give $(H_2O)_5CrO_2CNH_2{}^{2+}$ as product. Admittedly this mechanism does not seem favorable compared to hydration by a free water molecule when reactant charges and the relative nucleophilicity of free and coordinated water molecules are considered. In any case, if hydration from the coordination sphere of another metal ion were operative, then metal ions should catalyze the hydrolysis of $(NH_3)_5CoNCO^{2+}$ to $Co(NH_3)_6{}^{3+}$. However no catalysis by aqueous copper(II) at pH 4 has been observed and it is concluded that this type of hydration is not important in the electron-transfer reaction with chromium(II).

It is concluded that the k_1 path for reduction of $(NH_3)_5CoNCO^{2+}$ involves a simple inner-sphere mechanism with $-NCO^-$ acting as the bridging ligand. The $(H_2O)_5CrOCN^{2+}$ formed initially must hydrate to give the observed product $(H_2O)_5CrO_2CNH_2{}^{2+}$.

The k_1 value can be compared to that for other isoelectronic bridging ligands. The rate constants (25°), with ΔH^* and ΔS^* values in parentheses, for the chromium(II) reduction of $(NH_3)_5CoN_3{}^{2+}$, $(NH_3)_5CoNCNH^{2+}$, $(NH_3)_5CoNCS^{2+}$, and $(NH_3)_5CoNCO^{2+}$ are $\sim 3 \times 10^5$ M^{-1} sec^{-1},[6] 3.3×10^3 M^{-1} sec^{-1} (4.3 kcal mol^{-1}, -28 eu),[4] 19 M^{-1} sec^{-1} (6.9 kcal mol^{-1}, -29 eu),[6] and 0.5 M^{-1} sec^{-1} (8.8 kcal mol^{-1}, -30 eu), respectively. The ΔS^* values are remarkably constant, indicating a common mechanism. It has been noted by Burmeister and DeStefano[1] that N-bonded cyanate is not likely to be a good bridging group because the negative charge of the ligand is largely localized on the nitrogen atom bonded to cobalt(III). Therefore the oxygen atom will not be very basic and will not form a very stable bridge to the reducing agent. This may explain the low rate for cyanate bridging.

It should be noted that the conclusions about charge density in the NCO^- ion are based on the theoretical calculations of Wagner[7] in which only the π system was considered. In fact pK_a correlations with the theory predict that HSCN should have a pK_a of 5.4, which is certainly not the case. Such a result should be cause for more caution than seems to have been the case in applying Wagner's results.[8]

In any case it may still be that the strength of the bridge to chromium(II) is largely responsible for the difference in reactivity of these complexes, as has been argued previously[9,10] for the $-N_3$ and $-NCS$ complexes. This factor would be consistent with the fact that the rate differences are primarily due to ΔH^* differences. However changes in the electronic energy levels of the ligands and the cobalt may also be important factors.

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The Microwave Spectrum of Trimethylamine–Boron Trifluoride. The Boron–Nitrogen Distance

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Very few donor–acceptor complexes between boron and nitrogen have been studied by microwave spectroscopy because they are often either very involatile or highly dissociated compounds.[1-3] Trimethylamine–boron trifluoride, however, is sufficiently volatile and is undissociated at 177°.[4] We have observed the spectra of three isotopic species and have determined the boron–nitrogen bond distance of the complex in the gas phase.

Prokhorov and Shipulo[2] have reported an average B value of 1750 MHz for this complex based on the observation of ten rotational transitions. They stated that the low J lines appeared as broad unresolved transitions. We have investigated the $J = 8 \rightarrow J = 9$ and the $J = 9 \rightarrow J = 10$ rotational transitions for $(CH_3)_3N \cdot BF_3$, $(CH_3)_3{}^{15}N \cdot BF_3$, and $(CH_3)_3N \cdot {}^{10}BF_3$ at sufficiently low pressures to resolve the broad bands into the typical pattern expected for a symmetric-top molecule. Each transition region consisted of an intense ground-state line and a number of weaker lines arising from rotational transitions in excited vibrational states. Although the vibrational satellite patterns were similar for both J regions in each isotopic species, no extensive attempt was made to measure and assign these transitions. At the pressures employed, line widths were reduced to half-widths of about 1 MHz. No splitting of the ground state was observed due to centrifugal distortion, boron quadrupole coupling, or methyl torsion.

Experimental Section

The transitions were measured at room temperature with a Stark-modulated spectrometer described previously.[5] The uncertainties in the frequency measurements were estimated as ± 0.2 MHz. The assigned transitions and the average B values are listed in Table I. The effect of centrifugal distortion was

TABLE I
OBSERVED TRANSITIONS AND ROTATIONAL CONSTANTS (MHz)

$J \rightarrow J + 1$	$(CH_3)_3N \cdot BF_3$	$(CH_3)_3N \cdot {}^{10}BF_3$	$(CH_3)_3{}^{15}N \cdot BF_3$
8–9	31,609.35	31,675.94	31,529.18
9–10	35,121.42	35,195.38	35,032.40
B	1,756.073	1,759.772	1,751.621

small ($D_J \simeq 0.1 \pm 0.1$ kHz) and was neglected. The assignments were facilitated by the isotopic enrichment of the samples: $(CH_3)_3{}^{15}N \cdot BF_3$ was 90% ^{15}N and 99% ^{11}B; $(CH_3)_3N \cdot {}^{10}BF_3$ was

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92% [10]B. The samples were prepared by Dr. Patty Clippard using standard preparations.[6]

Results and Discussion

Since the boron and the nitrogen atoms lie on the symmetry axis, the B–N distance could be evaluated reliably even though the structure of the remainder of the molecule was not determined. The coordinates of the nitrogen and boron were calculated by the substitution method using Kraitchman's equations.[7] The coordinates obtained for the boron and the nitrogen, respectively, were |0.7761| and |0.8599| Å. These resulted in a B–N bond distance of 1.636 ± 0.004 Å. The uncertainty is associated with the experimental uncertainty in the frequency measurements.

The B–N distance determined here is somewhat longer than that determined from the X-ray analysis from which Geller and Hoard[8] reported a value of 1.585 ± 0.03 Å. It is difficult to ascertain whether this difference unequivocally indicates a change in the B–N bond length between the gas and the solid. Geller and Hoard pointed out in their report that their structure determination was inferior to that normally obtained by X-ray diffraction.

A recent crystallographic study in this department of some boron trihalide complexes of trimethylamine resulted in the following B–N bond distances:[9] $(CH_3)_3N \cdot BCl_3$,[10] 1.610 ± 0.006 Å; $(CH_3)_3N \cdot BBr_3$, 1.603 ± 0.02 Å; $(CH_3)_3N \cdot BI_3$, 1.584 ± 0.025 Å. Although the uncertainties in the values for the bromo and the iodo complexes are rather large, there appears to be a small decrease in the bond lengths in the series. The 1.636 ± 0.004 Å distance for the fluoro complex correlates quite smoothly with this trend. It is interesting to note that this decrease is consistent with the results of various dipole moment,[11] calorimetric,[12] and displacement[13] studies on the acceptor power of the boron trihalides toward trimethylamine.

The structure of trimethylamine–borane has been obtained from the analysis of the microwave spectra of eight isotopic species.[3] A value of 1.65 ± 0.02 Å was obtained for the B–N distance which is comparable to that of the fluoro complex. The results of several stability studies indicate that the acceptor strengths of boron trifluoride and borane toward trimethylamine are approximately the same.[4] Therefore, similar B–N bond distances would be expected for $(CH_3)_3N \cdot BH_3$ and $(CH_3)_3N \cdot BF_3$.

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Basicity of Nitrogen Trifluoride in the Gas Phase by Ion Cyclotron Resonance

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The study of acid–base phenomena deservedly remains an important area of endeavor in chemistry. The determination of acidities and basicities of molecules in the gas phase is especially valuable because complicating effects of solvation phenomena are avoided.[3-7] The new technique of ion cyclotron resonance spectroscopy (icr) is especially suited for the determination of gas-phase thermochemical quantities such as the acidity and basicity of molecules.[4-7] In contrast to ammonia, nitrogen trifluoride, NF₃, has been described as completely lacking in basic properties.[8] We report here the quantitative determination of the gas-phase proton affinity (basicity) of NF₃ based on the observation by icr of the course of ion–molecule reactions occurring in binary mixtures of NF₃ with CH₄ and HCl.

Experimental Section

The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail.[6] Commercial samples of NF₃ (Air Products), CH₄ (Matheson), and HCl (Baker) were subjected to repetitive freeze–pump–thaw cycles before use.

Results

The ion chemistry of NF₃ alone and in binary mixtures with CH₄ and HCl was examined between 10⁻⁷ and 10⁻³ Torr at 70 eV. Nitrogen trifluoride chemically attacks the rhodium-plated metal surfaces of the icr cell and filament wire, making pressure studies difficult. It was found necessary to change the icr cell drift and trapping voltages with nearly every scan. Such operating conditions make impossible the extraction of reaction rate constants for processes observed. However, it was still possible to monitor the course of reaction by pressure variation and icr double-resonance experiments.

Nitrogen Trifluoride.—The icr single-resonance spectrum at 10⁻⁷ Torr was in agreement with the known

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