

resented by the somewhat idealized structure,  $(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{OSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ .

***m*-Nitrophenylsilatrane.** Triethanolamine can be trimethylsilylated by reaction with  $(\text{Me}_3\text{Si})_2\text{NH}$  to give  $\text{N}(\text{CH}_2\text{CH}_2\text{OSiMe}_3)_3$ : bp  $126^\circ$  (2.7 mm);  $n_D^{25}$  1.4269; neut equiv 366 (calcd value 365). This product (3.7 g, 0.010 mol) was placed in a 1-oz vial with *m*-nitrophenyltrifluorosilane (2.1 g, 0.010 mol) and 5.0 g of *o*-xylene. After heating the xylene solution for 30 min at about  $110^\circ$ , during which time  $\text{Me}_3\text{SiF}$  was allowed to escape, the vial was removed from the hot plate and, upon cooling, crystallization occurred to give 2.83 g of the desired product (95% yield) whose infrared spectrum, neutralization equivalent, and other characteristics were identical with those of authentic material prepared by the more conventional method utilizing triethanolamine and the triethoxyarylsilane.

**$\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_3$ , Preparation and Reaction with  $\text{PhSi}(\text{OMe})_3$ .** The 3,3',3''-nitrotripropanol was prepared by heating 3-amino-1-propanol with 3-bromo-1-propanol and  $\text{K}_2\text{CO}_3$  at reflux in absolute ethanol as per the instructions of Tishler,<sup>11</sup> *et al.*, for a similar synthesis. Distillation afforded a 65% yield of the desired triol: bp  $180^\circ$  (0.2 mm);  $n_D^{25}$  1.4862. Subsequent condensation of this material (5.09 g, 0.0266 mol) with  $\text{PhSi}(\text{OMe})_3$  (5.30 g, 0.0268 mol) in the presence of 26 g of *o*-xylene as a diluent led to gelation; *i.e.*, there does not appear to be any tendency to form the monomeric cage structure.

**Syntheses Involving Displacement Reactions on Ethoxysilatrane Substrate.** (A) **Acetoxysilatrane (3).** Ethoxysilatrane **1** (21.8 g, 0.100 mol), acetic acid (6.0 g, 0.10 mol), and acetic anhydride (10.2 g, 0.10 mol) were heated at  $160^\circ$  for 16 hr. Recrystallization of the resulting product from a chloroform–heptane mixture afforded 60% (14 g) of the desired product, mp  $172$ – $175^\circ$ ; the infrared spectrum had the anticipated strong absorption at  $5.9 \mu$ .

*Anal.* Calcd for  $\text{SiC}_8\text{H}_{15}\text{O}_5\text{N}$ : C, 41.2; H, 6.44; Si, 12.0, neut equiv, 233. Found: C, 40.8; H, 6.24; Si, 12.1; neut equiv, 238.

(B) **Triphenylsiloxysilatrane (5).** When triphenylsilanol (27.5 g, 0.10 mol) was heated with ethoxysilatrane **1** (22 g, 0.10 mol) and 0.2 g of  $\text{Zn}(\text{OAc})_2$  in *o*-dichlorobenzene (50 g) at  $150^\circ$  for 2 hr, the desired compound **5** formed, and upon cooling it was isolated in 70% yield, mp  $256^\circ$ ; this material had a neutralization equivalent of 450 (calcd 449) and was identical with that described elsewhere herein.

(11) E. Wilson and M. Tishler, *J. Amer. Chem. Soc.*, **73**, 3635 (1951).

*Anal.* Calcd for  $\text{Si}_2\text{C}_{18}\text{H}_{27}\text{O}_4\text{N}$ : C, 64.1; H, 6.01; Si, 12.5; N, 3.11. Found: C, 63.8; H, 6.3; Si, 12.4; N, 3.10.

If a mixture of  $\text{Ph}_3\text{SiOH}$  and **1** is recrystallized without being heated long enough to permit reaction to occur, a 1:1 complex of the two compounds may be isolated; mp  $135$ – $138^\circ$ ; neut equiv, 500 (calcd 495).

**Synthesis of Polymers with Silatrane Backbone Units.** (A) **Reaction of 3-Glycidyloxypropyltrimethoxysilane with Diethanolamine.** Diethanolamine (10.5 g, 0.10 mol) and 3-glycidyloxypropyltrimethoxysilane (23.6 g, 0.100 mol) were heated under a Vigreux–Claisen assembly which was suitably protected from atmospheric moisture. Upon heating to  $70^\circ$ , the pot contents were pale yellow, but still immiscible. At about  $80^\circ$  miscibility resulted and an exotherm caused the temperature to increase very rapidly to  $130^\circ$ , whereupon the flask contents gelled. Gentle refluxing of the gel for several hours caused the gel to pass back into solution; the resulting solution was diluted with 25–30 ml of dry methyl ethyl ketone. This solution exhibits the delayed neutralization characteristic of silatrane structures.<sup>1b,2</sup> The methyl ethyl ketone solution deposited a crystalline product melting at  $143$ – $150^\circ$ . Recrystallization of this solid from benzene yielded what appeared to be a polymorphic form melting at  $85$ – $90^\circ$ . In both cases the crystalline solids melted to yield extremely viscous liquids and were merely polymorphs, as evidenced by their essentially identical infrared spectra.

*Anal.* Calcd for  $\text{SiC}_{10}\text{H}_{19}\text{O}_4\text{N}$ : C, 48.9; H, 7.81; N, 5.71. Found: C, 48.6; H, 7.62; N, 5.96.

(B) **Preparation of a Novel Polymer From  $\text{PhSi}(\text{OMe})_3$ ,  $\text{HOCH}_2\text{CH}_2\text{NH}_2$ , and *sym*-Bis(3-glycidyloxypropyl)tetramethyldisiloxane.**  $\text{PhSi}(\text{OMe})_3$  (99 g, 0.50 mol), ethanolamine (30.8 g, 0.50 mol), and the diepoxide (181 g 0.500 mol) were heated in a 1-l. three-necked flask fitted with an agitator, dropping funnel, condenser *via* a Dean Stark trap, and  $\text{N}_2$  purge. After about 15 min at  $90^\circ$ , the contents were becoming quite viscous, so 400 ml of *o*-xylene was added. During the following 2-hr period, approximately 150 g of volatiles was distilled from the system. These volatiles presumably included the anticipated 48 g of methanol produced by the reaction. The viscosity of the resulting resin solution did not undergo further change upon additional heating. Weight loss measurement confirmed that the solution was approximately 52.8% nonvolatile material, and titration of the solution confirmed the presence of silatrane-type amine (*i.e.*, delayed neutralization effect). Evaporation of a small portion of this polymer solution in an aluminum foil cup yielded a tacky film.

## Reaction of Triphenylmethylenamines with Boron Trihalides

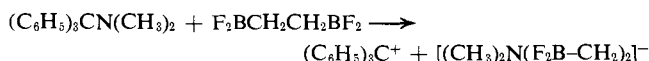
Richard J. Ronan,<sup>1</sup> John W. Gilje,\* and Michael J. Biallas

*Contribution from the Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822, and Northern Illinois University, Dekalb, Illinois 60115. Received February 8, 1971*

**Abstract:** Triphenylmethylenamines react with boron trifluoride to form stable 1:1 adducts,  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{R}_2\text{NBF}_3^-$  ( $\text{R} = \text{CH}_3$  or H). A similar reaction which produces  $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{CH}_3)_2\text{NBF}_3^-$  occurs between triphenylmethylenedimethylamine and boron trichloride. Tensimetric titrations at  $-78^\circ$  demonstrate the existence of an unstable  $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{CH}_3)_2\text{N}(\text{BF}_3)_2^-$ . No further coordination of either  $\text{BF}_3$  or  $\text{BCl}_3$  to  $(\text{C}_6\text{H}_5)_3\text{C}^+(\text{CH}_3)_2\text{NBF}_3^-$  could be detected. The basicity of  $(\text{CH}_3)_2\text{NBF}_3^-$  and  $(\text{CH}_3)_2\text{NBF}_3^-$  is discussed.

The difunctional Lewis acid 1,2-bis(difluoroboryl)ethane,  $\text{F}_2\text{BCH}_2\text{CH}_2\text{BF}_2$ , reacts with triphenylmethyl ethers<sup>2,3</sup> and triphenylmethylenamines<sup>4</sup> to form

“chelated” 1:1 adducts. For example



Similarly, boron trifluoride reacts with triphenylmethyl ether<sup>3</sup> to form  $(\text{C}_6\text{H}_5)_3\text{C}^+\text{CH}_3\text{O}(\text{BF}_3)_2^-$ . Since complexes in which two boron Lewis acids are coordinated to a single donor atom are relatively rare, the reactions of boron trihalides with triphenylmethyl-

\* To whom correspondence should be addressed at the University of Hawaii.

(1) NASA Trainee, 1968–1969; NSF Trainee, 1970.

(2) M. J. Biallas and D. F. Shriver, *J. Amer. Chem. Soc.*, **88**, 375 (1966).

(3) D. F. Shriver and M. J. Biallas, *ibid.*, **89**, 1078 (1967).

(4) M. J. Biallas, *ibid.*, **91**, 7290 (1969).

Table I. Infrared Spectra

$(C_6H_5)_3C^+(CH_3)_2NBF_3^-$	$(CH_3)_3NBF_3^a$	$(C_6H_5)_3C^{+b}$	$(CH_3)_3NBCl_3^a$	$(C_6H_5)_3C^+(CH_3)_2NBCl_3^-$
3260 (w)				3200 (w)
3050 (mw)	3013 (m)	$\approx 3040$	2964 (m)	2950 (mw)
	2954 (s)			2920 (mw)
1960 (w)		1815 (w)		
1890 (w)		1706 (w)		
1820 (w)		1645 (w)		
1590 (s)		1587 (s)		
1490 (s)		1488 (s)	1485 (s)	1495 (m)
			1465 (s)	1455 (m)
1450 (s)		1453 (s)	1451 (s)	1440 (sh)
			1412 (m)	1410 (s, br)
			1408 (m)	
1380 (s)		1359 (s)		1360 (w)
1300 (mw)		1311 (m)		1350 (w)
		1299 (s)		
			1263 (m)	
1210 (m)		1192 (m)	1232 (s)	1220 (m)
	1142 (s)	1168 (m)		1170 (s, br)
1100 (s, br)	1104 (m)		1116 (s)	1100 (sh)
1040 (s)		1037 (m)		1050 (m)
		996 (w)		1020 (m)
		980 (w)		
940 (m)	932 (s)	949 (w)	965 (vs)	
910 (w)		915 (m)		920 (m)
860 (mw)	841 (s)	845 (m)		
820 (mw)		809 (s)		830 (m)
765 (m)		767 (s)		760 (s)
745 (m)				
710 (m)	692 (m)	701 (s)		720 (s)
		658 (m)		680 (s)

<sup>a</sup> R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, **20**, 1487 (1964). <sup>b</sup> R. E. Weston, Jr., A. Tsukamoto, and M. N. Lichtin, *ibid.*, **22**, 433 (1966).

amines were investigated as possible simple routes to such compounds.

### Experimental Section

All manipulations were performed using high-vacuum and/or inert-atmosphere techniques. Triphenylmethylamine and triphenylmethylmethylamine were prepared by the method of Krause.<sup>4,5</sup>  $BF_3$  (Matheson Co.) was purified by distillation from NaF.  $BCl_3$  (Matheson Co., CP grade) was distilled on the vacuum line immediately before use. Other reagents were dried and/or purified by appropriate means.

Tensimetric titrations were performed using standard procedures.<sup>6</sup> The tensimeters used in gas-solid titrations were of all-glass construction and were sealed immediately after sample preparation. This prevented the boron trihalide from coming in contact with stopcocks, grease, or rubber O-ring seals and positively prevented leakage over the long periods (up to 30 days) required for the equilibration of some samples. Samples of the adducts for spectroscopic investigation were obtained after the tensimetric titrations were completed as before.<sup>4</sup>

Visible spectra were obtained on mulls and of toluene or benzene solutions using a Cary model 14, and ir spectra were run as mulls and KBr pellets using Beckman IR 5 and 12 spectrometers. Nmr spectra were recorded in benzene and toluene solutions on a Varian A-60 spectrometer. Chemical shifts are referenced to internal tetramethylsilane. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tenn.

**The Reaction of  $(C_6H_5)_3CN(CH_3)_2$  with  $BF_3$ .** The stoichiometry of the reaction between  $BF_3$  and  $(C_6H_5)_3CN(CH_3)_2$  was determined by tensimetric titrations. In a typical titration  $BF_3$  (measured using a gas weighing bulb) was added incrementally, using the standard procedure,<sup>6</sup> to a 0.0850-g (0.294 mmol) sample of  $(C_6H_5)_3CN(CH_3)_2$  which was dissolved in a few milliliters of toluene and contained in a tensimeter. After each addition the solution was stirred and after equilibration at 0° the pressure was measured. The break

in the plot of pressure vs. mole ratio of  $BF_3$  to  $(C_6H_5)_3CN(CH_3)_2$  occurred after the addition of 0.293 mmol of  $BF_3$  (moles of  $BF_3$ /moles of  $(C_6H_5)_3CN(CH_3)_2 = 0.998$ ). Other titrations performed at temperatures ranging from -23 to 27° also indicated a 1:1 stoichiometry for the reaction. At 27°, in the absence of solvent, no dissociation pressure could be detected for the adduct,  $(C_6H_5)_3CN(CH_3)_2 \cdot BF_3$ . (Pressure within the tensimeters was measured using a Sargent S-14780 cathetometer; while pressure differences of 0.1 mm could be detected, the accuracy of any given measurement was about  $\pm 0.5$  mm because of the tensimeter design.) Typical tensimetric titrations are shown in Figure 1. The products obtained from these reactions were identical regardless of whether or not a solvent was employed.

$(C_6H_5)_3CN(CH_3)_2 \cdot BF_3$  is a bright yellow moisture-sensitive solid. Visible spectra taken of mulls and solutions in benzene and toluene exhibited twin absorption peaks at 410 and 430  $\mu$ . Ir spectra are tabulated in Table I. Repeated attempts to obtain good elemental analysis on this compound gave irreproducible results. Typical values obtained are as follows. *Anal.* Calcd for  $(C_6H_5)_3CN(CH_3)_2 \cdot BF_3$ : C, 70.90; H, 5.91; N, 3.94. Found: C, 72.36; H, 6.32; N, 1.78. Reliable molecular weight measurements could not be obtained because of the compound's limited solubility in all solvents investigated.

**Reaction of  $(C_6H_5)_3CN(CH_3)_2$  with  $BCl_3$ .** The stoichiometry of the reaction between  $(C_6H_5)_3CN(CH_3)_2$  and  $BCl_3$  was also determined by tensimetric titrations. In one titration 0.1–0.25-g samples of  $(C_6H_5)_3CN(CH_3)_2$  were placed in the reaction tubes of seven tensimeters. Sufficient  $BCl_3$  (measured from a gas weighing bulb) was frozen into each of the tubes at -196° so that the  $BCl_3/(C_6H_5)_3CN(CH_3)_2$  molar ratio varied from about 0.1 to 2.5. The tubes were then sealed, removed from the vacuum line, thermostated at 26°, and stirred until equilibrium had been reached. The results of this titration (Figure 1) clearly indicate the formation of a 1:1 adduct,  $(C_6H_5)_3CN(CH_3)_2 \cdot BCl_3$ , whose dissociation pressure is less than 1 mm. The  $(C_6H_5)_3CN(CH_3)_2 \cdot BCl_3$  obtained from this titration was identical in every respect with that formed in reactions run using benzene or toluene as a solvent.

The color of  $(C_6H_5)_3CN(CH_3)_2 \cdot BCl_3$  is yellow, and its visible spectrum shows two peaks, one at 410 and the other at 430  $\mu$ . Ir spectra are listed in Table I. This adduct gave good carbon

(5) C. A. Krause and R. Rosen, *J. Amer. Chem. Soc.*, **47**, 2739 (1925).

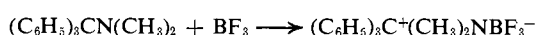
(6) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, pp 58–63.

and hydrogen analysis. Nitrogen values, however, were irreproducible and low. Typical values follow. *Anal.* Calcd for  $(C_6H_5)_3CN(CH_3)_2 \cdot BCl_3$ : C, 62.3; H, 5.19; N, 3.46. Found: C, 62.2; H, 5.04; N, 1.54. Molecular weight was not determined because of the compound's limited solubility in suitable solvents.

**The Reaction of  $(C_6H_5)_3CNH_2$  with  $BF_3$ .** The stoichiometry of the reaction between  $(C_6H_5)_3CNH_2$  and  $BF_3$  was investigated by tensimetric titration using procedures analogous to those used for the titrations described above. These titrations also indicated the formation of a 1:1 complex,  $(C_6H_5)_3CNH_2 \cdot BF_3$ . Visible spectra run on mulls and in toluene solutions showed peaks at 410 and 430  $m\mu$ .

## Results

Tensimetric titrations of  $(C_6H_5)_3CN(CH_3)_2$  with  $BF_3$  (typical titrations are shown in Figure 1), either with or without solvent, indicate the formation of a 1:1 complex,  $(C_6H_5)_3CN(CH_3)_2 \cdot BF_3$ , whose dissociation pressure is negligible at 27°. As in the other reactions of triphenylmethyldimethylamine with boron Lewis acids<sup>4</sup> the  $(C_6H_5)_3C-N$  bond is cleaved and this reaction can be written as



$(C_6H_5)_3C^+(CH_3)_2NBF_3^-$  is a yellow solid whose visible spectrum, taken on solutions in benzene or toluene or on mulls, displays the characteristic absorption peaks on the  $(C_6H_5)_3C^+$  cation at 410 and 430  $m\mu$ .<sup>7</sup> The presence of  $(C_6H_5)_3C^+$  and the formulation of the complex as  $(C_6H_5)_3C^+(CH_3)_2NBF_3^-$  are also supported by its ir spectrum (Table I), where bands typical of  $(C_6H_5)_3C^+$  and tetrahedral (*e.g.*, coordinated)  $BF_3$ <sup>4,9</sup> can be discerned. Qualitatively, the ir spectrum of  $(C_6H_5)_3C^+(CH_3)_2NBF_3^-$  is quite similar to a superposition of the  $(C_6H_5)_3C^+$ <sup>8</sup> and  $(CH_3)_3NBF_3$ <sup>9</sup> spectra (Table I), providing additional supportive evidence for the proposed formulation of the complex. The adduct is moisture sensitive and decomposes into dimethylamine  $\cdot BF_3$  and a derivative of triphenylmethane in solvent systems containing active protons. The only solvents discovered in which it was appreciably soluble without decomposition were toluene and benzene, where the solubility was at most a few weight per cent. The resolution of nmr spectra obtained in these solvents was not good, although a singlet with unresolved fine structure was observed at  $\delta -1.3$ , a typical value for an  $N-CH_3$  group, and a complex multiplet in the phenyl region, centered at about  $\delta -7$ , could be distinguished.

In the tensimetric titrations run in toluene, a white precipitate, which ultimately redissolved, often formed. Qualitatively, the intensity of the yellow color of the triphenylmethyl cation in the solution appeared to be inversely proportional to the amount of this precipitate which was present. The formation of white solid itself seemed to be favored when the  $BF_3$  concentration in solution was low and little formed if the ratio of  $BF_3$  to  $(C_6H_5)_3CN(CH_3)_2$  was high or at the lower temperatures where the boron trifluoride's solubility in toluene is relatively high. At  $-78^\circ$  and below  $BF_3$  was absorbed by solid  $(C_6H_5)_3CN(CH_3)_2$  without the appearance of any yellow coloration if care was taken to avoid localized heating during the reaction and the  $BF_3/(C_6H_5)_3CN(CH_3)_2$  molar ratio was less than about 0.3. The resultant white solid is quite unstable and

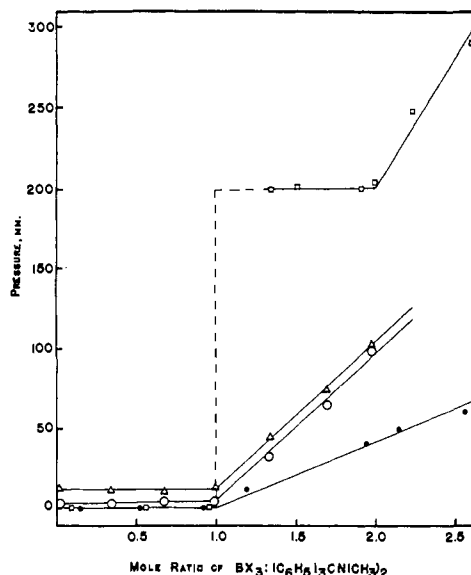
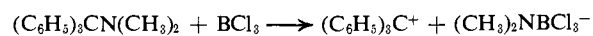


Figure 1. Tensimetric titrations of  $(C_6H_5)_3CN(CH_3)_2$  with  $BF_3$ , toluene solvent,  $0^\circ$  ( $\Delta$ );  $BF_3$ , toluene solvent,  $-23^\circ$  ( $\circ$ );  $BF_3$ , no solvent,  $-78^\circ$  ( $\square$ ); and  $BCl_3$ , no solvent,  $26^\circ$  ( $\bullet$ ).

decomposed rapidly into  $(C_6H_5)_3C^+(CH_3)_2NBF_3^-$  during all attempts to isolate it and obtain stoichiometries on its formation. Although positive identification was not accomplished, the solid probably is the amine  $\cdot BF_3$  complex,  $(C_6H_5)_3C(CH_3)_2N \cdot BF_3$ . Failure of boron Lewis acids to cleave the  $C-N$  bond in triphenylmethyldimethylamine is not unknown, as the simple addition product  $(C_6H_5)_3C(CH_3)_2N:B(F_2)CH_2CH_2BF_2$  has also been observed.<sup>4</sup>

Boron trichloride also reacts with triphenylmethyldimethylamine (Figure 1) to form a 1:1 adduct. The presence of the  $(C_6H_5)_3C^+$  cation in this complex is clearly indicated by the twin absorption peaks at 410 and 430  $m\mu$  in its visible spectrum (taken in benzene and toluene solution) and characteristic bands in the ir spectrum (Table I). The ir spectrum of the adduct itself is quite similar to a combination of  $(C_6H_5)_3C^+$ <sup>8</sup> and  $(CH_3)_3NBCl_3$ <sup>9</sup> spectra, which further supports the idea that the adduct should be written as  $(C_6H_5)_3C^+(CH_3)_2NBCl_3^-$ . The reactivity of this complex toward solvents containing active protons, in which it rapidly decomposed giving a derivative of triphenylmethane and dimethylamine  $\cdot BCl_3$ , prevented the acquisition of good nmr spectra. Proton spectra run in toluene or benzene, in which its solubility was at most a few weight per cent, did exhibit a singlet with unresolved fine structure at  $\delta -1.4$  in the  $N-CH_3$  region and a complex multiplet at about  $\delta -7$  in the phenyl region. It thus appears that the reaction of triphenylmethyldimethylamine with  $BCl_3$  is analogous to this amine's reaction with  $BF_3$ , that is



The behavior of this system is similar to that of the  $BF_3-(C_6H_5)_3CN(CH_3)_2$  system except that no evidence for the formation of  $(C_6H_5)_3C(CH_3)_2N:BCl_3$  was obtained.

Tensimetric titrations of triphenylmethyldimethylamine,  $(C_6H_5)_3CNH_2$ , with  $BF_3$  also produce a 1:1 adduct containing the  $(C_6H_5)_3C^+$  ion. This reaction also appears to be analogous to the  $(C_6H_5)_3CN(CH_3)_2 \cdot BF_3$

(7) B. Branch and H. Walba, *J. Amer. Chem. Soc.*, **76**, 1564 (1954).

(8) R. E. Weston, Jr., A. Tsukamoto, and N. N. Lichtin, *Spectrochim. Acta*, **22**, 433 (1966).

(9) R. L. Amster and R. C. Taylor, *ibid.*, **20**, 1487 (1964).

system except that no evidence was obtained for the formation of  $(C_6H_5)_3CH_2N:BF_3$ . Since amines containing active hydrogens have been observed<sup>10</sup> to undergo dehydrohalogenation with  $BCl_3$ , behavior which would appreciably complicate the  $(C_6H_5)_3CNH_2-BCl_3$  reaction, no studies were performed using these reactants.

At room temperature and slightly below no complexes of stoichiometry  $(C_6H_5)_3CNR_2 \cdot 2BX_3$  formed. However, tensimetric titrations of  $(C_6H_5)_3CN(CH_3)_2$  or  $(C_6H_5)_3C^+(CH_3)_2NBF_3^-$  with  $BF_3$  (Figure 1) demonstrate the existence of an unstable 2:1 complex,  $(C_6H_5)_3C^+(CH_3)_2N(BF_3)_2^-$ , with  $P_{diss}(-78^\circ) = 202 \pm 2$  mm. The formation of a similar  $BCl_3$  complex could not be detected, nor would  $(C_6H_5)_3C^+(CH_3)_2NBCl_3^-$  react with  $BF_3$ , either in toluene or without solvent, at  $-78^\circ$  over a 1-month period or at lower temperature over several hours. No exchange between  $BF_3$  and  $BCl_3$  could be detected, and tensimetric titrations indicate that if  $(C_6H_5)_3C^+(CH_3)_2N(BCl_3)(BF_3)^-$  does exist, its dissociation pressure must exceed 600 mm at  $-78^\circ$ .

## Discussion

$(CH_3)_2NBF_3^-$  is clearly a stronger base than  $(CH_3)_2NBCl_3^-$  toward the reference acid  $BF_3$ . Considering the fact that the basicity of similar bases can commonly be inversely related to the electron-withdrawing ability of the groups attached to the donor atoms,<sup>11</sup> this order is intuitively wrong in view of the electronegativity differences between fluorine and chlorine.<sup>12</sup> However, the heats of formation of  $BCl_3$ :base complexes are known to exceed those of the analogous  $BF_3$  adducts,<sup>16</sup> and spectroscopic and structural evidence<sup>17-23</sup> which implies that the acceptor strength of  $BCl_3$  exceeds that of  $BF_3$  is accumulating. EHMO calculations,<sup>20</sup> which indicate that  $\pi$  back-bonding from the halogen to boron is much less important in  $BCl_3$  than in planar or pyramidal  $BF_3$  (the configuration the molecule

must assume during dative bond formation), also argue for the lower basicity of the trifluoride. A similar conclusion<sup>18</sup> is based on CNDO/2 calculations which imply that the energy of the lowest unfilled MO (the  $BX_3$  orbital most involved in dative  $\sigma$ -bond formation) on  $BCl_3$ , after rearrangement to the configuration it must assume during bond formation, may be lower than that of the less distorted  $BF_3$ . Assuming that steric effects are not the overriding factors in determining the basicity of the  $(CH_3)_2NBX_3^-$  species,<sup>24</sup> the donor strengths observed here indicate that the electron-withdrawing ability of boron trifluoride is less than that of the trichloride.

Extended Hückel MO calculations<sup>25</sup> based on reasonable "guessed" structures of  $(CH_3)_2NBF_3^-$  and  $(CH_3)_2NBCl_3^-$ <sup>26</sup> also support the conclusion that  $BF_3$  is not significantly more electron withdrawing than  $BCl_3$ . The charge on the nitrogen in  $(CH_3)_2NBCl_3^-$  is calculated to be  $-0.32$ , which is identical, within the uncertainties of the calculation, with the value of  $-0.30$  for nitrogen's charge in  $(CH_3)_2NBF_3^-$ . The Mulliken overlap population of 0.732 for the B-N bond in  $(CH_3)_2NBF_3^-$  contrasted to 0.803 for the bond in  $(CH_3)_2NBCl_3^-$  demonstrates a higher B-N bond order in the trichloride complex, indicative of a greater acceptor strength for  $BCl_3$ . As reported previously,<sup>20</sup> EHMO calculations indicate that this order of acceptor strengths results from more effective halogen-to-boron  $\pi$  back-donation in  $BF_3$ , with a concomitant loss in the ability of the boron to serve as an acceptor in Lewis acid-base complexes. Hence, while some of the basicity differences observed between  $(CH_3)_2NBF_3^-$  and  $(CH_3)_2NBCl_3^-$  may be due to steric effects, the electron-withdrawing ability of  $BF_3$  is probably not significantly greater and quite likely is less than that of  $BCl_3$ .

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(12) This discussion presupposes that both  $BF_3$  groups in  $(CH_3)_2N(BF_3)_2^-$  bond to the nitrogen. While the coordination of  $BF_3$  to  $BF_3$  complexes *via* fluorine bridges has been reported,<sup>13,14</sup> such addition is unlikely in this case for several reasons. First, the nitrogen in  $(CH_3)_2N^-$  can and will accommodate the coordination of two boron Lewis acids, as demonstrated by the existence of the stable  $(CH_3)_2N(BH_3)_2^-$ <sup>15</sup> and  $[(CH_3)_2N(F_2B-CH_2)_2]^-$ .<sup>4</sup> Secondly, coordination of a  $BF_3$  group *via* fluorine bridges is unusual and does not seem to occur<sup>14</sup> when an acyclic amine  $\cdot BF_3$ ,  $(C_2H_5)_2N \cdot BF_3$ , is allowed to react with  $BF_3$ .

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