
$(CH_2)_4OBCl_3$	+ 7.9			THF
$(CH_2)_4SBCl_3$	+10.2			$(CH_2)_4S$

[a] These data are in good agreement with results of other investigations: D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **86,** 1505 (1964); C. W. Heitsch, *Inorg. Chem.*, **4,** 1019 (1965). [b] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81,** 4496 (1959). [c] Because of the instability of these compounds at room temperature, the B^{11} nmr spectra were obtained at −25° for $\underline{OCH_2CH_2OB}NH(CH_3)_3$ and from −25 to −85° for $(CH_3)_2OBH_3$. [d] Chemical shift values are in general ±0.5 ppm; values of J are in general about ±1 cps.

An interesting feature of the spectra is that the chemical shift for the adduct of a given reference acid with a sulfur base is significantly different from that of an adduct of the same acid with the analogous oxygen base. With the exception of $(CH_3)_3NBF_3$ and $(CH_3)_3PBF_3$, significant differences in the chemical shift are also observed for the trimethylamine and trimethylphosphine adducts of given reference acids. Furthermore, with the exception of the BF_3 adducts, the shift involving the sulfur or phosphorus base is to a higher field than the corresponding adduct involving the oxygen or nitrogen base, suggesting, perhaps, that the electron density on boron is greater in the sulfur and phosphorus adducts than the corresponding oxygen or nitrogen adducts. If this is indeed the case, then one might expect to observe a reverse order of base strength when BCl_3 or BBr_3 is the Lewis acid.

To test the suggestion given above, homogeneous displacement reactions and equilibration reactions involving equimolar amounts of trimethylamine and trimethylphosphine with Lewis acids were studied, using nmr spectra of the equilibrium mixtures to obtain relative distributions of amine and phosphine adducts. The same procedure was used to determine the relative base strengths of $(CH_3)_2O$ and $(CH_3)_2S$ with respect to BCl_3. Figure 1 shows the B^{11} nmr spectra of the individual adducts and the spectrum of an equilibrium mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3PBH_3$. Spectra taken of the day-to-day progress of the equilibrium showed that equilibrium was attained in 3 days at 25°. Clearly, $(CH_3)_3PBH_3$ exists in larger concentration. The areas under the curves give relative amounts of adducts (77% $(CH_3)_3PBH_3$ and 23% $(CH_3)_3NBH_3$) which are in very good agreement with analytical data obtained by direct chemical analysis of the equilibrium mixture. Figure 2 shows the H^1 nmr spectrum of the same equilibrium mixture. The signals in the figure are due to the methyl hydrogens of the adducts, and integration of the curves gives a 4:1 ratio of $(CH_3)_3PBH_3$ to $(CH_3)_3NBH_3$, in excellent agreement with the analytical data.

Figure 3 shows the B^{11} nmr spectra of the individual adducts and the spectrum of an equilibrium mixture of trimethylamine–boron trifluoride and trimethylphosphine–boron trifluoride. The concentration of the trimethylphosphine–boron trifluoride in the equilibrium mixture is so small as to be undetectable by B^{11} nmr. Equilibrium was reached rapidly in this experiment requiring only a few minutes. The results of this experiment are in accord with earlier work done on this system.[3]

Figure 4 shows the B^{11} nmr spectra of the individual adducts of BCl_3, the spectrum of a mixture of trimethylamine–boron trichloride and trimethylphosphine–boron trichloride after 1 day of equilibration time, and the spectrum of the same mixture after 3 days. The concentration of the trimethylamine–boron trichloride in the equilibrium mixture is so small as to be undetectable by B^{11} nmr. As the system approached equilibrium, the peak attributed to the trimethylamine adduct diminished in size until it disappeared. This result has been duplicated in two solvents ($CHCl_3$ and $C_6H_5NO_2$), providing strong evidence that when BCl_3 is the reference acid the reverse order of apparent base strength, P > N, occurs. It is of interest to note the marked difference in time to reach equilibrium for the BF_3 system as opposed to the $\underline{SCH_2CH_2SB}H$, BH_3, and BCl_3 systems.

The only signal observed in the B^{11} nmr spectrum of an equilibrium mixture of equimolar amounts of $(CH_3)_2O$ and $(CH_3)_2S$ with BCl_3 was that due to $(CH_3)_2SBCl_3$, indicating that with BCl_3 the order of apparent base strength S > O occurs.

Discussion

The results of this investigation provide new examples of Lewis acids which cause apparent reversal of base strength. For the acids $\underline{SCH_2CH_2SB}H$ and BCl_3, trimethylphosphine is a stronger Lewis base than trimethylamine, while the normal order of base strength is observed for $\underline{OCH_2CH_2OB}H$.

Base strength reversal in the case of BH_3 adducts has been accounted for by the suggestion that the three hydrogens of BH_3 form a group orbital of π symmetry which can overlap with a vacant d orbital on a ligand atom such as phosphorus or sulfur, thereby supplementing the σ bond and enhancing the stability of the compound.[3] Other than the observed relative sta-

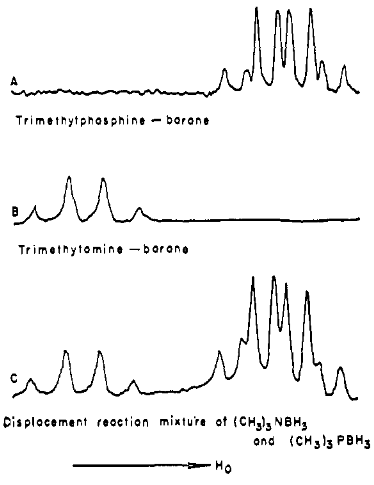

Figure 1. B^{11} nmr spectra of: A, $(CH_3)_3PBH_3$; B, $(CH_3)_3NBH_3$; C, equilibrium mixture of the two adducts from displacement reaction.

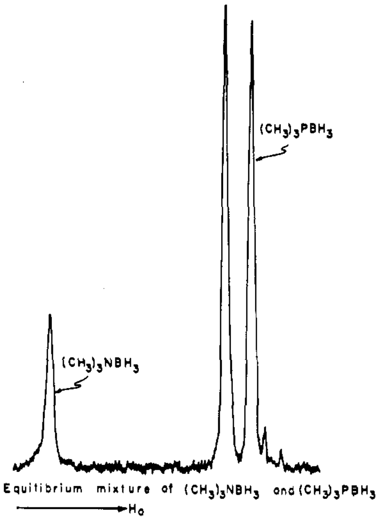

Figure 2. Proton nmr spectrum of same equilibrium mixture as shown in Figure 1. The signals are due to the methyl hydrogens of the two adducts.

bilities, there is little in the way of physical evidence to support the contention that π bonding, which is possible in principle, is the prime reason for base strength reversal.

Shifts to higher stretching frequencies in the compound $(CH_3)_2SBH_3$ compared to $(CH_3)_2OBH_3$ have been considered to offer some support for back-bonding.[7] Similar shifts have been noted in the complex $(CH_3)_3PBH_3$ compared to $(CH_3)_3NBH_3$. It has been suggested that "If back-donation occurs, the net charge transfer to boron will be reduced, and this could account for the high B–H stretching frequency."[7] However, detailed analyses of the vibrational spectra of these systems have not yet been reported. If is of interest to note that a shift to a lower stretching frequency is observed in the systems cited below.

$\underbrace{\mathrm{SCH_2CH_2SB}}\mathrm{HN(CH_3)_3}$ (solution) 2421 cm^{-1}

$\underbrace{\mathrm{SCH_2CH_2SB}}\mathrm{HP(CH_3)_3}$ (solution) 2358 cm^{-1}

Proton chemical shift data suggest that less charge transfer from sulfur to boron occurs in BH_3 complexes

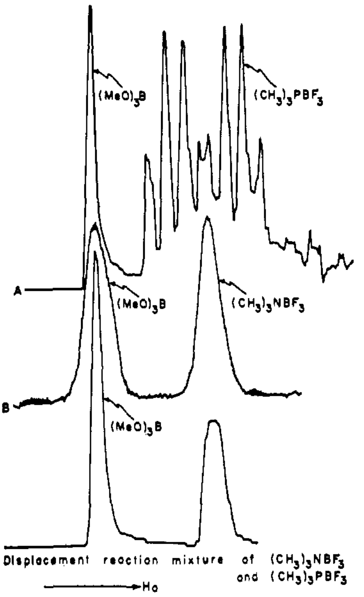

Figure 3. B^{11} nmr spectra of: A, $(CH_3)_3PBF_3$; B, $(CH_3)_3NBF_3$; C, equilibrium reaction mixture of the two adducts from displacement reaction.

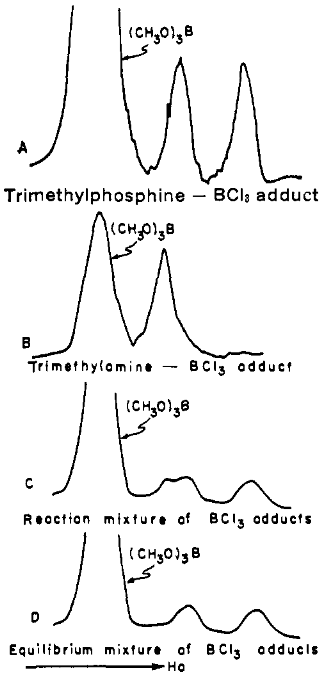

Figure 4. B^{11} nmr spectra of: A, $(CH_3)_3PBCl_3$; B, $(CH_3)_3NBCl_3$; C, reaction mixture of the two adducts 24 hr after the start of the equilbration; D, equilibrium mixture of the two adducts 3 days after the start of the equilbration.

than in sulfur complexes of weaker Lewis acids.[7,11] Bearing in mind the inherent danger in interpreting the chemical shift on a simple basis or in terms of one principal factor, when we examine the difference in B^{11} chemical shift (see Table II) for an oxygen adduct compared to a sulfur adduct of BH_3 or an acid stronger than BH_3, the shift is to a higher field for the sulfur adduct than the corresponding oxygen adduct, implying greater transfer of charge to the boron by sulfur than

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[11] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4318 (1961).

oxygen. When the acid is weaker than BH_3 the relative positions of the chemical shifts are reversed, suggesting that less charge is transferred from sulfur to boron than from oxygen to boron in the corresponding compounds. The same general observations hold true for phosphorus and nitrogen adducts also.

The magnitude of spin coupling through a bond has been shown, on theoretical grounds, to depend upon the s character of the bond.[12–15] In principle, therefore, spin-coupling values should reflect the hybridization in the B–H bond. An interesting point concerning the spectra of the BH_3 adducts is that the B–H coupling constants for the phosphorus and nitrogen adducts and for the sulfur and oxygen adducts show little or no difference (see Table III). These data can be compared with analogous cases in C^{13} nmr spectroscopy where it has been shown that there is little difference in the C–H coupling constants in going from $-OCH_3$ to $-SCH_3$ and in going from FCH_3 to $ClCH_3$.[16] The H–C–H bond angles have been shown to be very nearly equal in each pair of compounds, indicating that elements in the same subgroup can have quite similar influences on C^{13} hybridization. A similar interpretation of the B–H coupling constant data suggests that the hybridization of boron is the same in the phosphorus and nitrogen adducts and in the sulfur and oxygen adducts, thus providing some argument against back-bonding since one might expect π involvement of B–H hydrogen with phosphorus or sulfur to alter significantly the hybridization of boron in these compounds compared to the corresponding nitrogen and sulfur adducts. Unfortunately the qualitative implications of the spin-coupling data with respect to hybridization are not necessarily assured a basis in fact.

Table III. B–H Spin–Spin Coupling Constants

Complex	J_{B-H}, cps
$(CH_3)_3NBH_3$	98
$(CH_3)_3PBH_3$	95
$(CH_3)_2OBH_3$	106
$(CH_3)_2SBH_3$	104
$(CH_2)_4OBH_3$	103
$(CH_2)_4SBH_3$	106

It is generally believed that the normal order N > P and O > S would be observed for adducts of the boron halides.[17] However, there is no previous published record of studies of apparent base strengths of trimethylamine and trimethylphosphine or dimethyl ether and dimethyl sulfide with respect to a boron halide other than boron trifluoride. In view of the absence of strong evidence that π bonding of the B–H bonding electrons with d orbitals of phosphorus and sulfur is the principal cause of base-strength reversal, plus the fact that the order P > N and S > O is observed for BCl_3, we prefer, for the time being, to minimize the importance of this type of interaction in determining the order of base strength in systems of the type studied in this investigation. In effect our approach to the question of base strength reversal is a correlative one in which it is assumed that the apparent order of base strength of trimethylamine and trimethylphosphine or dimethyl ether and dimethyl sulfide depends upon the ability of the Lewis acid to form a σ bond between boron and the donor atom. In essence it is thought that as the Lewis acid becomes increasingly stronger (*e.g.*, the boron halides) the tendency to reverse the normal order of base strength increases.

Consider the oxygen- and sulfur-containing heterocycles which were studied in this investigation. 1,3,2-Dioxaborolane is a very weak Lewis acid. The apparent order of base strength is N > P when it serves as the reference acid. On the other hand, in the case of 1,3,2-dithioboralane which is a strong Lewis acid, the apparent order of base strength is P > N. Boron trichloride which is a stronger Lewis acid than boron trifluoride produces P > N while the latter compound produces N > P. This trend suggests that BH_3 and $\underline{SCH_2CH_2SBH}$ should be stronger Lewis acids than BF_3 since they produce the order P > N. Indeed, if we accept recent values for the dissociation energy of the bridge system of B_2H_6, then BH_3 is a stronger Lewis acid than BF_3 on the basis of thermodynamic data which have been reported for the following reactions.

$$\tfrac{1}{2}B_2H_6(g) + C_5H_5N\,(\text{in nitrobenzene}) = C_5H_5NBH_3\,(\text{in nitrobenzene}) \qquad \Delta H = -17.9\ \text{kcal/mole}^{18}$$

$$BH_3(g) = \tfrac{1}{2}B_2H_6(g) \qquad \text{Recent value } \Delta H = -\tfrac{1}{2}[35\ \text{kcal/mole}]^{19} \qquad \Delta H = -\tfrac{1}{2}[37\ \text{kcal/mole}]^{20}$$

$$BH_3(g) + C_5H_5N\,(\text{in nitrobenzene}) = C_5H_5NBH_3\,(\text{in nitrobenzene}) \qquad \Delta H \sim -36\ \text{kcal/mole}$$

$$BF_3(g) + C_5H_5N\,(\text{in nitrobenzene}) = C_5H_5NBF_3\,(\text{in nitrobenzene}) \qquad \Delta H = -32.9\ \text{kcal/mole}^{21}$$

$$BCl_3(g) + C_5H_5N\,(\text{in nitrobenzene}) = C_5H_5NBCl_3\,(\text{in nitrobenzene}) \qquad \Delta H = -44.0\ \text{kcal/mole}^{4,22}$$

Furthermore, the rates at which equilibria are achieved in the systems studied in this investigation provide

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(12) N. Muller and D. E. Pritchard, *J. Chem., Phys.*, **31**, 768 (1959).

(13) N. Muller and D. E. Pritchard, *ibid.*, **31**, 1471 (1959).

(14) J. N. Shoolery, *ibid.*, **31**, 1472 (1959).

(15) R. E. Williams, K. M. Harmon, and J. R. Spielman, *U. S. Govt. Res. Rept.* **39** (19), 22 (AD 603782) (1964).

(16) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(17) The statement that the order of base strength with BX_3 should be $R_2O > R_2S > R_2Se$ and $R_3N > R_3P > R_3As > R_3Sb$ has been attributed to H. C. Brown in the literature by other authors *via* private communication: T. D. Coyle, H. D. Kaesz, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 2989 (1959); R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(18) H. C. Brown and L. Domash, *J. Am. Chem. Soc.*, **78**, 5384 (1956).

(19) A. B. Burg and Y.-C. Fu, *ibid.*, **88**, 1147 (1966).

(20) (a) T. D. Fehler and W. S. Koski, *ibid.*, **87**, 409 (1965); (b) M. E. Garabedian and S. W. Benson, *ibid.*, **86**, 176 (1964). These authors have set an upper limit of 38 kcal/mole and a lower limit of 35–32 kcal/mole for the dissociation energy of diborane.

(21) R. C. Brown and O. Gintis, *ibid.*, **78**, 5378 (1956).

(22) The value obtained here was calculated from the original value of Brown and Holmes taking into consideration the heats of vaporization of BCl_3 according to the following thermodynamic cycle.

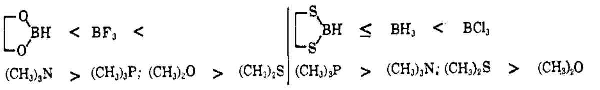
$$BCl_3(l) + C_5H_5N\,(\text{in nitrobenzene}) = C_5H_5NBCl_3\,(\text{in nitrobenzene}) \qquad \Delta H = -39.5\ \text{kcal/mole}$$

$$BCl_3(g) = BCl_3(l) \qquad \Delta H = -4.5\ \text{kcal/mole}$$

$$BCl_3(g) + C_5H_5N\,(\text{in nitrobenzene}) = C_5H_5NBCl_3\,(\text{in nitrobenzene}) \qquad \Delta H = -44.0\ \text{kcal/mole}$$

support for the contention that BF_3 is a weaker Lewis acid than $\underline{SCH_2CH_2S}BH$, BH_3, and BCl_3. The equilibration reactions with $(CH_3)_3N$ and $(CH_3)_3P$ appeared to be complete within minutes for the systems involving BF_3. On the other hand, the equilibration reactions with $(CH_3)_3N$ and $(CH_3)_3P$ in which the other Lewis acids were involved required days to achieve equilibrium.

The following order (3) of acceptor character and orders of base strength are suggested from the results of this investigation and earlier studies. Although



(3)

equilibration reactions were not carried out using the bases $(CH_3)_2O$ and $(CH_3)_2S$ in the present study for any of the Lewis acids other than BCl_3, earlier work on BH_3 and BF_3 plus the correlation of chemical shift data in Table II suggest an ordering of base strength similar to trimethylamine and trimethylphosphine with the acids shown above. However, because relatively few systems have been studied to date, application of the chemical shift as the sole criterion of whether normal or reverse order of base strength occurs should be used with reservation in spite of the consistency in results observed in the present investigation.

Because the equilibration reactions are measures of free-energy differences rather than enthalpy differences, the order of apparent base strength might not reflect orders based on enthalpy measurements because of entropy effects. However, there are very few examples in boron acid–base chemistry in which enthalpy and free-energy measurements do not parallel each other.[7]

By taking into account the polarizabilities of acids and bases, a great many qualitative observations can be correlated.[23] The most recent treatment employs the terminology hard and soft acids and bases. The results of this study can be correlated in a similar manner. It is of interest to note, however, that BCl_3 would be considered a soft acid instead of a hard one as previously suggested.

Experimental Section

Trimethylamine and Trimethylphosphine. Reagent grade trimethylamine was dried at 0° with CaH_2 under a high vacuum system. The dry material was measured as a gas by standard methods in a calibrated distillation train and was distilled into the cold reaction vessel at room temperature.

Trimethylphosphine was prepared from the reaction of methylmagnesium bromide with PCl_3 in ether. The trimethylphosphine was stabilized as the solid tetrameric monoiodotrimethylphosphine–silver complex, $[(CH_3)_3PAgI]_4$, by reaction with silver iodide in aqueous potassium iodide solution.[24,25] The trimethylphosphine was freed from the complex at elevated temperatures. The vapor pressure of the pure substance was measured as 161 mm at 0°. It was measured as a gas in a calibrated distillation train and was distilled into the cold reaction vessel at room temperature.

Dimethyl Ether, Dimethyl Sulfide, and Tetrahydrothiophene. Reagent grade dimethyl ether was dried at $-80°$ with $LiAlH_4$ under high vacuum. The dry material was measured as a gas by standard methods in a calibrated distillation train and was distilled into the cold reaction vessel at room temperature.

Dimethyl sulfide and tetrahydrothiophene were dried at room temperature with CaH_2 under high vacuum. The dry material was distilled into the cold reaction vessel at room temperature. Only excesses of tetrahydrothiophene were used so that accurate measurement of the material was not necessary. Dimethyl sulfide was measured in the same manner as dimethyl ether.

Trimethylamine Borane and Trimethylphosphine Borane. Trimethylamine borane was obtained from Callery Chemical Co. and purified by sublimation. Trimethylphosphine borane was prepared by the reaction of diborane and $P(CH_3)_3$ in rigorously dried glyme or tetrahydrofuran as the solvent. About 10 ml of solvent was condensed in a reaction tube on the vacuum line. Equivalent amounts of the reactants were then distilled into the tube and the contents allowed to warm to room temperature with stirring. The solvent was then distilled away from the solid $(CH_3)_3PBH_3$ which was purified by sublimation.

1,3,2-Dioxaborolane and Its Adducts with $N(CH_3)_3$ and $P(CH_3)_3$. 1,3,2-Dioxaborolane was prepared from B_2H_6 and ethylene glycol.[2] The adducts of the compound with $N(CH_3)_3$ and $P(CH_3)_3$ were prepared at $-78°$ in reaction vessels on the vacuum system, and the composition of the vapor above the solid adducts was determined by infrared spectroscopy.[9]

1,3,2-Dithiaborolane and Its Adducts with $N(CH_3)_3$ and $P(CH_3)_3$. 1,3,2-Dithiaborolane was prepared from B_2H_6 and 1,2-ethanedithiol.[2] The adducts with $N(CH_3)_3$ and $P(CH_3)_3$ were prepared from 1,3,2-dithiaborolane and an excess of the base in glyme and tetrahydrofuran.[2] The vapor pressures of the adducts were determined by Professor Tamres at the University of Michigan.

Boron Trifluoride and Boron Trichloride. BF_3 and BCl_3 were fractionated in a standard vacuum distillation train. The substances were measured as gases in a calibrated system and distilled into cold reaction vessels at room temperature.

Homogeneous Displacement Reactions. The displacement reactions between trimethylamine borane and trimethylphosphine and between trimethylamine 1,3,2-dithiaborolane and trimethylphosphine and the reverse reactions between trimethylphosphine borane and trimethylamine and between trimethylphosphine 1,3,2-dithiaborolane and trimethylamine were carried out with equimolar amounts of the adduct and the base at room temperature in glyme or THF solvent.

$$(CH_3)_3NBH_3 + P(CH_3)_3 \rightleftharpoons (CH_3)_3PBH_3 + N(CH_3)_3$$

$$\underline{S(CH_2)_2S}BHN(CH_3)_3 + P(CH_3)_3 \rightleftharpoons \underline{S(CH_2)_2S}BHP(CH_3)_3 + N(CH_3)_3$$

The systems were stirred continuously for periods ranging from 3 days to 2 weeks. The results were the same regardless of the length of time the system was stirred.

In the nitrogen atmosphere of a drybox, a 2–3-mmole quantity of sublimed adduct was measured by weighing and placed in a greaseless reaction vessel fitted with a vacuum stopcock adaptor. The reaction tube was removed to the vacuum system where 10–20 ml of solvent was distilled into the tube to dissolve the adduct. Then an equimolar amount of $N(CH_3)_3$ or $P(CH_3)_3$ was distilled into the system and the displacement was allowed to proceed to equilibrium. The free amine in the system was distilled from the reaction vessel along with all volatile material at $-5°$. The amount of free amine was determined by standard Kjeldahl procedures. In the case of the displacement reactions involving BH_3, the residues left in the tube after distillation of all volatile material were redissolved and the distribution of BH_3 was determined by B^{11} and proton nmr.

Homogeneous Equilibration Reactions with BCl_3. Equimolar amounts of $N(CH_3)_3$ and $P(CH_3)_3$ were measured in the vacuum system and distilled into a tube which contained 10–15 ml of nitrobenzene or chloroform. The contents were stirred to ensure thorough mixing. An equimolar amount of pure BCl_3 was then condesnsed into the tube. A typical reaction involved 2 mmoles of BCl_3 and 2 mmoles of both $P(CH_3)_3$ and $N(CH_3)_3$. The contents of the tube were then allowed to warm to room temperature and the equilibration was allowed to proceed for periods ranging from 24 hr to 3 days with stirring. The distribution of the adducts was determined through the use of B^{11} nmr.

In the case of the reactions involving $O(CH_3)_2$ and $S(CH_3)_2$ with BCl_3, both displacement and equilibration reactions were carried out directly in a 15-mm nmr tube containing about 2 ml of rigorously dried nitrobenzene and an external reference tube containing

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(23) R. W. Parry and R. W. Keller, "The Chemistry of Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, Chapter 3; R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(24) F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937).

(25) F. G. Mann and A. F. Wells, *ibid.*, 708 (1938).

trimethyl borate. The same results were obtained when the BCl_3 was allowed to react with equimolar amounts of the two bases thoroughly premixed in the nmr tube and when $S(CH_3)_2$ was allowed to displace the $O(CH_3)_2$ from an equimolar amount of $(CH_3)_2OBCl_3$. The distribution of the adducts was determined through the use of B^{11} nmr.

Homogeneous Displacement Reaction with BF_3. Equimolar amounts of $P(CH_3)_3$ and BF_3 were measured in the vacuum system and distilled into a 15-mm nmr tube containing CH_2Cl_2 solvent and a 5-mm tube containing trimethyl borate to be used as an external standard. The contents were allowed to warm, and the adduct, $(CH_3)_3PBF_3$, formed and went into solution. This solution was quickly frozen and an equimolar amount of $N(CH_3)_3$ was distilled into the cold tube. A typical reaction involved approximately 2 mmoles of all reactants. The nmr tube was then sealed with a torch and the contents were kept frozen until the B^{11} nmr spectrum could be obtained. The tube was then warmed and the spectrum was obtained immediately.

Nuclear Magnetic Spectroscopy. All B^{11} nmr spectra were obtained using a Varian HR-60 high-resolution spectrometer. The spectra were obtained from samples in 15-mm tubes and were calibrated by use of side bands of known frequency separation from a standard resonance signal due to an external reference of trimethyl borate. Proton spectra were obtained with a Varian A-60 spectrometer. The concentration of adduct in the nmr sample varied with the reference acid. For borane and BF_3 adducts the concentration range was 0.4–1.5 *M*. For all other acids the concentration range was 0.1–0.2 *M*.

Infrared Spectroscopy. Infrared spectra were obtained in the gas phase using a cell with windows of Eastman Kodak's infrared transmitting optical material, IRTRAN-4. Spectra were obtained in solution using matched liquid cells with NaCl windows. The Perkin-Elmer 237 recording grating spectrometer was used.

Low-Temperature Boron-11 Nuclear Magnetic Resonance Spectra. The B^{11} nmr spectrum of $(CH_3)_2OBH_3$ was obtained in $(CH_3)_2O$ solvent at temperatures ranging from −25 to −85°. An external reference of $(CH_3O)_3B$ was placed in the tube used to obtain the spectrum. The reference signal could not be seen at temperatures below −30° because trimethyl borate is frozen below this temperature. The spectrum of $\underbrace{OCH_2CH_2OB}HN(CH_3)_3$ was obtained at −25° using $BF_3O(C_2H_5)_2$ as an external reference.

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Boron–Nitrogen Chemistry. I. Syntheses and Properties of New Cycloborazanes, $(BH_2NH_2)_n$[1,2]

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Abstract: Cyclic species, cycloborazanes, of composition $(BH_2NH_2)_n$ have been synthesized by the reaction of $NaNH_2$ with $BH_2(NH_3)_2{}^+BH_4{}^-$ in liquid ammonia. Rings with $n = 2, 3$, and 5 have been isolated; evidence is also cited for the formation in small amounts of $(BH_2NH_2)_4$. Infrared, X-ray powder diffraction, and molecular weight data provide evidence for unique species. The principal cyclic product of the synthesis is $(BH_2NH_2)_5$, while lower members are found in only small per cent yields. Under certain conditions $(BH_2NH_2)_2$ isomerizes to $(BH_2NH_2)_3$. Cycloborazanes are significantly more stable thermally and hydrolytically than chain-like $(BH_2NH_2)_n$ species.[2] Possible mechanisms of formation are considered. Evidence is given for the formation of monomeric BH_2NH_2 upon pyrolysis of cyclodiborazane.

The concept of isosterism between the atom groupings B–N and C–C, when introduced almost 40 years ago, implied the expectation that a relatively extensive "boron–nitrogen system" of compounds which are analogs of hydrocarbons should be forthcoming. With reference to the principal classes of aliphatic hydrocarbons, Wiberg subdivided the boron–nitrogen system into the three groups of amine boranes, empirical composition BH_3NH_3, aminoboranes, BH_2NH_2 (referred to as cycloborazanes when known to be cyclic), and borazines, BHNH.[4] Although most of the known unsubstituted boron–nitrogen compounds are indeed isosteric analogs of hydrocarbons, their number is still small and largely confined to cyclic structures.

The least well-known of the three groups are the unsubstituted aminoboranes of empirical composition BH_2NH_2. Species of this composition had been encountered from the beginning of research in the boron–nitrogen system, and several reactions producing these materials have been reported.[5–9] The products were usually described as "highly polymeric, amorphous solids which split out hydrogen readily," and the composition of these "inorganic polyethylenes" was more often than not inferred from the stoichiometry of the reactions. Closer investigation of one of these materials[2] has indicated a chain-like structure consisting of three to four aminoborane units with end groups of uncertain nature.

The properties of the first truly characterized aminoborane, cyclotriborazane, $(BH_2NH_2)_3$, contrasted

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[1] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

[2] Part II is concerned with chain-like $(BH_2NH_2)_n$ species. To be published.

[3] To whom inquiries should be directed.

[4] E. Wiberg, IUPAC, 16th Conference, Paris, 1957.

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(9) A. K. Holliday and N. R. Thompson, *J. Chem. Soc.*, 2695 (1960).