$(BH_4)_3$, which is monomeric with a planar AlB_3 arrangement,[15] to the trimethylamine adduct. A similar tetrahedral symmetry around the aluminum atom has been observed in the adduct $C_6H_5C(Cl)O{\cdot}AlCl_3$,[16] the only other reported X-ray analysis on an $L{\cdot}AlX_3$ system (where L = ligand). It has been previously argued that the aluminum atom need use only one bonding orbital for each tetrahydroborate group,[17] and the mean positions of the boron atoms at room temperature suggest that the aluminum atom is essentially sp^3 hybridized. The distorted geometry around the aluminum atom at low temperature appears to represent a compromise with the boron and hydrogen atoms distorted from tetrahedral and pentagonal-bipyramidal sites, respectively, so that the planar geometry of each AlH_2B bridge system is preserved. The attempt by the boron atoms to occupy the tetrahedral sites may represent some degree of direct bonding between the aluminum and boron atoms; this is illustrated in Figure 3 in which the circles represent the normal (Sidgwick) covalent radii of atoms. Clearly the concept of coordination number must be used with care in any discussion of the stereochemistry of metal tetrahydroborates since the contribution of the bridge hydrogen atoms and boron atom may vary considerably depending on the size of the metal atom.

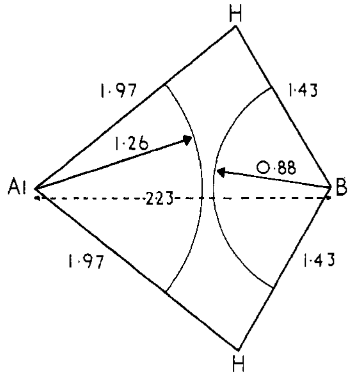

Figure 3.—Mean molecular geometry of AlH_2B system.

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A Variable-Temperature Proton Magnetic Resonance Study of Complexes of Pyridine, Methylpyridines, Ethylpyridines, Imidazole, 1-Methylimidazole, and Pyrimidine with Boron Trifluoride and Boron Trichloride

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A variable-temperature proton magnetic resonance chemical shift and coordination number study of complexes of pyridine, methylpyridines, ethylpyridines, imidazole, 1-methylimidazole, and pyrimidine with BF_3 and BCl_3 has been completed. In the presence of excess base, separate resonance signals are observed for bulk and complexed ligand molecules in all cases. The chemical shift data are interpreted in terms of paramagnetic shielding and polarization of the ligand molecules by complex formation. Integration of the bulk and complexed ligand signals for all systems shows conclusively that only one ligand molecule is complexed to BF_3 or BCl_3 from +35 to $-40°$. Mixed coordination number studies indicate a decreasing Lewis base strength in the order pyridine > 1-methylimidazole > imidazole and pyrimidine.

Introduction

Numerous nuclear magnetic resonance (nmr) studies of interactions of Lewis acids with a variety of ligands have been made in an attempt to assess the strength and structure of the complex formed. These investigations of the interactions of diamagnetic cations[1-3] and boron trihalides[4-12] with several Lewis bases are made by observing the chemical shifts of the ligand proton signals upon the addition of an equimolar amount of Lewis acid, usually in another solvent. The observed chemical shifts, however, reflect temperature and ionic strength effects, are influenced by interactions of the complexing species with solvent molecules, and frequently provide only qualitative information about the structure of the complex in solution.

It has been demonstrated recently that the spectra of solutions of various diamagnetic cations, such as

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Al(III), Be(II), and Ga(III), in N,N-dimethylformamide,[13-19] dimethyl sulfoxide,[13,14,20] methanol,[21,22] and even water or aqueous mixtures at low temperatures,[23-27] exhibit separate proton magnetic resonance (pmr) signals for bulk solvent and solvent molecules in the first coordination shell of the cation. In these solutions, solvent exchange[13-22] or proton exchange[22-27] is slow enough to permit this observation. Thus, accurate coordination number measurements can be made, more reliable estimates of the effect of complex formation on chemical shifts are possible, and the interaction site in the ligand can be more readily assigned. Each of these advantages was clearly demonstrated in recent applications of this pmr method to studies of complexes of the boron trihalides with several oxygen-containing organic bases.[28,29] The technique has now been extended to heterocyclic compounds, namely, pyridine, methyl- and ethyl-substituted pyridines, and compounds of biological importance, such as imidazole, 1-methylimidazole, and pyrimidine.

Experimental Methods

Chemical shifts and peak areas were measured with a Varian A-60 nmr spectrometer equipped with a variable-temperature system which permits studies from −100 to +200°. Tetramethylsilane (TMS) was used as an internal chemical shift standard. The pyridines were reagent grade, while the imidazole, 1-methylimidazole, and pyrimidine were commercial grade (II) biochemicals (Cyclo). All were used as received with no further purification. Samples were prepared *in vacuo* by adding fractionated BF_3 or BCl_3 to the pure solvent. With all samples studied, high amplitude pmr measurements gave no evidence of sample decomposition. The chemical shifts and peak areas were measured at least three times for each sample.

Results

The chemical shift and coordination number data for all single complex pyridine systems are summarized in Table I, while analogous results are listed in Table II for 1-methylimidazole and pyrimidine. The mole ratios of ligand to boron trihalide are listed first and the temperatures of study are given in column 2 in each table. In the next four columns of Tables I and II, the separations, δ^{BC}, of the alkyl and ring proton signals of bulk and complexed ligand molecules are given. Finally, the number of ligand molecules complexed to the boron trihalide, hereafter referred to as the coordination number of the trihalide, appear in the last column of each table.

TABLE I

PROTON CHEMICAL SHIFT AND COORDINATION NUMBER DATA FOR COMPLEXES OF BF_3 AND BCl_3 WITH PYRIDINE (Py), METHYLPYRIDINES (MePy), AND ETHYLPYRIDINES (EtPy)

System	Temp, °C	δ_R^{BC}	$\delta_{2,6}^{BC}$	$\delta_{3,5}^{BC}$	δ_4^{BC}	CN
10:08:1 $Py \cdot BF_3$	+35		13	30	33	Broad
	−40		15	29	33	1.13
9.90:1 $Py \cdot BCl_3$	+35		48	37	40	0.98
	−40		49	38	41	1.01
10.03:1 3-$MePy \cdot BF_3$	+35	8.7	10	32	35	0.95
	−50	9.1	17	33	35	1.03
8.95:1 3-$MePy \cdot BCl_3$	+35	13.4	44	40	42	0.99
	−40	12.8	47	41	44	1.04
10.05:1 4-$MePy \cdot BF_3$	+35	13.8	8	29		0.97
	−50	11.9	11	29		1.06
10.08:1 4-$MePy \cdot BCl_3$	+35	16.1	43	36		0.98
	−50	17.0	45	39		0.86
9.81:1 2-$EtPy \cdot BF_3$	+35	0 (CH_3) 31.5 (CH_2)	18	Overlap	33	0.95
	−40	0 (CH_3) 32.8 (CH_2)	21	Overlap	36	1.06
10.00:1 2-$EtPy \cdot BCl_3$	+35	5.9 (CH_3) 57.9 (CH_2)	68	40	38	0.98
	−40	15.1 (CH_3) 59.5 (CH_2)	67	45	42	1.03
9.93:1 3-$EtPy \cdot BF_3$	+35	0 (CH_3) 0 (CH_2)	12	33	37	Broad
	−40	0 (CH_3) 2.0 (CH_2)	17	40	39	1.08
10.00:1 3-$EtPy \cdot BCl_3$	+35	2.5 (CH_3) 12.4 (CH_2)	47	44	47	1.01
	−40	2.6 (CH_3) 12.7 (CH_2)	48	48	50	1.06
9.63:1 4-$EtPy \cdot BF_3$	+35	3.4 (CH_3) 11.8 (CH_2)	8	30		1.08
	−40	2.3 (CH_3) 11.8 (CH_2)	12	34		0.96
10.18:1 4-$EtPy \cdot BCl_3$	+35	4.5 (CH_3) 16.1 (CH_2)	44	38		1.01
	−40	3.1 (CH_3) 16.0 (CH_2)	43	43		1.01

TABLE II

PROTON CHEMICAL SHIFT AND COORDINATION NUMBER DATA FOR COMPLEXES OF BF_3 AND BCl_3 WITH 1-METHYLIMIDAZOLE (1-MeIm) AND PYRIMIDINE (Pym)

System	Temp, °C	δ_R^{BC}	δ_2^{BC}	$\delta_{4,5}^{BC}$	$\delta_{4,6}^{BC}$	δ_5^{BC}	CN
9.97:1 1-$MeIm \cdot BF_3$	+35	13.1	64	18			0.94
	−20	14.2	68	20			0.77
9.96:1 1-$MeIm \cdot BCl_3$	+35	20.8	96	45			1.04
2.54:1 $Pym \cdot BF_3$	+35		20		36	40	0.83
	0		22		38	43	0.80

The pmr spectra in Figures 1–4 are portions of those exhibited by solutions of BF_3 in pyridine, 2-ethylpyridine, 3-ethylpyridine, and 4-ethylpyridine, respectively. The comparable methylpyridine spectra are analogous in appearance to those shown in Figures 1–4. Since the spectra of the pyridines are complex, the examples shown in Figures 1–4 are included to identify the peaks chosen for chemical shift measurements. Usually the most dominant signal from each proton pattern was used to facilitate identification. Although much broader, the signals of the pyridines complexed to BF_3 resemble the bulk signals in appearance and, when measurable, in *J* coupling values. Likewise, the 3-, 4-, and 5-proton signal patterns of the pyridines complexed to BCl_3 are similar to the comparable bulk solvent signals and they are easily identified. However, as shown in Figure 5, the 2- and 6-proton patterns of these BCl_3 complexes differ markedly

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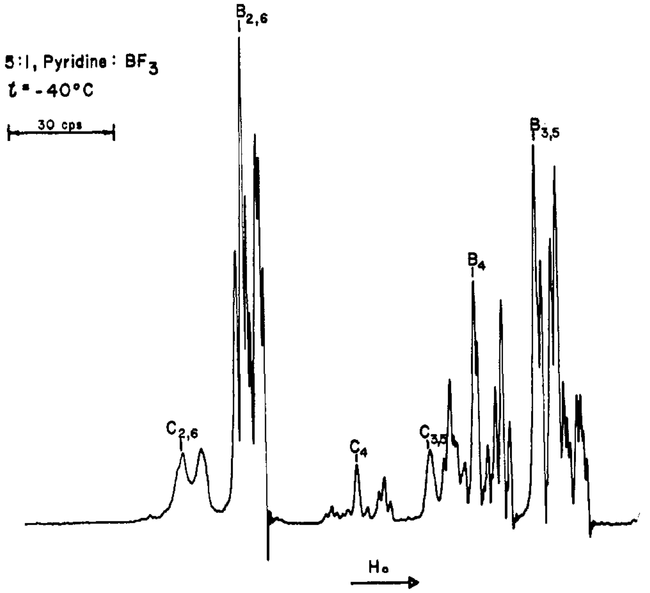


Figure 1.—The proton magnetic resonance (pmr) spectrum of a 5:1 mole ratio solution of pyridine to BF_3, recorded at −40° on a Varian A-60 spectrometer. The chemical shift data of Table I correspond to the bulk (B) and complexed (C) pyridine signals identified in the diagram.

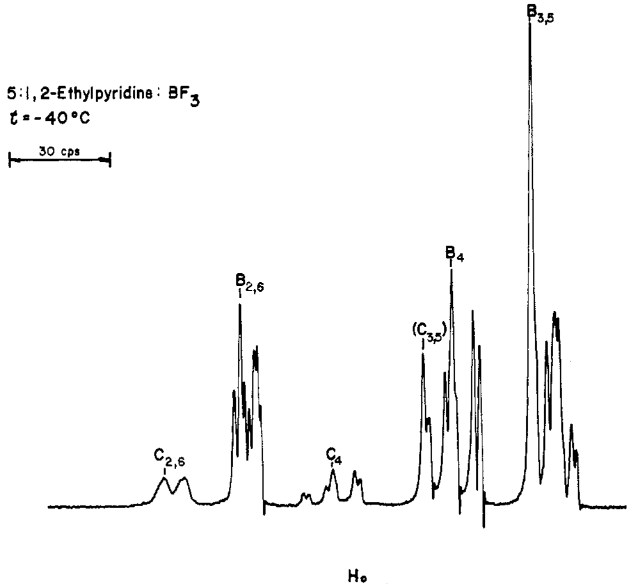


Figure 2.—The pyridine portion of the pmr spectrum of a 5:1 mole ratio solution of 2-ethylpyridine to BF_3 recorded at −40°. The chemical shift data of Table I correspond to the bulk (B) and complexed (C) 2-ethylpyridine signals identified in the diagram. Owing to overlap, the assignment of the 3- and 5-proton signal of complexed 2-ethylpyridine is somewhat doubtful.

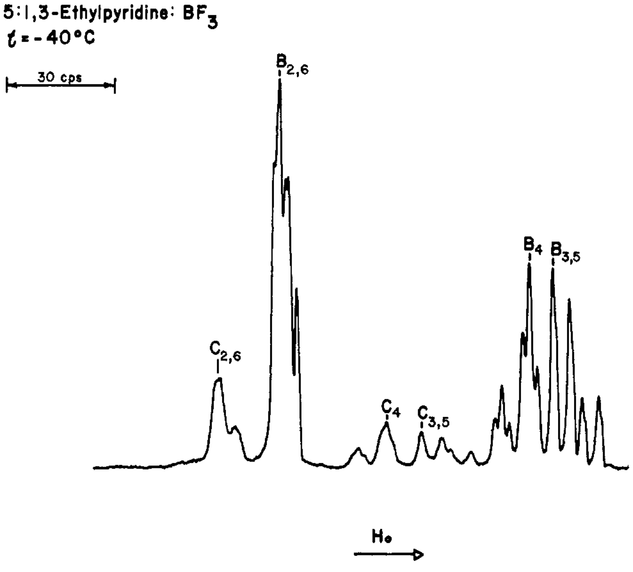


Figure 3.—The pyridine portion of the pmr spectrum of a 5:1 mole ratio solution of 3-ethylpyridine to BF_3 recorded at −40°. The chemical shift data of Table I correspond to the bulk (B) and complexed (C) 3-ethylpyridine signals identified in the diagram.

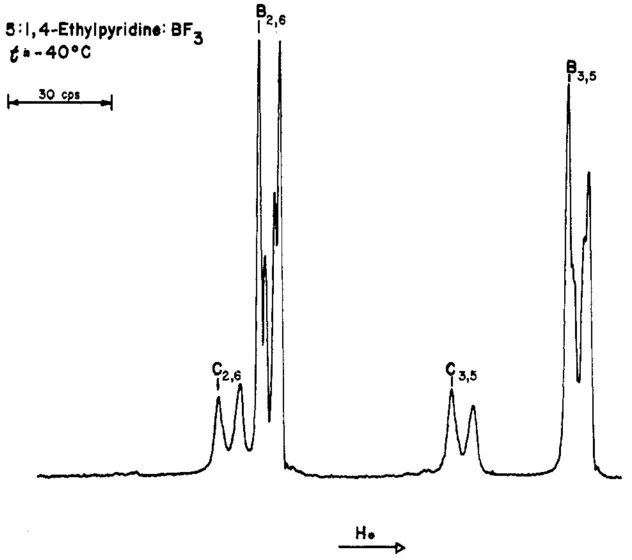


Figure 4.—The pyridine portion of the pmr spectrum of a 5:1 mole ratio solution of 4-ethylpyridine to BF_3 recorded at −40°. The chemical shift data of Table I correspond to the bulk (B) and complexed (C) 4-ethylpyridine signals identified in the diagram.

from the bulk signal. In these instances, the centers of the bulk and complexed 2- and 6-proton signals were approximated to gain a measure of the $\delta_{2,6}{}^{BC}$ values. Since the pmr signals of 1-methylimidazole and pyrimidine, as well as the alkyl proton signals of the substituted pyridines, are simple patterns, the centers were used for the chemical shift results shown in Tables I and II. The broadness of the 2- and 6-proton patterns of the complexed pyridines and the 2-proton signals of 1-methylimidazole and pyrimidine limited the precision of the separation measurements (δ^{BC}) to about 10% in both the BF_3 and BCl_3 systems. The remaining δ^{BC} values were measured with a precision of approximately 5%.

Peak areas of the ring or alkyl proton signals, or both when possible, were measured electronically with the Varian A-60 spectrometer, resulting in coordination numbers precise to about 5%. No indication of which peaks were used is made in Tables I and II since excellent agreement of the integrations was always obtained.

In Table III, several coordination number results are

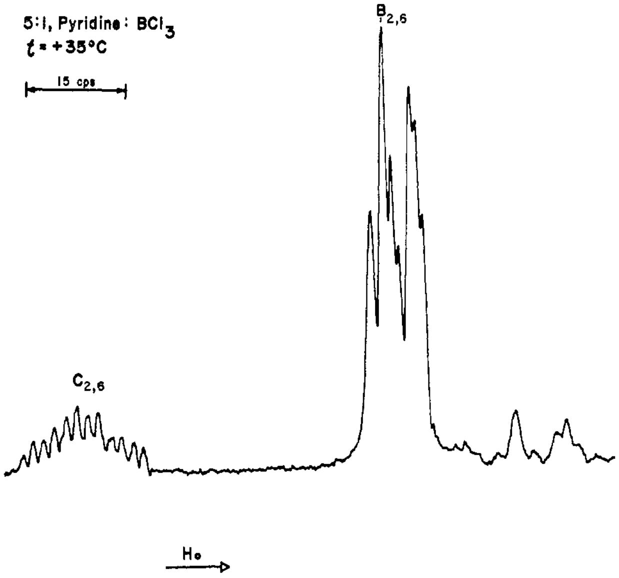


Figure 5.—The 2- and 6-proton magnetic resonance spectrum of bulk (B) and complexed (C) pyridine in a 5:1 mole ratio solution of pyridine to BCl_3, recorded at +35°.

TABLE III

COORDINATION NUMBER DATA FOR MIXED COMPLEXES OF BCl_3 WITH IMIDAZOLE (Im), 1-METHYLIMIDAZOLE (MeIm), PYRIDINE (Py), AND PYRIMIDINE (Pym) AT 35°

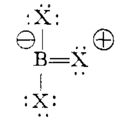
	—Coordination number contributions—			
System	Im	MeIm	Py	Pym
10.1 Py–5.0Im–1BCl_3	(0)		1.0	
5.8Py–5.8MeIm–1BCl_3		0.22	0.84	
5.0Py–5.0Pym–1BCl_3			0.82	(0.2)
5.0MeIm–5.0Pym–1BCl_3		0.90		(0.1)
10.0MeIm–5.0Im–1BCl_3	(0)	1.1		

listed for systems containing BCl_3 and two ligands, chosen from imidazole, 1-methylimidazole, pyridine, and pyrimidine. The ligand and BCl_3 concentrations are given in column 1 in mole ratios, and the coordination number contributions of the various ligands are listed in the next four columns. Parentheses indicate that the coordination number contribution could not be measured because of signal overlap or lack of an observable signal corresponding to complexed ligand. The numbers shown in parentheses were obtained by measuring the contribution of one of the solvent components and assuming a total ligand contribution of 1.

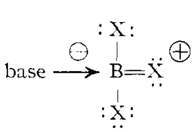
Discussion

Since resonance signals for bulk and complexed ligand molecules are being observed, the data of Tables I and II provide the most accurate measure of the effect of complexing with a boron trihalide on the chemical shift of a ligand proton. To assess the influence of concentration on the chemical shifts, two concentrations were studied in all cases but the 4-methylpyridine-BCl_3 (5:1) and the pyrimidine solutions, where crystallization, presumably of the complex, occurred. Only the results for the most dilute systems, the 10:1 solvent to boron trihalide solutions, are shown, since in these cases chemical shifts of the bulk ligand molecules differed by only 3–4 cps from the respective signals of the pure solvent. The bulk solvent chemical shifts in more concentrated (5:1) solutions differed by a slightly greater amount. However, the separations of bulk and complexed solvent signals δ^{BC}, showed essentially no dependence on concentration, changing by 2 cps or less in most cases for the 5:1 and 10:1 solutions. Thus, it may be reasonably assumed that the δ^{BC} values in Tables I and II are accurate measures of the chemical shifts of the boron trihalide complexes.

The chemical shift data of Tables I and II reflect several structural features of both the boron trihalides and the solvents. For instance, while BF_3 should be a stronger Lewis acid than BCl_3 on the basis of the greater electronegativity of the fluorine atom, much larger chemical shift displacements of the ligand proton signals are produced in the BCl_3 solutions. This is observed consistently throughout Tables I and II for every solvent listed. Although chemical shift displacements are not necessarily a measure of the strength of these complexes, other spectral features also indicate that the boron–nitrogen linkage is stronger in the BCl_3 complexes. The 2- and 6-proton signals of the pyridines complexed with BF_3 appear similar in appearance to the same signal of the bulk ligand, while this resonance pattern appears as in Figure 5 for the BCl_3 complexes. Although not completely resolved, the pattern in Figure 5 apparently results from a spin–spin interaction of the 2- and 6-protons with the boron nucleus in the BCl_3 complexes. This acidity trend agrees with other nmr[1,5,6,8,28,29] and calorimetric studies[30] of boron trihalide complexes, where BCl_3 appears to be a stronger Lewis acid than BF_3. Resonance structures such as



which would make the boron atom less acidic have been postulated to explain these observations.[30,31] Such structures would influence the chemical shift measurements summarized in Tables I and II only if species such as



are important. Since the boron atom exists in many compounds in which it is involved in five or more bonds,[32,33] such structures may be reasonable.

The chemical shift differences, δ^{BC}, of the bulk and complexed pyridine signals are much larger for the 3-, 4-, and 5-protons, usually by a factor of 2 or 3, than for the 2- and 6-protons, even though the interaction site in the molecule is closer to the latter. This result also has been noted in pmr studies of the interaction of

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pyridine with borane[34] and electrolytes.[35] In contrast, upon complex formation with BCl_3 the 2- and 6-proton signals are displaced further downfield, though only by a few cycles per second, than those of the 3-, 4-, and 5-protons. Explanations involving dipolar solvent interactions,[34] polarization of the ligand molecule,[35] electron density calculations,[36] and a paramagnetic effect[37,38] which arises from a mixing of low-lying energy levels at the nitrogen atom have been offered for the observations exemplified by the BF_3 chemical shift data of Table I, that is, a small perturbation of the 2- and 6-proton signal when pyridine is complexed. Obviously any definitive conclusions regarding the cause of the chemical shifts in these complexes will require more experimental information, such as the results of boron-11, fluorine-19, and nitrogen-14 nmr measurements. However, it may be worthwhile to mention some interesting features of the chemical shift results of Tables I and II.

For instance, the chemical shift displacements of the 3-, 4-, and 5-proton signals of pyridine are practically independent of complexing agent, that is, BF_3, BCl_3, and even BH_3,[34] while the 2- and 6-proton chemical shifts reflect the polarizing ability of these Lewis acids. The pyrimidine–boron trifluoride results of Table II are qualitatively similar to those of the boron trifluoride–pyridines, in that the greatest displacements are observed for the signals of the 4-, 5-, and 6-protons, those furthest removed from the interaction site. In contrast, polarization of the ligand molecule dominates in the 1-methylimidazole system as manifested by the greater displacement of the 2-proton signal. Since these results indicate that it may be possible to distinguish between polarization effects and effects which require extensive electron delocalization, such as that present in the pyridines and pyrimidine, a large number of heterocycles are presently being investigated.

In the 1-methylimidazole and pyrimidine systems the chemical shift displacements, δ^{BC}, are very large, amounting to $\sim$90 cps in two cases. This is in contrast to previous nmr studies of these and similar compounds with metal ions wherein attempts are made to deduce information regarding complex formation from chemical shift changes of 1 or 2 cps.[39] The results in Table II reveal the potential utility of this pmr technique for studying the complexing behavior of biologically important molecules in a less ambiguous manner.

The coordination number data of Table I indicate that with all of the pyridines studied, the boron trihalide is complexed by only one ligand molecule. The results for pyridine itself in the table refute the claim based on calorimetric measurements that the pyridine–boron trichloride complex adds another ligand molecule at temperatures below $-30°$.[30] A possible misinterpretation of the thermodynamic data is understandable since calorimetric techniques are susceptible to all processes occurring in solution when the boron trihalide is added. The pmr integrations, however, are unambiguous since they involve the observation of the separate species in solution. Coordination numbers were measured at probe temperature and at -40 or $-50°$ for the pyridines, and they were essentially 1 in all cases. The 1-methylimidazole value in Table II is less than 1 at low temperatures but this is probably due to excessive broadening of the signals. At $+35°$, however, the coordination number is definitely 1. Since pyrimidine could be studied at only one concentration and only with BF_3, owing to crystallization of the sample, the low value listed in Table II is inconclusive. At any rate, these coordination number data indicate that the pmr technique can be used to identify quantitatively the species being studied in these solutions.

This pmr method was also applied to the study of systems containing two Lewis bases and a boron trihalide in an attempt to assess the relative basicities of the ligands. In Table III the contributions of various pairs of bases to BCl_3 complexes are listed. As indicated previously the parentheses indicate that the value was obtained by subtraction from 1 when signal overlap or lack of an observable complexed ligand signal prevented the measurement. The results definitely reveal a decreasing base strength and complexing ability in the order pyridine > 1-methylimidazole > imidazole and pyrimidine. The last two could not be studied in the same solution owing to signal overlap. The data of Table III are preliminary in nature and sparse, but, since studies of competitive interactions of a wide variety of compounds of this type and some more complex in structure are presently underway, the list will be expanded soon.

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