w, 1020 m, 1010 m, 990 w, 970 m, 930 w, 880 w, 855 m, 835 m, 820 s, 805 w, 770 w, 720 w.

(e) $[(C_5H_5)_2Co][Co(C_2B_9H_{11})_2]$, **XII.** A dark yellow band was eluted with CH_2Cl_2. Recrystallization afforded 0.1863 g (0.35 mmol, 18%) of $[(C_5H_5)_2Co][Co(C_2B_9H_{11})_2]$.

Cobaltacarboranes from 3,1,2-$C_5H_5CoC_2B_9H_{11}$ using Na in NH_3(l). The polyhedral expansion of 3,1,2-$C_5H_5CoC_2B_9H_{11}$ was equally successful when the reduction was carried out with sodium in liquid ammonia; hence, a viable low-temperature method of polyhedral expansion is also available. 3,1,2-$C_5H_5CoC_2B_9H_{11}$ (1.369 g, 5.2 mmol) was placed in a previously dried, nitrogen-flushed, 500-ml, three-neck flask equipped with a nitrogen inlet and a magnetic stirring bar. The flask was cooled with a 2-propanol cold bath maintained at −50° by the periodic addition of Dry Ice. Ammonia (125 ml) was condensed into the flask and sodium (0.36 g, 15.6 mmol) was added turning the yellow solution a deep blue. After stirring for 4 hr the reaction mixture was very dark brown. Stirring was continued for 2 hr and NaC_5H_5 (78 mmol) in THF and a slurry of $CoCl_2$ (20 g) in THF were added. The reaction was gradually allowed to warm to room temperature over a 20-hr period. After air was bubbled through the reaction mixture for 45 min, the solution was poured onto silica gel and the solvents were removed by rotary evaporation. The solids were chromatographed on a column of silica gel (500 ml) in hexane. Several unstable yellow bands were initially eluted. Separated and isolated as described above were 0.1905 g (0.74 mmol, 14%) of 3,1,2-$C_5H_5CoC_2B_9H_{11}$, 95 mg (0.25 mmol, 5.5% based on starting material consumed) of $(C_5H_5)_2Co_2C_2B_9H_{11}$, X, and 32 mg (0.08 mmol, 2%) of $(C_5H_5)_2Co_2C_2B_9H_{11}$, XI.

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Registry No. I, 50803-36-6; II, 50803-43-5; III, 50803-44-6; IV, 50803-45-7; V, 50803-51-5; VI, 50803-46-8; VII, 50803-48-0; VIII, 39475-06-4; IX, 50803-47-9; (X–XI), 50639-82-2; XII, 50803-40-2; 2,1,7-$C_5H_5CoC_2B_9H_{11}$, 50803-38-8; 2,1,6-$C_5H_5CoC_2B_7H_9$, 50803-35-5; 1,2,3-$C_5H_5CoC_2B_8H_{10}$, 11072-15-4; 1,2,4-$C_5H_5CoC_2B_8H_{10}$, 50803-37-7; 3,1,2-$C_5H_5CoC_2B_9H_{11}$, 11056-78-3.

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Urea-Boron Trihalide Adducts. III. Mixed Boron Trihalide Adducts of Tetramethylurea and the Difluorobis(tetramethylurea)boron(III) Cation

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Under certain conditions the adduct tmu·BF_3 rearranges to give small amounts of the ionic adduct $(tmu)_2BF_2^+\cdot BF_4^-$. Mixed boron trihalide adducts of tetramethylurea, tmu·BF_2Cl and tmu·$BFCl_2$, form readily from tmu·BF_3 and tmu·BCl_3 in solution. tmu·BF_2Cl is shown to be a convenient source of larger amounts of $(tmu)_2BF_2^+$, *via* nucleophilic attack of tmu on the tmu·BF_2Cl adduct with displacement of chloride ion. All of the mixed fluorochloroborate anions are also present in these solutions as a result of halogen redistribution reactions.

Introduction

We have recently investigated donor site and restricted rotation in BF_3 adducts of alkylureas.[1,2] In the course of studies of the BF_3 adduct of tetramethylurea (tmu), we observed the appearance of an additional species under certain conditions. We tentatively identified this as an ionic form of the adduct $(tmu)_2BF_2^+\cdot BF_4^-$. Extension of our studies to halogen redistribution and the mixed boron trihalide adducts of tmu showed that the redistribution reactions were more complex than in the Me_2O, Me_3N, or Me_2S mixed boron trihalide adduct systems[3-5] and provided further evidence about the nature of the additional species which can exist in the tetramethylurea-boron trihalide adduct system. We now report a study of this system, giving evidence for the presence of the difluoroboron cation $(tmu)_2BF_2^+$ and various mixed tetrahaloborate anions,[6] as well as mixed boron trihalide adducts of tmu.

Experimental Section

Rigorous dryness was maintained in the synthesis of adducts and in the preparation of nmr samples.

Pure tmu·BF_3, which gave single ^1H and ^{19}F nmr peaks (δ 3.02 and 149.2 ppm, respectively) was prepared as described previously.[1] An excess of pure BF_3 was condensed onto a solution of tmu in dry, vacuum-distilled methylene chloride, followed by removal of solvent and drying of the residue.

A second method of preparing tmu·BF_3 was employed in which BF_3 was slowly added with constant stirring to liquid tmu, on the vacuum system. The temperature of the reaction mixture was maintained near room temperature with the aid of an ice bath. After uptake had ceased, the temperature was raised to 60° and the BF_3 pressure maintained at 0.5 atm until uptake was complete. Excess BF_3 was removed by pumping on the molten adduct at 80° with constant stirring for 1 hr. The adduct prepared by this method gave the same large ^1H and ^{19}F peaks and in addition small peaks, as described below, which are attributed to an ionic form of the adduct, $(tmu)_2BF_2^+\cdot BF_4^-$.

Pure tmu·BCl_3 was prepared under anhydrous conditions on a vacuum line. An excess of pure BCl_3 was condensed onto a solution of tmu in dry, vacuum-distilled methylene chloride. The dried product was recrystallized from methylene chloride a total of three times to remove occluded BCl_3 and finally dried overnight under vacuum, mp 145.5–146.0°.

Mixed boron trihalide adducts readily formed in methylene chloride solutions of tmu·BF_3 and tmu·BCl_3. The tmu·BCl_3 adduct was only moderately soluble in methylene chloride but dissolved over a period of several minutes in the presence of tmu·BF_3.

The ^1H and ^{19}F nmr instrumentation has been described previously.[1] Boron-11 nmr spectra were obtained on a Varian

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Associates HA-100 spectrometer operating at 25.1 MHz. The spectra were calibrated by the usual audio-side-band method.

Results

$(tmu)_2BF_2^+ \cdot BF_4^-$. tmu·$BF_3$ prepared in the absence of solvent gave small nmr peaks in addition to the single ^{1}H and ^{19}F peaks of the simple adduct. The ^{1}H spectrum had one additional peak, with an intensity that was 4.5% of the total, just to low field (δ 3.09) of tmu·BF_3. The ^{19}F spectrum had two additional peaks, both small and broad, of relative areas 1:2 and combined intensity 5.0% of the total fluorine intensity, to low field and high field of the tmu·BF_3 peak, respectively. The chemical shift of the small high-field peak (151.9 ppm) is consistent with the species being BF_4^-,[1] and the spectra are consistent with the presence of about 5% of the ionic adduct $(tmu)_2BF_2^+ \cdot BF_4^-$.

The spectra observed are quite unlike those of tmu·$H^+ \cdot BF_4^-$ which we previously found as a difficult-to-remove impurity in tmu·BF_3.[1] Unlike the methyl signal of tmu·H^+, the small proton signal in the above solution does not undergo exchange averaging with tmu when free tmu is present. tmu·$H^+ \cdot BF_4^-$ gave an identical BF_4^- signal in the ^{19}F spectrum, but there was no additional peak to low field of tmu·BF_3.

Mixed Boron Trihalide Adducts of Tmu. Proton and fluorine-19 nmr showed that halogen redistribution between tmu·BF_3 and tmu·BF_3 and tmu·BCl_3 does not occur at room temperature when free tmu is also present. In the absence of any free base, however, solutions of tmu·BF_3 and tmu·BCl_3 at 21° gave a series of five closely spaced peaks (Figure 1a). The highest and lowest field peaks have the chemical shifts of tmu·BF_3 and tmu·BCl_3, respectively. As in other mixed-adduct systems,[3-5] two of the intermediate peaks are assigned to tmu·BF_2Cl and tmu·$BFCl_2$. The fifth peak has the same chemical shift as the species which is sometimes present in addition to tmu·BF_3 when fluorine is the only halogen (δ 3.08) and is assigned to $(tmu)_2BF_2^+$. Evidence for this assignment is described below. Chemical shifts and assignments are given in Table I.

On warming to 37°, the tmu·BF_3 and tmu·BF_2Cl peaks coalesced. This is apparently the first stage of a coalescence of all of the adduct peaks due to rapid donor-acceptor bond breaking, similar to that observed in the Me_2O and Me_2S adduct systems at much lower temperatures.[3,5] In the present system studies at temperatures above 37° were not carried out in view of possible complications due to side reactions at elevated temperatures.

Fluorine-19 spectra confirmed that several species containing fluorine bonded to boron are present. In addition to a broad peak apparently corresponding to tmu·BF_3, but with a width at half-height of 15.4 Hz, four 1:1:1:1 quartets were present (Figure 2a). The highest field quartet has the same chemical shift as the smaller of the ^{19}F peaks assigned to the ionic tmu adduct and is assigned to $(tmu)_2BF_2^+$. Three additional quartets remain, so that at least one species in addition to the two fluorine-containing mixed boron trihalide adducts must be present. There must be a counterion for $(tmu)_2BF_2^+$. Although no BF_4^- peak is visible, the lowest field quartet has the chemical shift and coupling constant expected for $BFCl_3^-$.[6] The system is evidently complex. The broadness of the "tmu·BF_3" peak indicates that chemical exchange is occurring and hence that additional species are present which do not give separate ^{19}F peaks. Since fluorine-chlorine exchange involving the fluorines of BF_4^- is fast in certain mixed tetrahaloborate systems,[6] the remaining fluorochloroborate anions $BF_nCl_{4-n}^-$ are likely additional species. However, the middle quartet does not correspond to any of the fluorochloroborate anions and apparently arises from a mixed boron trihalide adduct of tmu. Addition of free tmu to the system, as described in the next section, is necessary to detect further species present in solution by ^{19}F nmr.

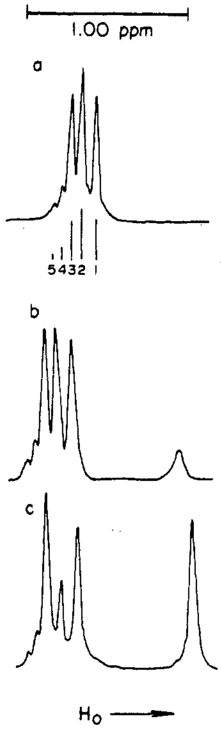

Figure 1. The 21° ^{1}H spectra of a methylene chloride solution of tmu·BF_3 and tmu·BCl_3 in the molar ratio 1.74:1.00: (a) initial spectrum; (b) after addition of 20 mol % tmu; (c) after addition of 50 mol % tmu. Peak assignments: 1, tmu·BF_3, 2, tmu·BF_2Cl; 3, $(tmu)_2BF_2^+$; 4, tmu·$BFCl_2$; 5, tmu·BCl_3.

Table I. Nmr Parameters

Soln compn[a]	Species	Chem shifts,[b] ppm ^{1}H	^{19}F	^{11}B	^{11}B–^{19}F J, Hz
1	tmu·BF_3	3.02	149.2	18.9	c
1	BF_4^-		151.9	c	c
1	$(tmu)_2BF_2^+$	3.09	146.1	~19	c
2	$(tmu)_2BF_2^+$	3.08	146.0	~19	12.5
2	tmu·BF_2Cl	3.06	124.3	15.9	28.2
2	tmu·$BFCl_2$	3.10	105.7	12.9	58.5
2	tmu·BCl_3	3.12		10.8	
2	BF_3Cl^-		126.1		24.3
2	$BF_2Cl_2^-$		105.5		59.0
2	$BFCl_3$		95.4		80.1
3	$(tmu)_2BF_2^+$		146.1		c
3	$(DMAC)(tmu)BF_2^+$		144.8		c
3, 4	$(DMAC)_2BF_2^+$		144.2		c
3, 4	DMAC·BF_3		148.6		c
3, 4	DMAC·BF_2Cl		125.0		28.4
3, 4	DMAC·$BFCl_2$		110.0		57.4

[a] All in methylene chloride: solution 1, tmu·BF_3 with small amounts of ions; solution 2, tmu·BF_3 and tmu·BCl_3 in a molar ratio 1.74:1 (total adduct concentration ~1 *M*); solution 3, DMAC added to solution 2; solution 4, DMAC·BF_3 and DMAC·BCl_3. [b] ^{1}H, ppm to low field of TMS, 21°; ^{19}F, ppm to high field of $CFCl_3$, 26°; ^{11}B, ppm to high field of external $(MeO)_3B$, 25°. [c] Not visible under these conditions.

Further confirmation of the presence of mixed boron trihalide adducts was provided by ^{11}B spectra. As in the ^{1}H spectra, chemical shift assignments were confirmed by skewing relative tmu·BF_3 and tmu·BCl_3 concentrations. In the ^{11}B spectra, skewing of the concentrations allowed the tmu·BF_2Cl 1:2:1 triplet and the tmu·$BFCl_2$ 1:1 doublet,

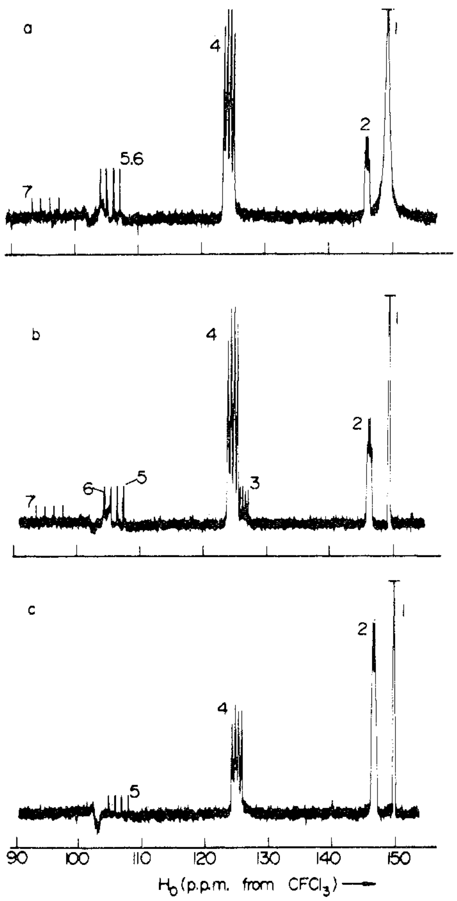

Figure 2. The 26° ^{19}F spectra of a methylene chloride solution of $tmu{\cdot}BF_3$ and $tmu{\cdot}BCl_3$ in the molar ratio 1.74:1.00: (a) initial spectrum; (b) after addition of 10 mol % tmu; (c) after addition of 56 mol % tmu. Peak assignments: 1, $tmu{\cdot}BF_3$; 2, $(tmu)_2BF_2^+$; 3, BF_3Cl^-; 4, $tmu{\cdot}BF_2Cl$; 5, $tmu{\cdot}BFCl_2$; 6, $BF_2Cl_2^-$; 7, $BFCl_3^-$.

arising from coupling with fluorine, to be observed (Figure 3). In some cases, additional overlapping peaks of low intensity that could be assigned to the mixed fluorochloroborate ions[6] were also observed.

Ligand Displacement by Addition of Free tmu to the Mixed Adducts. Confirmation of the Existence of $(tmu)_2BF_2^+$. Successive additions of tmu to solutions of the $tmu{\cdot}BF_nCl_{3-n}$ (n = 0-3) adducts resulted in a decrease in the intensity of the ^1H peak assigned to $tmu{\cdot}BF_2Cl$ and an increase in the intensity of the peak assigned to $(tmu)_2BF_2^+$ (Figure 1). A separate free-tmu peak of somewhat variable chemical shift was observed to high field as tmu was added, showing that all of the tmu added did not go to form the cation. The results are consistent with the equilibrium shown in eq 1. The relative chemical shifts of the adducts

$$tmu + tmu{\cdot}BF_2Cl \rightleftarrows (tmu)_2BF_2^+ + Cl^- \qquad (1)$$

showed a slight dependence on solution composition.

Changes in the ^{19}F spectrum in the presence of increasing proportions of tmu are shown in Figure 2. Addition of 5 mol % of tmu resulted in a sharpened $tmu{\cdot}BF_3$ peak (peak width at half-height 6.1 Hz) and the appearance of BF_3Cl^- and $BF_2Cl_2^-$ quartets.[6] $tmu{\cdot}BFCl_2$ is also clearly visible as a separate quartet (Figure 2b). There is still no BF_4^- peak; fluorine exchange, perhaps with $tmu{\cdot}BF_3$, seems to remain too fast. The presence of the mixed tetrahaloborate anions was confirmed by addition of a solution of the fluorochloroborate anions to one of the samples; perfect superposition of all three mixed tetrahaloborate quartets occurred.

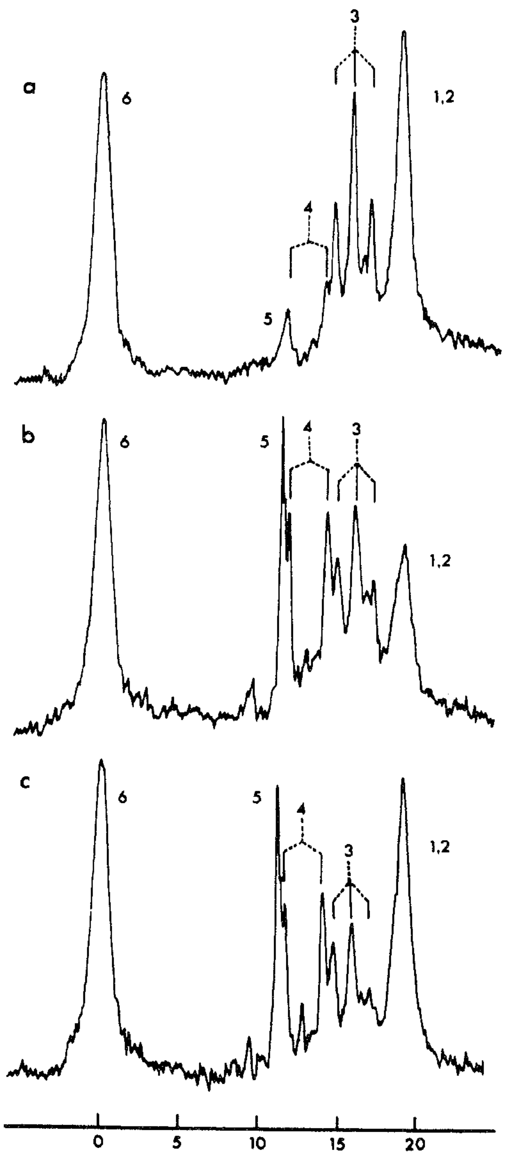

Figure 3. The 25° ^{11}B spectra of a methylene chloride solution of $tmu{\cdot}BF_3$ and $tmu{\cdot}BCl_3$ in the molar ratios (a) 3:1, (b) 1:1, and (c) 1:1 after the addition of approximately 50 mol % tmu. Peak assignments: 1 and 2, $tmu{\cdot}BF_3$ and $(tmu)_2BF_2^+$; 3, $tmu{\cdot}BF_2Cl$; 4, $tmu{\cdot}BFCl_2$; 5, $tmu{\cdot}BCl_3$; 6, external $(CH_3O)_3B$.

As a large excess of tmu was added, the $(tmu)_2BF_2^+$ quartet greatly increased in intensity, the $tmu{\cdot}BF_2Cl$ quartet showed a corresponding decrease in intensity, and the fluorochloroborate anion peaks disappeared. This is consistent with eq 1 and with a similar equilibrium involving the mixed tetrahaloborate anions

$$tmu + BF_nCl_{4-n}^- \rightleftarrows tmu{\cdot}BF_nCl_{3-n} + Cl^- \qquad (2)$$

The results of a quantitative titration of a mixed-adduct sample with free tmu, monitored by ^{19}F nmr, are given in Figure 4. The corresponding molar quantities of BF_3Cl^-, $BF_2Cl_2^-$, $BFCl_3^-$, and $tmu{\cdot}BFCl_2$ are not given in the figure owing to their low initial concentrations and the overlap of $BF_2Cl_2^-$ and $tmu{\cdot}BFCl_2$ quartets. Throughout the titration the fluorochloroborate signals decreased in intensity and finally vanished. This titration confirms that each molecule of $tmu{\cdot}BF_2Cl$ used up gives rise to one difluoroboron cation and thus supports the postulate that the reaction is the simple displacement equilibrium 1.

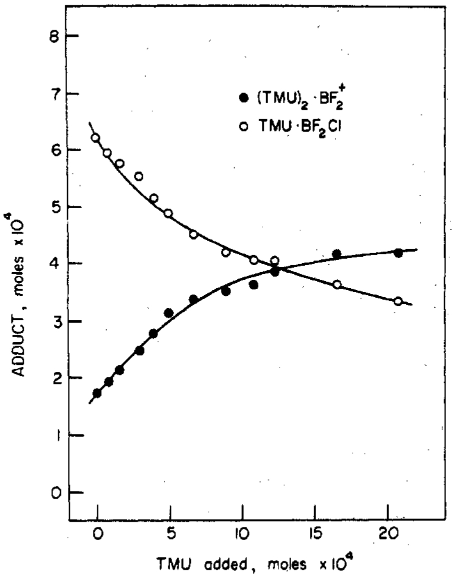

Figure 4. Titration of tmu·BF_2Cl (6.40×10^{-4} mol) with tmu, monitored by ^{19}F nmr.

The addition of a large excess of tmu to a mixed-adduct sample also caused a pronounced decrease in the intensity of the ^{11}B tmu·BF_2Cl triplet and a corresponding increase in the intensity of the combined signal due to $(tmu)_2BF_2^+$ and tmu·BF_3, which unfortunately could not be resolved further (Figure 3).

Both the ^{19}F and ^{11}B chemical shifts are consistent in showing that the cation contains tetrahedral boron rather than trigonal boron. Fluorine on trigonal boron absorbs far to low field of fluorine on tetrahedral boron,[7] well outside the position of the cation. The ^{11}B resonance of a well-authenticated trigonal boron cation[8] occurs very far to low field of all the tetrahedral ^{11}B resonances observed in this work. Thus, it is confirmed that the cation contains a second molecule of tmu and is indeed $(tmu)_2BF_2^+$.

Related Ligand Displacements. (tmu)(DMAC)BF_2^+ and $(DMAC)_2BF_2^+$ Ions. To provide additional proof of the nature of the displacement reactions, dimethylacetamide (DMAC) was added to an equimolar solution of tmu·BF_3 and tmu·BCl_3. Signals corresponding to tmu·BF_3, DMAC·BF_3, $(tmu)_2BF_2^+$, the mixed fluorochloroborate anions, and badly overlapping quartets arising from the BF_2Cl and $BFCl_2$ adducts of both bases were observed in the ^{19}F spectrum. The ^{19}F nmr parameters of DMAC adducts were confirmed from solutions containing no tmu and are included in Table I. In addition, two new peaks appeared somewhat to low field of $(tmu)_2BF_2^+$. These are assigned to (tmu)(DMAC)BF_2^+ and $(DMAC)_2BF_2^+$ as is shown in Table I. The $(DMAC)_2BF_2^+$ peak was also observed in solutions containing both DMAC·BF_3 and DMAC·BCl_3, confirming that the reactions in the DMAC adduct system are similar to those in the tmu adduct system. Further confirmation of the "$D_2BF_2^+$ structure" is provided by the regular trends in ^{19}F chemical shift that occur in the series $(tmu)_2BF_2^+$, tmu·BF_3, BF_4^-; $(DMAC)_2BF_2^+$, DMAC·BF_3, BF_4^-; $(tmu)_2BF_2^+$, (tmu)(DMAC)BF_2^+, $(DMAC)_2BF_2^+$. Unfortunately, no ^{11}B–^{19}F couplings could be observed for the difluoroboron cations in these solutions.

To determine the ability of chloride ion to act as a nucleophile on tmu and related adducts, tetraethylammonium chloride was added in equimolar amounts to separate solutions of tmu·BF_3, the mixed-adduct system tmu·BF_nCl_{3-n}, DMAC·BF_3, and $Me_3N\cdot BF_3$. Proton nmr showed that near-quantitative displacement of tmu from its mixed adducts and its BF_3 adduct took place, whereas no free DMAC or Me_3N could be detected.

The ^{19}F nmr spectrum of a tmu·BF_3 solution which had been treated with an equimolar amount of chloride ion showed only a small tmu·BF_3 peak remaining, and an intense BF_4^- quartet (151.0 ppm, $J_{^{11}B-^{19}F} = 0.9$ Hz). Although it is not clear why BF_4^- rather than BF_3Cl^- is formed in this case, it is clear that the BF_3 adduct is attacked.

Much further work remains to be done to determine relative nucleophilicities and equilibrium constants in these systems. However, it is clear that both DMAC and chloride ion are effective nucleophiles in the tmu adduct system.

Discussion

The Ionic Adduct $(tmu)_2BF_2^+\cdot BF_4^-$. Evidence for the ionic adduct rests on the ^1H, ^{19}F, and ^{11}B nmr spectra. Tetrafluoroborate ion has previously been observed to occur in varying amounts in solutions of tmu·BF_3, and its presence has been traced to HF impurity in the BF_3, which led to the formation of tmu·$H^+\cdot BF_4^-$.[1] Absence of protonated tmu in the present work is shown by (i) the absence of the low-field ^1H peak due to the added proton and (ii) the absence of a methyl resonance which coalesces with the free-tmu peak when free tmu is added.[1] The ^1H peak, which is assigned to $(tmu)_2BF_2^+$, is *not* coalesced with the free-tmu peak when excess base is present. The existence of a second ^{19}F peak, of half the intensity of the BF_4^- peak, helps to confirm the structure. The $(tmu)_2BF_2^+$, tmu·BF_3, and BF_4^- ^{19}F peaks are regularly spaced (Table I), as would be expected in a series where tmu is replaced in a stepwise fashion by F^-. All three ^{19}F peaks and the ^{11}B resonance of $(tmu)_2BF_2^+$ are in the usual region of the spectrum for fluorine on tetrahedral boron. All of the above are consistent with the presence of $(tmu)_2BF_2^+\cdot BF_4^-$ but not tmu·$H^+\cdot BF_4^-$.

Further confirmation of the "$D_2BF_2^+$ structure" is provided by the experiments with DMAC. The two additional species observed in the ^{19}F spectrum, with chemical shifts similar to that of $(tmu)_2BF_2^+$, are the correct number of species expected if the tmu molecules in the four-coordinate difluoroboron cation are displaced stepwise by DMAC molecules.

Poor ^{19}F resolution caused difficulties in studying $(tmu)_2BF_2^+\cdot BF_4^-$. The absence of spin-spin splittings on either the cation or anion peaks and the broadening of the tmu·BF_3 peak suggest moderately rapid fluorine exchange among the species. Attainment of better resolution on addition of tmu supports this, as discussed in the next section.

The breaking and re-forming of boron-fluorine bonds when fluorine is the only halogen is well established in BF_3 adducts of ketones[9] and in the tetrafluoroborate anion.[10] In one of our previous studies[9] we proposed a difluoroboron cation as a likely intermediate in the exchange process. The formation of difluoroboron species is certainly favored when chelation provides an additional driving force.[11,12]

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$(tmu)_2BF_2^+$ is of special interest because few cases of donor-for-fluorine exchange in BF_3 adducts of nonchelating Lewis bases have been reported.

The formation of the ionic adduct from the normal covalent adduct tmu·BF_3 occurred only to the extent of about 5% under the more favorable conditions (the adduct prepared without solvent) and occurred to no detectable extent under less favorable conditions (the adduct prepared in methylene chloride). It is not clear whether an equilibrium was attained or whether a slow reaction was driven further toward the ionic product in the absence of a solvent. An equilibrium would be more favorable to an ionic species in the higher dielectric constant medium tmu (and in molten tmu·BF_3, which is formed and should have an even higher dielectric constant), than in the low dielectric constant medium methylene chloride. It would be interesting to determine whether the system could be driven further toward the ionic product by higher temperatures and to determine which other covalent BF_3 adducts could be made to form detectable amounts of the ionic adducts under forcing conditions. A previous report[13] indicates that this should be possible through a suitable choice of conditions to maximize the formation of either an ionic or a covalent adduct.

Schmulbach and Ahmed[14] have reported, on the basis of conductivity studies, that small proportions of the ionic adduct species $(CH_3CN)_2BX_2^+\cdot BX_4^-$ (X = Cl, Br) are formed in addition to the simple covalent adducts when BCl_3 or BBr_3 are dissolved in acetonitrile. Such reactions are more likely to occur with halogens heavier than fluorine, since boron-heavy halogen bonds are weaker. As discussed by Fogelman and Miller,[15] ionic species are not formed to any appreciable extent when BF_3 is dissolved in acetonitrile.

The $(tmu)_2BF_2^+$ cation has not been isolated as a salt. This would be desirable as there is still much to be learned about relative stabilities and rates of displacement in these systems. It seems unlikely that the BF_4^- salt, *i.e.*, the ionic form of the adduct, could be isolated at room temperature since nmr indicates that chemical exchange remains fairly rapid. Reversion to the covalent form of the adduct would be likely. The PF_6^- or $B(C_6H_5)_4^-$ salts would be better possibilities. Preliminary work indicates that $(tmu)_2BF_2^+B(C_6H_5)_4^-$ is precipitated from methylene chloride solutions containing the $(tmu)_2BF_2^+$ cation.

Redistribution Reactions. With the observation of the formation of $(tmu)_2BF_2^+$ and counterions from a covalent adduct, all of the possible redistribution reactions about boron (eq 3-5) in boron trihalide adducts have been observed in a single adduct system for the first time.

$$D\cdot BX_3 + D' \rightleftarrows D'\cdot BX_3 + D \qquad (3)$$

$$D\cdot BX_3 + D\cdot BY_3 \rightleftarrows D\cdot BX_2Y + D\cdot BXY_2 \qquad (4)$$

$$2D\cdot BX_3 \rightleftarrows D_2BX_2^+ + BX_4^- \qquad (5)$$

Although there have been extensive studies of the breaking and re-forming of donor-acceptor bonds in boron trihalide adducts (eq 3),[7] the general case of ligand redistribution about tetrahedral boron has been very little studied. We have shown that boron-halogen bonds as well as donor-acceptor bonds can be labile in the tetrahedral boron compounds, so that halogen redistribution (eq 4) leads to the formation of mixed boron trihalide adducts[3,5] and mixed tetrahaloborate anions.[6] Reaction 5, in which an organic donor molecule is exchanged for a halogen, is not well known. Numerous dichlorobis(amine)boron cations have been prepared by various other routes,[16] and, as described above, heavy-halogen dihaloborane cations seem to form by reaction 5.[14] Difluoroboron cations seem to be preferred when a bidentate ligand can occupy the remaining two coordination positions about boron.[11,12] Nonchelated difluoroboron cations seem to be less readily formed; the only one reported to date was prepared by an indirect route.[17]

As discussed by Lockhart,[18] the probable first step in the redistribution of ligands about tetrahedral boron is the dissociation of one of the ligands. The trigonal-boron species so formed might then cause exchange by a number of different mechanisms. Our studies of halogen redistribution[3-6] support this. Thus, in the tmu system, dissociation of the weak tmu·BF_3 donor-acceptor bond would account for rapid fluorine exchange. From the ^{19}F spectra it appears that the freed BF_3 exchanges rapidly with BF_4^-, BF_3Cl^-, and $BF_2Cl_2^-$ and somewhat more slowly with $(tmu)_2BF_2^+$, $BFCl_3^-$, and the stronger donor-acceptor species tmu·BF_2Cl and tmu·$BFCl_2$. Addition of free tmu decreases the rate of fluorine exchange. The free base does this by inhibiting dissociation of the adduct and thus decreasing the concentration of free boron trihalide.

Larger amounts of free tmu cause extensive changes in the mixed-halogen system because tmu can displace Cl^- from boron-chlorine bonds. Thus, large amounts of $(tmu)_2BF_2^+$ are formed at the expense of tmu·BF_2Cl. Chloride is a much better leaving group than fluoride, expecially in low dielectric constant solvents like methylene chloride where free fluoride ion is unlikely to exist. Fluorine exchange would probably occur only by a bridging mechanism[6] which avoids the formation of fluoride ion, whereas simple nucleophilic displacement of chloride ion by tmu seems reasonable. Thus, it is not surprising that large amounts of the cation do not form when fluorine is the only halogen but do form when chlorine is present.

This rather specific reaction could result from especially ready dissociation of Cl^- from tmu·BF_2Cl because of maximized π bonding in the residue (SN1 reaction) as is proposed for BF_3Cl^- dissociation.[6] The alternative is a direct attack on tmu·BF_2Cl by tmu (SN2 reaction).

Once Cl^- is driven off, formation of BF_3Cl^- and eventually the entire series of fluorochloroborate anions is to be expected; however, the rapid rates at which these ions exchange halogen is somewhat surprising. In the $BF_nCl_{4-n}^-$ system alone halogen exchange is very slow at room temperature;[6] it becomes fast in the presence of BBr_4^- and, hence, of Br^- by dissociation.[19] It seems that the rapid exchange among the fluorochloroborate ions in the present case is due to tmu having a similar accelerating effect to Br^-, and the mechanism would be similar to that suggested previously.[6] As in the Br^- case, a separate BF_4^- signal cannot be distinguished.

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No evidence has been obtained for the formation of the cations $(tmu)_2BFCl^+$ and $(tmu)_2BCl_2^+$. The reason for this is not clear. Rapid chemical exchange may prevent detection of these species by nmr. Alternate possibilities are lower stabilities of these ions or higher activation barriers to their formation. Only the first of these species is amenable to detection by ^{19}F nmr; a similar species $(Me_3N)_2BFCl^+$ is reported in the literature.[17]

This work provides the first use for our nmr data on the mixed tetrahaloborate anions, and detection of these by nmr should help to clarify other complex exchanging boron trihalide adduct systems.

Comparison with Other Adduct Systems. Halogen redistribution in boron trihalide adducts in the absence of an excess of free boron trihalide depends on the ease of dissociation of the adduct to provide traces of free boron trihalide. Thus, no exchange occurs among Me_3N adducts because the donor-acceptor bond is too strong to allow appreciable dissociation.[4] The $BF_nCl_{4-n}^-$ system exchanges at high temperatures.[6] Owing to the weakness of the donor-acceptor bonds exchange occurs readily at room temperature in the Me_2O and Me_2S adduct systems even when an excess of Lewis base is present.[3,5] The tmu system shows intermediate behavior; halogen redistribution between adducts occurs readily at room temperature provided there is no excess tmu present. Thus, rates of chlorine-fluorine exchange increase in the order $Me_3N{\cdot}BX_3 < BX_4^- < tmu{\cdot}BX_3 < Me_2O{\cdot}BX_3 < Me_2S{\cdot}BX_3$. From the proposed mechanism the order of base strengths should then be Me_2O, Me_2S[20,21] $<$ tmu $< Cl^- < Me_3N$. This order is in accord with our results and (where results are available) with relative base strengths of similar compounds reported in the literature.[22]

It is interesting that a similar donor-halogen exchange giving ionic adducts has not been observed in the Me_2O and Me_2S adduct systems where reactions 3 and 4 have been studied in detail. Ionic species seem to be a possibility only in the Me_2O-BI_3 system, but extreme instability has prevented a detailed study. Both Me_2O and Me_2S are apparently not strong enough nucleophiles to displace halogen. Trimethylamine adducts do not undergo exchange reactions nearly as readily[4] and the absence of donor-halogen exchange is not too surprising. The $(Me_3N)_2BF_2^+$ ion has been isolated as the PF_6^- salt and is quite stable.[17] Thus, the absence of ionic adducts of Me_3N under our conditions seems to be a kinetic effect.

Perhaps reaction 5 requires a Lewis base of intermediate strength, so that dissociation of the adduct occurs to a sufficient extent to allow exchange reactions to occur, but the base which is freed by dissociation is a sufficiently strong nucleophile that it can displace halide ion from one of its boron trihalide adducts.

Nmr Parameters. Trends in the ^1H, ^{19}F, and ^{11}B nmr parameters of the mixed adducts $tmu{\cdot}BF_nCl_{3-n}$ follow those of the corresponding Me_2O adducts; *i.e.*, with increasing chlorine substitution the chemical shifts all move to lower field and the ^{11}B-^{19}F coupling constant increases. In the ^1H spectrum the shift to lower field as heavier halogens are substituted has been attributed to an increase in Lewis acid strength in the order $BF_3 < BF_2Cl < BFCl_2 < BCl_3$. By this criterion the moiety $tmu{\cdot}BF_2^+$ has a Lewis acid strength intermediate between that of BF_2Cl and $BFCl_2$. Since differences in Lewis acid strengths of the boron trihalides have been attributed to π-bonding effects,[23] it would appear that the tmu substituent has an effectiveness between fluorine and chlorine in decreasing the Lewis acidity of boron through π bonding.

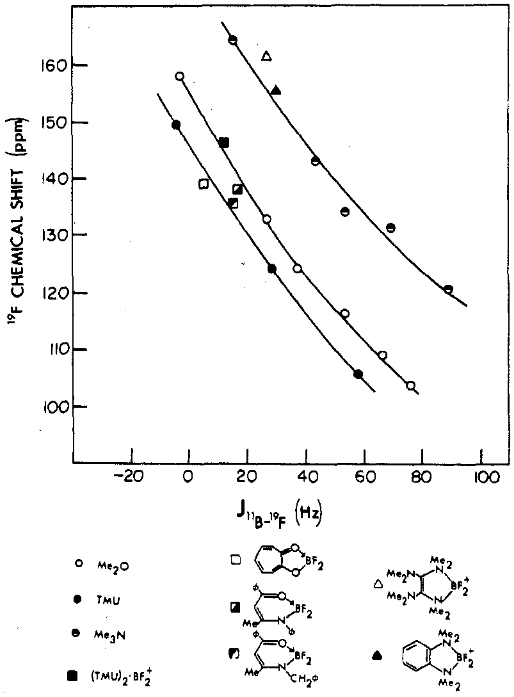

Figure 5. Variation of ^{19}F chemical shifts and ^{11}B-^{19}F coupling constants of some BF_3 and mixed boron trihalide adducts[3,4] and some difluoroboron compounds.[11,12]

Fluorine-19 chemical shifts and ^{11}B-^{19}F coupling constants in boron trihalide adducts can also be considered in terms of the survival of some boron-fluorine π bonding in the adducts.[3,6] The shift of the ^{19}F resonance to lower field and the increase in the ^{11}B-^{19}F coupling constant as fluorines are replaced by other substituents can be attributed to poorer competition of the nonfluorine substituents in π bonding to boron. Tetramethylurea should be able to provide some π bonding in competition with fluorine. From the ^{19}F parameters the ability of tmu to π bond to boron appears to be intermediate between that of fluorine and that of chlorine. Thus, ^1H and ^{19}F nmr data are consistent in placing tmu between fluorine and chlorine in terms of π-bonding ability in these adducts. Boron-11 spectra are not as clear-cut since $(tmu)_2BF_2^+$ and $tmu{\cdot}BF_3$ appear to have very similar ^{11}B chemical shifts.

Trends in ^{19}F chemical shift and ^{11}B-^{19}F coupling constant, such as are shown in Figure 5, seem to be general for boron trihalide adducts of oxygen and nitrogen donors. Thus, a plot of this type is useful in assigning nmr peaks, and the figure helps to confirm the $(tmu)_2BF_2^+$ assignment. Nmr parameters have been reported for several chelated difluoroboron species and these are included in Figure 5 along with $(tmu)_2BF_2^+$. The latter does indeed have the same range of values as the known difluoroboron species.

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(20) Me_2O and Me_2S are anomalous in that "base strength reversal" occurs.[5,21] The weakest adduct by far in either of these systems is $Me_2S{\cdot}BF_3$; thus, uncomplexed boron trihalide is most readily available in the Me_2S adduct system, and it exchanges more rapidly.

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Unfortunately, coupling constants for $(DMAC)_2BF_2^+$ and $(DMAC)(tmu)BF_2^+$ were not observed. Chemical shifts, however, are in the expected range. *Only* the coupling constant (37 Hz), and not the chemical shift, has been reported for $(Me_3N)_2BF_2^+$.[17] This value is in the expected range.

The insensitivity of the nmr parameters to the charge on the ion is notable in the series $(tmu)_2BF_2^+$, $tmu \cdot BF_3$, BF_4^-; $(DMAC)_2BF_2^+$, $DMAC \cdot BF_3$, BF_4^-. Much more sensitivity is shown to factors such as the nature of the donor, the number of heavier halogens, and whether boron is trigonal or tetrahedral.

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Registry No. $tmu \cdot BF_3$, 23389-91-5; $(tmu)_2BF_2^+ \cdot BF_4^-$, 50600-95-8; $tmu \cdot BCl_3$, 50599-70-7; $tmu \cdot BF_2Cl$, 50599-71-8; $tmu \cdot BFCl_2$, 50599-72-9; $(tmu)_2BF_2^+$, 50600-94-7; BF_3Cl^-, 36503-32-9; $BF_2Cl_2^-$, 36503-34-1; $BFCl_3^-$, 36503-36-3; $(DMAC)(tmu)BF_2^+$, 50600-96-9; $(DMAC)_2BF_2^+$, 50600-97-0; $DMAC \cdot BF_3$, 15876-98-9; $DMAC \cdot BF_2Cl$, 50790-57-3; $DMAC \cdot BFCl_2$, 50790-58-4; tmu, 632-22-4; DMAC, 127-19-5; BF_3, 7637-07-2.

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Complexes of Nucleophiles with Rare Earth Chelates. II.[1] Self-Association and Adduct Formation of the Lanthanide Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) Chelates $Pr(fod)_3$ and $Eu(fod)_3$

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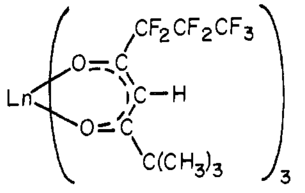
The self-association of the acidic chelates $Pr(fod)_3$ and $Eu(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) as well as the adduct formation of $Eu(fod)_3$ with methyl dimethylcarbamate (TMC) has been studied. All investigations were carried out in carbon tetrachloride solutions. The association quotients for the formation of dimers and trimers respectively are $140 \pm 8\ M^{-1}$ and $45 \pm 5\ M^{-1}$ for $Pr(fod)_3$ and $367 \pm 22\ M^{-1}$ and $12 \pm 2\ M^{-1}$ for $Eu(fod)_3$ at 37°. The association quotients for the formation of 1:1 and 1:2 adducts of $Eu(fod)_3$ with TMC are $(16 \pm 6) \times 10^2\ M^{-1}$ and $107 \pm 10\ M^{-1}$, respectively, at 32°. The effects of water of hydration on the above interactions are also discussed.

Introduction

The paramagnetic tris lanthanide(III) chelates of the anion of Hfod, $Ln(fod)_3$ (I),[2] have been finding ever increasing usage as nmr shift reagents[3] since the first report of Rondeau and Sievers.[4] The chemical property which allows their use as nmr shift reagents is the Lewis acidity which they possess as a consequence of their coordinative unsaturation. Thus the neutral tris chelates dissolve in organic solvents and form labile adducts with a large variety of nucleophilic substrates.[1,3b] The paramagnetic lanthanide ions cause isotropic hyperfine shifts in the resonance frequencies of magnetic substrate nuclei.[3] The Lewis acidity of these chelates also causes two side interactions which can interfere with their usage as nmr shift reagents. These are the formation of hydrates[5-7] and the formation of self-associated oligomers.[1,8,9] We report here the results of our investigations on the effects of these interactions on shift reagent studies.



I

Results

Self-Association of $Pr(fod)_3$, $Eu(fod)_3$, and Their Hydrates. We have studied the self-association of $Pr(fod)_3 \cdot {\sim}{}^3/_2OH_2$, $Pr(fod)_3 \cdot {\sim}{}^1/_2OH_2$, $Pr(fod)_3$, $Eu(fod)_3 \cdot {\sim}{}^3/_2OH_2$, $Eu(fod)_3 \cdot {\sim}{}^1/_2OH_2$, and $Eu(fod)_3$ in carbon tetrachloride by vapor pressure osmometry.[7] The results of the experiments with the praseodymium complexes are shown in Figure 1. The

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[1] Part I: B. Feibush, M. F. Richardson, R. E. Sievers, and C. S. Springer, *J. Amer. Chem. Soc.*, 94, 6717 (1972).

[2] In this paper, Ln symbolizes all of the lanthanide elements from La to Lu and includes Y. The ligand abbreviations used in this paper are as follows: fod, 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate; thd, 2,2,6,6-tetramethyl-3,5-heptanedionate, often referred to as dpm; dfhd, 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedionate; pta, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionate; hfhd, 1,1,1,2,2,3,3-heptafluoro-4,6-heptanedionate; tta, 1,1,1-trifluoro-4-thenoyl-2,4-butanedionate; hfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; acac, 2,4-pentanedionate.

[3] Reviews of lanthanide shift reagents: (a) R. von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, 11, 675 (1972); (b) R. E. Sievers, M. F. Richardson, and C. S. Springer, to be submitted for publication.

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[9] R. Porter, T. J. Marks, and D. F. Shriver, *J. Amer. Chem. Soc.*, 95, 3548 (1973).