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Stereochemistry of Octahedral *cis*-Tetrafluoro Titanium Complexes with $Ph_2P(O)CH(Me)CH_2C(O)Et$ Enantiomers in CH_2Cl_2

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Abstract—The complex formation of TiF_4 with the phosphorylated ketone $Ph_2P(O)CH(Me)CH_2C(O)Et$ (L), containing an asymmetric carbon atom in the aliphatic hydrocarbon group and representing a racemic mixture of enantiomers, was studied by $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The composition of complexes formed in the solution was determined; analysis of the ^{19}F NMR spectra resorting to the heterotropicity concept was used to assign the resonance lines to two chiral optically active racemic and *meso*-stereoisomers of *cis*-TiF_4L_2. The configurations of enantiomers of the monodentate ligand coexisting in the coordination sphere were found to have a crucial effect on the axial fluorine atoms of mixed octahedral *cis*-tetrafluoro d^0 transition metal complexes. A new efficient method was developed for the synthesis of ligand L.

Keywords: titanium tetrafluoride, complexes, diphenylphosphorylalkanones, enantiomers, optical stereoisomerism, NMR, solutions

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INTRODUCTION

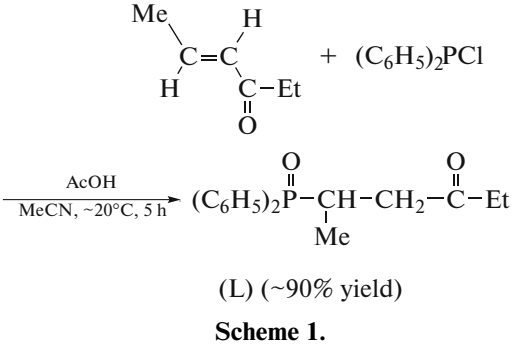
Coordination compounds of d^0-transition metal fluorides are used in important catalytic processes, as precursors for the synthesis of new classes of coordination compounds, in medicine, etc. [1–3]. In particular, they serve for activation of the fluorine–carbon bonds of organofluorine compounds, which is an important area of organic chemistry owing to its practical applications for solving environmental problems, and in pharmaceutics and catalysis (e.g., for defluorination of fluoroalkanes by combining a fluoride precatalyst and silane) [4]. Metal fluoride complexes hold promise as new agents for ^{18}F radioisotope transfer in medicine, which was initially based on the use of organofluorine compounds [5, 6]. Persistent interest of researchers is attracted by the development of nonplatinum antitumor therapy. For example, titanium fluoride compounds like $Cp^R_2TiF_2$ (Cp^R = 4-MeO–$C_6H_4(CH_2)C_5H_4$, 3-MeO–$C_6H_4(CH_2)C_5H_4$) possess high antitumor activity, which is only two times lower than that of the gold standard, cisplatin, with their toxicity being lower [7–9]. Complexes of d^0 transition metal fluorides have been actively studied [10] as model systems to establish the details of chemical bonding in the complexes of these elements. Phosphoryl-containing bases are reactive towards fluorides, which are hard Lewis acids. For studying new classes of coordination compounds of d^0 transition metal fluorides, it is of interest to use functionalized phosphine oxides differing in the number, nature (P=O, C(O)R, $C(O)NR_2$, C(O)OH, NH_2, NRH, etc.), and relative positions of functional groups. Previously, reactions of TiF_4 with representatives of a new class of ligands, diphenylphosphorylalkanones, $Ph_2P(O)CH_2C(O)Me$ (L^1) [11] and $Ph_2P(O)(CH_2)_2C(O)NMe_2$ (L^2) [12], were studied by $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. It was shown that with a twofold excess of the ligand, it is coordinated to TiF_4 via the P=O group to give *cis*-$TiF_4(L^{1,2})_2$. In an equimolar solution of TiF_4 and L^2, fluorine-bridged dimeric and polynuclear complexes are formed. When TiF_4 is taken in a twofold excess, L^2 acts as a bridge, apart from F^- ions, using the P=O and C=O groups for coordination [12]. The replacement of the methyl group at C=O by $-NR_2$ gives rise to chelating properties. Depending on the reactant ratio, the ligand $Ph_2P(O)CH_2C(O)NBu_2$ (L^3) is coordinated to TiF_4 either in the chelating mode to give $(\eta^2\text{-}L^3)TiF_4$ or in the monodentate mode via more basic P=O group to give *cis*-$Ti(L^3)_2F_4$ [12]. In addition to adducts, stereoisomers of the dimeric cation $\{(\mu\text{-}F)[Ti(\eta^2\text{-}L^3)F_3]_2\}^+$ were detected. In this cation, the chelated $[(\eta^2\text{-}L^3)TiF_3]^+$ fragments are linked by a fluorine bridge [13]. With increasing length of the hydrocarbon bridge in $Ph_2P(O)(CH_2)_2C(O)NMe_2$ (L^4), high chelating ability is retained, and the conformational isomerism

of the seven-membered TiOPCCCO heterocycle in $(\eta^2\text{-}L^4)TiF_4$ was observed by $^{19}F\{^1H\}$ and $^{13}P\{^1H\}$ NMR spectroscopy in solutions at low temperatures [14]. The single crystal of this complex was found to contain four crystallographically independent $(\eta^2\text{-}L^4)TiF_4$ molecules [15], in which the geometry of the TiOPCCCO chelate rings was virtually the same in pairs and, hence, two conformational isomers also existed in the crystal, like in solution [15]. In the reaction of L^4 with TaF_5, the ligand is not only coordinated in the chelating mode with displacement of the fluoride ion to give the cation $[(\eta^2\text{-}L)TaF_4]^+$, but also acts as a bridging group by linking two pentafluoride $(\mu\text{-}L)[TaF_5]_2$ molecules [16].

In this study, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR method is used to investigate the complex formation of TiF_4 with a diphenylphosphorylalkanone containing an asymmetric carbon atom, nanely, 5-diphenylphosphorylhexan-3-one, $Ph_2P(O)CH(Me)CH_2C(O)Et$ (L), representing a racemic mixture of enantiomers. The diastereotopicity of fluorine atoms in the ^{19}F NMR spectra of fluoro complexes with optically active bidentate chelating ligands was demonstrated in relation to dioxo [17] and oxo tungsten fluoride complexes [18, 19]. It was of interest to establish the applicability of ^{19}F NMR spectroscopy for identification and estimation of relative concentrations of the racemic and *meso*-stereoisomers of mixed fluoro complexes containing two monodentate optically active ligands, (*R* and *R*), (*S* and *S*), or (*R* and *S*), in the inner sphere. This also opens up prospects for determining the optical purity of some pharmaceuticals and biologically active compounds by fluorine labeling.

EXPERIMENTAL

TiF_4 was prepared by fluorinating a metal powder with elemental fluorine in a quartz system. The ligand L was synthesized by a procedure we specially developed from commercially available chlorophosphine and enone in the presence of AcOH in acetonitrile, as shown in Scheme 1:



(L) (~90% yield)

Scheme 1.

The reaction proceeds at high rate at room temperature, it is easily scaled, and affords analytically pure target compound in a nearly quantitative yield.

Synthesis of L. A solution of glacial AcOH (1.94 g, 32.3 mmol) in anhydrous MeCN (14 mL) and a solution of freshly distilled chloro(diphenyl)phosphine (6.42 g, 29 mmol) in anhydrous MeCN (10 mL) were successively added dropwise to a solution of hex-4-en-3-one (3.0 g, 30.5 mmol) in anhydrous MeCN (24 mL) under argon. The mixture was magnetically stirred for 5 h at room temperature. Then the solvent was distilled off, and the residue was kept for 2 h at 60°C in vacuo (~1 Torr) and dissolved in CH_2Cl_2 (40 mL). The solution thus formed was filtered through basic Al_2O_3 (5.0 g) and washed with CH_2Cl_2 (20 mL). The combined organic filtrates were evaporated in vacuo (~ 15 Torr), and the residue was triturated with a mixture of Et_2O (25 mL) and hexane (12.5 mL). The crystalline precipitate thus formed was separated, washed with a Et_2O–hexane mixture (2 : 1) (2 × 37.5 mL), and dried in air. This gave 6.44 g of ligand L. An additional amount of the product (1.39 g) was isolated from wash solutions. The total yield of L was 7.83 g (90%). T_m = 97.5–98.5°C.

For $C_{18}H_{21}O_2P$			
Anal. calcd., %	C, 71.99	H, 7.05	P, 10.31
Found, %	C, 72.25	H, 7.06	P, 10.21

^1H NMR (δ, ppm; *J*, Hz): 0.72 (t, $C\underline{H}_3CH_AH_B$, 3H, $^3J_{HH}$ = 7.3), 1.14 (dd, $C\underline{H}_3CH$, 3H, $^3J_{HH}$ = 7.1, $^2J_{HP}$ = 16.2), 1.64 (dq, $CH_3C\underline{H}_AH_B$, 1H, $^3J_{HH}$ = 7.3, $^2J_{HAHB}$ = 17.8), 1.68 (dq, $CH_3CH_A\underline{H}_B$, 1H, $^3J_{HH}$ = 7.4, $^2J_{HBHA}$ = 17.8), 2.45–2.57 (m, $C\underline{H}_2CH$, 2H), 3.16–3.25 (m, CH, 1H), 6.98–7.07 (m, *m*- + *p*-C_6H_5, 6H), 7.78–7.85 (m, *o*-C_6H_5, 2H), 7.86–7.92 (m, *o*-C_6H_5, 2H). ^{13}C NMR (δ, ppm; *J*, Hz): 7.34 (s, $\underline{C}H_3CH_2$), 12.76 (d, $\underline{C}H_3CH$, $^2J_{CP}$ = 2.7), 27.43 (d, CH, $^1J_{CP}$ = 74.5), 36.00 (s, $CH_3\underline{C}H_2$), 41.46 (s, $CH\underline{C}H_2$), 128.42 (d, *m*-C_6H_5, $^3J_{CP}$ = 10.9), 128.50 (d, *m*-C_6H_5, $^3J_{CP}$ = 10.9), 130.92 (d, *o*-C_6H_5, $^2J_{CP}$ = 8.2), 130.98 (d, *p*-C_6H_5, $^4J_{CP}$ = 2.7), 131.11 (d, *p*-C_6H_5, $^4J_{CP}$ = 2.7), 133.28 (d, *ipso*-C_6H_5, $^1J_{CP}$ = 94.5), 133.60 (d, *ipso*-C_6H_5, $^1J_{CP}$ = 93.6), 207.43 (d, C=O, $^3J_{CP}$ = 12.7). ^{31}P NMR (δ, ppm): 3353.

This procedure was successfully tested on an enlarged scale (three times larger reactant amounts).

The elemental analysis of L was performed at the Laboratory for Microanalysis of the Nesmeyanov Institute of Organoelement Compounds. The analysis for C and H was carried out on an Elementar vario Micro cube analyzer; phosphorus was determined using an Agilent Cary 100 spectrophotometer as a phosphomolybdic heteropolyacid after sample digestion with concentrated H_2SO_4 according to Kjeldahl.

The melting point was measured on an MPA 120 EZ-Melt automated melting point apparatus (Stanford Research Systems).

The $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of solutions were recorded on a Bruker AVANCE-300 spectrometer. The ^{19}F and ^{31}P NMR chemical shifts were referred to CCl_3F and 85% H_3PO_4, respectively. A solution with the L : TiF_4 ratio of 2.1 (somewhat higher than 2) was prepared for investigations, for the complex TiF_4L_2 to be formed as the major product. The specified amount of TiF_4 was added to a solution of L in dry CH_2Cl_2, and the mixture was magnetically stirred for 30 min at room temperature; TiF_4 completely dissolved. All operations were performed in a dry nitrogen atmosphere.

RESULTS AND DISCUSSION

The temperature dependence of the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the solution was studied in the 263–313 K range. At 313 K, the $^{19}F\{^1H\}$ NMR spectra (Fig. 1) exhibited a group of broad overlapping lines at 138.0–142.5 ppm and a broad signal at 200.5 ppm, which was indicative of ligand exchange processes. The positions of the signals in the regions observed previously for titanium tetrafluoride complexes with diphenylphosphorylalkanones *cis*-$TiF_4(L^{1,2})_2$ [11, 12] and the equal total relative intensities of the high-field A', B', and A'' lines and the signal at 200.5 ppm attested to the formation of titanium tetrafluoride complex *cis*-TiF_4L_2. We assigned the broad high-field lines to the F^1 fluorine atoms located in the *trans*-position relative to each other [11, 12]. The low-field signal at 200.5 ppm was assigned to F^2 fluorine atoms located in the *trans*-position to the P=O groups on the F–Ti–OP···L ordinates. The low-intensity signal C indicates the presence of a low amount of *trans*-TiF_4L_2.

When the temperature drops to 303 K and below, the signals in the fluorine F^1 region start to move apart. At 293 K, five resonance lines were detected, which developed a triplet fine structure at 283 K (Fig. 1). The total intensity of two pairs of triplets A' and A'' is equal, to within the error, to the intensity of the triplet B'. A triplet fine structure was also manifested for the low-field line that was assigned to F^2 atoms located in the *trans*-position to the P=O group of the ligand. The best spectral resolution is observed at 283 K (Fig. 2), while further decrease in the temperature leads to signal broadening.

In the $^{31}P\{H\}$ NMR spectrum at 300 K, the phosphorus atoms of the coordinated ligands in *cis*-TiF_4L_2 give rise to an intense singlet at 48.5 ppm (Fig. 3).

Usually, the first-order ^{19}F NMR spectra of *cis*-tetrafluoro complexes with monodentate ligands, TiF_4X_2, consist of two triplets of equal intensity corresponding to two pairs of non-equivalent fluorine atoms on the F^1–Ti–F^1 and F^2–Ti–X ordinates of the octahedron [20–22]. The appearance of a larger number of resonance multiplets in the region of *trans*-arranged F^1 atoms can be attributed to the presence of stereoisomeric *cis*-TiF_4L_2 in solution, since the ligand L with an asymmetric carbon atom exists as a racemic mixture of *R* and *S* enantiomers. The formation of conformational isomers of the complex due to hindered rotation of the coordinated ligands L cannot be ruled out either. In order to assign the observed resonance lines and establish the cause for the unusual group of resonance lines in the F^1 region, we will consider the temperature dependence of the ^{19}F {1H} NMR spectra (Fig. 1) in more detail.

Attention is attracted by the temperature behavior of signal pairs A' and A'': shift to opposite directions with decreasing temperature, with retention of the frequency difference ($\Delta\nu$ = 284.4 Hz) between the multiplets in the A' and A'' pairs and decrease in the relative intensity difference. These factors, together with equal total integrated intensities of the A' and A'' line pairs, allow the lines to be assigned to XY components of the second-order ^{19}F NMR spectrum (A_2XY) of the octahedral complex *cis*-TiF_4L_2, in which the fluorine atoms in the *trans*-position to each other are non-equivalent, F^1–Ti–$F^{1'}$. This assignment is also confirmed by a decrease in the difference (equalization) between the relative intensities of the "outer" and "inner" lines of the A' and A'' pairs of triplets with increasing chemical shift difference between them, i.e., the spectrum approaches the first-order spectrum comprising two doublets of triplets of equal intensity. The resonance frequency difference between the multiplets in the A' and A'' pairs, which is retained as the temperature decreases, was interpreted as the spin-spin coupling constant between the non-equivalent fluorine nuclei $J_{F^1F^{1'}}$ = 284.4 Hz on the F^1–Ti–$F^{1'}$ ordinate.

Thus, we assigned the two pairs of multiplets A' and A'' to the *trans*-arranged F^1 fluorine atoms of the *cis*-TiF_4L_2 stereoisomer (**I**) in which these atoms are non-equivalent, F^1–Ti–$F^{1'}$, while the B' triplet was assigned to the *cis*-TiF_4L_2 stereoisomer (**II**) in which the *trans*-arranged fluorine atoms are equivalent, F^1–Ti–$F^{1'}$. Both stereoisomers are present in solution in equal concentrations. The ^{19}F NMR signals of the F^2 atoms located in the *trans*-position to the ligand on the F^2–Ti–L ordinates of stereoisomers **I** and **II** (A and B) could not be resolved by lowering the temperature; they give rise to a low-field signal (A + B) resembling a triplet (Fig. 1). The line intensity is equal to the total intensity of the F^1 signals of **I** and **II** (A', A'', B'), which have different chemical shifts. The spin-spin coupling constants between the non-equivalent terminal fluorine atoms located in the *cis*-positions to each other ($J_{F^2F^1}$ and $J_{F^2F^{1'}}$) in stereoisomers **I** and **II** were equal to within the experimental error (38.2 Hz). This value is more than seven times lower than the spin-spin cou-

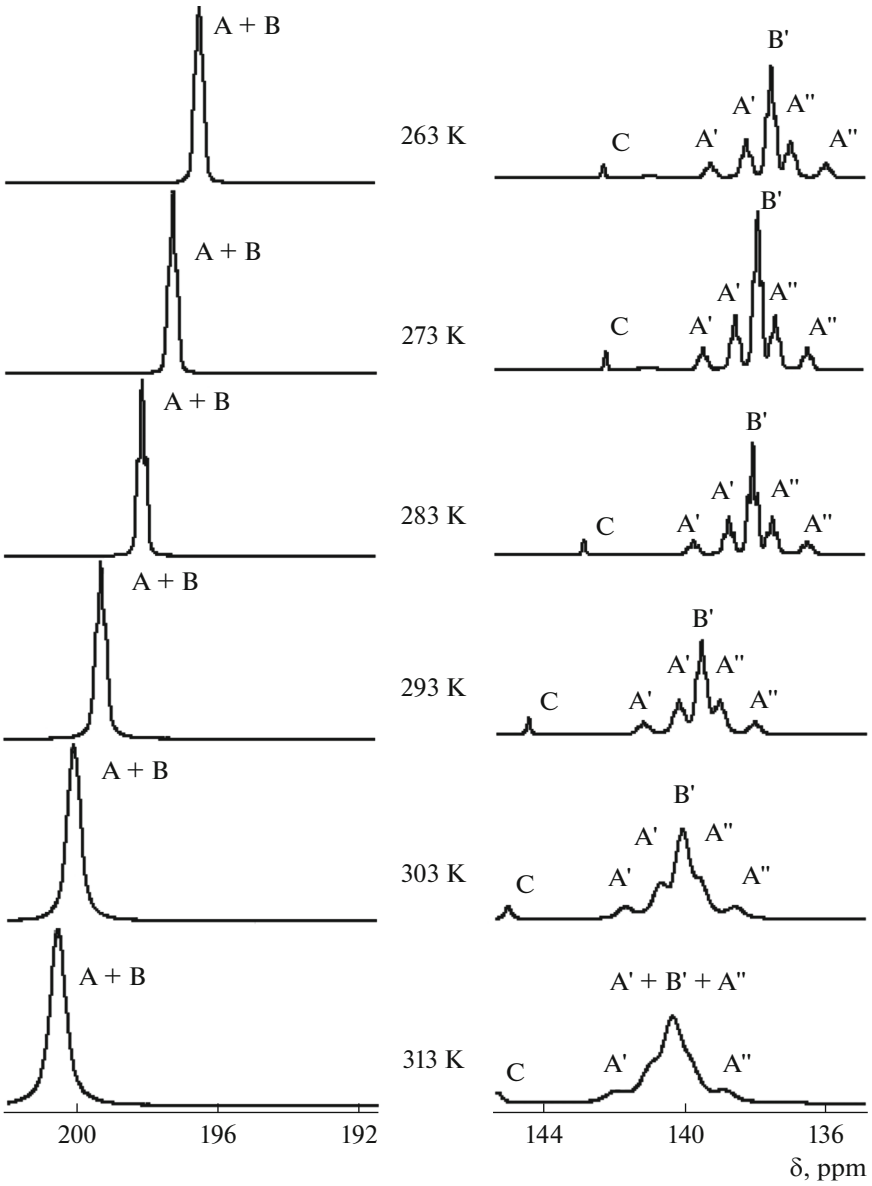


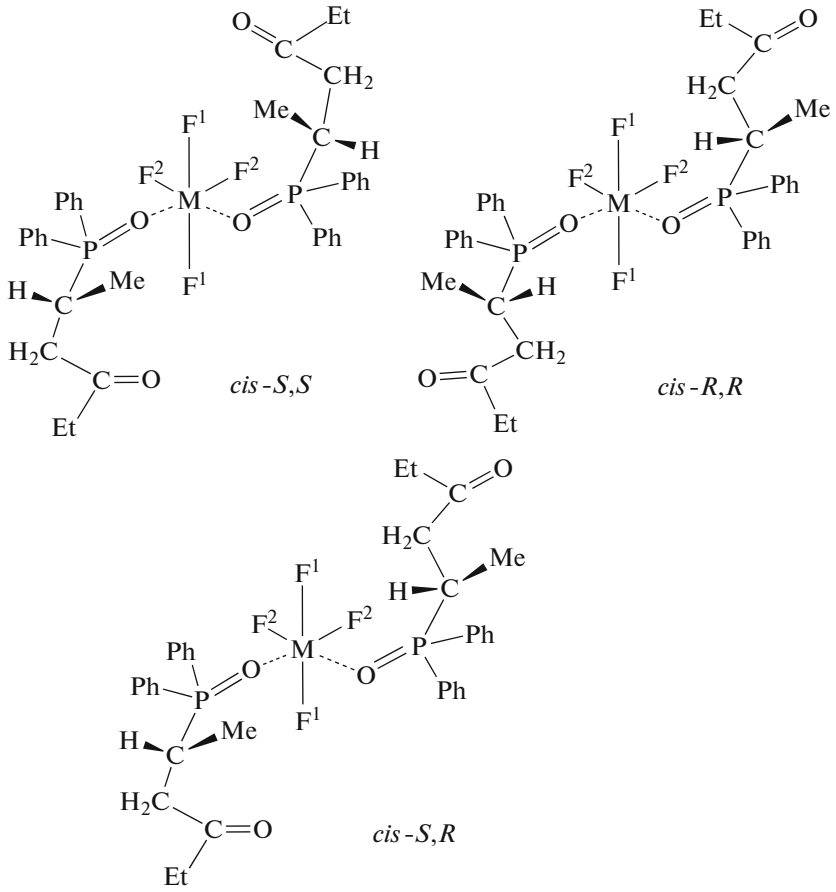
Fig. 1. Temperature dependence of the $^{19}F\{^1H\}$ NMR spectra of a TiF_4 + 2L solution in CH_2Cl_2. A, A', A" are F^2, F^1, $F^{1'}$; B, B' are F^2, F^1 of optical stereoisomers **I** and **II** of *cis*-TiF_4L_2; C is F^1 of *trans*-TiF_4L_2.

pling constant between *trans*-arranged fluorine atoms ($J_{F^1F^{1'}}$ = 284.4 Hz) in **I**. This confirms the conclusion based on summarized experimental data on the stereochemistry of Group IV–VI mixed fluorides in the crystalline state and in solutions [23], indicating the predominance of interligand interactions via the central atom in octahedral complexes of d^0 transition metals between ligands located in *trans*-positions to each other. The observed $J_{F1F1'}$ value is much higher than the coupling constant between the bridging and *trans*-terminal fluorine atoms in the ^{19}F NMR spectra of $[M_2F_{11}]^-$ (M = Nb, Ta, Sb, Ti) [23–27] and $M_2F_{10}L$ (M = Nb, Ta) [28] dimers, which are in the range of 150–175 Hz.

The formation of stereoisomers **I** and **II** of *cis*-TiF_4L_2 in solutions is, in our opinion, attributable to the existence of ligand L as a racemic mixture of *R*- and *S*-isomers.

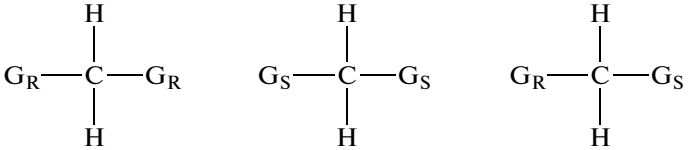
In solution, *cis*-TiF_4L_2 can form three optical stereoisomers: *cis*-$TiF_4L_RL_R$, *cis*-$TiF_4L_SL_S$, and *cis*-$TiF_4L_RL_S$ (Scheme 2). According to the theory of statistical ligand distribution [29], the probability of formation of stereoisomers containing two ligand molecules with the same optical activity, either dextrorotary or levorotatory (*cis*-$TiF_4L_RL_R$

or *cis*-$TiF_4L_SL_S$), is two times lower than that for stereoisomers containing ligand molecules with opposite optical activities, *cis*-$TiF_4L_RL_S$. Hence, the total concentration of the two former complexes should be equal to the concentration of the latter complex, which is actually observed. Since the ligand is a racemic mixture of enantiomers, this confirms the possibility of existence of three optical stereoisomers of *cis*-TiF_4L_2 in solution (Scheme 2):



Scheme 2.

For the assignment of A, A', A" and B, B' groups of lines in the ^{19}F NMR spectra to particular optical stereoisomers of *cis*-TiF_4L_2, we resorded to the fundamental studies on determination of the stereochemical configurations of chiral organic molecules by NMR spectroscopy [30, 31]. In particular, this concerns organic molecules in which two asymmetric centers are separated by one carbon atom. The organic molecules containing symmetrically arranged chiral groups (G_R, G_S) can exist in two forms called *meso*, or optically inactive isomer and optically active racemic isomers, which occur as two enantiomers (Scheme 3) [30]. For these symmetrical molecules, it was assumed [32] that symmetry relations between protons would allow one to distinguish between *meso* and racemic stereoisomers by NMR spectroscopy (Scheme 3):



Enantiomers of the racemic isomer *meso*-Isomer

Scheme 3.

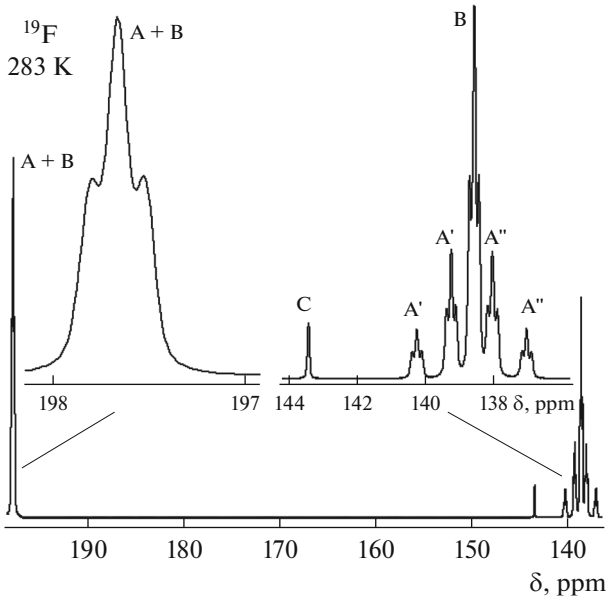


Fig. 2. $^{19}F\{^1H\}$ NMR spectrum of a TiF_4 + 2L solution in CH_2Cl_2 at 283 K.

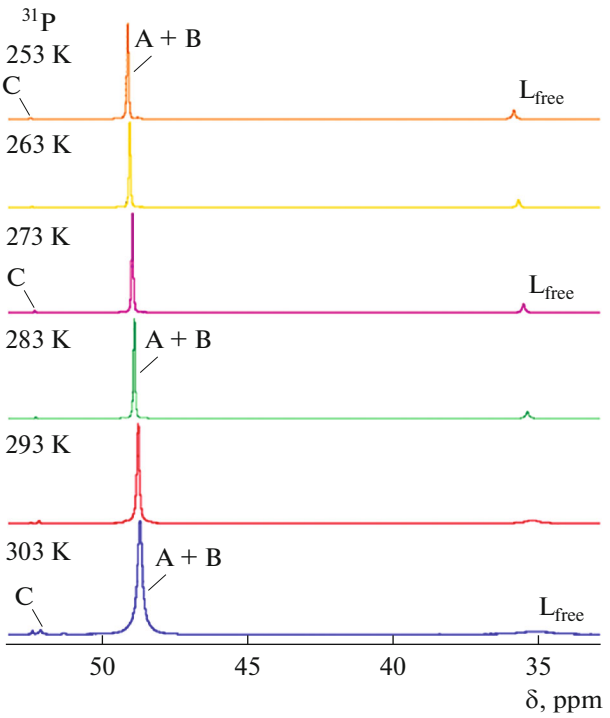


Fig. 3. Temperature dependence of the $^{31}P\{^1H\}$ NMR spectra of a TiF_4 + 2L solution in CH_2Cl_2. A + B is the ^{31}P signal of L for optical stereoisomers **I** and **II** of *cis*-TiF_4L_2; C is ^{31}P signal of L in *trans*-TiF_4L_2.

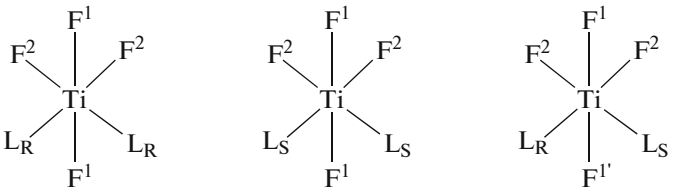
In the enantiomers of the racemic molecules, two chiral groups (G_R or G_S) have the same absolute configuration, whereas in the *meso*-form, they have opposite configurations [30]. From this, it follows that in the enantiomers of the racemic isomer, two protons at the bridging carbon atom can exchange positions via C_2 symmetry operation; therefore, they have to be isochronic [30] and do not differ in the ^{1}H NMR spectra. In the *meso*-isomer, the protons at the bridging carbon atom cannot be superimposed by any symmetry operation; therefore, they are diastereotopic and should be anisochronic [30]; hence, they can be distinguished in the ^{1}H NMR spectra.

We applied these conclusions to possible optical stereoisomers **I** and **II** of the octahedral tetrafluoro complex *cis*-TiF_4L_2 (Scheme 4), with the carbon atom being replaced by titanium and hydrogen atoms being replaced by axial F^1 fluorine atoms. In the enantiomers of *cis*-$TiF_4L_RL_R$ and *cis*-$TiF_4L_SL_S$ racemic stereoisomer of the octahedral TiF_4L_2 complex containing symmetrically arranged same enantiomers of the ligand; they can be superimposed by rotation about the twofold axis C_2, the bisector of the OTiO angle (Scheme 2), which lies in the equatorial plane of the octahedron perpendicular to the F^1–Ti–F^1 ordinate. Thus, in the enantiomers with the same absolute configuration of the coordinated ligands L, the axial fluorine atoms can exchange places via C_2 symmetry operation; they should be isochronic and have equal chemical shifts.

In the *meso*-stereoisomer of the octahedral complex *cis*-$TiF_4L_RL_S$, the ligands coordinated to the central ion have opposite configurations and are not related by any symmetry operation; therefore, the axial fluorine atoms are anisochronic and may have different chemical shifts.

In view of the foregoing, stereoisomer **I** in which the axial fluorine atoms are *trans*-arranged, sterically non-equivalent, and differ in the chemical shifts of F^1 and $F^{1'}$ and which gives rise to the A, A', and A" lines in the ^{19}F NMR spectrum is, in our opinion, the *meso*-stereoisomer *cis*-$TiF_4L_RL_S$.

Stereoisomer **II** in which the fluorine atoms in the *trans*-position are equivalent and which gives rise to two triplets, B and B', of equal intensity in the ^{19}F NMR spectrum was identified as the sum of optically active enantiomers of the *racemic* stereoisomer *cis*-$TiF_4L_RL_R$ (**IIa**) and *cis*-TiF_SL_S (**IIb**) present in equal concentrations. Since the geometric positions of ligands L relative to the F^1 atoms are symmetrical, the fluorine atoms are equivalent, isochronic, and cannot be distinguished in the ^{19}F NMR spectrum.



Enantiomers **IIa** and **IIb** of the racemic isomer *meso*-Isomer **I** of *cis*-TiF_4L_2

Scheme 4.

The total concentration of optically active enantiomers **IIa** and **IIb** of the racemic isomer should be equal to the concentration of the *meso*-stereoisomer **I**, *cis*-$TiF_4L_RL_S$ [18], which is actually the case. The signals of the phosphorus atoms of optically active stereoisomers **IIa** and **IIb** and *meso*-stereoisomer **I** of *cis*-TiF_4L_2 could not be distinguished in the ^{31}P NMR spectra (Fig. 2).

The complex *trans*-TiF_4L_2 can also form *meso*-*trans*-$TiF_4L_RL_S$ and optically active enantiomers, *trans*-$TiF_4L_RL_R$ and *trans*-$TiF_4L_SL_S$, of the racemic stereoisomer in solutions; however, their separate signals could not be observed. This may be due to averaging of the effects of optical stereoisomerism of chiral ligands when they are *trans*-arranged in the coordination sphere, which ensures their free rotation.

Thus, we established the formation of optical stereoisomers of the octahedral complex *cis*-TiF_4L_2 with a representative of phosphorylated ketones containing an asymmetric carbon atom in the aliphatic radical. On the basis of analysis of ^{19}F NMR spectra using the heterotopicity concept, the conclusion was made about the relative stereochemical configurations of the chiral and *meso*-optically inactive stereoisomers present in the solution. In the *meso*-stereoisomer *cis*-$TiF_4L_RL_S$, the F^1 atoms located on one octahedron ordinate (in the *trans*-positions to each other) are sterically non-equivalent and differ in the chemical shifts; a spin-spin coupling constant $J_{F^1F^{1'}}$ is observed between them. In the enantiomers of the optically active racemic stereoisomer, *cis*-$TiF_4L_RL_R$ and *cis*-$TiF_4L_SL_S$, the *trans*-located fluorine atoms are equivalent and the complex gives rise to two triplets of equal intensity in the ^{19}F NMR spectrum. A new procedure for the synthesis of phosphorylated ketones in high yields from commercially available reactants was developed.

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