dation states by complex formation in molten salts has been discussed previously.[15] Evidence for retention of some In^0 in solution in the melt was provided by the fact that indium metal separated out from the solid on cooling. The question remains as to the state of combination of the In^0 in solution; we suggest that this may be coordinated to In^{III} or, more likely, to $InCl_4^-$. The strong, polarized Raman band at *ca.* 170 cm^{-1} observed for both molten In_2Cl_3 and molten $InCl_{1.2}\cdot 4(Li,K)Cl$ could then be explained as due to the stretching mode of an In–In bond; In^{3+} is isoelectronic with Cd^{2+}, and the latter has been shown to coordinate with Cd^0 to form Cd_2^{2+} in the molten state. The Cd–Cd stretching frequency was found[15] at 183 cm^{-1}, quite close to the above-mentioned band in these indium-containing melts. Association of In^0 with In^I seems improbable since it was shown in separate experiments that there is no appreciable solubility of indium metal in molten $InAlCl_4$, which contains only In^I.

Unfortunately the present results do not provide sufficient information to deduce the actual structure of the proposed In^0–In^{III} species, and more extensive Raman studies were severely hindered by the deep red color of the melts. The presence of the strong band at 281 cm^{-1} may be indicative of competitive coordination of $InCl_4^-$ by free Cl^- to form $InCl_5^{2-}$ and $InCl_6^{3-}$, but broadness of the band suggests that it may also contain contributions from the In–Cl stretching modes of a complex of the type $(InCl_4In^0)^{2-}$. It is worth noting at this stage that in the molten Bi–$BiCl_3$ system which, like InCl and In_2Cl_3, is very deeply colored, there is strong evidence[17] to substantiate the existence of such moieties as Bi_5^{3+}, which probably are further coordinated to chloride ligands.

We should point out that although the above conclusions may be speculative, the evidence for disproportionation of In^I in the presence of free chloride is quite strong, and if further studies of the indium chloride melts confirm the existence of metal–metal bonds, then this is an entirely novel feature of the chemistry of indium.

Since the preparation of this work for publication, another paper offering Raman evidence for the formulation of molten $InCl_2$ as $In^+InCl_4^-$ has appeared.[18] However, the spectra in this paper are much less complete than ours, and the authors failed to observe the important new band at *ca.* 170 cm^{-1} in their spectra on addition of excess chloride. We have observed this band for molten mixtures of $InCl_2$ and KCl, thus confirming our conclusion that it is a feature typical of melts containing In^+ and excess chloride.

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A Fluorine-19 Nuclear Magnetic Resonance Study of Some Titanium Tetrafluoride–Substituted Pyridine 1-Oxide Adducts[1]

BY DANIEL S. DYER[2a,b] AND RONALD O. RAGSDALE[2c]

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A fluorine-19 nmr study of several substituted pyridine 1-oxide adducts of titanium tetrafluoride is reported. Evidence for the existence of a number of *trans*-$TiF_4\cdot 2$(donor) complexes is presented and discussed. Mixed adducts of TiF_4 in which the donor molecules are oriented *trans* to each other in solution are reported for the first time. The factors which determine the stereochemistry of the $TiF_4\cdot 2$(donor) complexes are discussed. It appears that *trans*-$TiF_4\cdot 2$(donor) is formed only when there is sufficient steric interaction to overcome symmetry effects and the tendency to maximize pπ–dπ bonding.

Introduction

Recently several reports of research on transition metal complexes of substituted pyridine 1-oxides have appeared in the literature. Of particular interest was the infrared study of some diadducts of titanium tetrafluoride with *para*-substituted pyridine 1-oxides ($TiF_4\cdot 2(4\text{-}ZC_5H_4NO)$).[3] The N–O and Ti–O stretching modes of this series of $TiF_4\cdot 2D$ (D = donor) complexes were investigated as a function of the *para* substituent. The observed linear correlation of these two vibrational modes with the substituent constant σ^+ was used to elucidate the nature of the titanium–ligand bonds. The present paper describes an ^{19}F nmr study of $TiF_4\cdot 2(4\text{-}ZC_5H_4NO)$ and other titantium tetrafluoride–substituted pyridine 1-oxide complexes.

Previous ^{19}F nmr studies of the $TiF_4\cdot 2D$ adducts include the work of Muetterties[4] and of Ragsdale, *et al.*[5,6]

(1) Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) (a) Abstracted in part from the Ph.D. thesis of D. S. D. submitted to the University of Utah. (b) Wright-Patterson Air Force Base. (c) Chemistry Department, University of Utah.

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TABLE I

NMR DATA FOR SOME *cis*- AND *trans*-$TiF_4 \cdot 2D$ COMPLEXES IN CHLOROACETONITRILE AT −40°

	Chemical shift, δ (±0.5 ppm) (internal $CFCl_3$ ref)			F–F coupling constant (±1), cps	% *trans* (±2%)
	δ(*cis*)		δ(*trans*)		
Donor	Triplet	Triplet	Singlet		
C_5H_5NO	−156.9	−133.9		35	0
$2\text{-}CH_3C_5H_4NO$	−155.0	−129.5	−127.8	36	7
$2\text{-}C_2H_5C_5H_4NO$	−155.2	−129.3	−128.1	37	14
$4\text{-}CH_3C_5H_4NO$	−151.0	−131.3		35	0
$2,4\text{-}(CH_3)_2C_5H_3NO$	−149.7	−127.4	−125.4	36	15
$2,6\text{-}(CH_3)_2C_5H_3NO$			−133.3		100
$3,5\text{-}(CH_3)_2C_5H_3NO$	−152.2	−131.9		35	0
C_9H_7NO[a]	−156.3	−130.7	−128.3	36	9

[a] At −60°.

The data reported by Muetterties[4] contain chemical shift values for only one complex ($TiF_4 \cdot 2C_2H_5OH$). Ragsdale and Stewart[5] gave nmr data for the three $TiF_4 \cdot 2ROH$ complexes where R is methyl, ethyl, and isopropyl. More recently Ragsdale and Dyer[6] reported an ^{19}F nmr study of some mixed adducts of TiF_4 ($TiF_4 \cdot DD'$ complexes). In all these studies the two donor molecules were found to occupy positions *cis* to each other in the octahedra. Evidence for a *trans* orientation in some titanium tetrafluoride–substituted pyridine 1-oxide complexes has also been reported.[7] In this paper we have presented further evidence for the existence of *trans*-$TiF_4 \cdot 2D$ in solutions of some substituted pyridine 1-oxide–titanium tetrafluoride adducts and discussed the factors which determine the stereochemistry of $MF_4 \cdot 2D$ complexes.

Experimental Section

Titanium tetrafluoride adducts were formed by the method described by Muetterties[1] with 4-methylpyridine 1-oxide, pyridine 1-oxide, 2-methylpyridine 1-oxide, 2-ethylpyridine 1-oxide, 2,4-dimethylpyridine 1-oxide, 2,6-dimethylpyridine 1-oxide, 3,5-dimethylpyridine 1-oxide, quinoline 1-oxide ("C_9H_7NO"), dimethylacetamide, and tetramethylurea. Mixed-adduct complexes[6] were prepared *in situ* by addition of the appropriate substituted pyridine 1-oxide to a solution of the $TiF_4 \cdot 2D$ complex in chloroacetonitrile. All solutions were prepared in such a way as to exclude moisture. These adducts, were studied as chloroacetonitrile solutions by low-temperature ^{19}F nmr spectroscopy. All spectra were obtained using a Varian A-56/60A nmr spectrometer equipped with a variable-temperature accessory.

Results

The results of the low-temperature ^{19}F nmr study for some *cis*- and *trans*-$TiF_4 \cdot 2D$ complexes are listed in Table I. In Figure 1 a diagrammatical representation of the ^{19}F spectra of the $TiF_4 \cdot 2D$ complexes with various pyridine 1-oxides is shown.

The ^{19}F spectrum of the *cis* complexes consists of two triplets of equal intensity. Only *cis* adducts were found in solution for pyridine 1-oxide and 4-methylpyridine 1-oxide. Two triplets of equal intensity were also observed in each of the spectra of the 2-methylpyridine 1-oxide, 2-ethylpyridine 1-oxide, 2,4-dimethylpyridine 1-oxide, and quinoline 1-oxide complexes, but in addition a singlet resonance was observed upfield from each pair of triplets. Only a single line was seen for the 2,6-dimethylpyridine 1-oxide complex.

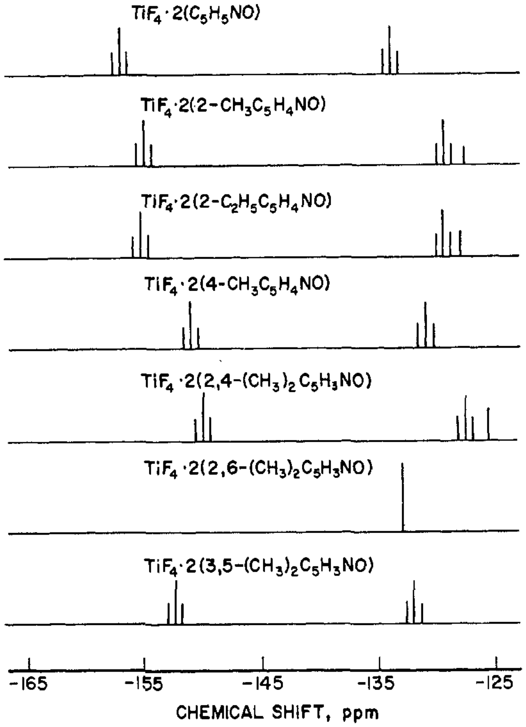

Figure 1.—Diagrammatic representation of the ^{19}F nmr signals observed for the titanium tetrafluoride–substituted pyridine 1-oxide adducts in chloroacetonitrile at −40° . (The chemical shifts are recorded in parts per million displacements from the resonance of internal $CFCl_3$.)

Since fast exchange can collapse an nmr multiplet into a single line, it is usually difficult to justify a structural assignment on the basis of a singlet. Nevertheless, the singlets observed in the spectra of the above solutions are assigned to the respective *trans*-$TiF_4 \cdot 2D$ complexes. This assignment can be justified on the following bases. (1) Since two triplets were resolved in each nmr spectrum except that of $TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$, a fast exchange at −40° involving a *cis* isomer is eliminated for all solutions except those containing the latter adduct. If the single line observed in the spectrum of $TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$ were due to fast fluorine exchange in the *cis* isomer, the resonance would be expected to occur approximately halfway between the upfield and downfield triplets of the *cis* complexes (see Figure 1). Instead it occurs in the region of the upfield triplets. (2) In the *cis* complex the fluorines, which have only a *cis* relationship to the two donor molecules, have been assigned to the upfield triplet.[5,6] Consequently, it is expected that the resonance for the *trans*-isomer fluorines, which are all *cis* to the two donor

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[7] D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966).

molecules, would occur in the region of the upfield triplet. (3) None of the observed singlets were due to the hexafluorotitanate ion. This ion were prepared by the addition of fluoride ion to the $TiF_4 \cdot 2D$ solutions, and its resonance appears several parts per million upfield from any of the $TiF_4 \cdot 2D$ resonances.

trans isomers were also observed when certain substituted pyridine 1-oxides were added to solutions of $TiF_4 \cdot 2DMA$ (DMA = N,N-dimethylacetamide) and $TiF_4 \cdot 2TMU$ (TMU = tetramethylurea) in chloroacetonitrile. When 2,6-dimethylpyridine 1-oxide was added to $TiF_4 \cdot 2DMA$–chloroacetonitrile solutions and the low-temperature ^{19}F spectrum recorded, nine lines were observed in the region where the upfield triplet of $TiF_4 \cdot 2DMA$ occurs. A spectrum of this region is reproduced in Figure 2. Three of these lines constitute the upfield 1:2:1 triplet of $TiF_4 \cdot 2DMA$. The line which occurs farthest upfield has the same chemical shift as the singlet which was assigned to *trans*-$TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$. The remaining five lines constitute the singlet and the upfield doublet of doublets of *trans*- and *cis*-$TiF_4 \cdot [(DMA)(2,6\text{-}(CH_3)_2C_5H_3NO)]$, respectively. The molar ratio of *cis* isomer to *trans* isomer concentration for $TiF_4 \cdot [(DMA)(2,6\text{-}(CH_3)_2C_5H_3NO)]$ in these solutions was approximately 8:1.

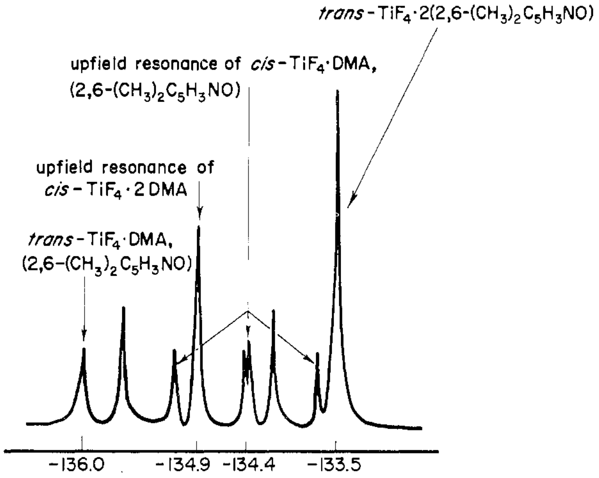

Figure 2.—Partial ^{19}F spectrum of a $TiF_4 \cdot 2(CH_3)_2NC(O)CH_3$–$2,6\text{-}(CH_3)_2C_5H_3NO$ solution in chloroacetonitrile at −40°. (In this spectrum is shown the region of the upfield triplet of $TiF_4 \cdot 2DMA$. The chemical shifts are listed in parts per million displacements from internal $CFCl_3$.)

When 4-methylpyridine 1-oxide was added to a $TiF_4 \cdot 2TMU$ solution, the upfield portion of the spectrum consisted of nine major peaks. This spectrum is reproduced in Figure 3. Four of the peaks are also present in the spectra of chloroacetonitrile solutions which contain only $TiF_4 \cdot 2TMU$. The absorbances in Figure 3 which are assigned to $TiF_4 \cdot 2TMU$ are the lowest field peak, which is the singlet of *trans*-$TiF_4 \cdot 2TMU$, and the upfield triplet of *cis*-$TiF_4 \cdot 2TMU$. The highest field peak appears to be a singlet and is assigned to *trans*-$TiF_4 \cdot [(TMU)(4\text{-}CH_3C_5H_4NO)]$. The four remaining major peaks constitute a doublet of doublets which is the upfield portion of the resonance of *cis*-$TiF_4 \cdot [(TMU)(4\text{-}CH_3C_5H_4NO)]$. One of the triplets of $TiF_4 \cdot 2(4\text{-}CH_3C_5H_4NO)$ is buried under the doublet of doublets, but the upfield member can be seen in the figure.

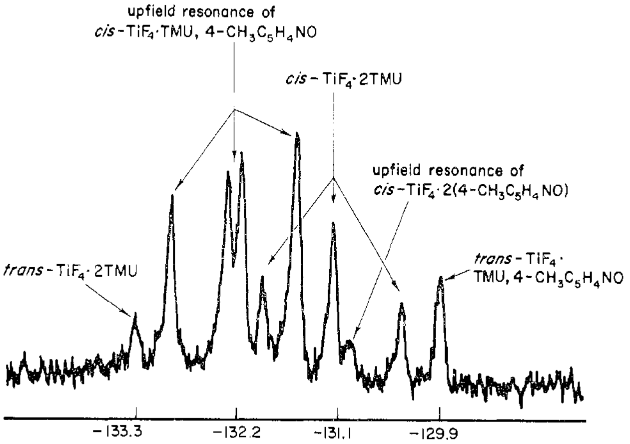

Figure 3.—Partial ^{19}F spectrum of a $TiF_4 \cdot [(TMU)(4\text{-}CH_3C_5H_4NO)]$ solution in chloroacetonitrile at −50°. (In this spectrum is shown the region near the upfield triplet of $TiF_4 \cdot 2TMU$. The chemical shifts are in parts per million displacements from internal $CFCl_3$.)

The same spectral region of a $TiF_4 \cdot 2TMU$–$4\text{-}O_2NC_5H_4NO$ solution is shown in Figure 4. *cis*- and *trans*-$TiF_4 \cdot 2TMU$ and *cis*-$TiF_4 \cdot [(TMU)(4\text{-}O_2NC_5H_4NO)]$ were present, but *trans*-$TiF_4 \cdot [(TMU)(4\text{-}O_2NC_5H_4NO)]$ was not observed. The $TiF_4 \cdot 2TMU$ fluorine chemical shift seems to be somewhat dependent on the temperature and on the concentrations of other species in the solution.

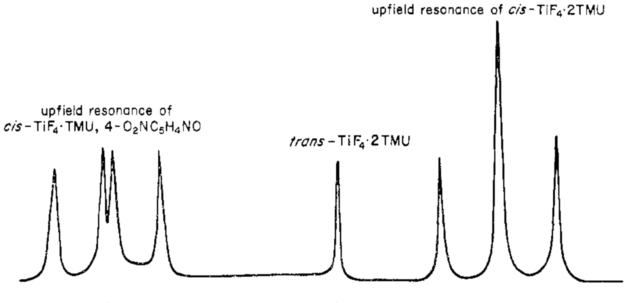

Figure 4.—Partial ^{19}F spectrum of a $TiF_4 \cdot 2(CH_3)_2NC(O)(N)(CH_3)_2$–$4\text{-}O_2NC_5H_4NO$ solution in chloroacetonitrile at −40°. (In this spectrum is shown the region near the upfield triplet of $TiF_4 \cdot 2TMU$. The chemical shifts are in parts per million displacements from internal $CFCl_3$.)

Discussion

In a fluorine-19 nmr study[4] of some $MF_4 \cdot 2D$ adducts (M = Ti or Sn, D = donor) it was reported that solutions of titanium tetrafluoride or tin tetrafluoride in ethanol contain primarily the *cis*-$MF_4 \cdot 2C_2H_5OH$ complexes. No *trans*-$MF_4 \cdot 2C_2H_5OH$ was detected for either of the two metals. A subsequent study[5] of TiF_4–C_2H_5OH solutions confirmed the *cis* orientation of the donor molecules in $TiF_4 \cdot 2C_2H_5OH$. However, it was reported that SnF_4–C_2H_5OH solutions contain *cis*- and *trans*-$SnF_4 \cdot 2C_2H_5OH$ in equilibrium.[8] The *cis* and *trans* isomers were found to be of approximately the

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(8) R. O. Ragsdale and B. B. Stewart, *Proc. Chem. Soc.*, 194 (1964).

same concentration at −50°, but the equilibrium shifted in favor of the *cis* isomer as the sample was warmed. Since Sn and Ti are chemically similar, it seemed reasonable to assume that with some donor molecules the $TiF_4 \cdot 2D$ complexes could also exist in a *trans* configuration. In an examination of this assumption, the factors[9] which might be expected to influence the stereochemistry of $MF_4 \cdot 2D$ complexes in solution were reviewed. The factors considered are steric repulsion, symmetry effects, and $p\pi$–$d\pi$ bonding. Although these factors are interrelated to some extent, they will be considered separately for the most part.

Steric repulsion between the fluorines, if present, would be expected to favor the *trans* configuration, because there are five F–F interactions in a *cis* complex and four in a *trans* complex. However, the fluorines are relatively small, and appreciable steric interaction between them might not occur when M is Ti or Sn unless a decrease (from 90°) in the FMF bond angles of a *cis*-$MF_4 \cdot 2D$ complex were induced by donor molecule–fluorine repulsion. As the size of M decreases, F–F repulsion would, of course, become more important. Any interference between two large donor molecules or between the donors and the fluorines would decrease the entropy of a complex, with steric interference between the donors favoring *trans* configuration.

The symmetry of an $MF_4 \cdot 2D$ complex is higher for the *trans* isomer than for the *cis* isomer. Therefore, in the absence of steric effects ΔS for the equilibrium

$$trans\text{-}MF_4 \cdot 2D \rightleftarrows cis\text{-}MF_4 \cdot 2D$$

should be positive. If so, as the temperature is increased, this equilibrium will shift to the right, since ΔG ($= \Delta H - T\Delta S$) would become more negative. In the study[8] of $SnF_4 \cdot 2C_2H_5OH$ the concentration of the *cis* isomer increased as the temperature was raised. An estimate for ΔS can be obtained, since on a statistical basis *cis*-$MF_4 \cdot 2D$ is four times more probable than *trans*-$MF_4 \cdot 2D$. The expression $\Delta S = R \ln (W_2/W_1)$, where W_1 and W_2 are the thermodynamic probabilities of the *trans* and *cis* isomers, respectively, gives 2.8 eu for ΔS (*i.e.*, it was assumed that $W_2/W_1 = 4$). However, this statistical analysis will be valid only in the absence of steric effects.

If metal d orbitals of low enough energy and proper symmetry are available, the fluorines will tend to arrange themselves so as to maximize fluorine–metal $p\pi$–$d\pi$ bonding.[9] Capacity for F–M π bonding apparently favors the *cis* isomer. Overlap of the fluorine p orbitals with the metal d_{xy}, d_{xz}, and d_{yz} orbitals may be more effective in the *cis* structure. However, it is more likely that competition among the ligands for the available $d\pi$ orbitals makes the *cis* configuration energetically more favorable. The ^{19}F chemical shift data of the *cis*-$TiF_4 \cdot DD'$ complexes have previously been interpreted by a π mechanism.[6] It was suggested[6] that competition between a fluorine and the ligand *trans* to it for the available $d\pi$ orbitals determines the amount of F–M bonding and hence the ^{19}F chemical shifts in the $TiF_4 \cdot 2$(donor) complexes. For these complexes the nmr signals of the two fluorines that are *trans* to the donor molecules occur downfield from the resonance of the other two fluorines, which are *trans* to each other. Likewise, in the study of the $TiF_5 \cdot ROH^-$ complexes,[5] the downfield resonance was found to be due to the fluorine *trans* to the donor molecule. It appears, therefore, that a fluorine can compete more successfully for the available $d\pi$ orbitals with a *trans* oxygen than with a *trans* fluorine.

Additional support for F–M π bonding has been suggested[6] by comparison of the ^{19}F chemical shift data for $TiF_4 \cdot 2C_2H_5OH$[5] and *cis*-$SnF_4 \cdot 2C_2H_5OH$.[8] The fluorine resonances in the titanium complex (d^0) are separated by 60 ppm whereas in the tin complex (d^{10}) the chemical shift between the two types of fluorine is approximately 1 ppm. The difference in the chemical shift has been interpreted by a reduced $p\pi$–$d\pi$ interaction for d^{10} electronic configuration. Since both the *cis* and *trans* isomers of SnF_4 in ethanol have been detected as compared to only the *cis* TiF_4 isomer, we suggest that there is decreased π bonding for the tin complexes. Other studies have also implied that stannate ion lacks the tendency to form $p\pi$–$d\pi$ bonds with first-row atoms. For instance, studies of hydrogen bond formation between ether or phenol and the compounds $(C_6H_5)_3MOH$ (M = Si, Ge, Sn, or Pb) indicate that π bonding from oxygen to M is greatest when M is silicon, weaker when M is germanium, and negligible when M is tin or lead.[10]

From the experimental data it appears that *trans*-$TiF_4 \cdot 2D$ is formed only when there is sufficient steric interaction to overcome symmetry effects and the tendency to maximize $p\pi$–$d\pi$ bonding. Fischer–Hirschfelder–Taylor models of the *cis* and *trans* forms of $TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$, the complex for which only the *trans* isomer was observed, were examined. In the *cis* structure the model showed considerable steric hindrance between the methyl groups and the fluorines. This, in turn, would cause steric interaction between the fluorines which could be relieved by isomerization to the *trans* structure. This model also indicated that the donor molecules do not interact with each other in the equilibrium configuration. It seems, therefore, that $TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$ exists primarily as the *trans* isomer because of donor-induced repulsion between the fluorines in the *cis* structure. This conclusion is substantiated by the observation that $TiF_4 \cdot 2(3,5\text{-}(CH_3)_2C_5H_3NO)$ has predominantly the *cis* configuration in solution. For the latter adduct molecular models showed no steric interaction between the methyl groups and the fluorines.

Although no *cis*-$TiF_4 \cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$ was detected, a *cis* complex containing a 2,6-dimethylpyridine 1-oxide molecule, *cis*-$TiF_4 \cdot [(DMA)(2,6\text{-}(CH_3)_2C_5H_3NO)]$, was observed in the $TiF_4 \cdot 2DMA$–$2,6\text{-}(CH_3)_2C_5H_3NO$ solutions. Detectable quantities of both the *cis* and *trans* isomers of $TiF_4 \cdot [(DMA)(2,6\text{-}$

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[9] I. R. Beattie, *Quart. Rev.* (London), **17**, 382 (1963).

[10] R. West, R. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).

$(CH_3)_2C_5H_3NO)]$ can exist in these solutions. It seems, therefore, that steric interaction in *cis*-$TiF_4\cdot[(DMA)(2,6\text{-}(CH_3)_2C_5H_3NO)]$ is somewhat less than for the *cis*-$TiF_4\cdot 2(2,6\text{-}(CH_3)_2C_5H_3NO)$ structure, as might be expected.

The existence of *trans*-$TiF_4\cdot[(TMU)(4\text{-}CH_3C_5H_4NO)]$ when no *trans*-$TiF_4\cdot[(TMU)(4\text{-}O_2NC_5H_4NO)]$ could be found might seem puzzling, because the *para*-substituted pyridine 1-oxides should have the same steric requirement. However, it has been suggested that a strongly basic ligand will favor the *trans* isomer.[9] The weakly basic nature of 4-nitropyridine 1-oxide[11] should then favor formation of the *cis* isomer.[9] In fact, this effect was also observed in the study of the adducts of 2-methylpyridine 1-oxide and 2,4-dimethylpyridine 1-oxide. The former donor molecule, which from resonance considerations would be expected to be the weaker donor of the two, formed the $TiF_4\cdot 2D$ complex with a higher *cis*:*trans* ratio (see Table I). At this time it is not known what effect specific solvation may have on the *cis* and *trans* isomers, and there is a lack of quantitative studies. Thus, many questions concerning the factors which determine the $TiF_4\cdot 2$(donor) stereochemistry warrant further study.

Acknowledgment.—The financial support of this work by the U. S. Air Force Material Laboratory is gratefully acknowledged by R. O. R.

(11) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

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Mössbauer Spectroscopy of Organometallic Compounds: Alkyltin Cyanides, Thiocyanates, and Related Molecules

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Mössbauer, infrared, and nuclear magnetic resonance data are reported for a number of related alkyl- and aryltin thiocyanates and cyanides. From ^{119}Sn isomer shift and quadrupole splitting data it is inferred that the R_3SnCN and R_3SnSCN compounds in the solid state adopt a trigonal-bipyramidal configuration involving a planar R_3Sn moiety linked by bridging bidentate –CN– or –SCN– groups. The quadrupole splittings which are observed arise largely from the C_{3v} symmetry around the metal atom and the difference in donor properties of the equatorial and axial ligands, rather than from p_π–p_π or p_π–d_π interactions. The Mössbauer and infrared data for the $R_2Sn(SCN)_2$ species are consistent with nearly octahedral symmetry around the metal atom in which the two R groups occupy *trans* coordination sites. Mössbauer data for frozen solutions of $(C_4H_9)_2Sn(SCN)_2$ in MHF (glassy matrix) and CH_3CN (crystalline matrix) are interpreted in terms of an octahedral complex structure in which two solvent molecules occupy two of the six (equatorial) coordination sites. Nuclear magnetic resonance data for methyl- and ethyltin compounds can be correlated with ^{119}Sn isomer shift data, an increase in the proton shift from TMS being reflected in an increase in the isomer shift, referred to SnO_2.

I. Introduction

The details concerning the structure and bonding in organotin cyanides and thiocyanates have received considerable attention in the recent literature in an attempt to correlate the structural parameters of such species with their observable physical and chemical properties. Mössbauer effect spectroscopy—used in conjunction with other molecular structure spectroscopic techniques such as nuclear magnetic resonance, infrared, and X-ray diffraction methods—can serve to shed considerable light on these problems, and the present study was undertaken to examine the detailed relationships between the Mössbauer parameters of a number of organotin cyanides and thiocyanates and the structural and bonding parameters determined by other methods.

II. Experimental Section

The compounds examined in the present study were prepared by methods reported in the earlier literature. The organotin thiocyanates were obtained[2] by mixing ethanol solutions of the corresponding organotin bromide or chloride with an ethanolic solution of KSCN, filtering off the insoluble halide, and isolating the organotin thiocyanate from the C_2H_5OH filtrate. The products were purified by recrystallization from benzene [$(CH_3)_3SnSCN$, $(C_6H_5)_3SnSCN$] or from acetonitrile [$R_2Sn(SCN)_2$] or by distillation [$(C_2H_5)_3SnSCN$ and $(C_4H_9)_3SnSCN$] and gave satisfactory elemental analyses[3a] for C, N, H, and S. The organotin cyanides were prepared[3b] by contacting ether solutions of the corresponding alkyltin halide with aqueous solutions of KCN, recovering the crude product from the ether layer, and recrystallizing from benzene.

$Sn(SCN)_4$ was prepared by refluxing an acetonitrile solution containing 0.11 mol of $SnCl_4$ through a Soxhlet extractor containing 0.44 mol of KSCN for 30 hr under nitrogen. The resultant white, hygroscopic solid (which yellows on exposure to air) was analyzed spectrophotometrically using the absorbance of the ferric thiocyanate complex at 480 μ. The observed SCN:Sn

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(1) Senior Research Participant.

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