cis–trans-Isomerism in Titanium Tetrafluoride–Substituted Pyridine 1-Oxide Adducts

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cis-CONFIGURATIONS for a number of TiF_4,2B complexes in various solvents have been established by means of fluorine-19 nuclear magnetic resonance (n.m.r.) studies.[1–3] To our knowledge, *trans*-TiF_4,2B adducts have not been reported previously.

The occurrence of *cis–trans*-isomerism in MF_4,2B adducts depends upon steric effects and p_π–d_π-bonding.[4] In general, small ligands or bases tend to give *cis*-adducts, while any reduction in p_π–d_π-interaction between the fluorines and M favours the *trans*-configuration. The effect of M can be found in the n.m.r. studies of SnF_4,2EtOH[5] and TiF_4,2EtOH.[1,2] In the former, p_π–d_π-interaction is reduced since the stannate ion has a $4d^{10}$ electronic configuration, and both the *trans*- and *cis*-adducts are in equilibrium in an excess of ethanol. In contrast, only the *cis*-complex was observed for titanium tetrafluoride and ethanol because fluorine–metal π-bonding is greater than with the tin complexes.

In order to form the *trans*-complex, it was necessary to select some bulky ligands. Titanium tetrafluoride adducts were formed with pyridine 1-oxide, 2-methylpyridine 1-oxide, and 2,6-dimethylpyridine 1-oxide. The complexes were studied in chloroacetonitrile by fluorine-19 n.m.r. at $-40°$. The results are shown in the Figure. For the pyridine 1-oxide complex the ^{19}F spectrum consists of two triplets of equal intensity, indicating that the pyridine 1-oxide molecules are *cis* to each other. In the spectrum of the 2-methylpyridine 1-oxide complex, two triplets are again observed, but in addition there is a single-line resonance upfield from the two triplets. Only a single line is seen for the 2,6-dimethylpyridine 1-oxide complex.

The singlets observed in the above solutions are assigned to the respective *trans*-TiF_4,2B complexes. Since fast exchange can collapse a multiplet into a single line, it is usually not possible to assign a structure on the basis of a singlet. Assignment was made to the *trans*-isomers for the following reasons:

(1) Since the two triplets in the n.m.r. spectrum of TiF_4,2(2-MeC_5H_4NO) were completely resolved, a fast exchange involving that

complex is eliminated. If the single line observed in the spectrum of $TiF_4,2(2,6\text{-}Me_2\text{-}C_5H_3NO)$ were due to fast fluorine exchange in the *cis*-isomer, the resonance would be expected to occur approximately half-way between the upfield and downfield triplets of the two *cis*-complexes (see the Figure). Instead it occurs between the upfield triplets.

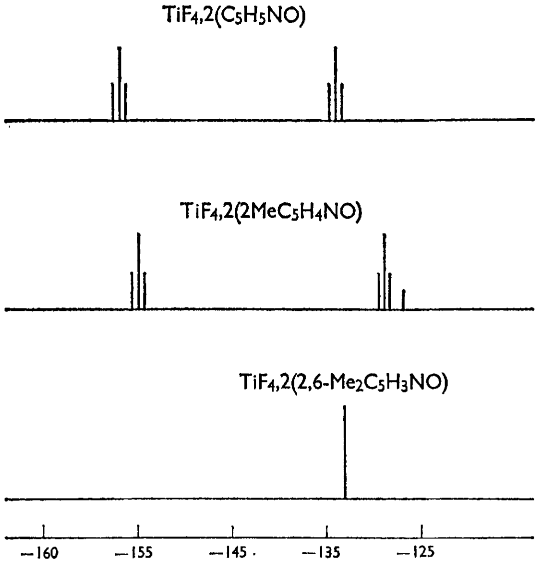
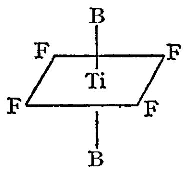
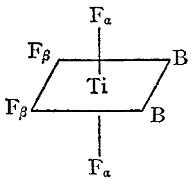


FIGURE. *Diagrammatic representation of the* ^{19}F *n.m.r. signals observed for the* $TiF_4,2B$ *adducts in chloroacetonitrile at* −40° C. *The chemical shifts are recorded in parts per million (p.p.m.) displacements from the resonance of internal* $CFCl_3$.

(2) In the *cis*-complex the F_α fluorines, which have only a *cis*-relationship to the two donor molecules, have been assigned to the upfield triplet.[2,3] Consequently, it is expected that the resonance for the *trans*-isomer fluorines, which are all *cis* to the two donor molecules, would occur near the upfield triplet.



trans-Isomer



cis-Isomer

(3) The single-line resonance is not due to the hexafluorotitanate ion since it was prepared and identified by the addition of fluoride ion to the $TiF_4,2B$ adducts.

From a consideration of the complexes discussed, it appears that the *trans*-$TiF_4,2B$ isomer is formed because of steric repulsion between the bulky ligands. Approximately 90% of the 2-methylpyridine 1-oxide complex is present as the *cis*-adduct whereas, the 2,6-dimethylpyridine 1-oxide adduct occurs in only the *trans*-configuration in solution.

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