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Stereochemistry of the *cis*-Tetrafluoro Complexes of Titanium with 1-Ac-2-[$Ph_2P(O)$]-Cyclohexane (1RS,2SR) Stereoisomers in CH_2Cl_2

E. G. Il'in[a, *], **A. S. Parshakov**[a], **V. I. Privalov**[a], **A. V. Churakov**[a], **G. V. Bodrin**[b], **and E. I. Goryunov**[b]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*

[b] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*

**e-mail: eg_ilin@mail.ru*

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Abstract—The monodentate phosphoryl-containing ligand 1-Ac-2-[$Ph_2P(O)$]-cyclohexane (L) bearing two asymmetric carbon atoms is synthesized. The study of its crystal structure shows that L is a racemic mixture of (1R,2S) and (1S,2R) stereoisomers. The complex formation of L with TiF_4 in CH_2Cl_2 is studied by $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The compositions of the complexes formed in the solution are determined. Racemic and *meso*-diastereomers of the octahedral complex *cis*-TiF_4L_2 are formed in the solution as found by an analysis of the ^{19}F and ^{31}P NMR spectra taking into account the concept of heterotropy of organic compounds. The influence of the optical configuration of stereoisomers of the monodentate ligand coexisting in the coordination sphere of the [MF_4L_2] octahedral tetrafluoro complexes of transition d^0 metals on the chemical shifts of the fluorine atoms arranged in the *trans* positions relative to each other is shown. In the *meso*-diastereomer of *cis*-TiF_4L_2, this results in a nonequivalence of the fluorine atoms on the F–Ti–F' ordinate of the octahedron, and the spin-spin coupling constant $J_{FF'}$ = 286.1 Hz is observed in the $^{19}F\{^1H\}$ NMR spectrum.

Keywords: titanium tetrafluoride, complex formation, NMR, stereochemistry

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INTRODUCTION

Phosphoryl-containing ligands find wide use in the separation and purification of transition and rare-earth metals and in the technology of radioactive elements [1]. The polarity of the P=O group imparts it a high complexation ability toward metal compounds of this class. As for basic research of organophosphorus compounds playing the role of ligands, the most interesting objects are diorganylalkyl phosphine oxides, especially the P,P-diphenyl derivatives containing various functional groups (X = C(O)R, C(O)NR_2, OH, COOH, NRH, NH_2, and others) in the alkyl moiety. This makes it possible to vary the nature of nonequivalent donor centers, their number, and relative arrangement and type of the bridging groups linking the centers (saturated and unsaturated hydrocarbon spacers, cyclic (including nitrogen-containing) heterocycles). The first complexes of representatives of the recently discovered class of organophosphorus compounds (diorganylphosphorylalkanones) were synthesized: active extracting agents for actinides [2] with transition d^0-metal fluorides. The reactions of their simplest representatives, $Ph_2P(O)CH_2C(O)Me$ and $Ph_2P(O)(CH_2)_2C(O)Me$, with fluorides of Groups IV and V transition elements were studied: TiF_4 [3, 4] and TaF_5 [5]. An unusually high stability of the seven-membered chelate heterocycle $TiF_4[Ph_2P(O)CH_2CH_2C(O)NMe_2]$ was established, and its conformational isomerism in the solution [6] and in the crystalline state [7] was studied. The formation of the chiral tetrafluoro complex was observed for the chelate coordination of $PhP(O)[CH_2C(O)NMe_2]_2$ via the P=O and C=O groups to TiF_4, which was reflected in the ^{19}F NMR spectra [8].

Stereoisomers of the octahedral *cis*-tetrafluoro complex of the transition d^0 element were first observed by the ^{19}F NMR method when studying the products of the reaction of TiF_4 with the monodentate ligand $Ph_2P(O)CH_2CH(OH)Me$ (L') [9] containing one asymmetric carbon atom in the hydrocarbon radical and representing a racemic mixture of two enantiomers. Racemic ($TiF_4L'_RL'_R$ + $TiF_4L'_SL'_S$) and *meso*-($TiF_4L'_RL'_S$) diastereomers of the *cis*- and *trans*-$TiF_4L'_2$ complexes were shown to be formed in the solution. The stereochemistry of the complex formation of TiF_4 with acyclic diphenylphosphorylalkanone $Ph_2P(O)$-$CHMeCH_2C(O)Et$ (L'') in which the chiral carbon

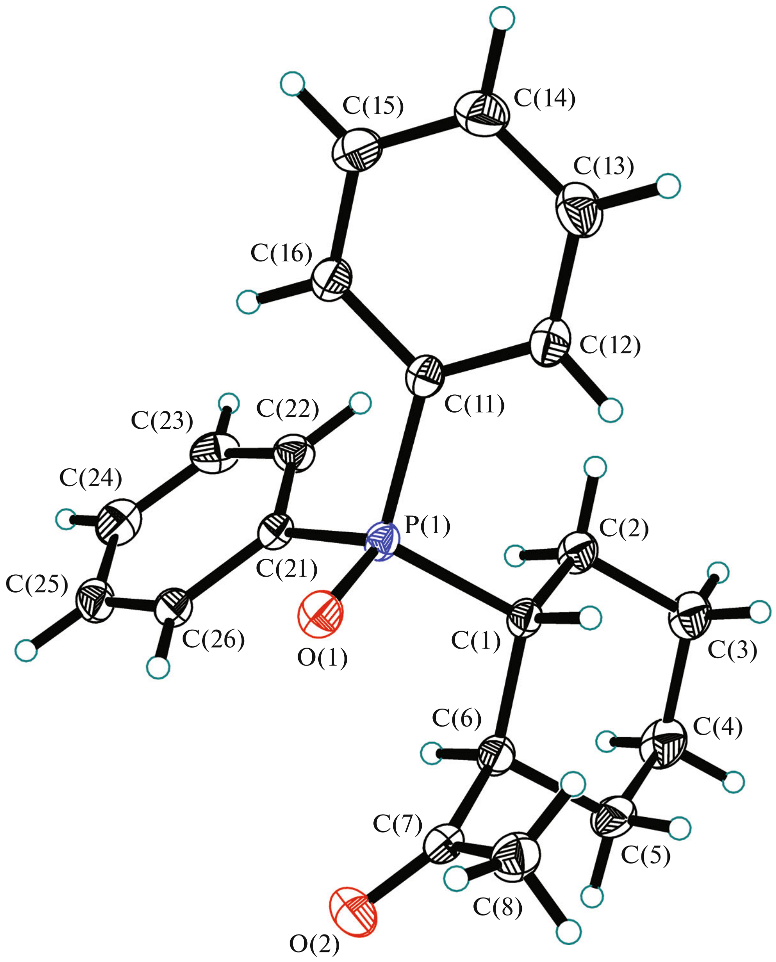


Fig. 1. Molecular structure of ligand L. Thermal ellipsoids with 50% probability.

atom is directly bound to the phosphorus atom of the ligand is analogous [10].

The purpose of this work was the $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR study of the complex formation of TiF_4 with cyclic diphenylphosphorylalkanone: 1-acetyl-2-diphenylphosphorylcyclohexane (1-Ac-2-[$Ph_2P(O)$]-C_6H_{10}) (L). This compound is the monodentate ligand bearing two asymmetric carbon atoms: C(1) and C(6) (Fig. 1). As determined by X-ray diffraction (XRD), L is a racemic mixture of the (1R,2S) and (1S,2R) stereoisomers.

EXPERIMENTAL

Titanium tetrafluoride TiF_4 was synthesized by the fluorination of the powdered metal with elemental fluorine. 1-Acetylcyclohexene (Aldrich, 97%) was used as received. Diphenylchlorophosphine (DPCP, Aldrich, 98%) was distilled in vacuo prior to use. All procedures were carried out in an argon atmosphere.

A solution with the L : TiF_4 ratio somewhat higher than 2 was prepared for the study aimed at preparing the TiF_4L_2 complex as the main form in the solution. The calculated amount of TiF_4 was introduced into a solution of L in CH_2Cl_2, and the reaction mixture was magnetically stirred at room temperature for 30 min. The complete dissolution of TiF_4 was observed. All procedures were carried out in a dry nitrogen atmosphere.

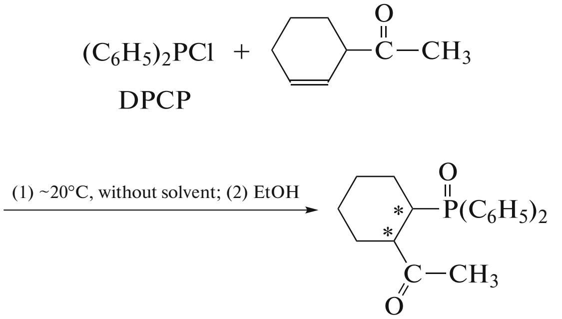
The $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the reaction products of TiF_4 with L in a temperature range of 298–213 K were recorded on a Bruker AC-300 spectrometer. The ^{19}F and ^{31}P NMR chemical shifts were measured relatively to CCl_3F and 85% H_3PO_4, respectively.

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of the phosphorylcarbonyl ligand (L) were recorded on a Bruker AV-500 instrument (working frequency 500.13 MHz (^1H), 125.77 MHz ($^{13}C\{^1H\}$), and 202.46 MHz ($^{31}P\{^1H\}$)) in a $CDCl_3$ solution (c = 0.1 mol/L). Signals of residual protons of the deuterated solvent (δ_H = 7.27 ppm) served as the internal standard for ^1H NMR spectra, signals of carbon nuclei of the deuterated solvent (δ_C = 77.00 ppm) served as the internal standard for $^{13}C\{^1H\}$ NMR spectra, and 85% H_3PO_4 was the external standard for $^{31}P\{^1H\}$ spectra. Signal assignment in ^1H and $^{13}C\{^1H\}$ spectra was carried out using the COSY, HMQC, and HMBC correlations.

XRD of compound L was conducted on a Bruker D8 Venture automated diffractometer at 220 K (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The crystals of L ($C_{20}H_{23}O_2P$, *FW* = 326.35) were monoclinic, space group $P2_1/n$, a = 12.4626(3), b = 9.1152(2), c = 15.6019(4) Å, β = 96.854(1)°, V = 1759.70(7) Å^3, Z = 4, ρ_{calc} = 1.232 g/cm^3, μ(MoK_α) = 0.164 mm^{-1}, F(000) = 696. Intensities of 19 066 reflections (of which 3842 were independent reflections, R_{int} = 0.0281) were measured in the ω scan mode in the range 1.98° < θ < 27.00° ($-14 \leq h \leq 15$, $-11 \leq k \leq 11$, $-19 \leq l \leq 19$). An absorption correction was applied by measuring equivalent reflection intensities [11]. The structure was solved by a direct method, and all non-hydrogen atoms were refined by full-matrix anisotropic least squares for F^2 (SHELXTL [12]). All hydrogen atoms were revealed from the difference Fourier synthesis and refined isotropically. The final R factors were R_1 = 0.0362 for 3247 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0968 over the whole data set using 300 refinement parameters. GOOF = 1.028, $\Delta\rho$(min/max) = –0.360/0.365 e Å^{-3}.

The crystallographic parameters were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2233632; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of 1-Ac-2-[$Ph_2P(O)$]C_6H_{10} (L) (undescribed earlier) was conducted from commercially available DPCP using the two-stage one-pot process (Scheme 1).



(L) (62.0% yield)

Scheme 1.

1-Acetylcyclohexene (2.15 g, 0.0173 mol) was added to DPCP (3.7 g, 0.0168 mol), and the mixture was thoroughly stirred and stored at room temperature for 70 h without light. The solidified reaction mixture (3.9 g, 0.085 mol) was decomposed in absolute EtOH. An alcohol excess was removed in vacuo, and the residue was consequently extracted with boiling hexane (3 × 20 mL) and boiling heptane (3 × 20 mL). The extracts were joined and cooled to room temperature, and the formed precipitate was separated and dried in vacuo (~10 Torr) at 110°C for 1 h. The yield of L was 3.4 g (62.0%). T_m = 143–144°C (cyclohexane).

For $C_{20}H_{23}O_2P$			
Anal. calcd., %	C, 73.60	H, 7.10	P, 9.49
Found, %	C, 73.56	H, 7.17	P, 9.44

At the first stage of the process, DPCP reacts with 1-acetylcyclohexene at room temperature without solvent to form a solid adduct, the treatment of which with absolute ethanol transforms it into the corresponding target compound. The process is stereospecific. According to the NMR spectral data, the formed ligand L represents only one of two theoretically possible racemic diastereomers.

^1H NMR (δ_H, ppm): 1.25–1.44 m (3H, $^3CH_2$- + $^4CH_2$- + $^6CH_2$-cyclohexane); 1.50–1.62 m (1H, $^3CH_2$-cyclohexane); 1.62–1.85 m (3H, $^4CH_2$- + $^5CH_2$-cyclohexane); 1.90 s (3H, CH_3); 2.00–2.09 m (1H, $^6CH_2$-cyclohexane); 2.96–3.06 m (2H, ^1CH- + ^2CH-cyclohexane); 7.44 dt (2H, *m*-C_6H_5, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-P}$ = 2.8 Hz); 7.46–7.55 m (4H, *m*- + *p*-C_6H_5); 7.76–7.86 m (4H, *o*-C_6H_5).

$^{13}C\{^1H\}$ NMR (δ_C, ppm): 24.40 s (C^5-cyclohexane); 24.64 d (C^3-cyclohexane, $^2J_{C-P}$ = 1.8 Hz); 24.83 d (^4C-cyclohexane, $^3J_{C-P}$ = 10.9 Hz); 29.13 s (CH_3); 29.63 d (^6C-cyclohexane, $^3J_{C-P}$ = 9.1 Hz); 36.12 d (C^2-cyclohexane, $^1J_{C-P}$ = 69.9 Hz); 48.33 d (^1C-cyclohexane, $^2J_{C-P}$ = 1.8 Hz); 128.41 d (*m*-C_6H_5, $^3J_{C-P}$ = 11.3 Hz); 128.60 d (*m*-C_6H_5, $^3J_{C-P}$ = 11.4 Hz); 131.18 d (*o*-C_6H_5, $^2J_{C-P}$ = 9.1 Hz); 131.60 d (*o*-C_6H_5, $^2J_{C-P}$ = 9.1 Hz); 131.64 d (*p*-C_6H_5, $^4J_{C-P}$ = 2.3 Hz); 131.78 d (*ipso*-C_6H_5, $^1J_{C-P}$ = 95.8 Hz); 131.80 d (*p*-C_6H_5, $^4J_{C-P}$ = 2.7 Hz); 132.24 d (*ipso*-C_6H_5, $^1J_{C-P}$ = 94.0 Hz); 210.87 d (C=O, $^3J_{C-P}$ = 3.6 Hz). $^{31}P\{^1H\}$ NMR (δ_P, ppm): 35.87 s.

Single crystals of ligand L were prepared by recrystallization from cyclohexane.

RESULTS AND DISCUSSION

The molecular structure of ligand 1-Ac-2-[$Ph_2P(O)$]C_6H_{10} (L) is shown in Fig. 1. The bond lengths and bond angles have values usual for organic compounds [13]. The cyclohexane ring adopts the chair conformation. The $Ph_2P=O$ and MeC=O substituents are neighboring and occupy the equatorial positions.

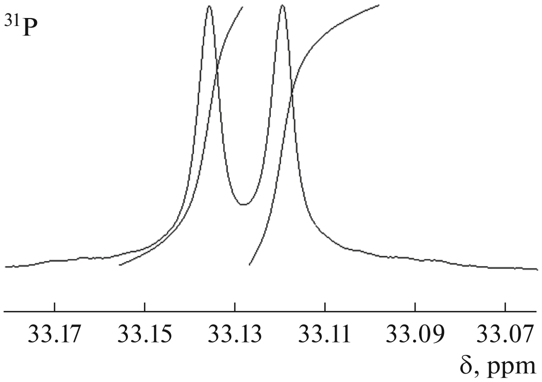


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of a 0.1 M solution of the ligand in L-PhCHMeNH$_2$.

According to the XRD data, L has two asymmetric carbon atoms and represents a racemic mixture of (1R,2S) and (1S,2R) enantiometers (Fig. 1).

The existence of the ligand in the solution as a racemic mixture of two enantiomers was confirmed by $^{31}P\{^1H\}$ NMR. Two singlet signals of equal intensities are observed (Fig. 2) in the spectrum of a solution of L in L-PhCHMeNH$_2$ (c = 0.1 mol/L).

Since the predominant formation of TiF_4X_2 complexes with monodentate ligands by titanium tetrafluoride is observed upon the introduction of two and more moles of ligands per mole of TiF_4 [3, 4], the corresponding solutions were prepared and studied by the ^{19}F and ^{31}P NMR method. The temperature dependence of the $^{19}F\{H\}$ NMR spectrum of the CH_2Cl_2 solution with the TiF_4 : L ratio somewhat higher than two is shown in Fig. 3.

Two groups of resonance lines are observed in the $^{19}F\{^1H\}$ NMR spectrum at room temperature: A and B in a range of 205 ppm and A', B', and B'' at 145 ppm (Fig. 3). The positions of these signals and equal total intensities indicate that the solution contains two titanium tetrafluoro complexes *cis*-TiF_4L_2. Comparing the chemical shift ranges with the known data [4–6], we assigned downfield lines A and B to the resonance signals of the fluorine atoms F^2 arranged in the trans position to the P=O groups on the octahedron ordinates F^2–Ti–OP...L, and signals B', A', and B'' in a stronger field are assigned to the F^1 fluorine atoms arranged in the *trans* position relatively to each other on the F^1–Ti–F^1 ordinate.

The first order ^{19}F NMR spectrum of the *cis*-MF_4X_2 octahedral complex represents two triplets of equal intensities corresponding to two pairs of nonequivalent fluorine atoms: on the F^1–Ti–F^1 and F^2–Ti–X ordinates of the octahedron [4–6, 13]. In our opinion, many multiplet resonance lines indicate that the solution contains diastereoisomers of the *cis*-TiF_4L_2 tetrafluoro complex, the formation of which can be due to the fact that L is a racemic mixture of two enantiomers (1R,2S) and (1S,2R).

Two triplets A and A' of equal intensities are assigned to the *cis*-TiF_4L_2 diastereomer having two nonequivalent positions of the fluorine atoms in which the fluorine atoms on the F^1–Ti–F^1 ordinate are equivalent. Three groups of lines (doublet of doublets B and doublets of triplets B' and B'') with an intensity ratio of 2 : 1 : 1 (second order NMR spectrum A_2XY) are related to the existence in the solution of the *cis*-TiF_4L_2 diastereomer in which the fluorine atoms in the trans positions to each other (F^1–Ti–$F^{1'}$) are equivalent. The difference in resonance frequencies between triplets in doublets B' and B'' equal to 286.1 Hz, which is retained with changing chemical shifts of doublets of triplets B' and B'' as the temperature of the sample decreases, makes it possible to assign it to the spin-spin coupling constant (SSCC) between the nonequivalent F^1 and $F^{1'}$ atoms arranged in the trans position to each other (SSCC $J_{F1F1'}$).

The low-intensity singlet B in this range but in somewhat weaker field (Fig. 3) was assigned to the *trans*-TiF_4L_2 isomer. In the ^{19}F NMR spectra of the tetrafluoro complexes of transition d^0 metals MF_4X_2, the signals of the *trans*-isomers lie in the range of chemical shifts of signals of the F^1 fluorine atoms on the F^1–M–F^1 ordinate of the *cis*-isomers [14]. As mentioned above, the signals of the F^2 fluorine atoms arranged in the trans positions to the molecular donor lie on the F^2–Ti–O=P ordinate in a substantially weaker field (lines A and B of the racemic and *meso*-diastereoisomers *cis*-TiF_4L_2, respectively). A relatively low intensity of the signal from *trans*-TiF_4L_2 compared to the lines of the TiF_4L_2 *cis*-isomer is associated with strengthening in the *cis*-isomer of the bonds of two F^2 fluorine ions (arranged in the trans position to a weaker molecular donor: P=O group of F^2–Ti–O=P) with the central titanium ion, whereas in the *trans*-isomer the fluorine atoms are arranged in the trans positions to each other: F^1–M– F^1 [14].

In the general case, for the *cis*-TiF_4L_2 complex containing two ligands L, each of which has two asymmetric carbon atoms, the formation of 2^4, i.e., 16, optical diastereoisomers is theoretically possible [9]. However, L is a racemic mixture of two enantiomers (1R,2S) and (1S,2R) and, hence, only four diastereomers of the *cis*-TiF_4L_2 complex can exist: $TiF_4L_{1R,2S}L_{1R,2S}$, $TiF_4L_{1S,2R}L_{1S,2R}$, $TiF_4L_{1R,2S}L_{1S,2R}$, and $TiF_4L_{1S,2R}L_{1R,2S}$.

The $^{19}F[^1H]$ NMR spectrum exhibits signals of two *cis*-TiF_4L_2 diastereoisomers: in one of which the fluorine atoms arranged in the *trans* positions to each other are equivalent, and they are nonequivalent in the second diastereoisomer.

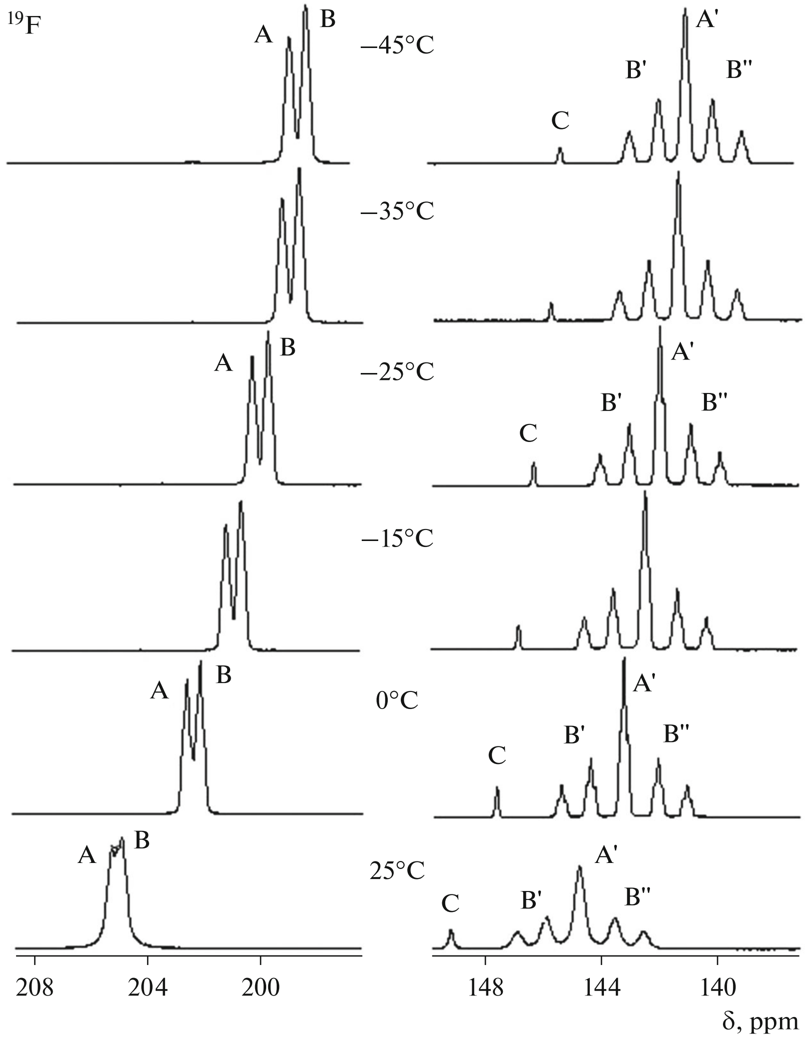
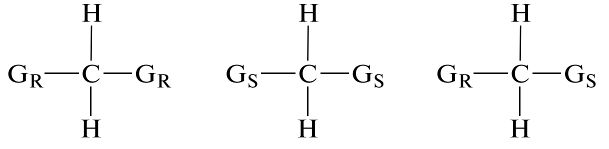


Fig. 3. Temperature dependences of the $^{19}F\{^1H\}$ NMR spectra of a TiF_4 + 2L solution in CH_2Cl_2: A, A' are the lines of the racemic diastereomers of *cis*-TiF_4L_2; B, B', B'' are those of the *meso*-diastereomers of *cis*-TiF_4L_2; and C is the line of *trans*-TiF_4L_2.

The fundamental works on the determination of the stereochemical configuration of chiral molecules of organic compounds by NMR spectroscopy were used to assign the groups of lines A, A' and B, B', B'' in the ^{19}F NMR spectra to possible diastereoisomers of the *cis*-TiF_4L_2 complex [15, 16]. In particular, the organic molecules having two asymmetric centers separated by the carbon atoms are considered. The molecules containing symmetrically arranged chiral groups (G_R, G_S) separated by one carbon atom exist as a *meso*- or optically inactive isomer and optically active racemic isomers (Scheme 2) [17]. For these molecules, the symmetry ratios between protons allow one to distinguish *meso*- and racemic isomers by the NMR method [18].

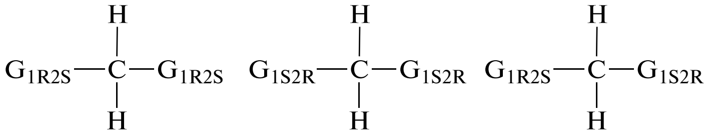

$$G_R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-G_R \qquad G_S-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-G_S \qquad G_R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-G_S$$

Racemic isomers of molecule *meso*-Isomer

Scheme 2.

In the racemic isomers, the chiral groups (G_R or G_S) have the same absolute configuration and can change the symmetry procedure C_2, and the protons at the bridging carbon atom are isochronous [16] and indiscernible in the ^{1}H NMR spectra. The chiral groups in the *meso*-isomer have opposite configurations [16] and cannot be matched by any symmetry procedure and, hence, the protons at the bridging carbon atom are diastereotopic and should be anisochronous [16], i.e., can be distinguished in the ^{1}H NMR spectra.

In our opinion, similar considerations can be extended to organic molecules containing, like ligand L, only two types of stereoisomers: (1S,2R) and (1R,2S). Their racemic and *meso*-isomers (Scheme 3) can also be distinguished using NMR spectroscopy.

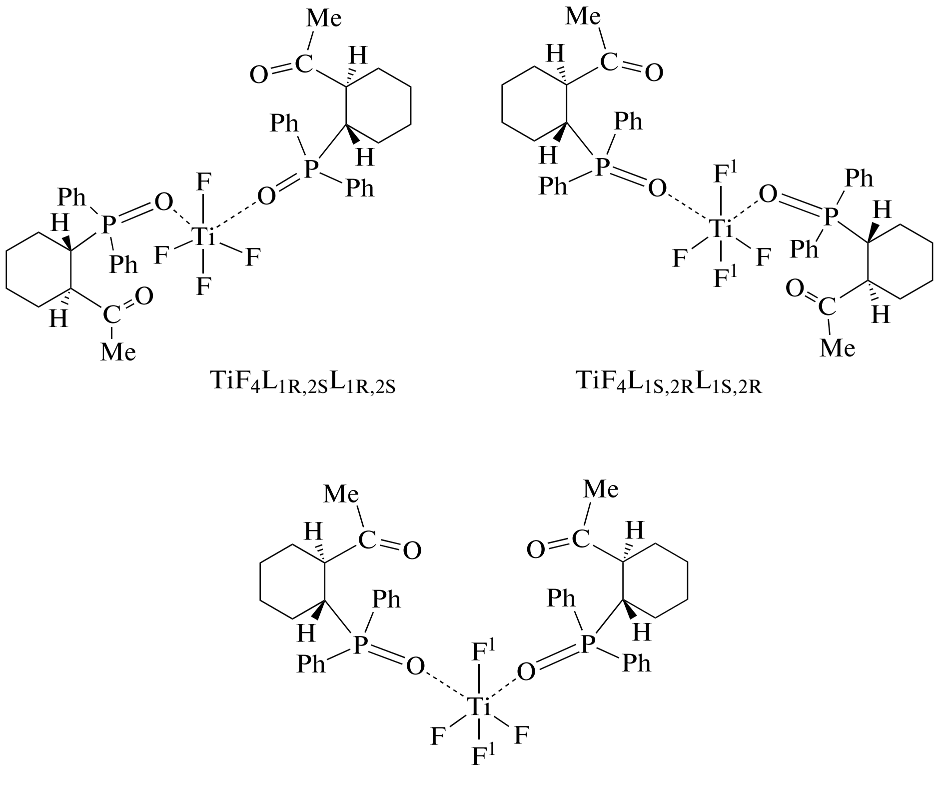


$$G_{1R2S}-\overset{H}{\underset{H}{C}}-G_{1R2S} \quad G_{1S2R}-\overset{H}{\underset{H}{C}}-G_{1S2R} \quad G_{1R2S}-\overset{H}{\underset{H}{C}}-G_{1S2R}$$

Racemic isomers of molecule *meso*-Diastereomer

Scheme 3.

Replacing the carbon atom by the titanium atom and hydrogen atoms by the axial fluorine atoms F^1, we applied this principle to diastereoisomers of the *cis*-TiF_4L_2 octahedral complex and assigned two signals of equal intensities A, A' to the racemic diastereomer being a mixture of enantiomers *cis*-$TiF_4L_{1R,2S}L_{1R,2S}$ and *cis*-$TiF_4L_{1S,2R}L_{1S,2R}$, and the group of lines B, B', and B'' was assigned to the $TiF_4L_{1R,2S}L_{1S,2R}$ *meso*-diastereomer (Scheme 4).



$TiF_4L_{1R,2S}L_{1R,2S}$ $TiF_4L_{1S,2R}L_{1S,2R}$

$TiF_4L_{1R,2S}L_{1S,2R}$

Scheme 4.

In the $^{31}P\{^1H\}$ NMR spectrum at 25°C (Fig. 4), the broad intense line at 51.8 ppm was assigned to the exchange signal of the phosphorus atoms of the coordinated ligands of the *cis*-TiF_4L_2 diastereomers B + C.

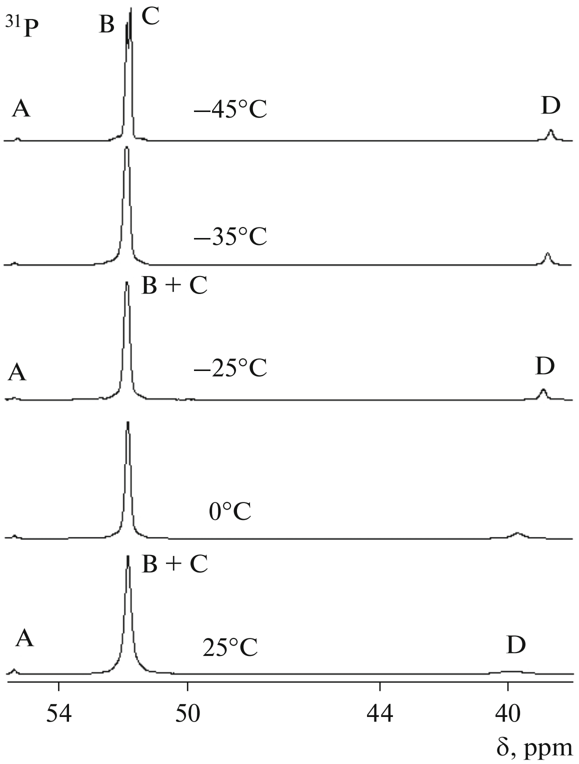


Fig. 4. Temperature dependences of the ^{31}P{^{1}H} NMR spectra of a $\mathrm{TiF_4}$ + 2L solution in $\mathrm{CH_2Cl_2}$: A is the signal of *trans*-$\mathrm{TiF_4L_2}$; B, C are the lines of the racemic and *meso*-diastereoisomers of *cis*-$\mathrm{TiF_4L_2}$; and D is the signal of the free ligand.

The low-intensity line A in a weaker field at 55.2 ppm was assigned to the phosphorus atoms of *trans*-$\mathrm{TiF_4L_2}$.

The signal at 40 ppm shows an insignificant excess of free ligand L, and its width indicates that the ligands participated in the exchange process. As the temperature decreased to –45°C, the signal of free ligand L became narrower and underwent the upfield shift, and the exchange signal in a range of ~55 ppm underwent separation. We also succeeded to distinguish the lines of the phosphorus atoms of the ligands belonging to individual diastereomers of *cis*-$\mathrm{TiF_4L_2}$.

Thus, an analysis of the ^{19}F NMR spectra using the concept of heterotropy allowed us to conclude about the relative stereochemical configurations of the racemic and *meso*-diastereoisomers of the *cis*-$\mathrm{TiF_4L_2}$ octahedral complex in the solution. In the *cis*-$\mathrm{TiF_4L_{1R,2S}L_{1S,2R}}$ *meso*-diastereomer, the fluorine atoms $\mathrm{F^1}$ arranged on one ordinate of the octahedron in the trans positions to each other are sterically nonequivalent, differ by chemical shifts, and are characterized by SSCC $J_{\mathrm{F1F1'}}$.

It is noteworthy that the nonequivalence of the $\mathrm{F^1}$ fluorine atoms in the trans positions to each other in the *meso*-diastereomer of *cis*-$\mathrm{TiF_4L_2}$ is manifested in the ^{19}F{^{1}H} NMR spectra already at room temperature, whereas the $\mathrm{F^1}$ signals for the earlier studied *meso*-stereoisomers *cis*-$\mathrm{TiF_4[Ph_2P(O)\text{-}CH_2CH(OH)Me]_2}$ (*cis*-$\mathrm{TiF_4L'_2}$) [9] and *cis*-$\mathrm{TiF_4[Ph_2P(O)\text{-}CHMeCH_2C(O)Et]_2}$ (*cis*-$\mathrm{TiF_4L''_2}$) [10] represented a group of overlapped broad resonance lines. Moreover, with decreasing temperature to – 45°C the signals of the phosphorus atoms of the racemic and *meso*-diastereoisomers of *cis*-$\mathrm{TiF_4L_2}$ were separated in the ^{31}P{^{1}H} NMR spectra of *cis*-$\mathrm{TiF_4L_2}$ (Fig. 4), whereas an exchange signal was observed down to freezing of the solution in the case of the *cis*-$\mathrm{TiF_4L'_2}$ and *cis*-$\mathrm{TiF_4L''_2}$ enantiomers. In our opinion, in the case of *cis*-$\mathrm{TiF_4L_2}$, the retardation of the dynamic and exchange processes in the solution is related to the bulky cyclohexane ring in L that restricts the mobility of the ligand in the coordination sphere of the central ion. In addition, unlike *cis*-$\mathrm{TiF_4L'_2}$ and *cis*-$\mathrm{TiF_4L''_2}$ for which the overall concentrations of racemic enantiomers and concentrations of *meso*-enantiomers are equal, i.e., obey the statistical distribution, the relative concentration of *meso*-diastereoisomers of *cis*-$\mathrm{TiF_4L_2}$ is somewhat higher, which can be related to fine effects of intrasphere interactions of the optical centers of the (1R,2S) and (1S,2R) stereoisomers in the ligand with fluorine ions.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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