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Dedicated to Professor Vladimir Fedorov
on the occasion of his 75th birthday

New Rhenium(III) Complexes with Fluorinated β-Diketones

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Abstract—Five new rhenium(III) complexes of the general formula $ReCl_2(R_FCOCHCOR_F)(PPh_3)(OPPh_3)$, where $R_F = CF_3$ (**I**), C_2F_5 (**II**), C_3F_7 (**III**), C_4F_9 (**IV**), and $CF_3CFOC_3F_7$ (**V**), were synthesized. The known rhenium(V) complex $ReOCl_2(OC_2H_5)(PPh_3)_2$, which can readily be obtained from metallic rhenium, was used as a precursor. Two polymorphous modifications of compound **I** were found and studied by X-ray diffraction analysis. The thermal properties of the synthesized complexes were characterized by the DTA–TG method.

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Complexes of many transition metals with polyfluorinated β-diketones are known to possess a high vapor pressure and can often be transformed into vapor without decomposition [1]. This makes it possible to use them, on the one hand, in the production of metal-containing film coatings by the MOCVD methods.

On the other hand, interest in the development of various rhenium-containing functional materials increases in recent years. The rhenium complexes with fluorinated β-diketones could be promising for the use in the CVD processes. However, data on fluorine-containing rhenium β-diketonates are restricted.

Three fluorine-containing rhenium(III) complexes with β-diketones have been described to the present time: two heteroligand complexes $ReCl_2(CF_3COCHCOCH_3)(PPh_3)_2$ and $ReCl_2(CF_3COCHCOCF_3)(PPh_3)_2$ [2–5] and one monoligand complex $Re(CF_3COCHCOCF_3)_3$ [6, 7].

Thus, an urgent problem and the task of the present work are the development of methods for the synthesis of the rhenium complexes with fluorinated β-diketones and the study of their structural characteristics and thermal properties.

EXPERIMENTAL

Complex $ReOCl_2(OCH_2CH_3)(PPh_3)_2$, being the precursor for the synthesis of the target products, was synthesized by a described procedure [8].

For $C_{38}H_{35}Cl_2O_2P_2Re$

anal. calcd, %:	C, 54.16;	H, 4.19;	Cl, 8.41;	P, 7.35.
Found, %:	C, 54.14;	H, 4.21;	Cl, 8.48;	P, 7.38.

Synthesis of rhenium dichloro(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)(triphenylphosphine oxide)(triphenylphosphine) (I). A solution of $ReOCl_2(OC_2H_5)(PPh_3)_2$ (1 g, 1.19 mmol) and an excess of $CF_3COCH_2COCF_3$ (3 g, 14.42 mmol) in benzene (40 mL) was refluxed for 20 min (dark blue solution). The reaction mixture was transferred to a beaker and diluted with petroleum ether (50 mL) at 70–100°C (octane can also be used). The dark blue plate-like crystals that formed were separated by filtration, washed with hexane, and dried in vacuo ($P = 9$ mm Hg). The yield was 1.1 g (90%), T_m = 200°C. Compound **I** is soluble in acetone, benzene, chloroform, and CCl_4; restrictedly soluble in ethanol and sulfuric ether; very restrictedly soluble in cyclohexane and hexane; and insoluble in petroleum ether (70–100°C) and octane.

For $C_{41}H_{31}Cl_2F_6O_3P_2Re$

anal. calcd, %:	C, 49.01;	H, 3.11;	Cl, 7.06;	F, 11.34;	P, 6.16.
Found, %:	C, 48.89;	H, 3.03;	Cl, 6.82;	F, 11.19;	P, 6.08.

Synthesis of rhenium dichloro(1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedionate)(triphenylphosphine oxide)(triphenylphosphine) (II). A solution of $ReOCl_2(OC_2H_5)(PPh_3)_2$ (0.96 g, 1.14 mmol) and $C_2F_5COCH_2COC_2F_5$ (0.37 g, 1.20 mmol) in benzene (40 mL) was refluxed for 20 min. The reaction mixture was transferred to a beaker, diluted with octane (50 mL), and left to stay for 5 days. The mother liquor was decanted, and the residue was dried in air. The dark blue plate-like crystals with T_m = 194°C and T_{decomp} = 250°C were obtained. The yield of compound **II** was 1.17 g (93%). Compound **II** is soluble in acetone, benzene, and chloroform; restrictedly soluble in CCl_4; and insoluble in alcohol, hexane, and octane.

For $C_{43}H_{31}Cl_2F_{10}O_3P_2Re$

anal. calcd, %:	C, 46.75;	H, 2.82;	Cl, 6.42;	F, 17.20;	P, 5.61.
Found, %:	C, 46.97;	H, 2.63;	Cl, 6.30;	F, 16.90;	P, 5.58.

Synthesis of rhenium dichloro(1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4,6-nonanedionate)(triphenylphosphine oxide)(triphenylphosphine) (III). Similarly to the synthesis of compound **II**, the gray-blue crystals of complex **III** with T_m= 160°C and T_{decomp} = 200°C were obtained from $ReOCl_2(OC_2H_5)(PPh_3)_2$ (0.7 g, 0.83 mmol) and $C_3F_7COCH_2COC_3F_7$ (0.41 g, 1.00 mmol). The crystals were dried in vacuo. The yield was 0.91 g (91%). Compound **III** is soluble in acetone, benzene, sulfuric ether, chloroform, dichloromethane, and CCl_4; restrictedly soluble in alcohol; and very restrictedly soluble in hexane.

For $C_{45}H_{31}Cl_2F_{14}O_3P_2Re$

anal. calcd, %:	C, 44.86;	H, 2.59;	P, 5.14.
Found, %:	C, 44.92;	H, 2.47;	P, 5.10.

Synthesis of rhenium dichloro(1,1,1,2,2,3,3,4,4,8,8,9,9,10,10,11,11,11-octadecafluoro-5,7-undecanedionate)(triphenylphosphine oxide)(triphenylphosphine) (IV). Complex **IV** was synthesized similarly from $ReOCl_2(OC_2H_5)(PPh_3)_2$ (1 g, 1.19 mmol) and $C_4F_9COCH_2COC_4F_9$ (0.7 g, 1.38 mmol). The best dark blue plate-like crystals were formed, when octane (~50 mL) was added to an equal volume of a hot benzene solution. Compound **IV** was dried in air. The yield was 1.36 g (88%), T_m = 171°C, and T_{decomp} = 235°C. Compound **IV** is soluble in acetone, benzene, sulfuric ether, chloroform, dichloromethane, and CCl_4; restrictedly soluble in alcohol; very restrictedly soluble in hexane; and insoluble in octane.

For $C_{47}H_{31}Cl_2F_{18}O_3P_2Re$

anal. calcd, %:	C, 43.26;	H, 2.39;	Cl, 5.43;	F, 26.20;	P, 4.74.
Found, %:	C, 43.11;	H, 2.33;	Cl, 5.22;	F, 25.96;	P, 4.77.

Synthesis of rhenium dichloro{1,3-*bis*(3-oxaperfluoro-2-hexyl)-1,3-propanedionate}(triphenylphosphine oxide)(triphenylphosphine) (V). Complex **V** was synthesized similarly from $ReOCl_2(OC_2H_5)(PPh_3)_2$ (0.5 g, 0.59 mmol) and $\{C_3F_7OCF(CF_3)CO\}_2CH_2$ (0.42 g, 0.65 mmol). Crystallization from the solution after the addition of octane occurred very slowly, and the most complete precipitation was attained after 18 days. Compound **V** was dried in air. The yield was 0.75 g (88%), T_m = 155°C, and T_{decomp} = 160°C. Compound **V** is a dark blue-violet powder soluble in acetone, benzene, sulfuric ether, chloroform, dichloromethane, CCl_4, and alcohol; very restrictedly soluble in hexane; and insoluble in octane.

For $C_{49}H_{31}Cl_2F_{22}O_5P_2Re$

anal. calcd, %:	C, 40.96;	H, 2.17;	Cl, 4.93;	F, 29.09.
Found, %:	C, 40.74;	H, 2.11;	Cl, 4.89;	F, 28.51.

Elemental analyses for complexes **I**–**V** were carried out at the Laboratory of Microanalysis of the Institute of Organoelement Compounds (Russian Academy of Sciences). The DTA–TG studies were carried out on a Derivatograph-C instrument (MOM, Hungary) at a heating rate of 10°C/min in argon and in air with ~15-mg samples. The temperature was measured with a platinum–platinorhodium thermocouple. The temperature corresponding to the 5% mass loss by the sample ($T_d^{5\%}$) was accepted as the temperature of mass loss onset. No intermediate products were isolated.

The X-ray diffraction analyses for two modifications of compound **I** (**a** and **b**) were carried out on a Bruker APEX II CCD automated diffractometer (T = 100 K, MoK_α radiation, graphite monochromator, φ- and ω scan modes). An X-ray radiation correction for the data obtained was applied using the SADABS program. Structures **Ia** and **Ib** were determined by a direct method and refined by the full-matrix least-square method in the anisotropic approximation for non-hydrogen atoms. The positions of all hydrogen atoms were calculated from the geometric concepts and included into the refinement in the isotropic approximation along with non-hydrogen atoms. All calculations were performed using the SHELXTL program package. The crystallographic characteristics and details of the X-ray diffraction experiment and structure refinement are given in Table 1. Selected interatomic distances and bond angles are listed in Table 2.

RESULTS AND DISCUSSION

In the most part of cases, the traditional methods for the preparation of fluorine-containing transition metal β-diketonates based on exchange reactions cannot be applied to rhenium compounds, since simple rhenium salts necessary for these processes to occur are poorly accessible or unknown.

We used the described and easily obtained complex: rhenium oxodichloroethoxybis(triphenylphosphine) [8]. The procedure of the synthesis includes the dissolution of metallic rhenium in 30% hydrogen peroxide with the formation of rhenium acid. The resulting colorless solution of $HReO_4$ was evaporated by ~10 times, and HCl and ethanol were added. Then the solution was heated, and boiling ethanol saturated with triphenylphosphine was poured to the solution. A green crystalline substance precipitated immediately, being the desired complex used for the synthesis of fluorine-containing rhenium β-diketonates.

The synthesis of all fluorinated complexes can be presented by the scheme

Table 1. Crystallographic data and the experimental and refinement parameters for two polymorphous modifications **a** (from acetone) and **b** (from alcohol) of complex **I**

Parameter	Value	
	Ia	**Ib**
FW	1004.70	1004.70
Space group	$C2/c$	$P2_1/n$
a, Å	42.357(2)	12.6176(9)
b, Å	10.4898(6)	23.9022(17)
c, Å	18.4349(10)	13.4285(10)
β, deg	106.851(1)	107.490(1)
V, Å^3	7839.3(8)	3862.7(5)
ρ_{calcd}, g/cm^3	1.703	1.728
Z	8	4
F(000)	3952	1976
Crystal size, mm	0.20 × 0.20 × 0.02	0.24 × 0.20 × 0.18
μ, mm^{-1}	3.385	3.435
θ range, deg	2.01–27.94	1.80–28.00
Number of measured/independent reflections/R_{int}	41820/9368/0.056	42155/9300/0.053
Number of reflections with $I > 2\sigma(I)$	7170	7930
Range of indices	$-55 \le h \le 55$ $-13 \le k \le 13$ $-24 \le l \le 24$	$-16 \le h \le 16$ $-31 \le k \le 31$ $-17 \le l \le 17$
Number of parameters	496	496
R factors ($I > 2\sigma(I)$)	$R_1 = 0.042$, $wR_2 = 0.095$	$R_1 = 0.029$, $wR_2 = 0.069$
R factors (all reflections)	$R_1 = 0.065$, $wR_2 = 0.106$	$R_1 = 0.038$, $wR_2 = 0.074$
Goodness-of-fit for F^2	1.001	1.003
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^3	2.930/–1.660	2.351/–1.496
T_{min}; T_{max}	0.551; 0.935	0.493; 0.577

Table 2. Selected interatomic distances and bond angles for two polymorphous modifications **Ia** and **Ib**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
		Ia			
Re(1)–O(2)	1.972(3)	P(1)–C(18)	1.817(4)	O(1)–C(1)	1.287(5)
Re(1)–O(1)	1.986(3)	P(1)–C(6)	1.821(4)	O(2)–C(3)	1.291(5)
Re(1)–O(3)	2.045(3)	P(1)–C(12)	1.824(4)	C(1)–C(2)	1.378(5)
Re(1)–Cl(1)	2.3518(10)	P(2)–O(3)	1.521(3)	C(1)–C(4)	1.525(6)
Re(1)–Cl(2)	2.3927(9)	P(2)–C(24)	1.776(4)	C(2)–C(3)	1.384(6)
Re(1)–P(1)	2.4348(10)	P(2)–C(36)	1.786(4)	C(3)–C(5)	1.507(6)
		P(2)–C(30)	1.789(4)		
		Ib			
Re(1)–O(2)	1.977(2)	P(1)–C(18)	1.822(3)	O(1)–C(1)	1.288(4)
Re(1)–O(1)	1.991(2)	P(1)–C(6)	1.821(3)	O(2)–C(3)	1.296(4)
Re(1)–O(3)	2.042(2)	P(1)–C(12)	1.820(3)	C(1)–C(2)	1.386(5)
Re(1)–Cl(1)	2.3431(8)	P(2)–O(3)	1.514(2)	C(1)–C(4)	1.515(5)
Re(1)–Cl(2)	2.3974(8)	P(2)–C(24)	1.793(3)	C(2)–C(3)	1.388(5)
Re(1)–P(1)	2.4387(8)	P(2)–C(36)	1.792(3)	C(3)–C(5)	1.511(5)
		P(2)–C(30)	1.794(3)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
		Ia			
O(2)Re(1)O(1)	91.34(11)	O(2)Re(1)P(1)	89.75(8)	C(1)O(1)Re(1)	124.5(2)
O(2)Re(1)O(3)	176.30(11)	O(1)Re(1)P(1)	93.41(8)	C(3)O(2)Re(1)	125.2(3)
O(1)Re(1)O(3)	85.25(11)	O(3)Re(1)P(1)	91.89(7)	P(2)O(3)Re(1)	152.16(17)
O(2)Re(1)Cl(1)	91.31(9)	Cl(1)Re(1)P(1)	88.73(4)	O(1)C(1)C(2)	127.9(4)
O(1)Re(1)Cl(1)	176.60(8)	Cl(2)Re(1)P(1)	175.72(3)	O(1)C(1)C(4)	111.7(3)
O(3)Re(1)Cl(1)	92.05(8)	C(18)P(1)Re(1)	109.47(13)	C(2)C(1)C(4)	120.4(4)
O(2)Re(1)Cl(2)	85.99(8)	C(6)P(1)Re(1)	114.86(13)	C(1)C(2)C(3)	122.8(4)
O(1)Re(1)Cl(2)	86.28(8)	C(12)P(1)Re(1)	116.77(14)	O(2)C(3)C(2)	127.3(4)
O(3)Re(1)Cl(2)	92.34(7)	O(3)P(2)C(24)	114.02(17)	O(2)C(3)C(5)	112.6(4)
Cl(1)Re(1)Cl(2)	91.78(4)	O(3)P(2)C(36)	109.51(16)	C(2)C(3)C(5)	120.0(4)
		O(3)P(2)C(30)	108.46(17)		
		Ib			
O(2)Re(1)O(1)	91.57(9)	O(2)Re(1)P(1)	87.30(6)	C(1)O(1)Re(1)	125.5(2)
O(2)Re(1)O(3)	174.58(9)	O(1)Re(1)P(1)	93.16(7)	C(3)O(2)Re(1)	124.6(2)
O(1)Re(1)O(3)	83.12(9)	O(3)Re(1)P(1)	91.91(6)	P(2)O(3)Re(1)	147.15(14)
O(2)Re(1)Cl(1)	93.35(7)	Cl(1)Re(1)P(1)	88.89(3)	O(1)C(1)C(2)	126.7(3)
O(1)Re(1)Cl(1)	174.75(7)	Cl(2)Re(1)P(1)	176.29(3)	O(1)C(1)C(4)	112.5(3)
O(3)Re(1)Cl(1)	91.99(7)	C(18)P(1)Re(1)	109.85(11)	C(2)C(1)C(4)	120.8(3)
O(2)Re(1)Cl(2)	89.04(6)	C(6)P(1)Re(1)	114.02(11)	C(1)C(2)C(3)	123.3(3)
O(1)Re(1)Cl(2)	87.50(7)	C(12)P(1)Re(1)	117.73(11)	O(2)C(3)C(2)	127.9(3)
O(3)Re(1)Cl(2)	91.80(6)	O(3)P(2)C(24)	114.30(14)	O(2)C(3)C(5)	111.8(3)
Cl(1)Re(1)Cl(2)	90.77(3)	O(3)P(2)C(36)	107.76(14)	C(2)C(3)C(5)	120.3(3)
		O(3)P(2)C(30)	110.19(14)		

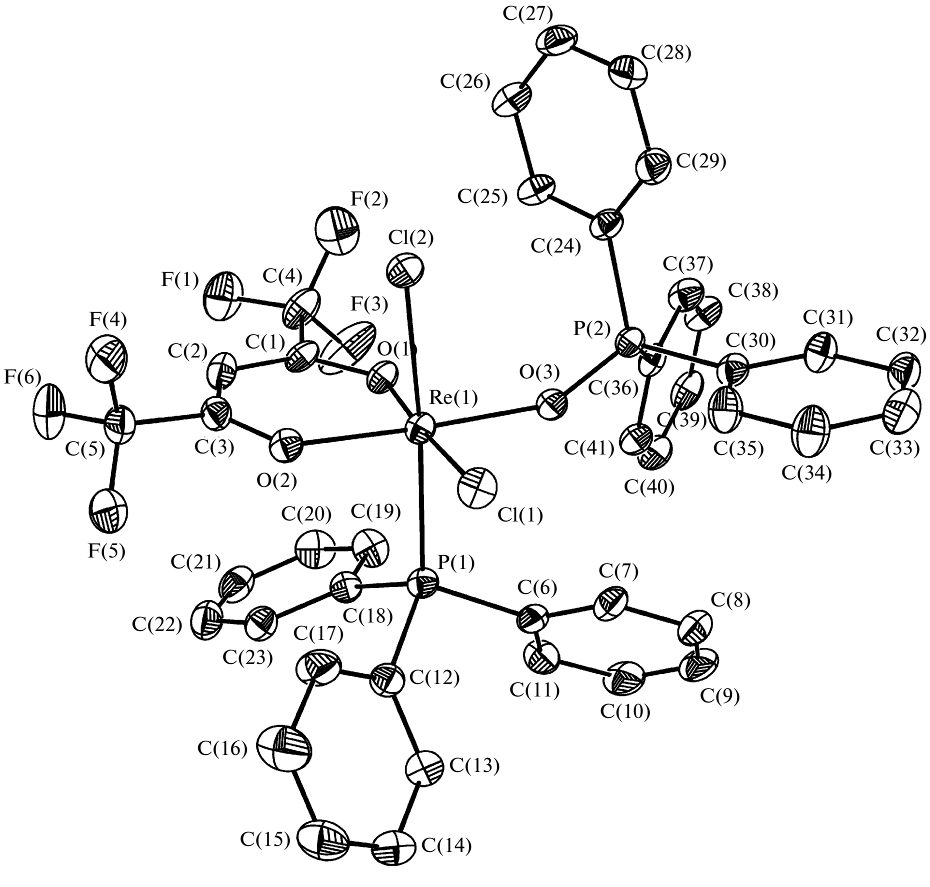
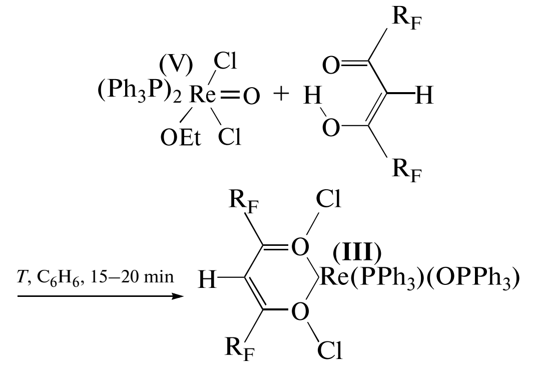


Fig. 1. Molecular structure of complex **Ia**.



$R_F = CF_3$(**I**), C_2F_5(**II**), C_3F_7(**III**), C_4F_9(**IV**), $C_3F_7OCF(CF_3)$ (**V**).

A solution of $ReOCl_2(OC_2H_5)(PPh_3)_2$ and a small excess of β-diketone was refluxed in benzene for 15–20 min. The compounds began to crystallize after octane was added to the obtained dark blue solution. It should be mentioned that we obtained just these complexes containing one triphenylphosphine ligand and one triphenylphosphine oxide ligand. It can be considered as established that the reduction of rhenium(V) to rhenium(III) is intramolecular due to the oxidation of triphenylphosphine.

Two polymorphous modifications were found for complex **I** $R_F = CF_3$: modification **a** (well soluble in ethanol) and modification **b** (moderately soluble in ethanol). Modifications **a** and **b** were obtained by crystallization from different solvents (**a** and **b** were crystallized from acetone and ethanol, respectively).

In the both structures (Figs. 1, 2), the rhenium atom has a distorted octahedral environment with the

Table 3. Thermal characteristics of complexes **I**–**V**

Compound	T_m, °C	T_{ox}, °C	$T_d^{5\%}$, °C		m_{res}, %	
			Air	Argon	Air	Argon
I	200	215	235	267	2	46
II	194	204	235	249	6	40
III	160	178	206	244	0.5	37
IV	171	195	235	247	0	29
V	155	162	180	177	0	37

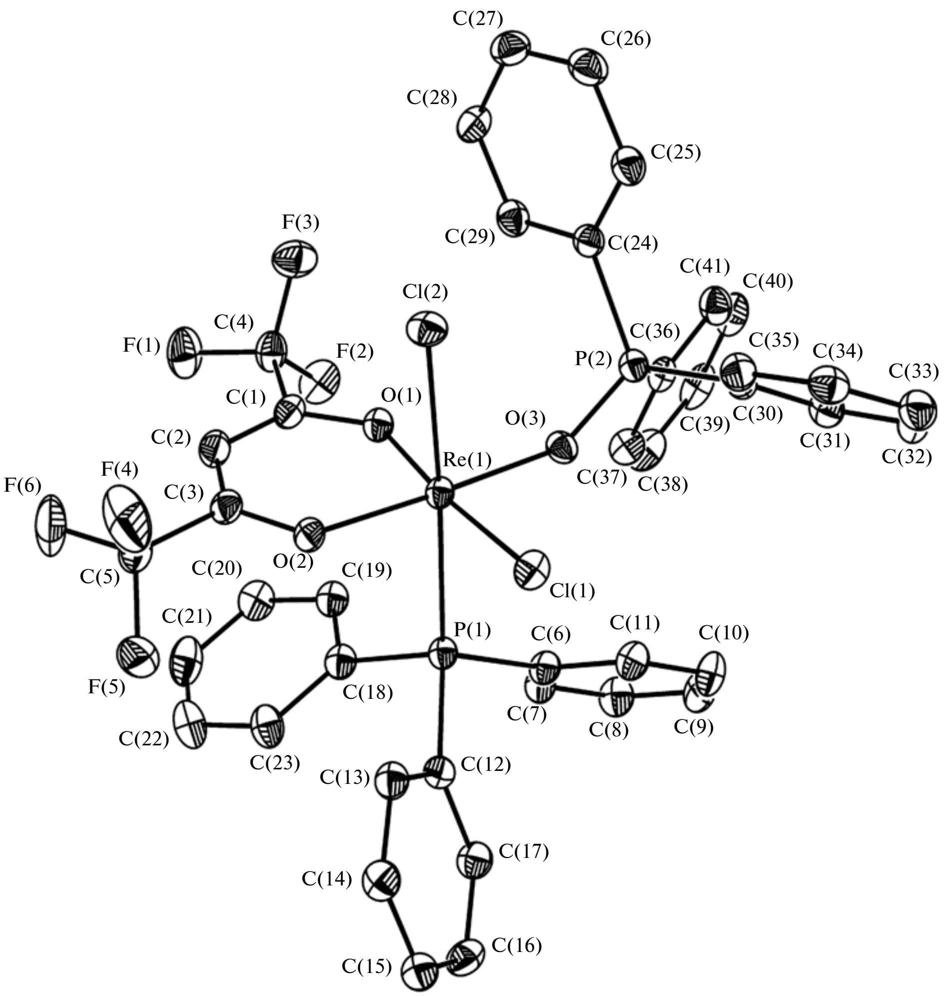


Fig. 2. Molecular structure of complex **Ib**.

same arrangement of the ligands. The chelating perfluorinated acetylacetonate, chloride, and coordinated triphenylphosphine oxide ligands form the equatorial plane of the octahedron, and the second chloride and coordinated triphenylphosphine substituents occupy the axial positions. A similar arrangement of the ligands is explained by their donor–acceptor properties. It is well known that the stronger the σ-acceptor properties of the ligand, the stronger σ-donor substituent is situated in the *trans* position to the ligand (*trans* effect). Correspondingly, the strongest σ donors (triphenylphosphine oxide and the carbonyl fragment of the chelating acetylacetonate substituent) are localized in front of the strongest σ-acceptor covalently bound acetylacetonate and chloride ligands. Although rather strong conjugation is observed in the acetylacetonate ligand, which is indicated by the alignment of the central C–C and C=C bond lengths, the Re–O (short) and Re ←O (long) distances differ, demonstrating the corresponding character of the fragments of the acetylacetonate substituent (σ-acceptor C–O– or σ-donor C=O→ fragments). According to the *trans* effect described above, the Re–$\mathrm{Cl_{equiv}}$ bond is shorter than Re–$\mathrm{Cl_{axial}}$.

The thermal properties of complexes **I–V** were studied by the TG and DTA methods. The corresponding curves are presented in Figs. 3 and 4. Some thermal characteristics are given in Table 3. The 5% mass loss of the sample was accepted to be the temperature of decomposition onset. The oxidation temperature was determined as shown in Fig. 3b.

The compounds synthesized decompose in several stages in both air and an inert atmosphere. The onset of mass loss starts above the melting point of the complexes. When the samples are heated in air, the DTA curves contain exotherms that appear in the temperature region of the mass loss onset. The influence of the number *n* in the fluoroalkyl substituent on the thermal characteristics of the studied complexes was analyzed. The curves of the dependences of several thermal parameters of complexes **I–IV** on the alkyl radical length are presented in Fig. 4. It is seen that they pass through a minimum at $n = 7$ (compound **III**). For TG of compounds **I–IV**, the temperature of decomposi-

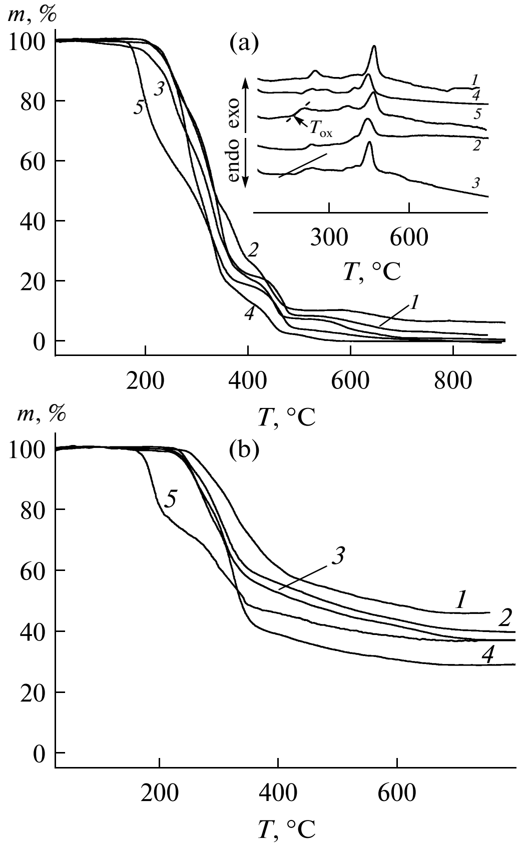


Fig. 3. (a) TG and DTA curves in air and (b) the TG curves in argon for complexes (*1*) **I**, (*2*) **II**, (*3*) **III**, (*4*) **IV**, and (*5*) **V** at a heating rate of 10°C/min.

tion onset in an inert atmosphere is higher than that in air. The temperature of oxidation onset is always higher by 10–15°C than the melting point and lower than $T_{\mathrm{d}}^{5\%}$ of the complexes. Thus, the initial stage of mass loss by the samples for TG in air is related to the thermal oxidation processes due, most likely, to the oxidation of the triphenylphosphine groups in the molecules of $ReCl_2(R_FCOCHCOR_F)(PPh_3)(OPPh_3)$ and their transformation into triphenylphosphine oxide followed by the decomposition of the molecules. Note that for compound **V** containing the γ-3-fluoropropyl groups $T_{\mathrm{d}}^{5\%}$ is almost independent of the experimental conditions (in air or in an inert atmosphere).

When TG is carried out in argon, the solid residue is formed (up to 46%). The solid residue weight in air

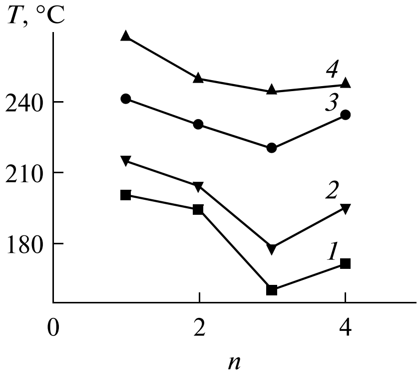


Fig. 4. Dependences of the (*1*) melting point, (*2*) oxidation temperature, and temperature of decomposition onset (*3*) in air and (*4*) in argon on the value of *n* in the fluoroalkyl radical.

is always lower than that in argon (Table 3). The molecules synthesized contain up to 20% of the metal; however, heating in air allows one to convert their oxidation products to the vapor phase more than by 94%. This makes it possible to use the new rhenium complexes with fluorinated β-diketones in the MO CVD processes.

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