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Some Pequliarities of Complex Formation of Tantalum Pentafluoride with $Ph_2P(O)(CH_2)_2C(O)NMe_2$: Stereochemistry of Hydrolysis Products

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Abstract—The compositions and structures of the products of the reaction of TaF_5 with $Ph_2P(O)(CH_2)_2C(O)NMe_2$ (L) in CH_3CN and CH_2Cl_2 are studied by the ^{19}F and ^{31}P NMR methods. As the hydrocarbon bridge between the P=O and C=O donor groups in carbamoylphosphine oxides elongates from $-CH_2-$ to $(-CH_2-)_2$, the chelation ability of the ligand is retained and the composition of the complexes formed in a solution is determined by the ratio of components. The compositions and structures of the hydrolysis products are studied. Distinctions in the coordination behavior of the considered ligand during complex formation with tantalum pentafluoride and titanium tetrafluoride are studied.

Keywords: tantalum pentafluoride, complex formation, NMR, carbamoylphosphine oxide

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INTRODUCTION

Some pequliarities of the influence of the central ion nature on the complex formation of d^0 transition metal fluorides on going from IV Group elements to V Group elements were established in this work by the ^{19}F and ^{31}P NMR methods using as an example the complex formation of tantalum pentafluoride with the simplest representative of diphenyl[2-(*N*,*N*-dialkylcarbamoyl)ethyl]phosphine oxides, namely, $Ph_2P(O)$-$(CH_2)_2C(O)NMe_2$ (L), in CH_2Cl_2.

Phosphoryl-containing compounds are important extracting agents for *f*-elements [1]. Phosphine oxides with the carbamoylmethyl fragments and methylene bridge, $Ph_2P(O)CH_2C(O)NR_2$, capable of forming stable six-membered chelate heterocycles in complexes of d^0-metals are of special interest [2]. The formation of the stable seven-membered chelate heterocycles in the complexes of d^0-transition elements has recently [3] been shown for the first time on the reaction of titanium tetrafluoride with L having a longer ethylene bridge between the functional groups. The earlier unknown conformational isomerism of the seven-membered chelate heterocycle TiOPCCCO in a solution at low temperatures was assumed on the basis of the data of NMR spectroscopy [3], which was further confirmed by the study of the structure of a single crystal of $[\eta^2\text{-}OPPh_2(CH_2)_2C(NMe_2)O]TiF_4$ [4].

The purpose of this work is the study of the reaction of L with pentafluoride of V Group element to tantalum establish the influence of the nature of the central ion on the coordination behavior of diphenyl[2-(*N*,*N*-dialkylcarbamoyl)ethyl]phosphine oxides in complexes of d^0-transition metals.

EXPERIMENTAL

Tantalum pentafluoride was obtained by the fluorination of the metal powder with elemental fluorine in a quartz system. Ligand $Ph_2P(O)$-$(CH_2)_2C(O)NMe_2$ (L) was synthesized from commercially available reactants, diphenylchlorophosphine and *N*,*N*-dimethylacrylamide, by the two-step one-pot process, which was earlier applied successfully in the synthesis of β-phosphorylalkanones [5] but used for the first time for the preparation of (2-carbamoylethyl)phosphine oxides.

Solutions with the ratios L : TaF_5 = 1 : 2 in CH_3CN and CH_2Cl_2 and 1 : 1 in CH_2Cl_2 were prepared for the investigation. For this purpose, a calculated amount of the ligand in CH_3CN or CH_3Cl_2 was added to a sample of weighed TaF_5, and the mixture was stirred for 30 min at ambient temperature. In all cases, TaF_5 passed into the solution completely. All procedures were conducted in a nitrogen atmosphere. ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AC-300 spectrometer at the Center for Collective Use at the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences). The ^{19}F and

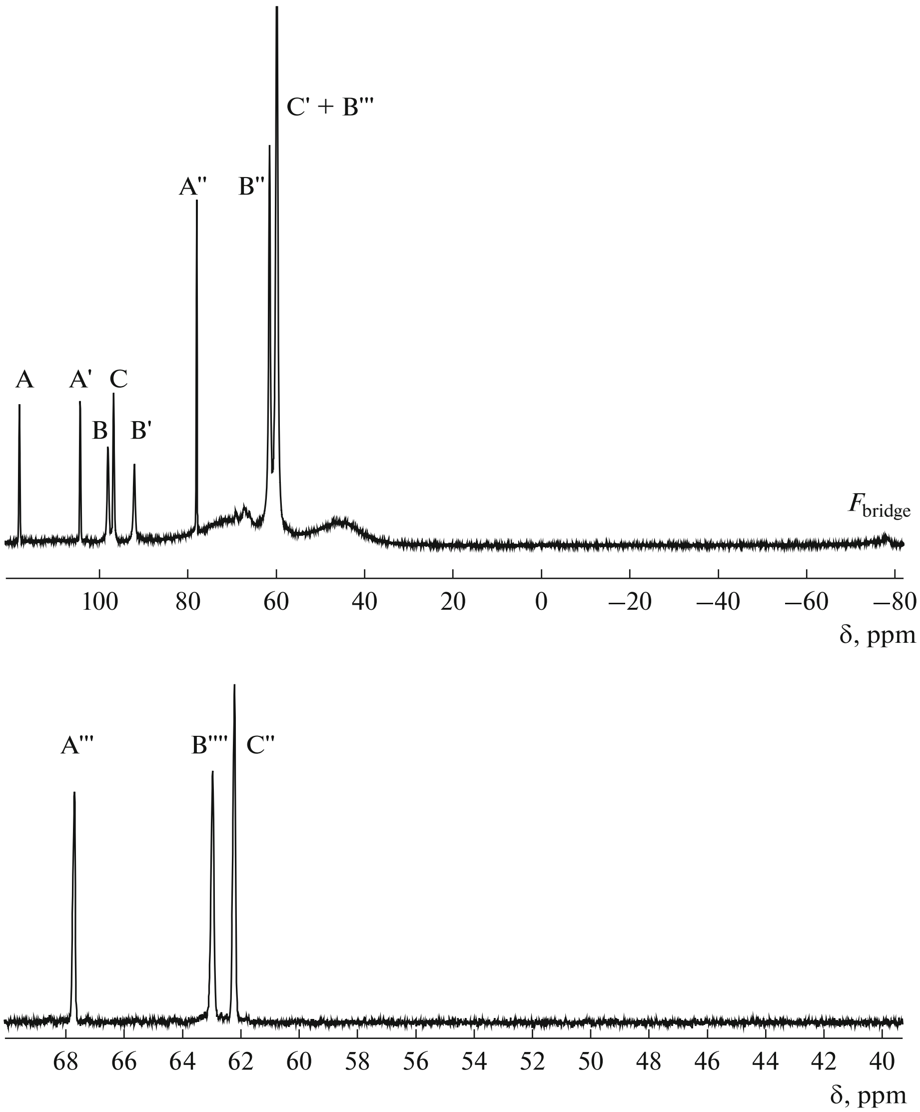


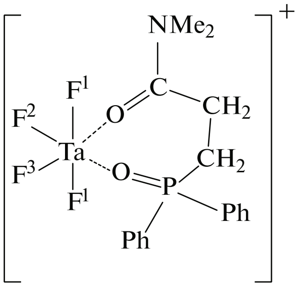
Fig. 1. ^{19}F and ^{31}P NMR spectra of a solution of $2TaF_5$: L in CH_3CN at –45°C: A, A', A'', A''' designate F^3, F^2, F^1, P from (η^2-L)TiF_4; B, B', B'', B''', B'''' designate F^3, F^2, F^1, F^{1a} from (μ-L)$(TaF_5)_2$; and C, C', C'' designate F^2, F^1 from TaF_5OP...L.

^{31}P NMR chemical shifts were measured relative to CCl_3F and 85% H_3PO_4, respectively.

RESULTS AND DISCUSSION

Ligand L has two donor centers: P=O and C=O groups. Pentafluoride has one vacant coordination place to achieve the octahedral configuration. Two moles of TaF_5 were introduced per mole of ligand L in order to the ligand could be use its coordination ability in a maximum extent. Taking into account a high solubility of TaF_5 in CH_3CN, the latter was chosen as a solvent (solution *a*). In the ^{19}F NMR spectrum of solution *a* on cooling to –45°C (Fig. 1), the resonance signals did not exhibit a fine structure and were assigned on the basis of the values of chemical shifts and intensity ratios.

Three groups of lines A, A', A'' with the intensity ratio 1 : 1 : 2 (Fig. 1, Table 1) were assigned to the cationic tetrafluoride complex $[(\eta^2\text{-L})TaF_4]^+$ (**I**) in which the ligand is coordinated to the central tantalum ion with the closure of the seven-membered chelate heterocycle through the P=O and C=O groups.



(**I**)

Table 1. Parameters of the ^{19}F and ^{31}P NMR spectra of the tantalum pentafluoride complexes with $Ph_2P(O)(CH_2)_2C(O)NMe_2$ (L) and hydrolysis products

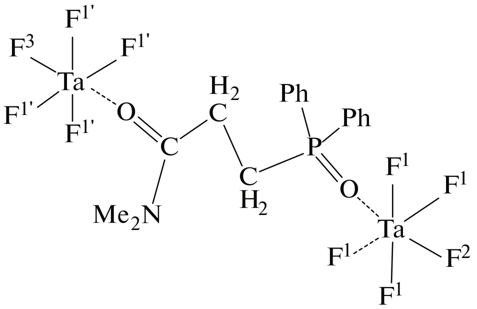
Complex	δF^1, ppm	δF^2, ppm	δF^3, ppm	δP, ppm	J_{F1F2}, Hz	J_{F1F3}, Hz	J_{F2F3}, Hz	Solution
*$[(\eta^2\text{-L})TaF_4]^+$ (**I**)	78.00	104.36	118.12	67.71	25	25	23	$2TaF_5$ + L in CH_2Cl_2
$(\mu\text{-L})[TaF_5]_2$ (II**)	59.83	92.15	98.08	62.97	26	26		
TaF_5OP...L (**III**)	58.69	85.39		65.18				$2TaF_5$ + L in CH_3CN
	59.83	96.76		65.11				TaF_5 + L in CH_2Cl_2
cis-$(\mu\text{-O})[TaF_4OP...L]_2$ (**IV**)	58.69	83.76	48.66	61.01	28	31	28	
cis-$TaF_4(OH)$OP...L (**V**)	53.19	76.04	32.94	63.5	26	26	31	
trans-$(\mu\text{-O})$ $(TaF_4OP...L)_2$ (**VI**)	54.54			58.93				
trans-$TaF_4(OH)$OP...L (**VII**)	47.79			64.41				
mer-$\{(\mu\text{-O})\ [TaF_3(OP...L]_2)_2\}^{+2}$ (**VIII**)	54.10	73.12		59.50	21			
face-$(\mu\text{-O})_2$ $(TaF_3OP...L)_2$ (**IX**)		50.48	63.74	56.95			26	
face-$TaF_3(OH)_2$OP...L (**X**)		56.00	44.88				31	
$(\mu\text{-O})_2(TaF_2OP...L)_2$ (**XI**)	65.09		39.16			39		

* $J_{F1'F3}$ = 26 Hz.

** $\delta F^{1'}$ = 63.53 ppm.

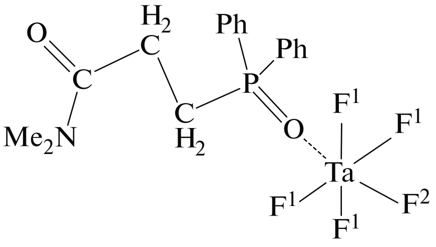
In the theoretical spectrum of the first order, the resonance signals of the fluorine atoms (A and A') arranged in the *trans*-position to the C=O and P=O groups should represent doublets of triplets, and the signal of the fluorine atoms (A'') in the *trans*-position to each other is a doublet of doublets.

In our opinion, four groups of lines B, B', B'', B''' with the intensity ratio 1 : 1 : 4 : 4 are attributed to the dimeric molecular complex $(\mu^2\text{-L})(TaF_5)_2$ (**II**) in which the ligand also uses both donor centers but acts as a bridge and coordinates two TaF_5 molecules. In the theoretical spectrum of the first order, B, B' are quintets and B'', B''' are doublets.



(**II**)

Two lines C and C' with the intensity ratio 1 : 4, being unresolved quintet and doublet, were attributed to the formation of the molecular pentafluoride complex TaF_5L (**III**) in which the ligand is coordinated to the central ion through a stronger (in basic properties) P=O group.



(**III**)

The broad lines in a range of 80–40 ppm at –35°C and lower temperatures corresponded to the exchange signals of the hexafluorotantalate ion $[TaF_6]^-$ and terminal fluorine atoms of the dimeric tantalum fluoride complexes: anion $[Ta_2F_{11}]^-$ [6] and molecular complex $[Ta_2F_{10}L]^-$ [7] with the bridging fluorine ions, whose signals were observed in a high field from –75 to –85 ppm (Fig. 1).

No signal of the free ligand was observed in the ^{31}P NMR spectrum of solution *a* (Fig. 1, Table 1), and three observed resonance lines A''', B'''', and C'' were assigned to the coordinated P=O groups of the ligand in the complexes formed. Based on a comparison of the relative intensities of the resonance lines in the ^{19}F and ^{31}P NMR spectra (Fig. 1), we attributed signal A''' in the weakest field to the P=O group of cation **I** (Table 1) in which L is coordinated to the central ion via the chelate mode. Line C'' in the highest field is assigned to the P=O group of complex **III** in which L is coordinated via the monodentate mode through the

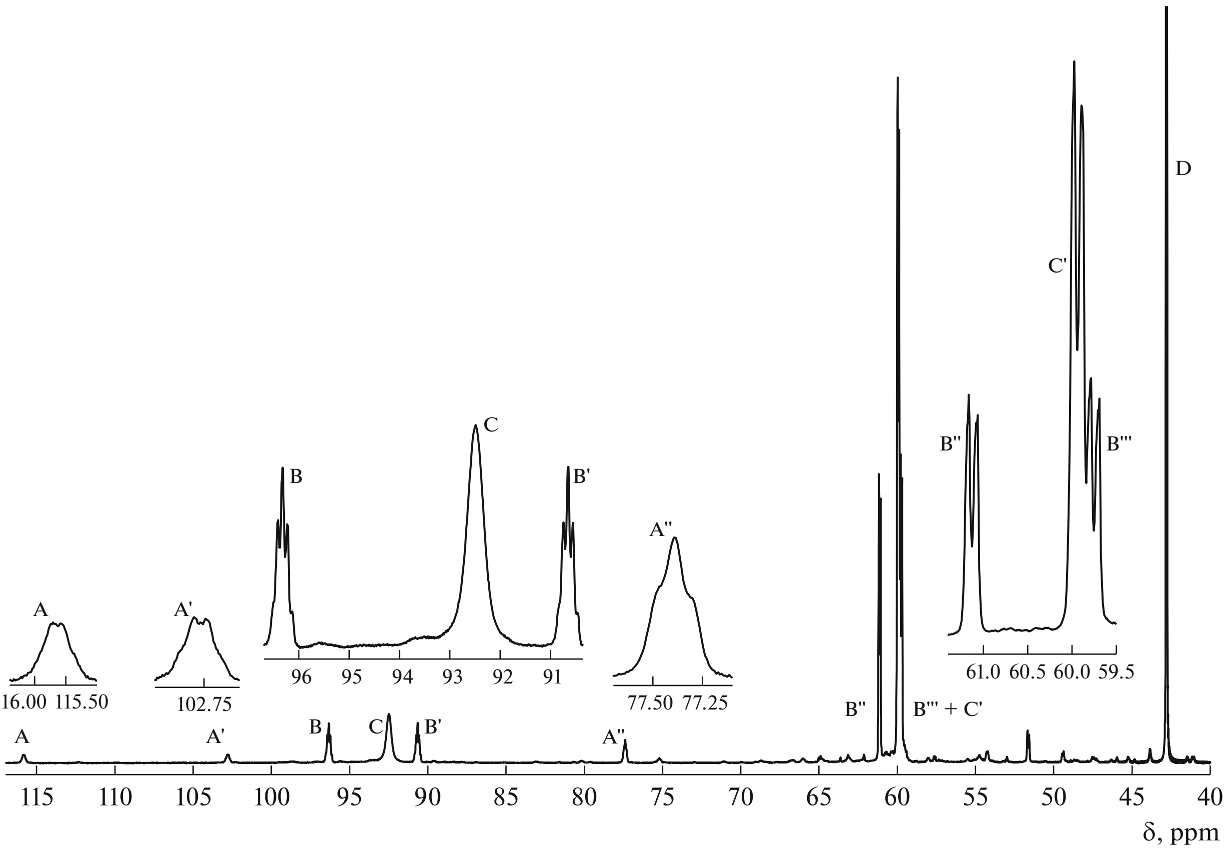


Fig. 2. ^{19}F and ^{31}P NMR spectra of a solution of 2TaF$_5$: L in CHCl$_2$ at –45°C: A, A', A'', A''' designate F^3, F^2, F^1, P from [(η^2-L)TaF$_4$]$^+$; B, B', B'', B''', B'''' designate F^3, F^2, F^1, F^{1a} from (μ-L)(TaF$_5$)$_2$; C, C', C'' designate F^2, F^1 from TaF$_5$OP...L; and J designates [TaF$_6$]$^-$.

P=O group and signal B'''' in somewhat weaker field belongs to the P=O group of the ligand acting as a bridging group in complex **II**. The absence of a fine structure of resonance lines can be attributed to the occurrence of fast intra- and intermolecular processes of ligand exchange in acetonitrile. Therefore, it seemed reasonable to study the reactions of the components at the same 2TaF$_5$: L ratio in CH$_2$Cl$_2$ (solution *b*).

In the ^{19}F NMR spectrum of solution *b* (Fig. 2), the main lines are the signals of the same complexes **I–III** present in the solution, but their relative concentrations have changed and a series of lines exhibited the fine structure.

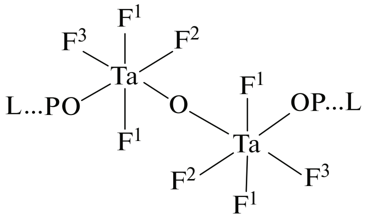
All signals of dimeric pentafluoride complex **II** exhibited the fine structure of quintets B, B' and doublets B'', B''' (Fig. 2), and we succeeded to measure the spin-spin coupling constant (J_{FF}) (Table 1). For the lines of monomeric pentafluoride complex **III**, the fine structure was observed only for doublet C' from the equatorial fluorine atoms F^1. Unlike acetonitrile solution *a*, the relative concentration of cation **I** in CH$_2$Cl$_2$ decreased sharply, but a number of new signals appeared in a higher field and were assigned to the hydrolysis products of this cation. The relative intensity of these signals increased with an increase in the ligand content in a CH$_2$Cl$_2$ solution to the equimolar value (solution *c*).

In the ^{19}F NMR spectrum of equimolar solution *c* (Fig. 3), the main lines are presented by two broad signals A, A' with the intensity ratio 1 : 4 of monomeric pentafluoride complex **III** in which the ligand is coordinated via the monodentate mode through the P=O group.

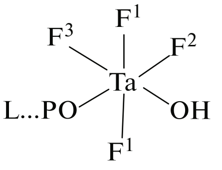
The difference in the chemical shifts of the ^{19}F and ^{31}P NMR signals of this species in CH$_3$CN and CH$_2$Cl$_2$ (Table 1) should be assigned to the solvent effect. The absence of the ^{19}F NMR fine structure can be related to exchange processes occurring due to the free ligand present in the solution. A broad singlet at ~40 ppm is attributed to the hexafluorotantalate ion TaF$_6^-$.

As mentioned above, numerous low-intensity lines are related, in our opinion, to hydrolysis processes due to a high hygroscopicity of TaF$_5$ and a possibility of getting moisture during sample preparation. Similar processes were obtained when studying the zirconium [8] and hafnium [9] tetrafluoride complexes with the phosphoryl-containing ligands X_3PO (X = Bu, Ph, Me_2N) in anhydrous solutions by the ^{19}F and ^{31}P NMR methods.

In spite of a low relative intensity of these resonance lines compared to the signals from complexes **III** and $[TaF_6]^-$, which are observed in the same range, the use of the modern program for NMR spectra processing (ACD/NMR Processor Academic Edition) allowed us to assign the main resonance lines. Three groups of lines B, B', and B'' with an intensity ratio of 1 : 2 : 1 (Fig. 3, Table 1) were assigned to the dimeric tantalum *cis*-tetrafluoride complex with the bridging oxygen atom (μ-O)(*cis*-$TaF_4L)_2$ (**IV**) on the basis of the earlier established regularities of a change in the ^{19}F NMR chemical shifts in the series of the tantalum oxo- and hydroxofluoride complexes formed in the stepwise base hydrolysis of tantalum fluorides [5]. In complex **IV**, ligands L are coordinated via the monodentate mode through the P=O group and are arranged in the *trans*-position to the fluorine atoms. Signal B in a low field is attributed to the fluorine atoms F^2 in the *trans*-position to the P=O groups of the ligands, and the line in a high field is assigned to the fluorine atoms F^3 in the *trans*-position to the bridging oxygen atom. The resonance line B' of the fluorine atoms in the ordinate F^1–Ta–F^1 is arranged between them in the range of the signal of the equatorial fluorine atoms of pentafluoride complex **III**. The theoretical spectrum of this species should consist of doublet of triplets B, doublet of doublets B', and doublet of triplets B'' with an intensity ratio of 2 : 4 : 2.



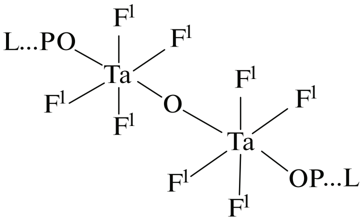
(IV)



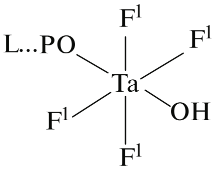
(V)

A similar group of lines in a higher field exhibiting the fine structure, namely, three signals C, C', and C'' with an intensity ratio of 1 : 2 : 1, represents doublet of triplets C, doublet of doublets C', and doublet of triplets C'' (Fig. 2, Table 1). They were assigned to the fluorine atoms F^2, F^1, and F^3 of the tantalum hydroxotetrafluoride complex *cis*-TaF_4(OH)OP...L (**V**) in which the ligand is also coordinated via the monodentate mode through the P=O group and is arranged in the *trans*-position to the fluorine atom.

Intense singlets H and I were assigned to the *trans*-isomers of the tetrafluoride complexes (μ-O)(*trans*-$TaF_4L)_2$ (**VI**) and *trans*-TaF_4(OH)OP...L (**VII**).

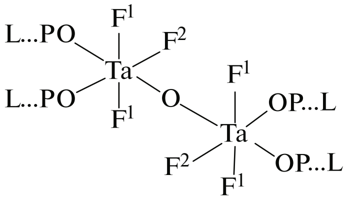


(VI)

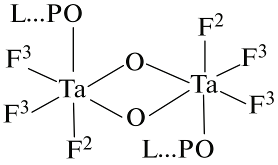


(VII)

Triplet J and doublet J' in a higher (relative to J) field (Fig. 3, Table 1) with an intensity ratio of 1 : 2 were attributed to the fluorine atoms F^2 and F^1 of the dimeric cationic tantalum complex with the bridging oxygen atom $[(\mu\text{-O})(mer\text{-}TaF_3OP...L)_2]^{+2}$ (**VIII**) in the fragments of which one ligand molecule is in the *trans*-position to the fluorine atom, the second ligand molecule is in the *trans*-position to the bridging oxygen atom, and the fluorine atoms occupy the meridian position. In our opinion, the fluorine atoms assigned to doublet E and broad line E' in a lower field with an intensity ratio of 2 : 1 are linked to the dimeric fluoride complex by two bridging oxygen atoms, arranged in the *trans*-position to the latter, and lie on the face of the octahedron $(\mu\text{-O})_2(face\text{-}TaF_3OP..L)_2$ (**IX**).

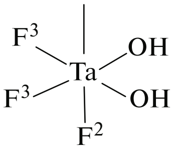


(VIII)



(IX)

Doublet G' and triplet G in a low field were attributed to the face isomer of the dihydroxotrifluoride complex *face*-$TaF_3(OH)_2$OP...L (**X**).



(X)

Two doublets of equal intensity D, D' (Fig. 3, Table 1) exhibiting the fine structure at −15°C, which indicates a high stability of the complex in the solution, were assigned to the *cis*-isomer of the difluoride complex $(\mu\text{-O})_2[TaF_2(OP...L)_2]$ (**XI**).

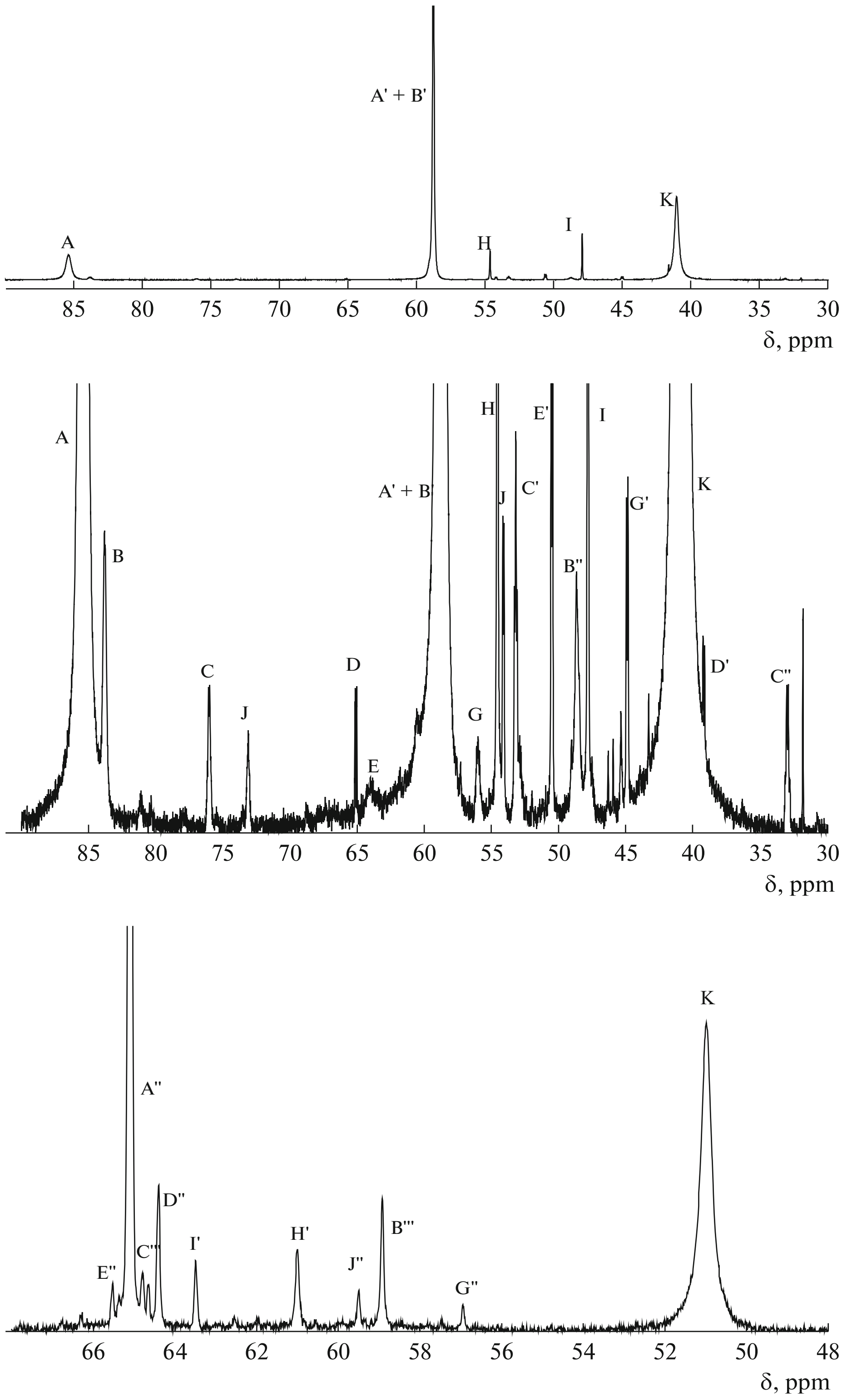
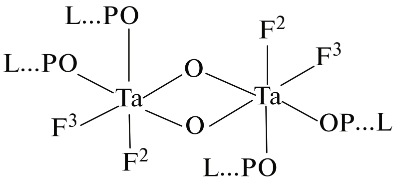


Fig. 3. ^{19}F and ^{31}P NMR spectra of an equimolar TaF_5—L solution in CH_2Cl_2: upper spectrum shows general ^{19}F NMR, medium spectrum shows ^{19}F NMR in the 87.5—30 ppm range, bottom spectrum shows ^{31}P NMR. A, A', A'' designate F^2, F^1, P from TaF_5OP...L; B, B', B'', B''' designate F^2, F^1, F^3, P from (μ-O)(*cis*-TaF_4OP...L)$_2$; C, C', C'', C''' designate F^2, F^1, F^3, P from cis-TaF4(OH)OP...L; J, J', J'' designate F^2, F^1, P from [(μ-O)(*mer*-TaF_3OP...L)$_2$]$^{+2}$; D, D', D'' designate F^2, F^3, P from (μ-O)[*cis*-TaF2 (OP...L)$_2$]; E, E', E'' designate F^2, F^1, P from (μ-O)(*mer*-TaF_3OP...L)$_2$; G, G', G'' designate F^2, F^1, P from (μ-O)2(*face*-TaF3OP...L)$_2$; H, H' designate F^1, P from (μ-O)(*trans*-TaF_4OP...L)$_2$; I, I' designate F^1, P from *trans*-TaF_4(OH)OP...L)$_2$; and K designates $[TaF_6]^-$.



(XI)

In the ^{31}P NMR spectrum of solution *c* (Fig. 3), the most intense line C'' at 50 ppm is assigned to the phosphorus atoms of the P=O groups of complex **III**. Based on a comparison of the relative integral intensities of the ^{31}P and ^{19}F NMR signals, we assigned lines J', A'', and B' to the phosphorus atoms of complexes **III–XI**, respectively (Table 1).

Thus, the composition of the products of the reaction of TaF_5 with $Ph_2P(O)(CH_2)_2C(O)NMe_2$ depends substantially on the ratio of components. In the case of a twofold excess of pentafluoride, the ligand predominantly uses both donor centers (groups P=O and C=O) in coordination and acts as both a bridge coordinating two molecules of pentafluoride $(\mu\text{-L})[TaF_5]_2$ and a chelate with the substitution of the fluorine ion and formation of the $[(\eta^2\text{-L})TaF_4]^+$ cation. Along with these species, the molecular pentafluoride complex TaF_5OP...L is formed in the solution in which the ligand is coordinated to the central ion through the P=O group, which is stronger in basicity. The tantalum fluoride complexes with the bridging fluorine atoms, namely, anion $[Ta_2F_{11}]^-$ and molecular complex $[Ta_2F_{10}L]$, as well as hexafluorotantalate ion $[TaF_6]^-$, are present in the solution in significant concentrations. They appear in the ^{19}F NMR spectrum as broad exchange signals of the terminal fluorine atoms in a range of 77–38 ppm. The resonance lines of the bridging fluorine atoms lie in a substantially higher field: from –75 to –80 ppm. In an equimolar solution, the ligand is coordinated to the central ion via the monodentate mode through the P=O group to form the adduct TaF_5OP...L as the major species. Since hydrolysis processes with fluorine ion formation occur during sample preparation and the acceptor ability of TaF_5 toward this ion is high, hexafluorotantalate, namely, ion $[TaF_6]^-$, is formed in a significant concentration in the solution. The hydrolysis products, the major of which are isomers of the oxo- and hydroxotetrafluoride complexes, namely, *cis*-, *trans*-$(\mu\text{-O})[TaF_4\text{OP...L}]_2$ and *cis*-, *trans*-$TaF_4(OH)\text{OP...L}_2$, respectively, are present in insignificant concentrations in the solution, as well as the deeper hydrolysis products: the oxo- and hydroxotrifluoride complexes. In all the hydrolysis products, the ligand is coordinated to the central ion through the P=O group. To study the influence of the nature of the substituent at the C=O group on the complex formation of modified ethylenephosphines with fluorides of V Group d^0-transition elements, we are planning to study the products of the reaction of TaF_5 with phosphorylated ketone $Ph_2P(O)\text{-}(CH_2)_2C(O)Me$.

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