Direct Carbon-13 Nuclear Magnetic Resonance Study of Boron Trifluoride and Boron Trichloride Complexes with Ethers [1]

By **Anthony Fratiello,* Robert Kubo, David Liu,** and **George Vidulich,** Department of Chemistry, California State University, Los Angeles, California 90032

A direct, low-temperature. ^{13}C n.m.r. study of the boron trifluoride and boron trichloride complexes with several ethers has been completed. At *ca.* −100°, ligand exchange is slow enough to permit the observation of separate signals for bulk and co-ordinated ether molecules. The chemical shift changes induced by complex formation reflect inductive and steric effects. Doublet patterns were observed for the signals of co-ordinated ethyl s-butyl, ethyl t-butyl, and di-isopentyl ether. The most reasonable interpretation of this result appears to be hindered rotation about the O–R bond in the complex.

THE advantages of using ^{13}C n.m.r. spectroscopy as a probe of molecular structure and interaction have been clearly demonstrated for many systems.[2,3] ^{13}C N.m.r. chemical shifts are sensitive indicators of electron density changes induced by structural modification and strong complex formation. All carbon-containing functional groups, including those which are not protonated, such as carbonyls, can be studied. In addition, the wide-band proton-decoupled ^{13}C n.m.r. spectrum consists of a single peak for each carbon atom, usually not obscured by signal overlap.

Boron trihalide complexes with organic bases have received much attention in attempts to determine the energetics and structural features involved in their formation.[4-18] The most efficient spectral approach to the study of these systems is the direct, low-temperature n.m.r. technique.[19-29] At temperatures low enough to slow ligand exchange, separate ^{1}H, ^{11}B, and ^{19}F n.m.r. signals can be observed for the boron trifluoride complex and the free ligand. Features such as the effect of complex formation on chemical shift, the stoicheiometry of the complex, the relative basic strengths of a series of molecules, and steric hindrance to interaction can be evaluated by this method. Recent reports of direct studies of solvated ions [30] and boron trihalide complexes [28] have demonstrated the feasibility and utility of ^{13}C n.m.r. spectroscopy in this area of research. The present work is an extension of the preliminary measurements on ethers.[28] These ethers provide a series of closely related molecules with one interaction site and structural features to introduce stereochemical effects in the complexing process.

EXPERIMENTAL

Methods.—Boron trifluoride, boron trichloride, and dichlorofluoromethane (Genetron) were CP grade (Matheson). Dichloromethane and all ethers were reagent grade and were dried ($CaSO_4$) before use. The purity of the ethers was verified by their ^{1}H and ^{13}C n.m.r. spectra. Boron trihalides were fractionated at −110 (BF_3) or −130° (BCl_3), and condensed *in vacuo* in the n.m.r. tube (Wilmad Glass Co., 504PP) in liquid nitrogen (−196°). When Genetron was used as the solvent, it too was transferred under vacuum. The sample tubes were sealed, warmed in an acetone–dry ice bath to dissolve all components, and stored in liquid nitrogen until the spectra could be recorded. These precautions were sufficient to prevent sample decomposition, as determined by the ^{1}H and ^{13}C n.m.r. spectra, in all but the boron trichloride–ethyl t-butyl ether solution.

^{1}H and ^{19}F n.m.r. spectra were recorded on Varian A-60 and Varian HA-100 spectrometers, the latter operating at 94.1 MHz for ^{19}F nuclei. ^{13}C N.m.r. spectra were obtained at 22.6 MHz with a Bruker HX-90-E instrument, equipped with a Bruker–Nicolet data system, model B-NC-12. Pulses of 3—10 μs width were applied at 1 s intervals. At

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the concentrations used, 1 000—2 000 pulses generally resulted in satisfactory signal intensity, although in a few cases, for example, ethyl s-butyl ether, 5 000 pulses were used.

The procedure used here is similar to that applied in the ^{1}H and ^{19}F n.m.r. studies of boron trihalide complexes,[20-26, 28] except the measurements are more time consuming when natural abundance ^{13}C spectra are sought. An estimate of the temperature at which exchange is slow enough to permit the observation of separate ^{13}C signals for co-ordinated and bulk ligand can be made from ^{1}H spectra, obtained more rapidly, and by calibration-type ^{13}C experiments involving the accumulation of a relatively small number of scans. For example, the ^{13}C spectrum resulting from 100 pulses may be sufficient to verify the slow exchange condition, but it would not be satisfactory for accurate chemical shift measurements. After a sequence of such spectra had been obtained and the optimal temperatures deduced, the final experiments were made.

RESULTS

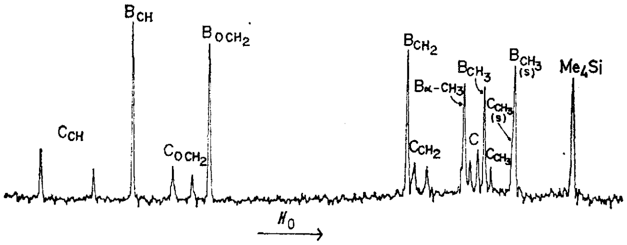
As demonstrated in a preliminary study,[28] signal overlap seriously complicates the ^{1}H n.m.r. spectra of these boron trihalide–ether mixtures. In the spectra of the larger ethers, only the α-proton signals for both bulk and co-ordinated ligand can be identified with certainty. Such observations are valuable in the determination of the stoicheiometry of the complex, and although they will not be discussed further here, they did verify the expected 1 : 1 mole ratio. Further, in all cases, the ether ^{1}H signal displacements are to lower field in the boron trihalide complexes. In general, the ^{1}H results do not provide much structural information for this group of complexes. The ^{19}F n.m.r. spectra of these boron trifluoride complexes also were not very useful since in most cases, the chemical shifts were similar, *ca.* 8.5 p.p.m. downfield from internal hexafluorobenzene. As a result, a competitive basicity study of the ethers would have been restricted. Thus, only the ^{13}C n.m.r. spectra of these systems were considered in detail.

^{13}C Chemical shift data for BF_3 and BCl_3 ether complexes

		Mole ratios		δ_B (p.p.m.)[c]				$\delta_C - \delta_B$ (p.p.m.)[d]			
BX_3	Ether	BX_3 : base : solvent[a,b]	t/°C	α	β	γ	δ	α	β	γ	δ
BF_3	Dimethyl	1.0 : 2.9 : 30[a]	−90	60.0				+3.3			
BCl_3	Dimethyl	1.0 : 3.9 : 90[a]	−95	60.8				+7.3			
BF_3	Diethyl	1.0 : 2.6 : 30[a]	−90	66.1	15.5			+3.9	−2.2		
BCl_3	Diethyl	1.0 : 5.6 : 50[a]	−90	66.3	15.5			+10.0	−1.5		
BF_3	Di-n-propyl	1.0 : 3.0 : 30[a]	−90	72.1	22.8	10.4		+3.4	−2.3	−1.4	
BCl_3	Di-n-propyl	1.0 : 5.4 : 50[a]	−90	72.6	23.1	10.8		+9.0	−1.8	−1.7	
BF_3	Di-isopropyl	1.0 : 3.9 : 30[b]	−90	67.6	22.4			+10.0	−2.0		
BCl_3	Di-isopropyl	1.0 : 3.0 : 30[b]	−90	67.8	22.6			+9.3	−0.4		
BF_3	Di-n-butyl	1.0 : 2.9 : 30[a]	−90	70.3	31.7	19.4	13.9	+3.7	−2.8	−1.4	−0.4
BCl_3	Di-n-butyl	1.0 : 5.1 : 50[a]	−90	71.2	32.1	19.7	14.5	+9.3	−2.2	−1.8	~0
BF_3	Ethyl isobutyl	1.0 : 2.6 : 30[a]	−90	(Et) 66.2	15.4			+5.3	−2.2		
				(Bu^i) 77.6	28.5	19.6		+1.6	−2.2	−1.2	
BCl_3	Ethyl isobutyl	1.0 : 4.3 : 60[a]	−90	(Et) 66.7	15.3			+12.4	+0.2		
				(Bu^i) 78.0	28.6	19.7		+8.4	−2.1	−1.3	
BF_3	Ethyl s-butyl	1.0 : 3.0 : 30[b]	−115	(Et) 63.6	15.7			+2.5	−1.0		
								+1.0[e]			
				(Bu^s) 76.9	29.1	10.3	19.0	+10.6	−2.0	+0.3	−1.0
							(α-CH_3)	+2.1[e]	−3.7[e]		
BCl_3	Ethyl s-butyl	1.0 : 3.0 : 30[b]	−100	(Et) 63.9	15.6			+6.4	−1.1		
								+3.0	+1.2[f]		
				(Bu^s) 77.5	29.1	10.3	19.0	+16.0[g]	−1.3	+0.3	−1.0
							(α-CH_3)	+6.8	−3.6		−2.2[f]
BF_3	Ethyl t-butyl	1.0 : 3.0 : 30[b]	−120	(Et) 57.0	15.9			+9.9	+0.7		
								+5.4	−0.6		
				(Bu^t) 73.5	27.4			+21.8	−0.4		
								+14.9			
BCl_3	Ethyl t-butyl	Decomposed									
BF_3	Di-n-pentyl	1.0 : 3.6 : 30[b]	−90	71.3	30.0	28.8	23.2(δ)	+3.3	−2.6	−1.8	−0.4(δ)
							14.6(ε)				−0.2(ε)
BCl_3	Di-n-pentyl	1.0 : 3.0 : 60[b]	−90	71.4	29.8	28.7	23.1(δ)	+9.0	−1.8	−2.1	−0.3(δ)
							14.5(ε)				~0(ε)
BF_3	Di-isopentyl	1.0 : 2.7 : 30[b]	−80	70.0	38.2	25.1	22.8	+3.8	−0.6	−0.3	−0.2
								−5.5	−2.6	−0.6	
BCl_3	Di-isopentyl	1.0 : 3.3 : 30[b]	−80	69.9	38.1	25.1	22.7	+10.8[g]	+1.6	−0.6	~0
								−5.4	−1.8[g]		
BF_3	2-Chloroethyl	1.0 : 3.3 : 30[b]	−95	70.7	44.2			+7.3	−2.4		
BCl_3	2-Chloroethyl	1.0 : 3.9 : 30[b]	−90	71.0	44.2			+10.6	−3.2		
BF_3	Ethyl phenyl	1.0 : 2.9 : 30[b]	−95	(Et) 63.8	14.9			+14.4	−2.0		
				(Ph) 158.5	114.2	130.2	121.2	−8.0	+8.7	+0.8	+8.4
BCl_3	Ethyl phenyl	1.0 : 3.3 : 30[b]	−100	(Et) 63.4	15.0			+20.5	−1.6		
				(Ph) 158.4	113.8	129.7	120.6	−6.6	+9.5	+0.8	(+9)[h]
BF_3	Dibenzyl	1.0 : 3.0 : 30[b]	−95	72.1	137.7	128—129[i]		~0	Not assignable		
BCl_3	Dibenzyl	1.0 : 2.9 : 30[b]	−95	71.9	137.5	128—129[i]		+4.3	Not assignable		

[a] Solvent dichloromethane. [b] Solvent Genetron. [c] Bulk ether chemical shifts were measured from internal tetramethylsilane which appeared at higher field in all cases. [d] Chemical shift difference between the co-ordinated and bulk ligand signals. A positive sign indicates a displacement of the signal to lower field with complex formation. [e] Signal intensity extremely low [f] Assignment of this peak to the α-CH_3 (Bu^s) or the CH_3 (Et) carbon atoms of bound ether is uncertain. [g] Area of this signal is twice that of the other doublet component. [h] This estimate assumes a superposition of this signal with the γ-carbon peak of free ether. [i] The γ-, δ-, and ε-carbon signals appeared in this range but an assignment is not possible.

The ^{13}C chemical shift results for all ethers are presented in the Table, and a representative spectrum is shown in the Figure. The n.m.r. data were obtained with at least two samples of each ether. Dichloromethane was used as a solvent whenever possible, but if this choice was precluded by solubility, viscosity, or temperature ($< -100°$) problems, Genetron was substituted. In the Table, the resonance positions of the free ether signals (δ_B) with respect to internal tetramethylsilane are given, along with the separation between each peak and the comparable signal in the boron trihalide complex ($\delta_C - \delta_B$). The δ_B values are accurate to within ± 0.1 p.p.m. Where a comparison is possible, specifically, with the published ^{13}C n.m.r. chemical shifts of pure dimethyl, diethyl, di-n-propyl, and di-n-butyl ether,[31,32] the bulk ligand data of the Table agree within 1 p.p.m. This difference can be attributed to solvent and temperature effects. Signal assignments for the other ethers were made by internal comparisons, for example, among the butyl ether isomers, and by the application of empirical rules described elsewhere.[2,3] A complete assignment was not possible in the dibenzyl ether case because of signal overlap.



^{13}C N.m.r. spectrum at $-100°$ of boron trichloride–ethyl s-butyl ether–Genetron (1 : 3.0 : 30). The spectrum is the accumulation of 4 000 pulses, obtained at 22.6 MHz on a Bruker HX-90-E Fourier transform spectrometer. The signals arising from bulk (B) and co-ordinated (C) ether molecules are identified, when possible (see Table)

DISCUSSION

In the usual considerations of ^{13}C n.m.r. chemical shifts produced by intermolecular interaction, displacements to lower magnetic field indicate charge withdrawal and deshielding of a particular carbon nucleus. It can be assumed that with the possible exception of ethyl phenyl ether, little change in the orbital hybridization will occur at the oxygen atom, and further, this atom will transmit electronic and structural effects much like a carbon atom. This latter point was demonstrated by studies of several ethers.[31,32] Although an inductive effect would be attenuated with increasing distance from the oxygen interaction site, it should be significant at the α-carbon. With the exception of ethyl phenyl ether, the α-carbon signals of all ether groups were displaced to lower field in the boron trihalide complexes. The larger shifts produced by boron trichloride, the stronger Lewis acid, also indicate the dominance of inductive effects at the α-carbon atoms.

The most likely molecular property which would be expected to correlate with these shifts is the relative basic strength of the ether. However, since the only quantitative estimates of this parameter are based on studies using the hydrogen ion as the Lewis acid,[33] thereby precluding steric effects, a comparison must be made with caution. For example, in the five di-n-alkyl ether systems, the α-carbon shift displacements varied little, averaging $+3.5 \pm 0.2$ p.p.m. In contrast, the pK_{BH^+} values of these molecules vary by two units, ranging from -3.7 for dimethyl and diethyl ether, to -5.4 for di-n-butyl ether. Also, the pK_{BH^+} value for di-n-propyl and di-isopropyl ether is *ca.* -4.4 in both cases, yet the α-carbon chemical shifts in the boron trifluoride complexes differ by 7 p.p.m. Thus, it is clear that while the α-carbon shifts reflect charge withdrawal, the strength of the complex is not the only factor which must be considered.

It is interesting to note that the magnitude of the inductive effect in the complexes, as estimated by the low-field displacements of the α-carbon signals, depends on the nature of the carbon atom, that is, whether the alkyl group is CH_3, RCH_2, R_2CH, or R_3C. In the boron trifluoride complexes, this displacement is $+3.3$ p.p.m. for dimethyl ether, and only slightly higher for the remaining di-n-alkyl ether molecules. However, the displacements increased to almost $+10$ p.p.m. in the di-isopropyl and ethyl s-butyl ether complexes, and to $+15$ and $+22$ p.p.m. in the complex of ethyl t-butyl ether. Thus, the increased electron density at the α-carbon produced by the replacement of hydrogen atoms with electron-donating methyl groups is reflected in the extensive charge withdrawal in the boron trihalide complex.

It can be expected that at carbon atoms beyond the α-position, charge withdrawal would be much less significant. In fact, the β- and γ-carbon signals for the alkyl groups of co-ordinated ethers were displaced to higher field in almost all cases. The increased upfield shifts of the γ-carbon signals in the boron trichloride complexes are probably due to the steric crowding and polarization produced by this larger Lewis acid. This is consistent with the postulate that through-space effects are more important at atoms several bonds removed from a site of substitution or interaction.[34]

The most interesting spectra were obtained with the boron trihalide complexes of ethyl s-butyl, ethyl t-butyl, and di-isopentyl ether, which exhibited doublets for most signals (see Figure). Spin coupling and the presence of adducts other than 1 : 1 can be ruled out as causes. Also, the existence of diastereoisomers produced by slow exchange of the boron trihalide between two oxygen *p*-orbitals could explain the ethyl s-butyl ether results, but not the ethyl t-butyl ether and di-isopentyl ether spectra. If the same phenomenon is operative in the three systems, it may be due to hindered rotation about the O–R bonds in these complexes. Models show that the presence of a boron trihalide

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molecule on these ethers, particularly those with methyl group substitution at the α-carbon, restricts the exchange between conformations and could lead to the observation of signals for two species.

It also is significant that the relative intensities of the doublet components were not equal in the spectra of all complexes. For example, in the boron trifluoride–ethyl s-butyl ether spectrum, one component was much more intense than the other, whereas in the boron trichloride complex, the intensities were comparable (see Figure). Similarly, in the boron trichloride–di-isopentyl ether spectrum, the intensity of one doublet component was twice that of the other. This probably reflects a steric preference for one of the conformations.

Finally, the ethyl phenyl ether entries in the Table illustrate the electron density changes which can occur in aromatic molecules. The chemical shift displacement of the ethyl group α-carbon was greater with this complex than with any other listed. The signs and relative magnitudes of these shifts are consistent for the most part with those produced by structural changes in phenol.[32,35,36] For instance, the change PhOH to PhO^- gives shifts of +13, +4, *ca.* 0, and −5 p.p.m., respectively, for the α-, β-, γ-, and δ-carbon signals.[35,36] In the boron trihalide complexes, as anticipated by the greater positive character of the oxygen atom, shifts of −8, +9, +0.8, and +8 p.p.m., respectively, are observed for these carbon signals. Charge delocalization of the unshared electron pair in a *p*-orbital to the ring system, could stabilize sp^2 hybridization at the ether oxygen atom. However, the charge withdrawal induced by interaction with the boron trihalide would minimize this occurrence, resulting in sp^3 hybridization in the complex. This could account for the larger shifts observed. Even larger shift changes have been seen with the boron trifluoride complexes of pyridines [37] and steroids with αβ-unsaturated keto-groups.[29]

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