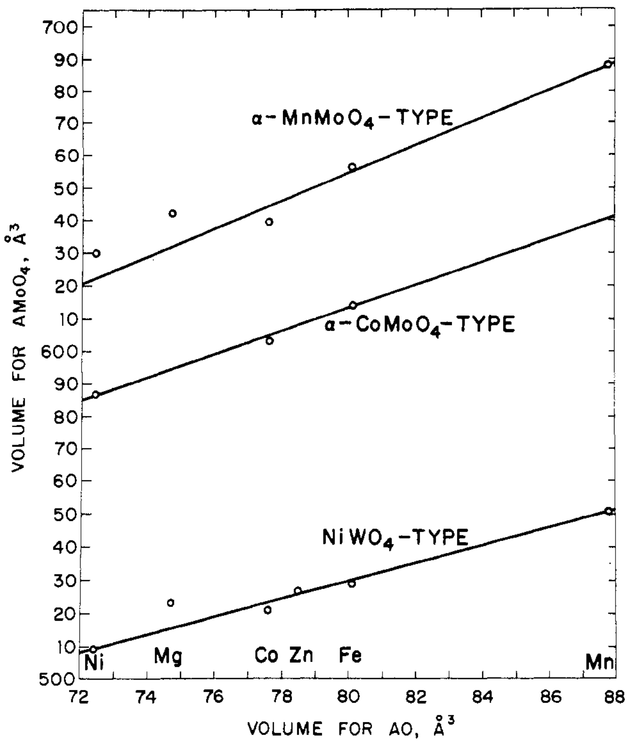

Figure 1.—Plot of the volumes of $AMoO_4$ molybdates *vs.* the volumes of corresponding AO oxides with the rock salt structure.

and the α-$MnMoO_4$ structure is the coordination of Mo which is tetrahedral in α-$MnMoO_4$ and essentially octahedral in α-$CoMoO_4$. Tetrahedral Mo also occurs in $AMoO_4$ molybdates where A is Ca, Sr, Ba, Cd, or Pb (scheelite structure). The occurrence of tetrahedral or octahedral Mo in $AMoO_4$ molybdates would thus appear to depend on the size and electronegativity of the A cation. The two most electropositive cations in the series, Mg, Mn, Zn, Fe, Co, and Ni are Mg and Mn, and of this series it is only Mg and Mn that form normal (STP) molybdates with tetrahedral molybdenum. While Mn is the largest of the above series, Mg is not the second largest.

In Figure 1 the cell volumes of the $AMoO_4$ molybdates are plotted against the cell volumes of the rock salt AO compounds.[12] The trends are relatively consistent although magnesium appears to be larger in the molybdates than in MgO. The figure dramatically shows the large density difference between the α-$CoMoO_4$ isotypes and the $NiWO_4$ isotypes. This is interesting because in both of these structure types the A and Mo atoms are in octahedral coordination. However, the oxygen atoms are nearly closed-packed in the $NiWO_4$ structure type whereas this is not the case in the α-$CoMoO_4$ structure. Smith and Ibers[3] describe the oxygen packing in α-$CoMoO_4$ as cubic-close-packed *except* that one out of nine oxygen sites is vacant. Thus, during the transformation from the α-$CoMoO_4$ structure to the $NiWO_4$ structure the oxygen atoms become nearly close-packed whereas the coordination numbers of the atoms remain unchanged.

Acknowledgment.—The 65-kbar experiments were supervised by C. L. Hoover, the X-ray data were obtained by K. R. Babcock, M. S. Licis, and J. F. Whitney, and the dta experiments were performed by H. W. Williams.

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[12] Data for the rock salt cell volumes were taken from R. W. G. Wyckoff, "Crystal Structures," Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, pp 86–91, except the value for ZnO which was obtained from C. H. Bates, W. B. White, and R. Roy, *Science*, **137**, 993 (1962).

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Complexes of Titanium Tetrafluoride with Substituted Pyridines

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Most of the titanium tetrafluoride complexes described in the literature have been with monofunctional oxygen donors. Usually the complexes are *cis* adducts of the type $TiF_4 \cdot 2$(donor), thus reflecting the tendency of titanium to achieve sixfold coordination. In contrast to the large number of oxygen-containing diadducts, very few complexes have been reported with other donor atoms. Reactions of various amines with TiF_4 have been investigated.[1–4] Reactions with secondary amines have resulted in aminolysis reactions with the formation of dialkylamidotitanium(IV) trifluorides and dialkylammonium hexafluorotitanates.[1,2] With tertiary amines and pyridine, addition compounds are formed.[2] Depending upon reaction conditions, it is possible to obtain both the 1:1 complex and 2:1 complex, $TiF_4 \cdot 2py$, with pyridine[2–4] (py = pyridine). The 2:1 complex slowly loses pyridine on standing in a dry atmosphere. The addition compound appeared to be polymeric and the titanium was postulated to be octahedrally coordinated through fluorine bridging.[4] No F^{19} nmr data were reported for the pyridine complexes. As a result, we felt it of interest to prepare complexes of several substituted pyridines in an attempt to clarify their structure(s) by nuclear magnetic resonance spectroscopy.

Experimental Section

Materials.—Dimethoxyethane obtained from Matheson Coleman and Bell was dried by distillation from sodium metal. Titanium tetrafluoride obtained from Allied Chemical Co. was used without further purification. 2-Chloropyridine, 2-bromopyridine, 3-bromopyridine, and 3-chloropyridine obtained from Aldrich Chemical Co., pyridine, 2-methylpyridine (Practical grade), 4-methylpyridine, and 2,6-dimethylpyridine (Practical grade) obtained from Eastman Organic Chemicals, and 2,4-dimethylpyridine (Practical grade) obtained from Matheson Coleman and Bell were dried by distillation from calcium oxide.

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Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, West Germany.

Preparations of Complexes.—The substituted pyridine was added slowly to a saturated solution of TiF_4 in dimethoxyethane until precipitation ceased. The solid was collected by filtration and dried under vacuum. *Anal.* Calcd for $TiF_4 \cdot 4\text{-}CH_3C_5H_4N$: C, 33.21; H, 3.25; N, 6.45. Found: C, 33.07; H, 3.77; N, 6.62. Calcd for $TiF_4 \cdot 2,6\text{-}(CH_3)_2C_5H_3N$: C, 36.39; H, 3.92; N, 6.06. Found: C, 37.72; H, 4.97; N, 6.68. Calcd for $TiF_4 \cdot 3\text{-}BrC_5H_4N$: C, 21.30; H, 1.42; N, 4.96; Br, 28.35. Found: C, 22.72; H, 1.84; N, 5.14; Br, 30.54.

Instrumental Data.—The fluorine nmr spectra were obtained on a Varian A56/60A spectrometer equipped with a V-6057 variable-temperature accessory. The chemical shifts were measured with respect to external standard trichlorofluoromethane.

Results

Complexes of TiF_4 with 4-methyl-, 2-methyl-, 2,6-dimethyl-, 3-chloro-, 2-chloro-, 3-bromo-, and 2-bromopyridines were prepared. Of these, only the 2-chloro- and 2-bromopyridine complexes were soluble upon addition of base to the TiF_4–dimethoxyethane solution; the other complexes precipitated immediately and were insoluble in a wide variety of solvents. Thus, it was possible to obtain the F^{19} nmr spectra of only the 2-halopyridine complexes. These spectra, obtained in dimethoxyethane at $-58°$, consisted of two triplets of equal intensity. The data from these spectra are given below. The chemical shifts are uncorrected for bulk susceptibility.

Ligand	Chem shifts, ppm (external $CFCl_3$ ref)	F–F coupling constants, cps
2-Chloropyridine	$-146, -214$	34
2-Bromopyridine	$-146, -214$	36

Discussion

The spectra of the 2-chloropyridine and 2-bromopyridine complexes are consistent with the previously reported *cis*-$TiF_4 \cdot 2$(donor) compounds.[4-7] The F^{19} spectra consist of two 1:2:1 triplets of equal intensity, indicating that the two donor molecules must be *cis* to each other. The chemical shifts[5] and coupling constants[8] are similar to those for other *cis*-TiF_4 diadducts.

Elemental analyses of the insoluble complexes (4-methylpyridine, 2,6-dimethylpyridine, and 3-bromopyridine) show them to be essentially 1:1 complexes. No evidence was found for the formation of 2:1 adducts with any of the substituted pyridines which formed 1:1 complexes. The 1:1 complexes have very little solubility in polar, nonprotonic solvents. A large range of solvents was employed, but it was not possible to dissolve enough of the compounds (for >0.02 *M* solutions) to obtain their spectra. The compounds are soluble with decomposition in protonic solvents such as water and ethanol. The 2-methylpyridine adduct was shown to be a 1:1 complex by decomposing the complex in water, obtaining the H^1 nmr spectrum, integrating the methyl resonance, and comparing it with data for standard 2-methylpyridine–water solutions. These complexes have high melting points which are not sharp. The intractability of the compounds and the absence of sharp melting points suggest that the 1:1 adducts are not pentavalent complexes. In all probability they are polymeric complexes with "fluorine bridging" so that the titanium is octahedrally coordinated. This phenomenon has been observed in antimony pentafluoride,[9,10] arsenic fluorosulfonate,[11] and other fluorides.[12] A similar conclusion was reached by Muetterties[4] for the $TiF_4 \cdot py$ complex.

To explain their conductometric titration curve for the titration of TiF_4 by pyridine in acetone, Chandler and Drago[2] proposed the mechanism

$$TiF_4 + py \longrightarrow [TiF_4 \cdot py] \qquad (1)$$

$$[TiF_4 \cdot py] + 2TiF_4 \longrightarrow pyTiF_3^+ + Ti_2F_9^- \qquad (2)$$

$$2py + pyTiF_3^+ + Ti_2F_9^- \longrightarrow (3/x)(pyTiF_4)_x \qquad (3)$$

In this reaction scheme one should consider that all the titanium species achieve sixfold coordination by complexing with the solvent. By also including an additional reaction

$$[TiF_4 \cdot py] + py \longrightarrow TiF_4 \cdot 2py \qquad (2')$$

the formation of the *cis* diadducts can be explained. There is competition between reactions 2 and 2′ and one would expect an increase in basicity of the ligand to favor reaction 2 thus influencing the extent of polymer formation, *i.e.*, insolubility. The stronger the base the more readily a fluoride ion could be transferred from $TiF_4 \cdot py$ to a TiF_4 molecule. In Table I are listed pK_a values of pyridine and some substituted pyridines. As can be seen from these data, the diadducts were formed with the two weakest bases.

TABLE I

RELATIVE BASICITY OF THE PYRIDINES AND THEIR COMPLEXES WITH TITANIUM TETRAFLUORIDE

Ligand	pK_a[a]	Solubility	Stoichiometry
2-Chloropyridine	1.31	Sol	2:1
2-Bromopyridine	1.60	Sol	2:1
3-Bromopyridine	2.20	Insol	1:1
3-Chloropyridine	2.16	Insol	1:1[b]
Pyridine	5.14	Insol	1:1[c]
2-Methylpyridine	6.12	Insol	1:1
4-Methylpyridine	6.15	Insol	1:1
2,6-Dimethylpyridine	6.73	Insol	1:1
2,4-Dimethylpyridine	6.74	Insol	1:1[d]

[a] I. I. Grandberg, G. K. Faizova, and A. N. Kost, *Khim Geterotsikl. Soedin*, **4**, 561 (1966). [b] Stoichiometry established by similarity of its physical properties with the other 1:1 complexes. [c] References 2–4. [d] Reference 4.

It is interesting that a 2:1 adduct was not obtained with 3-bromopyridine where there is not a large difference in its basicity as compared to 2-bromopyridine. The pK_a values give the relative basicity of the pyridines toward hydrogen ion, but with respect to the larger reference acid, TiF_4, the basicity of the 2-bromo-

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pyridine would be lessened by increased steric interaction with the 2-bromo substituent. A similar argument can be given in comparing the relative basicities of 2-chloropyridine and 3-chloropyridine.

It is surprising that only the *cis* adducts were detected by nmr for the 2-halopyridine complexes since it has been shown that both the *cis* and *trans* complexes are formed with 2-methylpyridine 1-oxide and only the *trans* compound is formed with 2,6-dimethylpyridine 1-oxide.[6] The occurrence of *cis–trans* isomerism in $MF_4 \cdot 2$(donor) depends upon steric effects and $p\pi$–$d\pi$ bonding.[13] Formation of *trans*-$TiF_4 \cdot 2[2,6\text{-}(CH_3)_2C_5H_3NO]$ was explained on the basis of a steric effect.[6] Since the pyridines are good π acceptors,[14,15] they should increase the ability of the fluorines to π bond to titanium and will stabilize the *cis* complexes. In contrast, a lone pair of electrons on the oxygen of the pyridine 1-oxides will be competing with the fluorines for the titanium π-bonding orbitals.

As indicated previously, most of the titanium tetrafluoride complexes studied have been with monofunctional oxygen donors. Most of these donors are weaker bases (comparison of pK_a values) than the weakest donor listed in Table I. A preliminary reaction of *p*-bromo-N,N-dimethylaniline N-oxide yielded an insoluble adduct which is suggestive of a 1:1 adduct. The basicity of the aniline N-oxide is much greater than that of the pyridine N-oxides. In conclusion it appears that 1:1 complexes are favored by strong bases whereas 2:1 adducts are formed only with weak bases.

Acknowledgment.—Support of this work by the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson AFB, Ohio, is gratefully acknowledged.

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The Hydrogen Exchange between Pentaborane-9 and Silane[1a]

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Little attention has been paid to the interaction between hydrides of boron and silicon. This work was attempted to determine whether silane-d_4 and pentaborane-9 would undergo hydrogen atom exchange and, if so, whether the transfer might occur preferentially at the apical position (believed to be the most susceptible to electrophilic attack[2]) or the basal positions of the latter.

Experimental Section

Apparatus and Equipment.—All chemical reactions were carried out in a vacuum line equipped with mercury-float valves. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer, Model 137. The samples were confined in a 5-cm gas cell with sodium chloride windows. Boron nmr spectra were obtained at 19.3 Mc/sec with a Varian DP-60 high-resolution spectrometer. Mass spectra were obtained with a Consolidated Engineering Corp. mass spectrometer, Model 21-620.

Chemicals.—Deuterated silane was prepared by a slight modification of the method of Finholt, *et al.*[3] Powdered lithium aluminum deuteride (99.9% D) was slowly dropped into a flask containing a solution of silicon tetrachloride in di-*n*-butyl ether. The silane-d_4 evolved was purified by passage through a −161° trap and its infrared spectrum was identical with that reported previously.[4] Pentaborane-9 (Olin Mathieson Co.) had a vapor pressure of 66 torr at 0° (lit. value 66 torr[5]) and was used without further purification. Deuterium chloride was prepared by the reaction of silicon tetrachloride and deuterium oxide.[6]

Hydrogen Exchange between Pentaborane-9 and Deuterated Silane.—Silane-d_4 (0.28 mmol) and 0.23 mmol of pentaborane-9 were condensed together in a U tube and allowed to equilibrate at room temperature for 10 min. Separation was then achieved by a single passage through a −161° trap. The more volatile silane was recovered quantitatively. An infrared spectrum of this distillate showed the presence of only silane-d_4 indicating that no exchange had occurred. The gases were then mixed together and allowed to remain at room temperature for 17 hr. They were separated as above, and again the infrared spectrum of the silane fraction indicated no evidence of hydrogen transfer.

The gases were then transferred to an all-glass reaction tube equipped with a seal-off and break-off; the tube was sealed and placed in an oven at 125° for 44 hr (total pressure in the tube was 0.45 atm). On opening, no noncondensable gas was observed. The products were separated as above. An infrared spectrum of the distillate confirmed the presence of mixed protonated and deuterated monosilane molecules. The condensate was also sampled for an infrared spectrum and the appearance of the B–D stretching frequency proved that exchange had occurred.

To determine whether proton exchange was selective in the pentaborane molecule, 0.82 mmol of silane-d_4 and 0.37 mmole of pentaborane-9 were placed in an all-glass reaction bulb and allowed to equilibrate for 21 hr at 125°. The total pressure in the bulb was calculated to be 1.2 atm. The gases were separated by a single pass through a −105° trap. The distillate (silane fraction) was sampled for an infrared spectrum and the components were identified as silane-d_4 and silane-d_3.[4] The infrared spectrum of the pentaborane-9 fraction agreed well with that reported by Onak and Williams[7] for pentaborane-9 with a deuterium atom substituted at the apical position. The spectrum is quite similar to that of normal pentaborane-9, the most distinguishing feature being the appearance of a new band at 5.06 μ.

A B^{11} nmr spectrum of the pentaborane-9 fraction was obtained. A comparison between the nmr spectra of the pentaborane-9 obtained from the above reaction and normal pentaborane-9 is shown in Figure 1.

The pentaborane-9 fraction was also sampled for a mass spectrum. The upper region of the spectrum is shown in Table I

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[1] (a) This work was taken from a dissertation submitted by M. L. Thompson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University. (b) Department of Chemistry, Lake Forest College, Lake Forest, Ill. 60045.

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