symmetric and asymmetric CN stretching vibrations. An X-ray diffraction study of the complex, currently in progress, should clarify this point.[34]

Solution conductivity studies in acetonitrile reveal nearly identical results for $L_3Cu(NCBH_3)$ and $L_2Cu(NCBH_3)$ (Figure 1). Equilibria 1 and 2 are postulated for the solution behavior of the monomeric and dimeric compounds, respectively. Because of the known tendency of triphenylphosphine–copper(I) complexes to dissociate phosphine ligands in solution,[21] no attempt was made to determine the molecular weight of the sparingly soluble cyanotrihydroboratobis(triphenylphosphine)copper(I) compound in chloroform or other noncoordinating solvents.

$$L_3Cu(NCBH_3) + CH_3CN = L_3Cu(NCCH_3)^+ + H_3BCN^- \quad (1)$$

$$[L_2Cu(NCBH_3)]_2 + 4CH_3CN = 2L_2Cu(NCCH_3)_2^+ + 2H_3BCN^- \quad (2)$$

(34) NOTE ADDED IN PROOF.—A structure similar to that shown in Figure 3a has been found by X-ray crystallography (S. J. Lippard and K. M. Melmed, to be submitted for publication), but the site symmetries of the two cyanide groups are distinctly different. The deuterated analog $\{[(C_6H_5)_3P]_2Cu(NCBD_3)\}_2$ has also been prepared (J. J. Mayerle, unpublished results) and found to contain two sharp ir bands at 2189 and 2206 cm^{-1}. We thank Dr. K. F. Purcell for a sample of NaD_3BCN.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CALIFORNIA STATE COLLEGE, LOS ANGELES, CALIFORNIA 90032

A Direct Proton and Fluorine-19 Nuclear Magnetic Resonance Study of Boron Trihalide Complexes with Pyrazine, Pyridazine, Pyrimidine, 4-Cyclopropylpyridine, 4-Ethylpyridine, Imidazole, 1-Methylimidazole, Pyrazole, and 1-Methylpyrazole

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A direct proton and fluorine-19 nuclear magnetic resonance chemical shift and integration study of boron trifluoride and boron trichloride complexes with pyrazine, pyridazine, pyrimidine, 4-cyclopropylpyridine, 4-ethylpyridine, imidazole, pyrazole, 1-methylimidazole, and 1-methylpyrazole has been completed. In these systems ligand exchange is slow enough to permit the direct observation of pmr signals for bulk ligand and molecules bound to the boron trihalide. The chemical shift differences between the bound and bulk ligand signals were interpreted in terms of an electrostatic effect and possible π-electron participation in the complexing process. Area measurements of the pmr and ^{19}F nmr signals provided an unambiguous determination of the stoichiometry of the complex, along with an estimate of the relative basic strengths of these species. The trends in basic strengths were as follows: pyridazine > pyrimidine > pyrazine; 4-cyclopropylpyridine $\simeq$ 4-ethylpyridine; and 1-methylimidazole > imidazole > pyrazole > 1-methylpyrazole.

Introduction

The utility of nuclear magnetic resonance (nmr) methods for studying a variety of Lewis acid–base systems has been demonstrated recently.[1-18] When samples containing an excess of base are cooled to reduce the rate of proton and molecular exchange, it frequently is possible to observe separate resonance signals for bound and bulk ligand molecules. This has been accomplished for electrolyte solutions, leading to quantitative determinations of cation hydration numbers,[1-3] competitive solvation,[4-6] and contact ion pairing;[7-12] for possible hydrogen-bonding interactions;[13] for Co^{2+} complexes with several bases;[14] and for boron trihalide interactions with organic bases.[15-18] The latter systems included oxygen-containing molecules,[15,18] substituted pyridines,[17] and compounds of biological relevance.[16]

Studies of similar systems have been attempted by calorimetric[19-22] and room-temperature ir and nmr techniques[23-29] and structural information has been ob-

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TABLE I

CHEMICAL SHIFT AND COORDINATION DATA FOR BORON TRIFLUORIDE AND BORON TRICHLORIDE COMPLEXES WITH PYRAZINE (Pyr), PYRIDAZINE (Pyd), PYRIMIDINE (Pym), 4-CYCLOPROPYLPYRIDINE (4-CyPy), 4-ETHYLPYRIDINE (4-EtPy), IMIDAZOLE (Im), 1-METHYLIMIDAZOLE (1-MeIm), PYRAZOLE (Pyra), AND 1-METHYLPYRAZOLE (1-MePyra) AT 60 MHz

Base	Solvent[a]	Mole ratios, base:BX_3:solv	Temp, °C	$\Delta\nu$(C–B), Hz 2	3	4	5	6	Complex mole ratio, base:BX_3
Pyr	A	1.24:1.00:10	−10	6	40	...	40	6	0.96:1.00
Pyr	A	2.18:1.00:20	0	13	47	...	47	13	0.98:1.00
Pyr	2-NP	2.93:1.00:29	−10	12	48	...	48	12	0.99:1.00
Pyd	A	3.00:1.00:29	−10	...	19	48	48	19	1.00:1.00
Pyd	2-NP	3.06:1.00:29	−10	...	18	44	44	18	0.99:1.00
Pym	A	3.00:1.00:29	0	19	...	39	41	19	1.10:1.00
Pym	2-NP	2.66:1.00:25	0	19	...	38	41	16	0.99:1.00
4-CyPy	DCM	2.64:1.00:25[b]	0	37	26	...	26	37	1.04:1.00
4-CyPy	2-NP	2.87:1.00:26	0	5	31	...	31	5	1.01:1.00
4-EtPy	DCM	2.80:1.00:27[b]	0	40	30	...	30	40	1.02:1.00
4-EtPy	DCM	2.80:1.00:27[b]	0	38	29	...	29	38	1.02:1.00
4-EtPy	2-NP	3.00:1.00:29	0	8	34	...	34	8	1.02:1.00
Pyra	2-NP	2.92:1.00:29	0	...	20	14	13	...	1.04:1.00
Im	2-NP	2.94:1.00:30	−10	17	...	5	5	...	0.97:1.00
1-MeIm	2-NP	3.15:1.00:31	+45	40	...	16	13	...	1.06:1.00
			−45						
1-MePyra	2-NP	3.10:1.00:31	+45	...	30	20	30	...	1.00:1.00
			−80						

[a] Solvents: A, acetone; 2-NP, 2-nitropropane; DCM, dichloromethane. [b] Boron trichloride was the Lewis acid.

tained in several cases. The nmr method of this study is somewhat more direct and quantitative in that the bound and bulk ligand signals can be observed simultaneously in the same spectrum. The information which can be derived from these boron trihalide investigations includes the ligand proton chemical shifts produced by complex formation, the stoichiometry of the complex, the relative basic strengths of a series of ligands toward the particular boron trihalide, steric hindrance to complex formation, and a direct measure of the ligand preference of a boron trihalide in a system containing more than one base. The relative basicity information can provide a valuable supplement to the protonation basicity studies carried out by calorimetric[30,31] and nmr methods.[32,33]

The molecules chosen for study all have the common structural feature of a nitrogen atom unshared electron pair, but they differ in ring size, substituents, and degree of unsaturation. This permitted an assessment of the effect of these parameters on complex formation.

Experimental Methods

With the exception of 4-cyclopropylpyridine, which was prepared as described in the literature,[34] all organic compounds were reagent grade. The liquids were distilled and dried over molecular sieves and CaH_2 before use, while the imidazole and pyrazole were recrystallized. The boron trifluoride and trichloride were purified by fractionation. The dryness of the solvents and the BF_3 was verified by the coordination number measurements and the absence of a signal for the water adduct of BF_3 in the ^{19}F nmr spectra. The absence of other BF_3 impurities also was checked by the ^{19}F spectra. The samples were prepared and sealed under vacuum and cooled in liquid nitrogen until the spectra could be recorded, always within a few hours. This procedure was critical only with solutions of the imidazoles and pyrazoles, which become colored and exhibited extraneous proton and ^{19}F nmr signals after standing for several days. None of these problems was evident in any of the systems to be described.

The chemical shift and integration measurements were made on a Varian A-60 and a Varian HA-100 spectrometer, the latter operating at 94.1 MHz for ^{19}F nuclei. The procedure has been described in more detail in previous publications[15-18] and it consists essentially of observing the nmr spectrum as the sample is cooled in the probe. In the systems of this study, ligand exchange was slow enough even at +35° in several cases to permit the observation of separate sets of base signals in the pmr spectra, and BF_3 peaks in the ^{19}F case. Chemical shift and area measurements were made at this point, the latter with the electronic integrator of the spectrometer.

Results

The proton chemical shift and coordination data for all ligands in several solvents are summarized in Table I. In most cases, BF_3 was the Lewis acid, but in addition, BCl_3 was used with the two pyridines to illustrate a chemical shift feature. The solvent was maintained in large excess (10:1) to minimize extensive bound–bulk ligand interactions and little chemical shift change was observed from one solvent to another. The chemical shifts listed represent the difference between the signals for the same proton in bulk ligand and ligand bound to the boron trihalide. The bulk ligand ring proton signal positions are not included in Table I, but they were measured in all cases and they were approximately 7–9 ppm downfield from internal TMS. Because of the complexity of the signal patterns and their partial superposition on the solvent signals, no attempt was made to determine the bound–bulk separations for the cyclopropane ring and ethyl peaks in the pyridine solutions. The bound–bulk separations were about 13 Hz for the methyl proton signals of 1-methylimidazole and 1-methylpyrazole. These peaks were used in the area measurements.

The $\Delta\nu$(complex–bulk) values were obtained by comparing the positions of the centers or one of the dominant peaks of the particular resonance pattern. The numerical designations of the proton sites in the various ligands are based on the diagrams in Figure 1.

The magnetic equivalence of protons in those ligands containing two nitrogen atoms was perturbed by complex formation. For example, although the bulk pyrazine signal for Figure 2 is a singlet arising from the four equivalent protons, two sets of peaks due to the 2,6-CH and 3,5-CH sites are exhibited by bound molecules of this compound. The broader pattern for bound pyrazine was assigned to the 2,6-CH protons because of the

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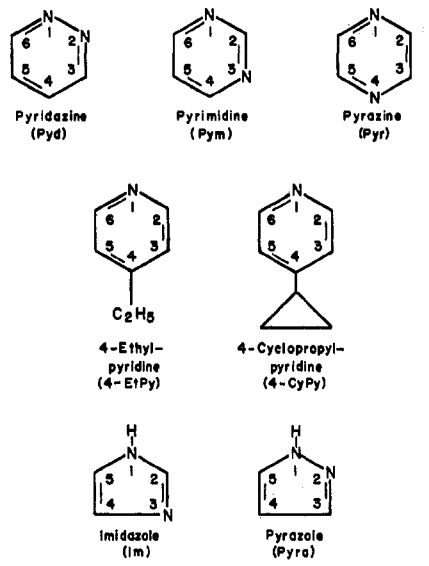

Figure 1.—Compound structure.

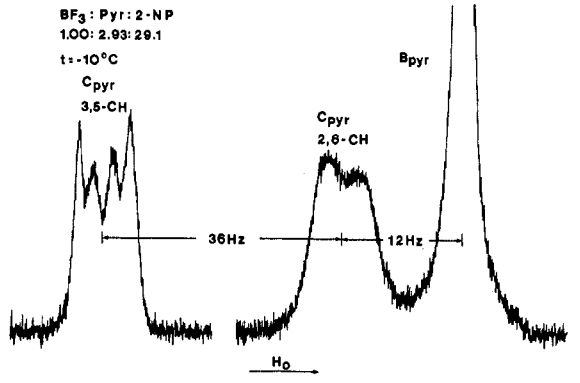

Figure 2.—The proton magnetic resonance spectrum of a BF_3–pyrazine mixture in 2-nitropropane, recorded on a Varian A-60 spectrometer. The signals arising from bulk (B_{pyr}) and coordinated (C_{pyr}) pyrazine molecules are labeled in the diagram, with the numerals identifying the particular proton in the molecule. The mole ratios of all species also are shown.

anticipated quadrupole interaction with the boron nucleus of BF_3. Similarly, the equivalence of the 4,6-CH positions in bulk pyrimidine is destroyed by complex formation and individual sets of signals appear for these protons as seen in the 100-MHz spectrum in Figure 3. The 4,6-CH assignments again were predicated on the greater quadrupole broadening expected at the site closer to the BF_3. Area considerations also were consistent with the assignments of Figure 3. Although not shown here, the bound pyridazine spectrum differed only slightly in appearance from that of bulk ligand, a consequence perhaps of rapid intramolecular exchange. In this case, the 3,6-CH and 4,5-CH protons were considered as equivalent in both environments. Individual signals are observed for the 3-, 4-, and 5-CH protons of bound pyrazole, whereas the 3,5-CH sites are equivalent in bulk ligand. Again, the broader signal was assigned to the 3-CH proton. Overlap of the bound and bulk 4,5-CH signals of imidazole prevented a similar observation in this case, but most likely these sites are not equivalent in the BF_3 adduct. Although bound 1-methylimidazole and 1-methylpyrazole signals were evident at +45°, only at the lower temperatures shown

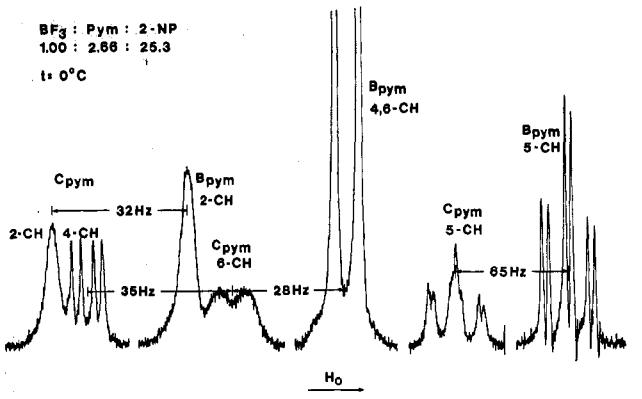

Figure 3.—The proton magnetic resonance spectrum of a BF_3–pyrimidine mixture in 2-nitropropane, recorded on a Varian HA-100 spectrometer. The signals arising from bulk (B_{pym}) and coordinated (C_{pym}) pyrimidine molecules are labeled in the diagram, with the numerals identifying the particular proton in the molecule. The mole ratios of all species also are shown.

in Table I was the nonequivalence of all ring protons clearly demonstrated. In the 1-methylpyrazole spectra at −80°, the 3- and 5-CH signals for bound and bulk molecules were separate doublets (eight peaks in all). Since the signals could not be assigned to a particular proton, the centers of the patterns were used to calculate the $\Delta\nu$(C–B) values. Similarly, separate signals were distinguishable for the 4- and 5-CH protons of bound 1-methylimidazole, but viscosity broadening prevented this observation for the bulk ligand signals.

The ^{19}F chemical shift data for all systems are summarized in Table II. It was observed that the signal of $CFCl_3$, the usual internal standard for ^{19}F nmr work, was about 150 ppm downfield from the BF_3 signals in these systems, whereas the C_6F_6 peak was only 10–12 ppm upfield from BF_3. Thus, C_6F_6 was used as an internal standard and the BF_3 chemical shifts were referred to $CFCl_3$ using the literature value of +162.3 ppm for $\delta(C_6F_6) - \delta(CFCl_3)$.[35] The BF_3 signals usually were broad so the precision of the Table II shift data is about 0.1–0.2 ppm. Also shown in Table II are the results for several systems containing two bases. In two cases, signal overlap prevented an unambiguous assignment of signals and the shift is designated an "average" value. The spectrum of Figure 4 illustrates the ^{19}F nmr signals arising from a BF_3–1-methylpyrazole–pyrazole mixture. Although broadened by complexing in several cases, including those shown in Figure 4, the ^{19}F spectrum of BF_3 generally is a quartet as a result of B–F spin-coupling. This agrees with previous experimental and theoretical reports of ^{19}F spectra for pure BF_3.[36]

The BF_3 ligand preference coordination data are summarized in Table III for various pairs of bases. Due to signal overlap in the pmr spectra, a direct measure of the fraction of BF_3 complexed by each base was not always possible. In those cases, the values shown in parentheses were obtained by subtraction of the measurable component from 1.00. When each contribution was directly measured, the sum totalled essentially 1 within 5%, the precision of these experiments. Since

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TABLE II

FLUORINE-19 CHEMICAL SHIFT DATA FOR BORON TRIFLUORIDE COMPLEXES WITH PYRAZINE (Pyr), PYRIDAZINE (Pyd), PYRIMIDINE (Pym), 4-CYCLOPROPYLPYRIDINE (4-CyPy), 4-ETHYLPYRIDINE (4-EtPy), IMIDAZOLE (Im), 1-METHYLIMIDAZOLE (1-MeIm), PYRAZOLE (Pyra), AND 1-METHYLPYRAZOLE (1-MePyra) AT 94.1 MHz

Base(s)			Mole ratios,	Temp,	δ, ppm	
A	B	Solvent[a]	Base(s):BF_3:solv	°C	A	B
Pyr		A	1.24:1.00:10	+5	+149.3	...
Pyr		2-NP	2.93:1.00:29	+5	+149.9	...
Pyd		A	3.00:1.00:29	+5	+149.5	...
Pyd		2-NP	3.06:1.00:29	+5	+150.0	...
Pym		A	3.00:1.00:29	+5	+148.0	...
Pym		2-NP	2.66:1.00:25	+5	+148.7	...
Pyr,	Pym	A	2.90:2.96:1.00:28	+5	+149.4	+148.1
Pyr,	Pym	2-NP	2.70:2.70:1.00:25	+5	+149.9	+148.6
Pyr,	Pyd	2-NP	2.66:2.84:1.00:28	+5	+150 (av)	
Pyd,	Pym	A	2.90:2.85:1.00:27	+5	+149.6	+148.0
Pyd,	Pym	2-NP	2.87:2.83:1.00:25	+5	+150.1	+148.6
4-CyPy		2-NP	2.87:1.00:26	+5	+149.7	...
4-EtPy		2-NP	3.00:1.00:29	+5	+149.6	...
4-CyPy,	4-EtPy	2-NP	2.88:2.81:1.00:28	+5	+150 (av)	
Im		2-NP	2.94:1.00:30	−20	+146.5	...
Pyra		2-NP	2.92:1.00:29	+5	+146.9	...
1-MeIm		2-NP	3.15:1.00:31	+45	+146.9	...
				−20	+146.7	...
1-MePyra		2-NP	3.10:1.00:31	+35	+145.0	...
				−20	+145.0	...
1-MeIm,	Pyra	2-NP	1.70:1.70:1.00:17	+35	+146.6	...
				−20	+146.4	...
1-MePyra,	Im	2-NP	1.60:1.60:1.00:16	+35	...	+146.5
				−20	...	+146.3
1-MePyra,	Pyra	2-NP	1.65:1.60:1.00:16	−20	+145.0	+146.5
1-MeIm,	1-MePyra	2-NP	1.60:1.60:1.00:16	+35	+146.6	...
				−20	+146.4	...

[a] Solvents: A, acetone; 2-NP, 2-nitropropane.

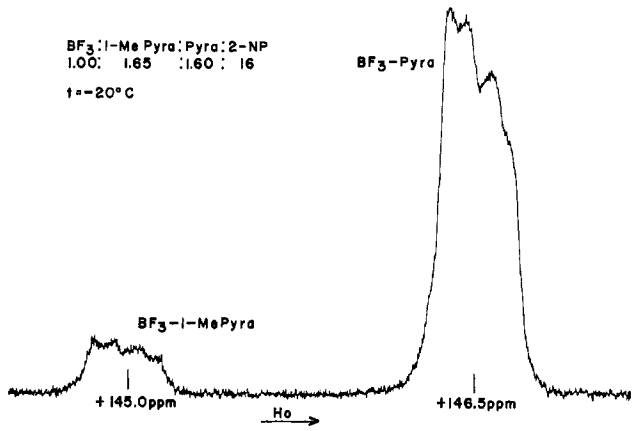

Figure 4.—The fluorine-19 nuclear magnetic resonance spectrum of a BF_3–1-methylpyrazole–pyrazole mixture in 2-nitropropane, recorded at 94.1 MHz on a Varian HA-100 spectrometer. The signals arising from the BF_3–1-methylpyrazole (BF_3–1-MePyra) and BF_3–pyrazole (BF_3–Pyra) adducts are labeled and the mole ratios of all species are shown.

all the BF_3 was complexed, the relative areas of the ^{19}F signals were compared. The distribution of the BF_3 between each complex calculated in this manner agreed with values derived from proton data. With three base pairs, only one ^{19}F signal was observed, an indication that complexing by one component was complete. These entries are shown as 1.00 values for the ^{19}F integrations.

Discussion

It is evident from the spectra of Figures 2–4 that the ability to slow ligand exchange in Lewis acid–base systems provides a valuable mechanism for directly studying several aspects of the complexing process. In these systems, the bound–bulk ligand proton chemical shift differences vary from ~0.1 to 1 ppm, indicating that the lifetime of a ligand molecule in a particular environment at 0° is of the order of $\tau \simeq 10/2\pi\Delta\nu \simeq 0.1$ sec.[37] Although it is not certain without a knowledge of the exchange mechanism, this slow exchange rate at a relatively high temperature for this type of study may reflect the strength of the BF_3–base complex. For example, the BF_3 complexes with acetone or diethyl ether,[15,18] both weaker bases, must be cooled to about −100° to produce a comparable exchange rate.

In the six-membered ring systems, the interaction site is the pyridine nitrogen atom or one of the two equivalent nitrogen atoms in the remaining compounds. However, the presence of a proton or methyl group on the imidazole and pyrazole rings presents the possibility of complexing at either nitrogen site in these molecules. One would anticipate that the BF_3 molecule and the proton, both strong Lewis acids, would be at different nitrogen atoms when complexing occurs with imidazole and pyrazole. Thus, if the 1-N position is assigned to the proton, the BF_3 would reside at the remaining nitrogen atom. Substitution of the proton with the electron donating methyl group should make the 1-N position more basic in 1-methylimidazole and 1-methylpyrazole. However, our chemical shift data, proton and probably ^{19}F, strongly imply that complexing occurs at the 2-N position in 1-methylpyrazole and the 3-N site in 1-methylimidazole, as a result of steric hindrance. In both systems, the bulk–bound methyl group separation is only about 0.2 ppm. In contrast to this result, methyl group separations are much larger in complexes of acetone (0.8 ppm),[15] dimethyl ether (0.6 ppm),[15] dimethyl sulfoxide (0.6 ppm),[18] dimethylformamide (0.4 ppm),[15,18] and tetramethylurea (0.3 ppm).[18] One might assume that if complexing were oc-

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TABLE III

PROTON AND FLUORINE-19 LIGAND PREFERENCE COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES WITH PYRAZINE (Pyr), PYRIDAZINE (Pyd), PYRIMIDINE (Pym), 4-CYCLOPROPYLPYRIDINE (4-CyPy), 4-ETHYLPYRIDINE (4-EtPy), IMIDAZOLE (Im), 1-METHYLIMIDAZOLE (1-MeIm), PYRAZOLE (Pyra), AND 1-METHYLPYRAZOLE (1-MePyra)

Bases			Mole ratios,	Temp,		BF_3 fraction component	
A	B	Solvent[a]	A:B:BF_3:solv	°C	Nucleus	A	B
Pyr	Pyd	2-NP	2.75:2.75:1.00:25	0	^{1}H	(0.05)[b]	0.95
Pyr	Pym	A	2.90:2.96:1.00:28	−20	^{1}H	(0.27)[b]	0.73
				+5	^{19}F	0.31	0.69
Pyr	Pym	2-NP	2.70:2.70:1.00:25	0	^{1}H	0.31	0.69
				+5	^{19}F	0.28	0.72
Pyd	Pym	A	2.90:2.85:1.00:27	0	^{1}H	0.77	(0.23)[b]
				+5	^{19}F	0.86	0.14
Pyd	Pym	A	3.02:2.90:1.00:29	0	^{1}H	0.80	(0.20)[b]
				+5	^{19}F	0.86	0.14
Pyd	Pym	2-NP	2.85:2.85:1.00:25	0	^{1}H	0.85	(0.15)[b]
				+5	^{19}F	0.86	0.14
4-CyPy	4-EtPy	2-NP	2.88:2.81:1.00:28	0	^{1}H	0.50	0.57
4-CyPy	4-EtPy	DCM	2.80:2.78:1.00:28	0	^{1}H	0.46	0.55
1-MeIm	Pyra	2-NP	1.70:1.70:1.00:17	+35	^{1}H	1.03	...
					^{19}F	1.00	...
				−20	^{19}F	1.00	...
1-MePyra	Im	2-NP	1.60:1.60:1.00:16	+35	^{1}H	...	1.05
					^{19}F	...	1.00
				−20	^{1}H	...	1.05
					^{19}F	...	1.00
1-MePyra	Pyra	2-NP	1.65:1.60:1.00:16	+35	^{1}H	0.11	0.87
				−20	^{19}F	0.13	0.87
1-MeIm	1-MePyra	2-NP	1.60:1.60:1.00:16	+35	^{1}H	1.10	...
					^{19}F	1.00	...
				−20	^{19}F	1.00	...

[a] Solvents: A, acetone; 2-NP, 2-nitropropane; DCM, dichloromethane. [b] Overlap or low intensity prevented a direct signal integration. Values in parentheses were obtained by subtraction of the second base contribution from 1.00.

curring at the 1-N position in these molecules, the displacement of the methyl signal would exceed 0.2 ppm. Also, the ^{19}F signal for the BF_3 complexes of these molecules differs significantly only in the case of 1-methylpyrazole, where the steric effect would be pronounced even with addition at the 2-N position. Although qualitative, the evidence seems to indicate complex formation at the 2-N and 3-N positions of 1-methylpyrazole and 1-methylimidazole, respectively. An attempt to add a second molecule of BF_3 to these complexes resulted in viscous samples and broad, inconclusive proton and ^{19}F spectra.

Although the proton chemical shift data of Table I cannot be interpreted in a rigorous, quantitative manner, there are several features of interest. For example, the observed bulk–complex chemical shift separations are not solvent dependent to any extent in those cases where a comparison is possible. Thus, the $\Delta\nu$(C–B) values are an accurate measure of the effect of complex formation on this nmr parameter. More importantly, in the six-membered ring systems, the greater displacements are observed for the signals of protons further removed from the nitrogen interaction site when complexing with BF_3 occurs. In the pyrimidine 60-MHz spectra, the 2- and 6-CH pmr signals undergo a displacement of about 20 Hz, while the 4- and 5-CH signals are displaced by about 40 Hz. This also is true with the coordinated pyridines, where the 3- and 5-CH pmr signals are displaced by twice the amount observed for the 2- and 6-CH peaks. In contrast to this result, when the partially unsaturated imidazoles and pyrazoles form BF_3 complexes, the signal arising from the proton closest to the nitrogen interaction site is displaced furthest. Finally, when the more acidic BCl_3 was used in place of BF_3 with the two pyridines, the situation was reversed and the greater displacement was observed for the 2- and 6-CH signals.

These results reflect the contribution of more than one process to the observed shifts. An electrostatic process dominates in the BCl_3–substituted pyridine cases, causing a decreased shielding at the 2- and 6-CH sites, with an attenuation of this effect at sites further removed. However, the BF_3–complex data for the completely unsaturated ligands reveal the presence of an effect which is of more importance at the protons closer to the nitrogen atom interaction site. Previous pyridine protonation,[38–40] cation solvation,[41] and boron trihalide complexation[16,17] studies gave similar results which were interpreted in terms of an energy level mixing of the unshared electron pair on the nitrogen atom of pure ligand.[42] The fact that the 2- and 6-CH pmr signal pattern of pure pyridine appears downfield from the remaining pmr peaks is attributed to this paramagnetic effect. Complex formation binds the electron pair thereby minimizing this process. A cancelation of these electrostatic and paramagnetic contributions causes a diminution of the low field displacement. This argument still is not sufficient, since the 3- and 5-CH proton shifts in the pyridines are similar in the BF_3 and BCl_3 complexes. One or more other effects also must be operative.

Although one would expect the paramagnetic effect to prevail in the imidazoles and pyrazoles, the chemical shift data of Table I indicate that this is not the case. An important structural difference between these ligands and the six-membered ring systems just discussed is the degree of π-electron character in the ring system. The more localized nature of the π bonds in imidazole and

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pyrazole may be the factor which removes the "paramagnetic" effect. At this point one can only state that π-electron participation in the complexing process is a possibility with completely unsaturated ligands. ^{14}N and ^{13}C nmr studies presently planned should prove to be a definitive supplement to these pmr results.

The data of Table II reveal that the ^{19}F chemical shifts of the BF_3 complexes all lie within a range of 3–4 ppm, and the position is solvent dependent to the extent of ~0.5 ppm. One would anticipate from the data for BF_3 complexes with pure pyrazine and pyridazine or pure 4-cyclopropyl- and 4-ethylpyridine that mixtures of these bases would produce superimposed signals. However, it was possible to study several combinations of bases to supplement the proton coordination measurements.

The pmr coordination data of Table I illustrate the principal advantage of this technique, namely, the ability to determine quantitatively the stoichiometry of the complex. Simple 1:1 complexes were anticipated in these systems, and within a few per cent, this was observed with each ligand. As shown in Table III, this approach also allows a direct comparison of the relative basic strengths of a series of ligands toward a boron trihalide. For example, the proton integration results for the pyrazine, pyridazine, and pyrimidine series clearly show that pyridazine is the most effective ligand of the three in binding BF_3. This compound binds essentially all the BF_3 in the presence of pyrazine and about 80% in the presence of pyrimidine. In turn, pyrimidine binds ~70% of the BF_3 in the presence of pyrazine. The ^{19}F nmr integration data support these observations. One must conclude, therefore, that toward BF_3 the relative basicities of these ligands decrease in the order pyd > pym > pyr. This trend correlates well with the pK_{BH^+} data for these species derived from protonation experiments. Thereto, the relative basicities decrease in the order: pyd (pK_{BH^+} = 2.3) > pym (pK_{BH^+} = 1.3) > pyr (pK_{BH^+} = 0.6).[43,44]

Similarly, protonation experiments demonstrate roughly equal basicities for 4-cyclopropylpyridine (pK_{BH^+} = 6.2)[34] and 4-ethylpyridine (pK_{BH^+} = 6.0).[44] This situation parallels their behavior toward BF_3, as seen from the pmr coordination data of Table III. Each ligand complexes roughly 50% of the BF_3 present in these systems.

The results obtained with combinations of the imidazoles and pyrazoles may be summarized as follows. The BF_3 combines solely with 1-methylimidazole when the second base is imidazole, pyrazole, or 1-methylpyrazole. The imidazole–1-methylimidazole pair was studied previously.[16] A competition for the BF_3 occurs when pyrazole and 1-methylpyrazole are paired, and, finally, imidazole complexes the BF_3 totally in the presence of 1-methylpyrazole. These conclusions are supported by the proton and ^{19}F shift and area data. For instance, only one ^{19}F signal is observed in each 1-methylimidazole solution spectrum, and the resonance position clearly identifies it with the BF_3 complex of this component. The proton spectra also exhibit bound ligand signals only for this base. Mixtures of pyrazole and 1-methylpyrazole show bound ligand signals for both components in the proton spectra, and two ^{19}F peaks (see Figure 4). The areas indicate that about 87% of the BF_3 is complexed by pyrazole and the remainder by 1-methylpyrazole. Finally, the one ^{19}F signal observed in the imidazole–1-methylpyrazole case corresponds closely to the BF_3–imidazole complex, while bound ligand signals were observed only for this base. The presence of extraneous proton and ^{19}F signals precluded the study of the imidazole–pyrazole pair. Although it is conceivable that this complication is caused by proton transfer and subsequent BF_3 complex formation with the resultant anion,[45] this feature was not explored. However, the data of Table III still lead to the following quantitative order of relative basicities toward BF_3: 1-MeIm (pK_{BH^+} = 7.1) > Im (pK_{BH^+} = 7.0) > Pyra (pK_{BH^+} = 2.5) > 1-MePyra (pK_{BH^+} = 2.0). This trend closely parallels the proton basicity data shown in parentheses,[43,44] although our data would suggest a greater basicity difference for the imidazole–1-methylimidazole pair than that arrived at by other methods.[44] An empirical estimate would be at least 1 pK unit.[16-18] Since the presence of a methyl group should make 1-methylpyrazole a more basic species than pyrazole, our results may reflect steric hindrance to complex formation in the former case. This is reasonable in view of the proximity of the two nitrogen atoms in this molecule.

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