likely that transitions both to $A_2(\pi^*)$ and to $B_2(\pi^*)$ are included in the charge-transfer band. Because of the pattern of sensitivity to substituents, the acceptor orbital must be the $B_2(\pi^*)$. The two transitions $B_2(\pi^*) \leftarrow B_2(d_{yz})$ and $B_2(\pi^*) \leftarrow A_2(d_{xy})$ could both comprise the absorption band, as the splitting between the d orbitals is probably small and should be relatively insensitive to perturbations on the pyridine ring.

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A Variable-Temperature Nuclear Magnetic Resonance Study of Complexes of Borane and Boron Trihalides with Acetone, Diethyl Ether, Dimethyl Ether, N,N-Dimethylformamide, Methanol, and Tetrahydrofuran

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Abstract: A proton and boron-11 chemical shift and coordination number study of complexes of diborane and the boron trihalides with dimethyl ether, diethyl ether, methanol, tetrahydrofuran, and, to a small extent, acetone and N,N-dimethylformamide has been completed. At low temperatures, separate proton resonance signals are observed for bulk solvent and solvent molecules complexed with the boron species. Coordination numbers were measured by the direct integration of the separate signals. The chemical shift separations for bulk and complexed solvent signals decreased in the order $BBr_3 > BCl_3 > BF_3 > BH_3$. An attempt is made to relate these separations to the coordinating abilities of the boron halides. The proton chemical shift data of the bases were correlated with some diborane ^{11}B and ^{1}H nuclear magnetic resonance results to obtain information concerning the species present in the ether–diborane solution.

Numerous attempts have been made to assess the relative strengths of donor–acceptor interactions in solution by nuclear magnetic resonance (nmr) chemical shift techniques. Although complexes of borane and the boron halides with a variety of Lewis bases have been the object of the most intensive study,[1–8] similar complexes of Ga(III)[9] and other ions[3,10] have been investigated by nmr methods. Using this technique, one relates the nmr signal displacements observed when the complexing species are mixed, often in another solvent, with the strength and the equilibrium of complex formation. However, at room temperature, only one set of resonance signals is usually observed for a particular ligand, since rapid exchange averages the signals arising from molecules in bulk medium and in the coordination shell of the complex. A study of the displacements of these averaged signals presents several disadvantages. The resonance positions of such signals are subject to all processes occurring in solution, including complex formation, ionic strength, temperature, and the nature of the solvent in which the complex is being studied. Further, systems which can be studied are limited to those that do not undergo reaction at room temperature. Such a limitation would have prevented the study of several of the boron halide complexes to be discussed here.

It has recently been demonstrated that in several systems involving complexes of Al(III) and other diamagnetic ions with N,N-dimethylformamide,[11,12] dimethyl sulfoxide,[13] and methanol[14,15] solvent exchange is slow enough to permit the observation of proton resonance signals for bulk solvent and molecules in the first coordination shell of the cation. In such systems, one obtains the most accurate value of the effect of complex formation on the chemical shift of a ligand proton. Integration of the separate resonance signals yields an unambiguous coordination number for the central ion.

We have applied this proton magnetic resonance technique to studies of complexes of borane and boron trihalides with several oxygen-containing organic bases, namely, dimethyl ether (Me_2O), diethyl ether (Et_2O), methanol (MeOH), tetrahydrofuran (THF), and, to a lesser extent, acetone and N,N-dimethylformamide (DMF). In addition, boron-11 room-temperature nmr

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

(2) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, 42, 1518 (1964).

(3) S. J. Kuhn and J. S. McIntyre, *ibid.*, 43, 375 (1965).

(4) E. Gore and S. S. Danyluk, *J. Phys. Chem.*, 69, 89 (1965).

(5) M. Okada, K. Suyama, and Y. Yamashita, *Tetrahedron Letters*, 28, 2329 (1965).

(6) P. N. Gates, E. J. McLauchlan, and E. F. Mooney, *Spectrochim. Acta*, 21, 1445 (1965).

(7) A. G. Massey and A. J. Park, *J. Organometal. Chem.* (Amsterdam), 5, 218 (1966).

(8) J. Paasivirta and S. Brownstein, *J. Am. Chem. Soc.*, 87, 3593 (1965).

(9) N. N. Greenwood and T. S. Srivastava, *J. Chem. Soc., Sect. A*, 703 (1966).

(10) A. J. Carty, *Can. J. Chem.*, 44, 1881 (1966).

(11) A. Fratiello, D. P. Miller, and R. E. Schuster, *Mol. Phys.*, 12, 111 (1967).

(12) A. Fratiello and R. E. Schuster, *J. Phys. Chem.*, 71, 1948 (1967).

(13) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, 44, 3148 (1966).

(14) J. H. Swinehart and H. Taube, *ibid.*, 37, 1579 (1962).

(15) S. Nakamura and S. Meiboom, *J. Am. Chem. Soc.*, 89, 1765 (1967).

Table I. Proton Chemical Shift Data for Complexes of Borane and Boron Trihalides with Organic Bases

System	Temp, °C	$\Delta\nu_{CH_3}{}^B$	$\Delta\nu_{CH_2}{}^B$	$\Delta\nu_{CH_3}{}^{BC}$	$\Delta\nu_{CH_2}{}^{BC}$	Coordn no.
$1BH_3$–$2.5Me_2O$	−70	198.6		23.9 (0.1)		0.85
$1BF_3$–$5Me_2O$	−90	202.0		38.3 (0.3)		1.01
$1BCl_3$–$5Me_2O$	−45	198.8		59.8 (0.2)		0.92
$1BBr_3$–$5Me_2O$				Decomposes		
$1BH_3$–$2.5Et_2O$	−95			No complex obsd		
$1BF_3$–$5Et_2O$	−80	70.0	210.0	15.4 (0.1)	53.9 (0.6)	1.01
$1BCl_3$–$5Et_2O$	−45	69.1	208.3	27.3 (0.2)	82.2 (0.2)	1.07
$1BBr_3$–$5Et_2O$	−30	71.6	215.0	30.4 (0.4)	89.3 (0.3)	
$1BH_3$–2.5THF	−45		(α) 220.4 (β) 108.4		(α) 20.1 (0.1) (β) 16.6 (0.1)	0.91
$1BF_3$–5THF	−80		(α) 226.0 (β) 111.3		(α) 40.5 (0.2) (β) 21.5 (0.1)	0.90
$1BCl_3$–5THF	−20		(α) 223.5 (β) 110.3		(α) 61.5 (0.3) (β) 27.6 (0.2)	
$1BBr_3$–5THF				Decomposes		
$1BF_3$–1.73MeOH	−40	220.0		5.4 (0.1)		0.71
$1BF_3$–2.38MeOH	−40	216.0		4.6 (0.1)		0.77
$1BF_3$–2.52MeOH	−40	215.9		4.6 (0.1)		0.76
$1BF_3$–5.0MeOH	−40	211.8		6.2 (0.1)		0.70
$1BF_3$–6.36MeOH	−40	208.3		8.0 (0.1)		0.67
$1BF_3$–18.2MeOH	−40	205.5		9.5 (0.1)		0.80
$1BF_3$–5(acetone)	−80	134.0		44.5 (0.3)		0.84
$1BF_3$–DMF	0	170.8 (*cis*)		22.8 (0.1) (*cis*)		1.10
		180.0 (*trans*)		27.3 (0.2) (*trans*)		

measurements have been made with several of these complexes. At low temperatures, separate proton resonance signals are observed for bulk and complexed solvent.[15a]

Experimental Section

All proton magnetic resonance chemical shift measurements and integrations were made with a Varian A-60 spectrometer equipped with a variable-temperature probe which permits studies from −100 to +200°. Chemical shifts were measured with reference to internal tetramethylsilane (TMS). The room-temperature boron-11 nmr spectra for several of the complexes were recorded using a Varian V-4300 spectrometer operating at 12.83 Mc.

Samples were prepared with vacuum-fractionated BF_3, BCl_3, BBr_3, and B_2H_6, and with reagent grade solvents. All of the ethers were distilled from $LiAlH_4$ before use. Dimethylformamide was dried over molecular sieves before use. The pmr spectra were recorded immediately thereafter. Evidence for decomposition of the samples was provided by high-amplitude proton magnetic resonance spectra. Only in the BCl_3-THF and BBr_3-Et_2O systems was there any indication of decomposition. Although the extent of reaction was small, reproducible integrations were not possible. Duplicate samples were prepared for each complex and the spectrum of each was recorded twice.

Results

Figure 1 illustrates the pmr spectrum, recorded at −45°, of a solution containing BCl_3 and Et_2O, in a 1:5 mole ratio, respectively, along with the recording of the electronic integration. As with every system listed in Table I, the signal arising from complexed solvent appears at a lower applied magnetic field than bulk solvent. The chemical shift and coordination number results for all the complexes studied are listed in Table I. In the first and second columns, respectively, the particular system and the temperature at which the spectra were recorded are listed. The quantities $\Delta\nu_{CH_3}{}^B$ and $\Delta\nu_{CH_2}{}^B$, in columns 3 and 4, respectively, of Table I, refer to the separations in cycles per second of the resonance signals of these particular bulk solvent protons from internal TMS, the latter always appearing at higher field. With the exception of the MeOH systems, the proton chemical shifts of the pure solvents at the same temperature agreed within 1–3 cps with those shown in columns 3 and 4 of Table I. Since the methyl proton signals of MeOH showed a significant concentration dependence, a sample containing a large mole ratio of MeOH to BF_3 was studied to ensure an "infinite dilution" result for the complex. The separations between the particular proton resonance signal (CH_3 or CH_2) of the complexed solvent molecules and bulk

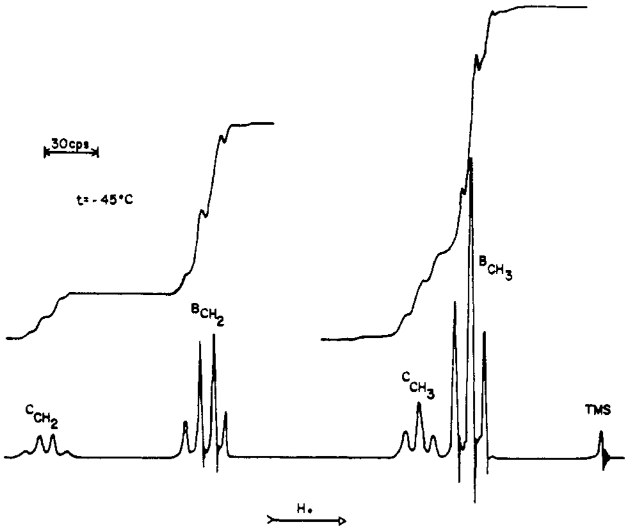


Figure 1. The proton magnetic resonance spectrum of a 1:5 mole ratio solution of BCl_3 to diethyl ether, recorded at −45° on a Varian A-60 spectrometer. The peaks are identified as bulk (B) or complexed (C) ether signals.

(15a) Note Added in Proof. A preliminary communication describing some of these measurements has recently been published: R. E. Schuster, A. Fratiello, and T. P. Onak, *Chem. Commun.*, 1038 (1967).

Table II. Chemical Shift Data for the Boron Hydride Moiety in Diborane–Ether Mixtures

System	Temp, °C	^{11}B nmr[a]	^{1}H nmr (H–B pattern)
$1B_2H_6$–$5Et_2O$	30	Broad singlet; δ −17 ppm[b]	
	−36	Spectrum of unaltered B_2H_6; δ −17 ppm[b] $J_{^{11}B-H_T}$ = 135 cps	Weak 1:1:1:1 quartet; δ 4.05 ppm $J_{H_T-^{11}B}$ = 133 cps
$1B_2H_6$–$5Me_2O$	30	1:6:15:20:15:6:1 septet; δ −15.9 ppm $J_{^{11}B-H_T}$ = 60 cps	Broad peak (total width = 400 cps); δ 2.4 ppm
	−60		1:1:1:1 quartet; δ 2.47 ppm $J_{H_T-^{11}B}$ = 104 cps
$1B_2H_6$–5THF	30	1:3:3:1 quartet; δ 1.9 ppm $J_{^{11}B-H_T}$ = 97 cps	1:1:1:1 quartet; δ 2.5 ppm $J_{H_T-^{11}B}$ = 95 ± 5 cps

[a] δ 0.0 for $BF_3\cdot(C_2H_5)_2O$. [b] See D. Gaines, *Inorg. Chem.*, **2**, 523 (1963), and references therein.

solvent are listed in columns 5 and 6 of Table I. The average deviations of these measurements, usually 1% or less, are shown in parentheses next to each entry. Not listed in Table I are the data involving the hydroxyl and formyl proton signals in the BF_3–MeOH and BF_3–DMF systems. A separate resonance signal was observed for the formyl proton of complexed DMF, displaced 28 cps downfield from the bulk signal. The latter, in turn, appears 484 cps downfield from TMS. A separate signal corresponding to the hydroxyl proton of complexed MeOH could not be observed even at −90°. The most reliable value of the separation between bulk and complexed MeOH is that obtained in the 1:18 mixture. At this concentration, the chemical shift of the methyl group of bulk MeOH is the same as that of pure MeOH at the same temperature.

The coordination numbers listed in column 7 of Table I were measured with a precision of ~10%, and they were approximately 1 in all but the BF_3–MeOH mixtures.

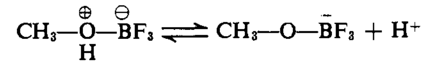
The temperatures of study shown in Table I are those at which the signals were sharpest. At higher temperatures the onset of solvent exchange resulted in line broadening. In general, however, again with the exception of the MeOH systems where hydrogen bonding and possibly proton exchange are complicating factors, the chemical shifts of bulk to complexed molecules, $\Delta\nu^{BC}$, did not vary over a ±20° range from that listed in Table I.

In Table II ^{11}B and ^{1}H nmr are tabulated for the boron hydride species present in several diborane–ether mixtures. Overlap of the H–C peaks of the ether occasionally masked part, or all, of one peak of the H–^{11}B quartets observed in the ^{1}H nmr. From the visible peaks, however, there was no doubt about the δ and J assignments. Further, the ^{1}H nmr J value checked out well with the reciprocal coupling observed in the ^{11}B nmr for those cases where such a correlation is to be expected.

Discussion

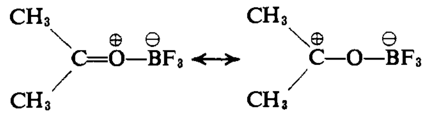
Boron Halide Systems. Since separate magnetic resonance signals are observed for the bulk and complexed solvent molecules, the quantity $\Delta\nu^{BC}$ listed in Table I, provides the most unambiguous measure of the effect of complex formation on the chemical shift of a particular solvent proton. With the use of pure solvents, the separations are not influenced by the presence of a diluent, and further, all but those representing the MeOH systems are independent of temperature over a 40° range. The complexes were studied at concentrations of base sufficiently great such that further dilution did not affect the $\Delta\nu^{BC}$ values. Also, in most cases, the coordination numbers permit an accurate qualitative and quantitative estimate of the species present in solution. This is far superior to the usual technique of mixing the components in a 1:1 mole ratio in a third solvent and then assuming the presence of 1 mole of complex.

Since the signals arising from complexed solvent always appear at lower applied magnetic field than the bulk solvent signals, the protons of the former must experience a decreased electronic shielding. This implies that the separation of the bulk and complexed solvent signals may reflect the extent of electron charge withdrawal from the ligand upon complex formation. For the simple oxygen-containing molecules listed in Table I, the chemical shift separations of the alkyl protons correlate well, qualitatively, with the amount of positive charge associated with the donor atom. The $\Delta\nu_{CH_3}{}^{BC}$ is much greater, for instance, for the dimethyl ether–boron trifluoride complex than with the methanol–boron trifluoride system. The latter complex can more easily distribute the accumulated formal charge on the oxygen to the proton by the following dissociation mechanism



$$CH_3-\underset{H}{\overset{\oplus}{O}}-\overset{\ominus}{B}F_3 \rightleftharpoons CH_3-O-\bar{B}F_3 + H^+$$

Also, the larger $\Delta\nu_{CH_3}{}^{BC}$ value for the acetone–BF_3 complex as compared to that of the diethyl ether–BF_3 complex might be accommodated by noting the greater polarizability of the carbonyl bond of acetone. Thus, resonance such as



results in a positive charge closer to the methyl groups of acetone than is possible in diethyl ether.

In view of the above correlation of the chemical shift separations of the alkyl hydrogens with the proximity and extent of neighboring positive charge, it is somewhat surprising that the $\Delta\nu^{BC}$ values decrease in the order $BBr_3 > BCl_3 > BF_3$. This trend has been noted before in related systems,[2-4,6,16] and attempts have been made to correlate it with the relative "acidities" of the BX_3 moieties. The acidities have been linked to

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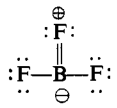
(16) H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, 78, 2173 (1956).

the enthalpy change associated with the reaction

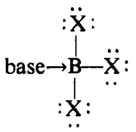
$$\text{base} + BX_3 \rightleftharpoons \text{base}\rightarrow BX_3$$

In such correlations, one must account for the relative stabilities of the starting materials. Fortunately, the low-temperature proton magnetic resonance data obtained for the complex itself are not especially influenced by the previous history of the complexing species.

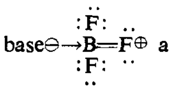
Considering the presumed near tetrahedral coordination about the boron atoms in the complexes, it is difficult to rationalize a trend in $\Delta\nu^{BC}$ values which is opposite to that expected on the basis of the halogen atom electronegativities. Thus, the strongly electronegative fluoride atom should serve to make BF_3 the strongest Lewis acid of the series. It has been postulated that the boron trihalides may exhibit resonance structures such as



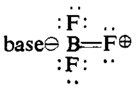
which would tend to make the boron site less acidic.[16,17] Since the tendency to form double bonds decreases with the heavier atoms, this resonance effect should make the largest structural contribution to BF_3 and the least to BBr_3. Since it comprises all the energy changes occurring in solution, ΔH values for complex formation in the boron trihalide series may reflect this resonance effect. For several reasons, however, an interpretation of the observed trend in $\Delta\nu^{BC}$ values in term of this resonance phenomenon is not entirely satisfactory. If the complex involves only a tetravalent boron



the chemical shift of the complex in no way is influenced by the prior structure of the trihalide. If structural contributions such as



and/or



are important, this resonance effect could account for the observed trend in signal separations.

Another approach involves a consideration of all the electronic changes that may occur in the base when a complex is formed. For instance, electron withdrawal at the oxygen atom results in a formal positive charge at this site and subsequent deshielding of neighboring protons. This is the only factor considered by previous workers when evaluating the magnitude of chemical shift displacements.[1-7,9,10] An unknown quantity, however, is the extent of paramagnetic effects at the oxygen atom in these bases. This effect, which involves a mixing of ground and low-lying excited electronic states, has been postulated to account for the large chemical shifts of fluorine nuclei,[18] the chemical shift displacements of the pyridine protons upon interaction with Lewis acids,[19-21] and the anomalous boron-11 chemical shifts of several BX_4^- species.[22]

The coordination numbers for the complexes of the first three solvents listed in Table I, that is, Me_2O, Et_2O, and THF, are essentially 1 ± 0.1 in all instances but one. These results rule out the existence of complexes involving two solvent molecules in the "coordination sphere" of borane or the boron trihalides. This is true in spite of the fact that the solvent is present in large excess. The addition of a second ligand to the addition complexes of boron trihalides with pyridine[16] and MeOH[8] has been reported on the basis of calorimetric data. The MeOH system will be discussed later in this paper. The other complexes are presently under investigation by means of this pmr integration technique with the hope of gaining conclusive information regarding the structure of the species present in these solutions.

As can be seen in Figure 1, the two sets of resonance patterns obtained for diethyl ether appear quite similar. This is consistent with the conclusion that the sets of signals arise from bulk ether and ether molecules complexed with BCl_3. It has been proposed[4] that the $BCl_3 \cdot OEt_2$ complex is actually present as the ethyl ethoxychloroborate salt, $(C_2H_5)^+(C_2H_5OBCl_3)^-$. This conclusion was based on the large displacement, 85 cps, of the averaged ether methylene proton resonance signals in a BCl_3 solution. The 85-cps displacement does not seem large enough to propose such a species to account for the deshielding. Several of the separations observed in this study and shown in Table I are comparable in magnitude. More importantly, the existence of such an ionic species does not correlate at all with the spectra of Figure 1. If this proposal were correct it would mean that the ethyl cation and the ethoxy portion of the anion would exhibit identical spectra. In view of the different electronic structures of the two ethyl groups, this does not seem probable. Further, their reported conductance values could easily be the result of a trace amount of hydrolysis of BCl_3.

The spectra of BF_3 solutions in MeOH show several interesting features. As indicated previously, only a single resonance peak could be observed for the hydroxyl proton even at temperatures as low as $-90°$. This most likely indicates that a rapid proton exchange is operative in this system. The chemical shift of the hydroxyl proton is very concentration dependent as illustrated by the 191-cps upfield displacement of the peak from the most dilute to the most concentrated MeOH solution (1:18) studied. This result means that the separation of the hydroxyl signals of bulk and complexed MeOH may be greater than 191 cps when observed. This is reasonable in view of the proximity of this proton to the oxygen interaction site in the alcohol. Further, a separation of ~250 cps has been reported for the signals of bulk and complexed water molecule protons in $AlCl_3$ solutions.[23]

As illustrated by the data in Table I, the methyl proton signals of bulk and complexed MeOH also demonstrate a small but definite concentration dependence. In a previous pmr study of the BF_3 complex of MeOH,

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(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 317.

(18) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

(19) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

(20) W. S. Brey, M. E. Fuller, G. E. Ryschkewitsch, and A. S. Marshall, "Boron-Nitrogen Chemistry," Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 100.

(21) A. Fratiello and E. G. Christie, *Trans. Faraday Soc.*, **61**, 306 (1965).

(22) R. J. Thompson and J. C. Davis, Jr., *Inorg. Chem.*, **4**, 1464 (1965).

(23) R. Schuster and A. Fratiello, *J. Chem. Phys.*, **47**, 1554 (1967).

the two upfield signals were attributed, not to bulk and complexed alcohol, as proposed here, but rather, to the methyl group signals of the mono- and dialcohol complexes, $BF_3 \cdot MeOH$ and $BF_3 \cdot 2MeOH$.[8,24] The supposed changes in the relative amounts of the two complexes were then used to calculate equilibrium constants for complex formation and also to account for the observed concentration dependence of the methyl signal chemical shifts. Further, they concluded that the observation of a signal corresponding to the methyl group of bulk MeOH was prevented by a rapid exchange of solvent molecules with each of the complexes. However, such an exchange would necessarily result in the observation of one, not two, methyl signals. It is our contention that the low-field methyl signal arises entirely from $BF_3 \cdot MeOH$. The peak at highest field is probably due to only bulk MeOH, but our data do not preclude the possibility of a small contribution from $BF_3 \cdot 2MeOH$. The fact that the coordination numbers are all less than 1 may mean that a portion of the BF_3 is present as the dimethanol complex. A rapid exchange of bulk solvent with only this species at low temperatures could account for the observation of only one signal at highest field. Another possibility is that the separation of the bulk and dicomplex methyl resonance signals may be extremely small. However, several points seem to minimize the likelihood that some dimethanol complex is actually present. First, all other systems in Table I form only 1:1 complexes. Also, the coordination number results for the MeOH system, while low, were nearly constant over the entire concentration range. If a competition between the 1:1 and 1:2 complexes were actually operative, a trend to lower coordination numbers should be observed with increasing MeOH concentration. At high MeOH content, the presence of the 1:2 complex would be favored. It is quite conceivable that the integrations, while reproducible to 10%, are not accurate because of the overlapping of the methyl signals. The separation of these signals is at most 10 cps, and both are slightly broadened. At any rate, until direct evidence for the existence of a higher complex is found, it is more reasonable to assume the presence of only the $BF_3 \cdot MeOH$ complex.

The data of Table I can perhaps be used to estimate the relative complexing abilities of the solvents used. For example, the magnitudes of the separations observed for bulk and complexed solvent molecules in the BF_3 and BCl_3 systems could lead one to conclude that Et_2O exhibits a greater complexing ability than Me_2O and THF, the latter two being about equal in this regard. However, since three chemically different types of protons are being considered, such a correlation should be made only with caution. A more valid approach should involve the consideration of the behavior of the same type of proton upon complex formation. For instance, the separations of the methyl group signals of bulk solvent and solvent complexed to BCl_3 are 60 and 30 cps for Me_2O and Me_2S, respectively. Thus, the ether appears to complex more readily than the sulfide with BCl_3, in contrast to their behavior toward the gallium halides.[9,25] More extensive studies of this type involving complexes of boron halides with nitrogen-, oxygen-, and sulfur-containing bases are presently underway.

A previous nmr investigation of the $BF_3 \cdot DMF$ complex in dichloromethane and 2-nitropropane revealed that the displacements of the methyl and formyl proton signals with respect to pure DMF in these solvents were approximately 23 and 10 cps, respectively.[3] While the methyl signal displacements compare favorably with those listed in Table I, the value of 10 cps for the formyl proton signal shift is meaningless. As stated previously, the actual separation for this signal is 28 cps. This result emphasizes the advantage of simultaneously observing the separate resonance signals of bulk and complexed solvent molecules rather than an average of the two.

A correlation of the data in Tables I and II provides convincing evidence for $R_2O \cdot BH_3$ complexes in excess coordinating solvent when the ether is tetrahydrofuran (30°) or dimethyl ether (−60°). Only one solvent signal is found for the diborane–ethyl ether system even when temperatures down to −80° are used. At the lowest measured temperature the boron species present exhibits a pmr spectrum almost identical with that of uncomplexed diborane. Also, only one solvent signal is found for the diborane–dimethyl ether system at 30°. However, the ^1H and ^{11}B nmr spectra exhibited by the boron moiety suggest that a significant portion of the diborane is present as a fast-equilibrating ether complex.[26]

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(24) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949, p 63.

(25) N. N. Greenwood and T. S. Srivastava, *J. Chem. Soc., Sect. A*, 270 (1966).

(26) For additional information on these and related systems, see (a) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959); (b) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963); (c) T. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959); (d) D. F. Gaines, R. Schaeffer, and F. Tebbe, *ibid.*, **67**, 1937 (1963).