finds a parallel in a similar lack of reaction between CH_3SeCl_3 and BCl_3.[1] The presence of three electron-withdrawing halogen atoms bonded to the chalcogen atom in each instance should reduce the possibility of the removal of a halogen as an ion. This electron-withdrawing effect is amply evident in the large downfield shift of the proton resonance of CH_3TeBr_3 in CCl_4 as compared to $(CH_3)_2TeBr_2$. In addition, the pronounced intermolecular association observed for solutions of CH_3TeBr_3 and of CH_3SeCl_3 may also be significant in preventing interaction with BX_3.

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A Scale of Relative Lewis Acidities from Proton Magnetic Resonance Data[1]

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Abstract: A scale of relative Lewis acidities has been set up for a number of inorganic halides and substituted inorganic halides based on the ratios of changes in the pmr chemical shifts of the α protons of ethers on complex formation. The sterically most favorable ether, tetrahydrofuran, was chosen as the reference base. Rapid exchange of Lewis acids among excess Lewis base sites occurs with all but the strongest acid–strongest base system studied. The pmr data on the complexes of boron fluoride and boron chloride indicate that back bonding persists in the complexes and that the bonding is dominantly electrostatic in character. When steric factors are not differentiating in either acid or base, relative Lewis acidities are unaffected by changes in the reference ether base. Steric inaccessibility in either acid or base causes pronounced changes in relative Lewis acidities toward ethers. For the chlorides of group IIIB elements, acidities increase with the electronegativity of the element. For the halides of group IVB elements steric rather than electronic factors appear to be controlling.

The relative strengths of Lewis acids have been compared using a variety of methods, and the results have been reviewed in the literature.[3,4] Although it has been reported by Diehl[5] that the interaction of a typical Lewis acid, boron fluoride, with ethers causes a marked downfield shift of the α-proton magnetic resonance, presumably due to electron withdrawal by the Lewis acid, this type of measurement has not been systematically used for the measurement of relative Lewis acidities. In the present paper are presented the results of some such measurements on a variety of inorganic halide- and substituted inorganic halide–ether systems.

To minimize steric effects, tetrahydrofuran was selected as a standard reference base for a scale of relative Lewis acidities. A value of 100 has been assigned to boron chloride, the strongest Lewis acid studied. The relative acidities of other Lewis acids are expressed as a percentage of the effect observed for boron chloride. Additional reference bases have been used to evaluate steric factors in Lewis acid–Lewis base interactions.

Experimental Section

The ethers used in this work were commercial products and were purified by fractional distillation. The inorganic halides were reagent grade chemicals and except for titanium tetrachloride were used as received. The titanium tetrachloride was fractionally distilled before use. The alkyl-substituted boron halides were products previously prepared in this laboratory.[6]

The boron fluoride complexes were prepared by direct synthesis and purified by vacuum distillation. The remaining Lewis acid–Lewis base systems were prepared by direct weighing of the components. No solvents were used other than excess of Lewis acid or base and approximately 5% tetramethylsilane. Samples for measurements were prepared and handled in an atmosphere of dry nitrogen.

Proton magnetic resonance spectra were obtained using a Varian Associates Model HR-60 high-resolution nmr spectrometer. Chemical shifts were obtained using the side-band technique with tetramethylsilane as internal standard. A Hewlett-Packard Model-521C electronic counter was used to measure side bands to 0.1 cps. The chemical shifts so obtained showed an average deviation of less than 0.4 cps. Measurements were made at ambient temperature (28 ± 1°). Liquids for measurement were kept at Dry Ice temperature until the spectra were run. None of the pmr spectra gave evidence of the presence of cleavage products.

Results and Discussion

The downfield shifts of the α-proton resonances of ethers on complexing with Lewis acids were determined, when solubility and melting point factors permitted, both for the pure complex and for solutions con-

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(1) J. F. Deters, P. A. McCusker, and R. C. Pilger, Jr., Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 6-V.

(2) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document COO-38-581.

(3) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958).

(4) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, Chapter 6.

(5) P. Diehl, *Helv. Phys. Acta*, **31**, 685 (1958).

(6) P. A. McCusker and J. H. Bright, *J. Inorg. Nucl. Chem.*, **28**, 2261 (1966).

taining excess ether. With the single exception of the boron chloride–tetrahydrofuran pair, all the Lewis acid–Lewis base systems gave a single set of signals as excess base varied over a wide range. It thus appears that to be a general characteristic of these systems the Lewis acid molecules move rapidly from one available base site to another, and that the observed field position represents an average electron withdrawal from the ether molecules. The single exception occurred with the strongest acid–base pair studied, boron chloride–tetrahydrofuran. Only in this case was the exchange slow enough at 28° to permit observation of resonance signals for both the complexed and uncomplexed ether. The next strongest pair studied, aluminum chloride–tetrahydrofuran, and all the others involving Lewis acids weaker than aluminum chloride gave only an average proton signal as the result of rapid exchange.

A quantitative estimate of the minimum rate of exchange for a typical Lewis acid, boron fluoride, among available base sites, may be obtained from the values for the chemical shifts of the ether and the complex and the fact that a single set of sharp signals is produced. For the case of a solution containing equimolar amounts of the ethyl ether–boron fluoride complex and ethyl ether, the equation[7] $\Pi(\sqrt{A} - \sqrt{B}) = 0.5$ was used to calculate a minimum lifetime of the Lewis acid on a base site of 0.00318 sec. This corresponds to a minimum rate of 314 exchanges/sec for a solution containing a 1:1 molar mixture of ethyl ether–boron fluoride and ethyl ether at 28°.

When the chemical shifts were plotted as a function of the ratio of acid (A) to base (B), two general results were obtained. Lewis acids, which form 1:1 complexes and have strengths 61% or more of that of boron chloride (such as aluminum chloride, boron fluoride and isobutyldichloroborane), gave straight line plots. Lewis acids of lower strengths and/or capable of forming 1:2 as well as 1:1 acid–base complexes gave plots with curvature showing a decreasing slope. This behavior is what would be expected if partial dissociation of the complex occurs and there is present some free Lewis acid not effectively interacting with Lewis base. When a large excess of base is present, the acid exists almost entirely in the form of a complex. As the number of acid molecules per base molecule increases, the proportion of uncomplexed acid molecules increases and the observed chemical shift for the base becomes less than that expected for complete interaction.

The chemical shifts used for the determination of relative Lewis acidities were those observed directly for 1:1 acid–base ratios or obtained by extrapolation from more dilute solutions of acid in base. In Table I are listed the acids studied, the reference bases used, the changes in chemical shifts in cps (60 Mc), and the relative acidities based on a value of 100 assigned to boron chloride.

Table I. Relative Acidity of Lewis Acids toward Various Reference Bases at 28°

Acid	Tetrahydrofuran J, cps	Tetrahydrofuran Acidity	*n*-Butyl ether J, cps	*n*-Butyl ether Acidity	Ethyl ether J, cps	Ethyl ether Acidity
BCl_3	64.0	100	75.2	100	79.0	100
$AlCl_3$	51.8	81	64.0	85	67.2	85
$i\text{-}C_4H_9BCl_2$	50.0	78	51.1	68	53.6	68
$BiCl_3$[a]	48.0	75	...	...	...	...
$TiCl_4$	...	...	52.6	70	60.0	76
$InCl_3$[b]	41.0	64	...	...	...	...
BF_3	39.1	61	45.8	61	49.8	63
$SnCl_4$	...	...	38.4	51	...	...
$SnBr_4$[c]	25.6	40	0.0	0	...	...
$(i\text{-}C_4H_9)_2BCl$	25.5	40	0.0	0	0.0	0
$AsCl_3$	11.0	11	...	...	...	...
SnI_4	0.0	0	...	...	0.0	0
$SiCl_4$	0.0	0	0.0	0	0.0	0
$GeCl_4$	0.0	0	0.0	0	0.0	0
PCl_3	0.0	0	0.0	0	0.0	0
$(i\text{-}C_4H_9)_3B$	0.0	0	0.0	0	0.0	0

[a] By extrapolation from 0.3 acid/base ratio. [b] By extrapolation from 0.25 acid/base ratio. [c] At 8.0 acid/base ratio.

The nature of the bond in Lewis acid–Lewis base complexes has been viewed by Mulliken,[8] in terms of molecular orbital theory, as involving the linear combination of a no-bond structure, in which the bonding would presumably be electrostatic, and an electron-transfer structure, in which the bonding would be essentially covalent.

The rapid exchange which is characteristic of many Lewis acids among available Lewis base sites and the proton resonance data on the boron chloride and fluoride complexes would suggest that the bonding is dominantly of the no-bond type and that back-bonding between halogen and boron persists in the complexes.

That the relative changes in the chemical shifts of ether protons on complex formation are a measure of the relative electron withdrawal by the acceptor atom and are not significantly affected by differences in the anisotropy of neighboring atoms is suggested by a number of considerations. The ratio of the shifts of the β protons is essentially the same as those of the α protons in a number of the cases where data are available for comparison. As an example, the relative acidity of boron fluoride toward ethyl ether is the same, within experimental error, whether determined from the ratio of the α-proton shifts or the β-proton shifts. Similar agreement is obtained for a number of other Lewis acids. Data reported by Cook[9] on the lowering of the carbonyl carbon–oxygen stretching frequency in xanthone, on complexing with various Lewis acids, may be used to calculate relative Lewis acidities. The value so obtained for boron fluoride from ir data is 60 compared to the pmr value of 61. The ir value for titanium tetrachloride is 76 and the same value is obtained from the pmr data. Stannic chloride and stannic bromide show larger relative acidities toward xanthone from ir data than toward ethers from pmr data. Such a difference would be expected, however, because of the steric factor resulting from the greater accessibility of the carbonyl oxygen in xanthone. The relative acidities obtained from the pmr data are also qualitatively in agreement with values obtained from many other types of measurement.[3,4] Finally the oxygen electrons in the complexes are much less free to precess in a magnetic field than those of the halogens in secondary alkyl halides where neighbor anisotropy effects are dominant. In the cases of the Lewis acid–ether complexes, dif-

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(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 223.

(8) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(9) D. Cook, *Can. J. Chem.*, **41**, 522 (1963).

ferences in the anisotropy of neighboring atoms are probably negligible.

Changes in relative Lewis acidities with different reference bases appear to be due almost entirely to steric factors. Marked effects may be noted for several examples which include both planar and tetrahedral Lewis acids. With tetrahydrofuran as reference base, the acidity of isobutyldichloroborane is 72, but, with the sterically less open bases *n*-butyl and ethyl ethers as reference bases, the acidity drops to 68. The branched alkyl group on boron apparently offers greater interference to interaction with *n*-butyl and ethyl ethers than with the sterically more accessible tetrahydrofuran. The steric effect of two isobutyl groups on boron is more extreme. With tetrahydrofuran, diisobutylchloroborane has an acidity of 25 relative to boron chloride, but with *n*-butyl and ethyl ethers as reference bases the acidity drops to a value which cannot be distinguished from zero. Similarly, stannic bromide has a significant acidity (25) toward tetrahydrofuran but an apparent zero acidity toward *n*-butyl ether. A further example of steric interference with complex formation is afforded by a comparison of the relative acidities of stannic bromide (25) and stannic iodide (0.0) toward tetrahydrofuran. The larger iodide atoms apparently completely block the oxygen atom of tetrahydrofuran from approaching near enough for complex formation to occur, but the smaller bromine atoms do not. A somewhat decreased acidity might be expected for stannic iodide for electronegativity reasons, but the observed extreme difference can hardly be due to electronic factors alone.

While the data are not available for gallium trichloride, a definite trend of decreasing acidity is shown for the trichlorides of boron, aluminum, and indium. This trend suggests that, when empty p orbitals are involved in the bonding, Lewis acidities toward ethers decrease with increasing size of the central atom in a periodic group. In periodic groups in which d orbitals are involved in complex formation, the opposite trend is noted. The acidity increases from silicon tetrachloride to tin tetrachloride and from arsenic trichloride to antimony trichloride. For the trichlorides of group III the sterically open planar structure makes the empty p orbital readily accessible to the donor molecule, and thus electronic factors are dominant in determining relative Lewis acidities. On the other hand the tetrahedral structure of the group V halides results in dominance of steric factors in relative Lewis acidities.

The relative basicities of ethers can also be conveniently determined from proton magnetic resonance data on solutions of different ethers and less than an equivalent amount of Lewis acid. The field positions of the α-proton resonances give directly the ratio of complexed to free ether in solution. The results of such a study will be reported in a later communication.

Boron–Fluorine Chemistry. II. The Reaction of Boron Monofluoride with Acetylenes

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Abstract: The cocondensation of boron monofluoride and acetylene at −190° yields a polymer and several volatile compounds. The most abundant of these volatiles has been shown by its proton and fluorine nmr spectrum to be $(F_2BCH{=}CH)_2BF$. This compound loses boron trifluoride in the vapor phase above room temperature to give quantitative yields of the compound $C_4H_4B_2F_2$, 1,4-difluoro-1,4-diboracyclohexadiene, which is isoelectronic and structurally similar to *p*-benzoquinone. The reaction of boron monofluoride with methylacetylenes yields $C_4(CH_3)_2H_2B_2F_2$ and $C_4(CH_3)_4B_2F_4$. These compounds of type $C_4R_4B_2F_2$ are all destroyed by air or water, and some polymerize in the condensed phase at room temperature.

It has been shown that boron monofluoride can be formed in preparative amounts by the action of boron trifluoride on boron at 1800–2000° at low pressure. Reaction of boron monofluoride has occurred with volatile inorganic and organic compounds by cocondensation at −196°.[2]

The present work was undertaken to find if a stable three-membered ring would result from the addition of boron monofluoride to an acetylenic bond, although caged carboranes also seemed likely products from such a reaction.

Only a few unsaturated organic compounds containing boron and fluorine have been reported previously. Brinckmann, Coyle, and Stone[3] studied the vinylfluoroboranes, and Schlesinger, *et al.*,[4] obtained the compound $C_2H_2B_2F_4$ from acetylene and diboron tetrafluoride. Relatively little has been published about the chemistry and spectroscopic properties of these compounds.

The Reaction of BF and C_2H_2

The initial product of cocondensation of BF and C_2H_2 at −196° was a yellow solid. On warming this

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[2] P. L. Timms, *J. Am. Chem. Soc.*, **89**, 1629 (1967).

[3] (a) F. E. Brinckmann and F. G. A. Stone, *ibid.*, **82**, 6218 (1960); (b) T. D. Coyle and F. G. A. Stone, *ibid.*, **82**, 6223 (1960).

[4] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6389 (1959).