Table II. Mass Spectrum of SF_5OCClO

m/e	Ion	Rel intensity	*m/e*	Ion	Rel intensity
129	$^{34}SF_5^+$	4.00	63	$CO^{35}Cl^+$	48.57
127	$^{32}SF_5^+$	100.00	51	SF^+	2.86
108	SF_4^+	3.71	44	CO_2^+	3.43
105	SF_3O^+	25.71	37	Cl^+	2.14
89	SF_3^+	24.71	35	Cl^+	7.14
86	SF_2O^+	4.86	32	S^+	1.92
70	SF_2^+	12.86	19	F^+	0.97
67	SFO^+	6.00	16	O^+	1.32
65	$CO^{37}Cl^+$	15.71	12	C^+	0.83

ment with the proposed structure. Differences between this fragmentation pattern and that of CF_3OCClO[3] are related to the breaking of the different carbon-oxygen single bonds of the compounds. The pentafluorosulfur compounds breaks at this bond giving fragments leading to the intense ion peaks, SF_3O and CClO. The trifluoromethyl compound breaks at the adjacent C-O bond giving strong CF_3 and OCClO peaks.

Pentafluorosulfur chloroformate is colorless and stable at room temperature in glass or metal equipment. Samples stored in infrared cells for several weeks did not decompose to a detectable degree.

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Some Exchange Reactions Involving Boron Lewis Acids

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Abstract: The ^1H nmr spectra of solutions of the adducts of $B(CH_3)_3$, BF_3, or BH_3 with $(CH_3)_3N$ or tertiary phosphines have been recorded at various temperatures in an effort to establish which of these systems undergo ambient-temperature intermolecular exchange reactions. The trimethylamine-trimethylborane system was selected for more detailed study. Concentration dependence studies together with the energies and entropies of activation establish that the reactions $(CH_3)_3NB(CH_3)_3 + B(CH_3)_3$ and $(CH_3)_3NB(CH_3)_3 + (CH_3)_3N$ proceed by dissociative mechanisms.

There is considerable interest in the relative Lewis acidities of boron compounds. One way of inferring orders of acceptor ability relates to the measurement of nmr chemical shifts.[1] A complicating feature which can arise in such a method is the possibility of rapid intermolecular exchange reactions of the following general categories

$$AB + B^* \rightleftharpoons AB^* + B \qquad (1)$$

$$A^*B + AB^* \rightleftharpoons A^*B^* + AB \qquad (2)$$

$$\begin{gathered} AB \underset{}{\overset{\text{slow}}{\rightleftharpoons}} A + B \\ A + B^* \overset{\text{fast}}{\rightleftharpoons} AB^* \end{gathered} \qquad (3)$$

where A and B denote the Lewis acid and base, respectively. In such cases the chemical shifts and coupling constants are sensitive to both changes in temperature and relative acid-base concentration. In order to assess the Lewis acidity of a particular acid or the Lewis basicity of a particular base or to measure the nmr parameters of the acid-base complex, it is necessary to cool the system to a temperature such that the intermolecular exchange becomes slow on the nmr time scale.

This point appears to have been appreciated first by Diehl and Ogg[2] in their study of the relative basicity of aliphatic alcohols toward BF_3. Subsequently other authors have studied the exchange between BF_3 and ethers and amines.[3]

Since $B(CH_3)_3$ and BH_3 are employed frequently as reference Lewis acids, we became interested in the possibility that these acids might also undergo rapid intermolecular exchanges. Trimethylamine and trimethylphosphine were selected as reference bases because of their simple ^1H nmr spectra. Of the systems investigated in this work, the trimethylamine-trimethylborane system was selected as the most suitable for more detailed study on the same basis. The reaction was studied with both excess acid and excess base. An additional point of interest concerns the fact that Oliver and coworkers have investigated the mechanisms of the corresponding trimethylamine exchange reactions with $Ga(CH_3)_3$[4] and $In(CH_3)_3$.[5]

Experimental Section

Diborane,[6] trimethylborane,[7] and trimethylphosphine[8] were prepared by previously described procedures and were fractionated

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[1] For a review of boron acids, see T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, 1, 83 (1964).

[2] P. Diehl, *Helv. Phys. Acta*, 31, 685 (1958); R. A. Ogg and P. Diehl, *J. Inorg. Nucl. Chem.*, 8, 468 (1958).

[3] (a) R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, 59, 1962 (1963); (b) S. Brownstein, A. M. Eastham, and G. A. Latremouille, *J. Phys. Chem.*, 67, 1028 (1963); (c) A. C. Rutenberg, A. A. Palko, and J. S. Drury, *J. Am. Chem. Soc.*, 85, 2702 (1963); (d) *J. Phys. Chem.*, 68, 976 (1964); (e) A. C. Rutenberg and A. A. Palko, *ibid.*, 69, 527 (1965); (f) E. Gore and S. S. Danyluk, *ibid.*, 69, 89 (1965).

[4] J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, 4, 1741 (1965); *J. Am. Chem. Soc.*, 89, 3970 (1967).

[5] K. L. Henold and J. P. Oliver, *Inorg. Chem.*, 7, 950 (1968).

[6] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *J. Am. Chem. Soc.*, 74, 901 (1952).

until their vapor tensions conformed to the literature values. Trimethylamine and the solvents CH_2Cl_2, C_6H_6, and glyme (1,2-dimethoxyethane) were procured commercially and distilled prior to use. The benzene was checked for the absence of thiophene by vpc.

Nmr sample preparation and purification of reagents were performed in a Stock-type high-vacuum manifold. An equal amount of solvent (1.0 ml) was used in each sample. In the qualitative work 0.5 mmole of both the acid and base was employed when the solubility of the complex was sufficiently large. Excess acid or base was used in quantities of 0.25 mmole. A small quantity of tetramethylsilane was used as internal standard in the cases where glyme and benzene were used as solvents. It is important that the CH_2Cl_2 solutions which contain $(CH_3)_3N$ or $(CH_3)_3P$ be kept at $-196°$ until the spectra are run because the amine and phosphine slowly react with CH_2Cl_2, precipitating a solid which is presumably a quaternary ammonium or phosphonium salt. This type of reaction has also been observed with ethyldimethylamine.[9] The qualitative exchange data (Table I) were obtained on a Varian Associates A-60 spectrometer. The criteria which were employed in ascertaining the presence or absence of exchange were: (a) the absence of anticipated peaks and/or coupling constants in the ambient temperature spectra, which then became apparent upon cooling; (b) the sensitivity of peak positions and/or coupling constants to changes in temperature; (c) the sensitivity of peak position and/or coupling constants to changes in acid/base ratios. In separate experiments it was determined that the chemical shifts of the free acid and the free base were independent of temperature and concentration within experimental error.

Table I. Results of Qualitative Exchange Experiments

Lewis acid	Lewis base	Solvent	Temp, °C	Exchanging?
BF_3	$(CH_3)_3N$	C_6H_6	Ambient	No
BF_3	$(CH_3)_3N$	CH_2Cl_2	Ambient	No
BF_3	$(CH_3)_3N$	Glyme	Ambient	No
BF_3[a]	$(CH_3)_3P$	CH_2Cl_2	Ambient	Yes
$(CH_3)_3B$	$(CH_3)_3P$	CH_2Cl_2	Ambient	Yes
$(CH_3)_3B$	$(CH_3)_3P$	CH_2Cl_2	−80	No
$(CH_3)_3B$	$(CH_3)_3N$	CH_2Cl_2	Ambient	Yes
$(CH_3)_3B$	$(CH_3)_3N$	CH_2Cl_2	−80	No
$(CH_3)_3B$	$(i\text{-}C_3H_7)_3P$	CH_2Cl_2	Ambient	Yes
$(CH_3)_3B$	$(i\text{-}C_3H_7)_3P$	CH_2Cl_2	−80	No
$(CH_3)_3B$	$(c\text{-}C_3H_5)_3P$	CH_2Cl_2	Ambient	Yes
$(CH_3)_3B$	$(c\text{-}C_3H_5)_3P$	CH_2Cl_2	−80	No
BH_3	$(CH_3)_3N$	C_6H_6	Ambient	Yes
BH_3	$(CH_3)_3N$	CH_2Cl_2	Ambient	No
BH_3	$(CH_3)_3N$	Glyme	Ambient	No
BH_3	$(CH_3)_3N$	Glyme	+80	No
BH_3	$(CH_3)_3P$	C_6H_6	Ambient	No
BH_3	$(CH_3)_3P$	CH_2Cl_2	Ambient	No
BH_3	$(CH_3)_3P$	Glyme	Ambient	No
BH_3	$(CH_3)_3P$	Glyme	+80	No

[a] Low solubility precluded the use of C_6H_6 and glyme as solvents.

The quantitative exchange data were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Temperatures, which are accurate to ±1°, were determined by CH_3OH calibration. Line widths were read directly off the chart paper.

$(CH_3)_3NB(CH_3)_3$ Exchange Reaction in Excess $B(CH_3)_3$. Since the peaks are not overlapping in this system, standard nmr line-broadening techniques[10] may be used to obtain mean lifetimes and hence rate constants. In the region of slow exchange, *i.e.*, well below the coalescence temperature, the approximation[10,11]

$$\frac{1}{\tau} = \pi(\nu_{1/2} - \nu_{1/2}{}^0) \tag{4}$$

was used, where $\nu_{1/2}$ is the peak width at half-height of the peak under exchange conditions, and $\nu_{1/2}{}^0$ is the peak width at half-height where no exchange exists. The inverse of the mean lifetime, $1/\tau_i$, is, of course, the first-order rate constant for transfer out of the *i*th state. The Arrhenius activation energy is obtained from a least-squares plot of first-order rate constant *vs.* inverse temperature.

$(CH_3)_3NB(CH_3)_3$ Exchange Reaction in Excess $(CH_3)_3N$. Because this system involves overlapping peaks, the above method cannot be employed. Instead we used the method of Rogers and Woodbrey.[12] Equations A1 and A2 of ref 12 were programmed for the CDC 6600 computer by M. W. Taylor of our laboratory. Input to the program includes a final peak separation, $\delta\omega$; the relative populations, P_A and P_B; and the final peak widths at half-height, T_{2A} and T_{2B}. The procedure starts with a trial value of the mean lifetime, τ, and computes two ν_{max}/ν_{min} ratios corresponding to the complexed and uncomplexed species which are then compared with the experimental values at a particular temperature. In subsequent calculations the τ value is adjusted until the agreement between the experimental and calculated ν_{max}/ν_{min} ratios is optimized. These τ values can then be used to obtain the Arrhenius activation energy in the usual manner. In such calculations $\delta\omega$, P_A, P_B, T_{2A}, and T_{2B} are treated as constants for a particular system and were taken from the lowest temperature spectrum (*i.e.*, where the system is effectively not exchanging on the nmr time scale).

Results and Discussion

For convenience the qualitative and quantitative exchange experiments are considered separately.

(i) Qualitative Exchange Experiments. It has been known for some time that BF_3 complexes of aliphatic alcohols,[2] ethers, and amines[3] undergo rapid intermolecular exchange reactions. In the present study it was found that $(CH_3)_3NBF_3$ does not exchange with $(CH_3)_3N$ in the solvents C_6H_6, CH_2Cl_2, or glyme. By contrast $(CH_3)_3PBF_3$ does exchange with $(CH_3)_3P$ in CH_2Cl_2. In the latter case low adduct solubility restricted our choice to this particular solvent. At ambient temperature the Lewis bases $(CH_3)_3N$, $(CH_3)_3P$, tricyclopropylphosphine,[13] and triisopropylphosphine all undergo rapid exchange reactions with their $B(CH_3)_3$ adducts in CH_2Cl_2. At $-80°$ the rate of exchange is slowed sufficiently on the nmr time scale such that all the anticipated resonances become apparent. The types of spectral changes which have been observed are illustrated in Figures 1 and 2 for the systems $(CH_3)_3P\text{–}B(CH_3)_3$ and $(CH_3)_3N\text{–}B(CH_3)_3$. Since triisopropylphosphine and tricyclopropylphosphine behave in a comparable manner, and further since Holmes and Carter[14] have noted previously that $B(C_2H_5)_3$ exchanges with $(CH_3)_3P$, it is likely that trialkylboranes undergo ambient-temperature exchange reactions with most alkylated group V(and probably group VI) Lewis bases. In Table II and Figure 1, we present data which are typical of the changes that can take place in the pmr parameters upon cooling an equimolar Lewis acid–base mixture. This means that the ambient-temperature nmr data of, *e.g.*, Heitsch,[15] concerning $B(CH_3)_3$ adducts must be viewed with caution. Furthermore these changes of chemical shifts are of the same order of magnitude as the differences of chemical shift (~0.1 ppm) upon which Coyle and Stone[9] have made arguments concerning Lewis acidity of vari-

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[7] W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

[8] F. G. Mann, A. F. Wells and D. Purdie, *J. Chem. Soc.*, 1828 (1937); F. G. Mann and A. F. Wells, *ibid.*, 768 (1938).

[9] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).

[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chapter 10, and references therein.

[11] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[12] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

[13] A. H. Cowley and J. L. Mills, submitted for publication.

[14] R. R. Holmes and R. P. Carter, *Inorg. Chem.*, **2**, 1146 (1963).

[15] C. W. Heitsch, *ibid.*, **4**, 1019 (1965).

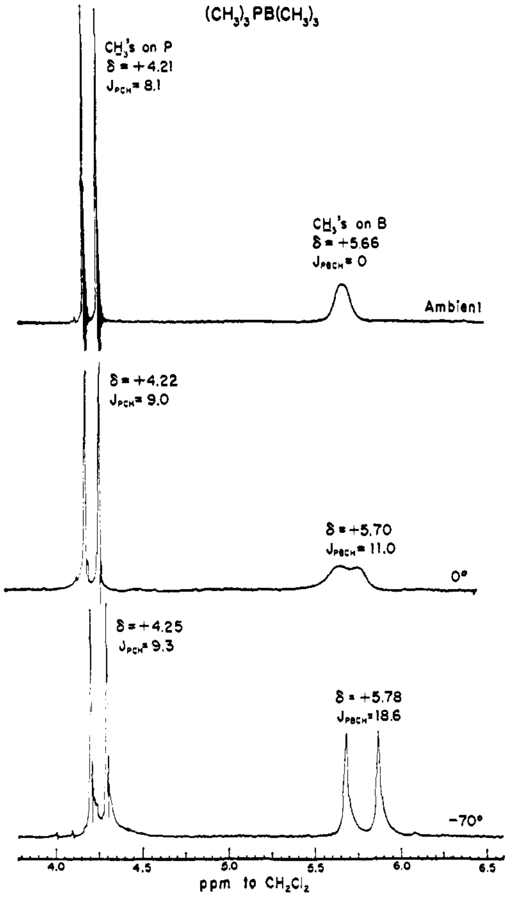

Figure 1. ^1H nmr spectra of $(CH_3)_3PB(CH_3)_3$ at ambient temperature, 0°, and −70°. Chemical shifts are relative to the solvent, CH_2Cl_2.

ous boron compounds. In view of the foregoing it is important that in making comparisons of Lewis acidity (or basicity) *that exchanging systems be cooled to a temperature such that the exchange process is slow on the nmr time scale.*

Table II. Changes in ^1H Chemical Shifts[a] and Coupling Constants with Temperature of the Systems $(CH_3)_3NB(CH_3)_3$ and $(CH_3)_3PB(CH_3)_3$

Temp, °C	$\delta_{(CH_3)_3P}$	$\delta_{B(CH_3)_3}$	J_{PCH}	J_{PBCH}
	$(CH_3)_3PB(CH_3)_3$			
Ambient	4.21	5.66	8.1	0
−70	4.25	5.78	9.3	18.6
	$(CH_3)_3NB(CH_3)_3$			
	$\delta_{(CH_3)_3N}$	$\delta_{B(CH_3)_3}$		
Ambient	2.96	5.69		
−70	3.02	5.80		

[a] All chemical shifts are in parts per million upfield from internal CH_2Cl_2.

A solvent effect was discovered in the borane complexes. Trimethylphosphine–borane underwent no detectable exchange in the solvents C_6H_6, CH_2Cl_2, or glyme. Similarly no exchange was apparent in the trimethylamine-borane system when this complex was dissolved in CH_2Cl_2 or glyme. However, exchange was detected in this system when benzene was employed as the solvent. Initially it was felt that this observation might be due to the presence of an impurity such as thiophene in the benzene. However, a vpc check of the purity of the benzene revealed no such impurity. Since $(CH_3)_3NBH_3$ underwent ambient temperature exchange in benzene, attempts were made to cause a similar exchange in the solvent glyme by raising the temperature. However, no exchange was detected up to 80°. A further peculiarity which was noted when benzene was employed as a solvent was that the proton resonances of the bases were at *higher field than the free bases* in the complexes $(CH_3)_3NBF_3$ and $(CH_3)_3PBH_3$. This is due presumably to the formation of a solvate with the magnetically anisotropic benzene.

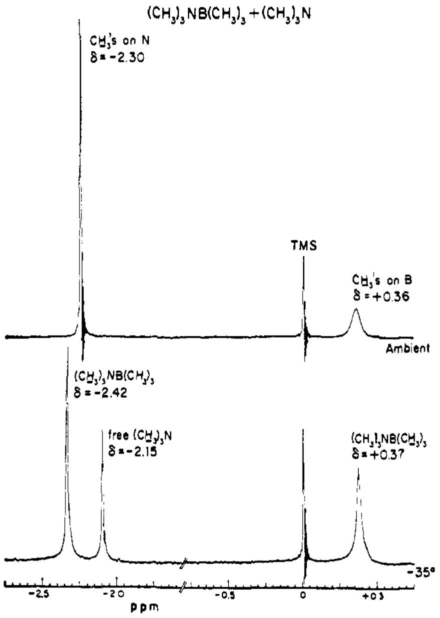

Figure 2. ^1H nmr spectra of $(CH_3)_3NB(CH_3)_3$ + excess $(CH_3)_3N$ at ambient temperature and −70°. Chemical shifts are relative to 5% internal TMS.

While recognizing that the effects observed here relate to the kinetic stability of the adducts, it is of interest to note a correlation with the acidity or basicity of the components. Thus the observation that all systems involving $B(CH_3)_3$ undergo intermolecular exchange at ambient temperature is consonant with this being the weakest Lewis acid[16] of the ones considered here. The observations with BF_3 (Table I) may be understood on the basis of Pearson's soft-hard acid-base theory.[17] Thus BF_3 is a hard acid and so prefers the hard base $(CH_3)_3N$. The soft base $(CH_3)_3P$ forms a weaker complex with BF_3 and is thus the most likely system to undergo an exchange reaction. The observation of solvent dependence with $(CH_3)_3NBH_3$ might also be rationalized in this manner. The BH_3 unit is considered a soft acid, and thus is most likely to undergo an exchange reaction with the hard base $(CH_3)_3N$. However, apparently in this case the assistance of the soft solvent benzene is required to lower the activation energy for the exchange process.

(ii) Quantitative Exchange Experiments. Of the systems described above the trimethylamine-trimethyl-

(16) Toward $(CH_3)_3N$ the order of Lewis acidity is $BF_3 > BH_3 > B(CH_3)_3$; see F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958), and references therein. Toward tertiary phosphines the order of Lewis acidity is $BH_3 > BF_3 > B(CH_3)_3$; see D. E. Young, G. E. McAchran, and S. G. Shore, *J. Am. Chem. Soc.*, **88**, 4390 (1966), and references therein.

(17) R. G. Pearson, *ibid.*, **85**, 3533 (1963).

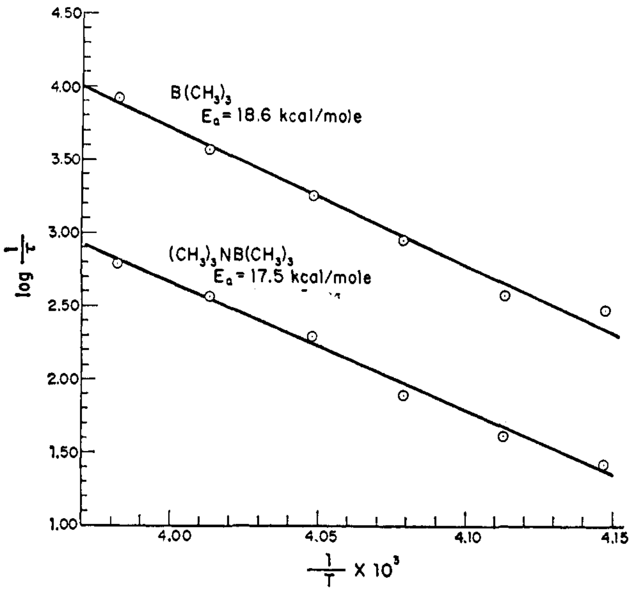

Figure 3. Least-squares plot of log $1/\tau$ *vs.* $1/T$ of the system $(CH_3)_3NB(CH_3)_3 + B(CH_3)_3$.

borane system appeared to be the most suited to more detailed study on account of its spectral simplicity. Furthermore, Oliver and coworkers[4,5] have studied the exchange reactions between $(CH_3)_3N$ and the other monomeric trimethyl group III compounds.

Table III. Concentration Dependence of the Lifetimes of $(CH_3)_3NB(CH_3)_3$ (τ_{AB}) and $(CH_3)_3B$ (τ_A) at −22°

C_{AB}[a]	C_A[a]	$1/\tau_{AB}$, sec^{-1}	$1/\tau_A$, sec^{-1}	C_{AB}/C_A	$(1/\tau_A)/(C_{AB}/C_A)$
0.228	0.228	11.6	15.7	1	15.7
0.285	0.570	12.2	8.5	0.5	16.9
0.913	0.228	11.9	42.7	4.0	10.7
0.279	0.837	12.6	4.4	0.33	13.2
0.474	0.237	12.2	28.6	2.0	14.3
0.555	0.555	12.6	16.6	1.0	16.6
		Av 12.2			Av 14.6

[a] Concentrations in moles/liter.

(a) Reaction of $(CH_3)_3NB(CH_3)_3$ with $B(CH_3)_3$. At ambient temperature the proton nmr spectrum of $(CH_3)_3NB(CH_3)_3$ in excess $B(CH_3)_3$ consists of only two peaks, one corresponding to N-methyl protons and the other to B-methyl protons. When the temperature is lowered to approximately −18°, an additional signal appears. Further cooling causes all three peaks to sharpen. In this region of slow exchange the three peaks are well separated, and the technique of line broadening[10,11] (see Experimental Section) may be used to obtain the mean lifetimes, τ, of $B(CH_3)_3$ and $(CH_3)_3NB(CH_3)_3$ by use of eq 4. The concentration dependence of the lifetimes of the adduct (τ_{AB}) and the acid (τ_A) were observed at −22°. It will be noted (Table III) that the lifetime of $(CH_3)_3NB(CH_3)_3$ is independent of concentration, while the lifetime of $(CH_3)_3B$ is proportional to the quotient C_{AB}/C_A. It has been shown elsewhere[4,5] that this type of concentration dependence is consistent only with a dissociative mechanism, *viz.*

$$\begin{gathered}(CH_3)_3NB(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3N + B(CH_3)_3 \\ (CH_3)_3N + B^*(CH_3)_3 \overset{\text{fast}}{\rightleftharpoons} (CH_3)_3NB^*(CH_3)_3\end{gathered} \tag{5}$$

for which

$$1/\tau_{(CH_3)_3NB(CH_3)_3} = k_1 \tag{6}$$

and

$$1/\tau_{(CH_3)_3B} = k_1 \frac{[(CH_3)_3NB(CH_3)_3]}{[(CH_3)_3B]} \tag{7}$$

A more complex reaction mechanism would manifest itself in a concentration dependence of τ_{AB}. Further support for a dissociative mechanism comes from the temperature dependence of τ_A and τ_{AB}. In Figure 3 is plotted ln $1/\tau$ *vs.* reciprocal temperature for both $(CH_3)_3NB(CH_3)_3$ and $(CH_3)_3B$ which leads to Arrhenius activation energies of 18.6 and 17.5 kcal/mole, respectively. The average of these two values (18.0 kcal/mole) exceeds the gas-phase dissociation energy (17.6 kcal/mole) of $(CH_3)_3NB(CH_3)_3$.[18] The positive entropy of activation (+17.0 eu at −22°) is also consistent with a dissociative rate-determining step. The $(CH_3)_3N$-$B(CH_3)_3$ results contrast with Brownstein's study[3b] of BF_3-OR_2 systems with excess BF_3. This study showed that the activation energy for the process is much less than the dissociation energy for the addition compound, thus suggesting that a bimolecular displacement reaction is occurring. An S$_N$2 process would be in accord with the observation of "double" adducts of amines of formula $R_3N \cdot 2BX_3$ at low temperature.[19]

(b) Reaction of $(CH_3)_3NB(CH_3)_3$ with $(CH_3)_3N$. In this system the separate peaks for free and complexed trimethylamine became apparent below approximately −22°. Since these peaks are overlapping, the usual line-broadening technique[10,11] (eq 4) is not applicable. Instead we employed the method of Rogers and Woodbrey,[12] the details of which have been discussed in the Experimental Section. This method provides access to the mean lifetimes of the absorbing species by matching calculated and experimental peak-maximum/peak-minimum ratios. Using the arguments presented in the previous section, it is clear that the concentration-dependence studies (Table IV) establish that a dissociative rate-determination step is also operative for this reaction. A least-squares fit of ln $1/\tau$ *vs.* $1/T$ for both $(CH_3)_3N$ and $(CH_3)_3NB(CH_3)_3$ yielded activation en-

Table IV. Concentration Dependence of the Lifetimes of $(CH_3)_3NB(CH_3)_3$ (τ_{AB}) and $(CH_3)_3N$ (τ_B) at −24°

C_{AB}[a]	C_B[a]	$1/\tau_{AB}$, sec^{-1}	$1/\tau_B$, sec^{-1}	C_{AB}/C_B	$(1/\tau_{AB})/(C_{AB}/C_B)$
0.228	0.228	11.0	10.4	1.0	10.4
0.555	0.555	11.6	11.0	1.0	11.0
0.285	0.570	11.3	5.35	0.5	10.7
0.279	0.837	11.6	3.1	0.33	9.4
0.474	0.237	11.0	19.4	2.0	9.7
0.913	0.228	11.0	42.8	4.0	10.7
		Av 11.2			Av 10.2

[a] Concentrations in moles/liter.

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(18) H. C. Brown and M. C. Taylor, *J. Am. Chem. Soc.*, **69**, 1332 (1947).

(19) H. C. Brown, P. F. Stehle, and P. A. Tierney, *ibid.*, **79**, 2020 (1957).

ergy values of 17.2 and 16.6 kcal/mole, respectively. Within experimental error this value agrees with the gas-phase dissociation energy of 17.6 kcal/mole for the adduct $(CH_3)_3NB(CH_3)_3$. At −24° the entropy of activation is +15.0 eu. This result contrasts with the findings of Oliver and coworkers on the corresponding $Ga(CH_3)_3$[4] and $In(CH_3)_3$[5] systems. Here no significant line broadening was apparent upon cooling, thus suggesting the availability of a low-energy reaction mechanism which is probably of the SN2 type, *viz.*

$$(CH_3)_3N^* + (CH_3)_3NGa(CH_3)_3 \rightleftharpoons (CH_3)_3N^*Ga(CH_3)_3 + (CH_3)_3N \tag{8}$$

The most obvious rationale for the difference in reaction mechanism between $(CH_3)_3B$ and the heavier group III alkyls would relate to the small size of boron and in inavailability of d orbitals. However, this cannot be the complete answer since the amine-BF_3 + excess amine reaction appears to go *via* an SN2 process.[3b] Thus, the reason might be simply one of lesser steric bulk around the boron atom in BF_3 than in $B(CH_3)_3$. Henold and Oliver[5] have shown that reducing the steric bulk around nitrogen can shift the reaction to a lower energy (bimolecular) mechanism. Clearly more effort needs to be expended in order to elucidate the course of this type of exchange reaction. Toward this end, Shore and coworkers are studying the corresponding trimethylphosphine–trimethylborane system.

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The Lewis Basicity and Ligand Behavior of Cyclopropylphosphines

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Abstract: The preparation and properties of tricyclopropylphosphine and cyclopropyldiphenylphosphine are described. Tricyclopropylphosphine is a stronger Lewis base than $(i\text{-}C_3H_7)_3P$ toward the Lewis acids $B(CH_3)_3$, BF_3, and BH_3. Tricyclopropylphosphine will react with cyclopropyl bromide to yield $(c\text{-}C_3H_5)_4P^+Br^-$, which appears to be stable only in the solid state. The P–S and P–Se stretching frequencies of $(c\text{-}C_3H_5)_3PS$, $(c\text{-}C_3H_5)_3PSe$, and $(i\text{-}C_3H_7)_3PS$ are all higher than the values reported previously[15] for tri(*n*-alkyl)- and tri(aryl)phosphine chalcogenides. The mono- and disubstituted tungsten carbonyl complexes of $(c\text{-}C_3H_5)_3P$ and $(c\text{-}C_3H_5)(C_6H_5)_2P$ have been prepared and the ^{31}P nmr chemical shifts of the free and complexed phosphines determined. The coordination chemical shifts of both phosphines are anomalously small. The ^{183}W–^{31}P coupling constants and E species CO stretching frequencies of the (phosphine)$W(CO)_5$ compounds fit the linear relationship of Grim, *et al.*, and suggest that the cyclopropylphosphines behave as π-acceptor ligands. Attempts to prepare an anion radical from $(c\text{-}C_3H_5)_3P$ or $(c\text{-}C_3H_5)_3PO$ were unsuccessful.

The cyclopropyl group can behave either as a π-electron donor or a π-electron acceptor. The former behavior is the best documented and is exemplified by a variety of structural studies which establish a preference for the "bisected" cyclopropyl conformation in π systems[1] and carbonium ions.[2] Acceptance of π electrons has been noted in certain cyclopropyl-substituted anion radicals.[3] Here conjugation from an external p orbital to the intraannular orbitals of the cyclopropyl moiety apparently results in the "symmetrical" conformation.

In principle then the cyclopropyl group should resemble an aryl group in its ability to conjugate with systems with low-lying vacant d orbitals. For tertiary phosphines the conjugative interaction is considered to involve a balance between phosphorus lone pair → ring (p_π–p_π) donation and ring → vacant phosphorus 3d orbital (p_π–d_π) acceptance.[4] While the present study was in its infancy, Denny and Gross[5] described the preparation of tricyclopropylphosphine and concluded that there is no conjugation between phosphorus and the cyclopropyl moiety on the basis of pK_a measurements. Recognizing that the presence of π bonding in the P–C linkage would be a very subtle effect which might not be manifest in the Brønsted basicity of a phosphine, we have directed our attention to assessing the Lewis basicity and ligand behavior of cyclopropyl-substituted phosphines.

Experimental Section

All volatile materials were handled in standard high-vacuum manifolds with U-traps interconnected with either Stock-type

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(1) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, 43, 647, (1965); J. P. Guillory and L. S. Bartell, *ibid.*, 43, 654 (1965); L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, **69**, 3043 (1965); G. L. Closs and B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965); G. R. DeMare and J. S. Martin, *ibid.*, **88**, 5033 (1966); G. A. Russell and H. Malkus, *ibid.*, **89**, 160 (1967).

(2) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965).

(3) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967).

(4) J. W. Rakshys, R. W. Taft, and W. A. Sheppard, *ibid.*, **90**, 5236 (1968), and references therein. For C_6F_5-substituted phosphines, see M. G. Hogben, R. S. Gay, and W. A. G. Graham, *ibid.*, **88**, 3457 (1966).

(5) D. B. Denny and F. J. Gross, *J. Org. Chem.*, **32**, 2445 (1967). Prior to this work the synthesis of cyclopropyltriphenylphosphonium bromide had been reported; see D. T. Longone and R. R. Doyle, *Chem. Commun.*, 300 (1967), and references therein.