Synthesis and Thermal Properties of Pd(II) Compounds with Perfluorinated Aromatic Thiols and Thiol Derivatives of Phenol

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Abstract

Compounds of Pd(II) of the PdL_2 formulation with perfluorinated thiols of aromatic series $4\text{-}CF_3C_6F_4SH$ (HL^1), $2,4\text{-}(CF_3)_2C_6F_3SH$ (HL^2), 4-nonafluorodiphenylthiol $C_6F_5C_6F_4SH$ (HL^3), 2-heptafluoronaphthalenethiol $C_{10}F_7SH$ (HL^4), and phenolic antioxidant $2,6\text{-}di(tert\text{-}C_4H_9)\text{-}4\text{-}(CH_2)_3SH$ (HL^5) have been obtained that feature a rather weak smell for mercaptans. The HL^3 structure has been determined by the X-ray diffraction analysis method. Thermal properties of $Pd(L^1)_2$–$Pd(L^4)_2$ compounds and the composition of their thermolysis products have been investigated. It has been found that depending on the conditions, Pd or a mixture of Pd and PdO is formed in the course of thermolysis of the compounds in the atmosphere of argon in crucible from porcelain and pyrex glass. When the thermolysis is conducted in nickel crucible, disperse palladium constitutes the thermolysis product.

INTRODUCTION

As of now, new technologies on the basis of platinum metals, palladium in particular [1], develop intensively, which stimulates the synthesis of new palladium compounds, the study of their physicochemical properties, and the application possibilities. Pd(II) that is the typical representative of "mild" acids (by Pearson) is typified by interaction with thiols (with "mild" bases) [2]. However, the study of reactions of Pd(II) with the lower aliphatic thiols and with aromatic benzenethiol becomes complicated because of their disgusting and strong smell. In this connection, the use of pentafluorobenzenethiol as a ligand that features rather weak smell [3, 4] became an important step in the improvement of the conditions of chemical experiment during the work with thiols. This reagent forms a compound of composition $Pd(C_6F_5S)_2$ during the interaction with Pd(II).

It turned out that compounds of metals with pentafluorobenzenethiol can act as precursors of inorganic materials. So, the thermolysis of $Pd(C_6F_5S)_2$ in a sealed tube has been studied [4]. Fugitiveness has been detected for $M(C_6F_5)_3$ compounds (M = Fe, Al, In, Rh, Tl) in vacuum at 65 °C [5, 6]. Of interest are synthesis and study of thermal properties of Pd(II) compounds with alternative perfluorinated aromatic thiols, as well as with thiol aromatic antioxidants.

The purpose of this work is to obtain Pd(II) compounds with perfluorinated thiols of aromatic series $4\text{-}CF_3C_6F_4SH$ (HL^1), $2,4\text{-}(CF_3)_2C_6F_3SH$ (HL^2), with 4-nonafluorodiphenylthiol $C_6F_5C_6F_4SH$ (HL^3), the structure of which as that of a representative of the class of perfluorinated thiols has been determined by the X-ray diffraction analysis method (XRD analysis), with 2-heptafluoronaphthalenethiol $C_{10}F_7SH$ (HL^4), and with phenolic antioxidant $2,6\text{-}di(tert\text{-}C_4H_9)\text{-}4\text{-}(CH_2)_3SH\text{-}C_6H_2OH$ (HL^5),

and also to examine thermal properties of compounds with HL^1–HL^4 reagents and the composition of products of their thermolysis.

EXPERIMENTAL

$PdCl_2$ of "ch." ("pure") qualification was used in the syntheses. Thiols HL^1–HL^4 and HL^5 were obtained by the procedures described in the works [7, 8] and [9], respectively. The syntheses were conducted in an ordinary extraction hood.

The synthesis of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzenethiolate of palladium (II), $Pd(L^1)_2$ (compound I). A solution of 0.17 g (1 mmol) $PdCl_2$ that was mixed with 30 ml H_2O and 4 drops of concentrated HCl was used to add a solution of 0.6 g (2 mmol) HL^1 in 10 ml EtOH. A brown deposit was filtered off on a glass filter with suction, washed with water, then with 1–2 ml EtOH, dried in the air atmosphere, and next in vacuum. The yield was equal to 0.35 g (58 %). It has been found (%): C 29.2, F 43.1, and S 10.0. For $C_{14}F_{14}S_2Pd$ it has been calculated (%): C 27.8, F 44.0, and S 10.6.

The freshly prepared compound I is dissolvable in EtOH, acetone, and MeCN. The substance that was let to stand for a certain time is slightly soluble in usual organic solvents. The IR spectrum (ν, cm^{-1}): 1641, 1482, 1466, 1377, 1330, 1184, 1166, 984, 827, 716 (weak bands are not present).

The synthesis of 2,4-bis(trifluoromethyl)-3,5,6-trifluorobenzenethiolate of palladium (II), $Pd(L^2)_2$ (compound II). The described above $PdCl_2$ solution was used to add a solution of 0.6 g (2 mmol) HL^2 in 10 ml EtOH. The mixture was stirred over 30 min, then left to stand for 2 h. The solution was separated, an oily deposit was washed twice with water; the water was decanted. Upon the addition of 1 ml of hexane, a solid deposit was obtained that was dissolved in 40 ml of acetone. The solution was filtered, and then acetone was evaporated until a solid phase appeared (almost to dryness). After adding several drops of hexane, the precipitated dark brown deposit was transferred onto a glass filter, was filtered off with suction, washed with hexane, and dried in the air atmosphere and then in vacuum. The yield was equal to 0.27 g (40 %). It has been found (%):

C 28.7, F 48.3, and S 8.7. For $C_{16}F_{18}S_2Pd$ it has been calculated (%): C 27.3, F 48.5, and S 9.1.

The compound is readily soluble in EtOH, acetone, MeCN, CH_2Cl_2, and DMSO and it is slightly soluble in toluene, benzene, hexane, and $CHCl_3$. The molecular mass in a solution (acetone): it has been found 657; it has been calculated 704. The IR spectrum (ν, cm^{-1}): 1633, 1586, 1478, 1450, 1360, 1331, 1238, 1189, 1138, 949, 880, 805, 735, 652.

The synthesis of 4-nonafluorodiphenylthiolate of palladium (II), $Pd(L^3)_2$ (compound III). The described above $PdCl_2$ solution was used to add a solution of 0.7 g (2 mmol) HL^3 in 30 ml EtOH. The mixture was stirred over 30 min, and then left to stand 30 min. 5 ml of hexane was added to the reaction mixture and the mixture was stirred. A brown deposit was filtered off with suction, washed with 1 ml EtOH, dried in the air atmosphere and then in vacuum. The yield was equal to 0.7 g (87 %). It has been found (%): C 36.6, F 41.4, and S 7.3. For $C_{24}F_{18}S_2Pd$ it has been calculated (%): C 36.0, F 42.7, and S 8.0.

Even the freshly prepared compound is slightly soluble in ordinary organic solvents. The IR spectrum (ν, cm^{-1}): 1655, 1637, 1529, 1502, 1466, 1377, 1263, 1002, 970, 724.

The synthesis of 2-heptafluoronaphthalenethiolate of palladium (II), $Pd(L^4)_2$ (compound IV). The described above $PdCl_2$ solution was used to add a solution of 0.57 g (2 mmol) HL^4 in 5 ml EtOH. The mixture was stirred over 30 min, and then left to stand for 2 h. A brown deposit was filtered off with suction, washed twice with water and hexane, dried in the air atmosphere and then in vacuum. The yield was 0.61 g (90 %). It has been found (%): C 36.1, F 39.0, and S 9.1. For $C_{20}F_{14}S_2Pd$ it has been calculated (%): C 35.5, F 39.3, and S 9.5.

Even the freshly prepared compound is slightly soluble in ordinary organic solvents. The IR spectrum (ν, cm^{-1}): 1663, 1638, 1598, 1525, 1490, 1410, 1263, 1155, 1112, 1045, 956, 915, 751, 697.

The synthesis of 3-(3,5-di-*tert*-butyl-4-hydroxybenzene)propanethiolate of Pd(II), $Pd(L^5)_2$ (compound V). A solution of 0.56 g (2 mmol) HL^5 in 8 ml EtOH was added to the described above $PdCl_2$ solution under stirring. A yellow deposit precipitated at once, and oil was formed, orange in colour. After 30 min, the deposit was filtered off on a glass filter

with suction (the oil remained in a beaker), washed with 5 ml of water, and dried in a vacuum desiccator. Then the deposit was washed with 1 ml MeCN, sucked off on the glass filter, air-dried, and then dried in vacuum. The yield was equal to 0.3 g (50 %). It has been found (%): C 61.3, H 8.6, and S 10.3. For $C_{34}H_{54}O_2S_2Pd$ it has been calculated (%): C 61.4, H 8.2, and S 9.6.

The compound is readily soluble in organic solvents. The molecular mass in a solution ($CHCl_3$): it has been found 1333; it has been calculated 665. The IR spectrum (ν), cm^{-1}: 3645, 3443, 2956, 2910, 2872, 1635, 1434, 1391, 1361, 1316, 1250, 1233, 1213, 1199, 1160, 1120. The UV spectrum (λ, nm, log ε): 208 (4.48), 275 (4.10), 324 (3.82), 377 (3.72).

The elemental analysis for C, H, F, N, and S content has been made in much the same manner as in [10]. Molecular masses of compounds II and V have been found by the vapour-phase osmometry method. The IR spectra were taken in a Specord 75 IR spectrophotometer in the field of 400−3800 cm^{-1}. Samples were prepared in the form of suspensions in Vaseline oil and fluorinated oil.

HL^3 single crystals have been grown by slow evaporation of a solution of a compound in the mixture CH_2Cl_2 : hexane = 1 : 1 at ambient temperature. A transparent colourless crystal of lamellar shape with the dimensions of 0.40 × 0.32 × 0.24mm has been selected for XRD analysis. Parameters of the unit cell and intensities of 1634 reflexes that were collected in an interval of indices: $0 \le h \le 25$, $0 \le k \le 9$, $-16 \le l \le 16$, $R(\text{int}) = 0.0182$ have been measured in an Enraf-Nonius CAD-4 autodiffractometer by the standard procedure at ambient temperature (λMoK_α, a graphite monochromator, $\theta/2\theta$-scanning, $2\theta_{\text{max}} = 50°$). The crystals were classed with the monoclinic syngony; the parameters of the unit cell: $a = 21.238(4)$, $b = 8.026(1)$, $c = 14.014(2)$ Å, $\beta = 97.29(1)°$, $V = 2369.5(6)$ Å^3, $Z = 4$, $\rho_{\text{calc}} = 1.952$ г/см^3, $F(000) = 1360$, $M = 696.38$. Space group $C2/c$ has been chosen on the basis of the analysis of extinctions in the file of intensities and has been confirmed by the performed computations. The structure has been deciphered by a direct method and adjusted by a full-matrix LSM under an anisotropic approximation for non-hydrogen atoms according to SHELX-97 programme package

TABLE 1

Coordinates of the basis atoms ($\times 10^4$) and their equivalent isotropic heat parameters (in 10^3 Å^2) in the structure of $C_6F_5C_6F_4SH$

Atom	x	y	z	U_{equiv}
S(1)	4263(1)	5578(4)	1145(2)	87(1)
F(2)	5664(3)	6204(7)	1379(4)	79(2)
F(3)	6593(2)	3965(7)	1503(4)	73(2)
F(5)	5086(2)	−328(7)	1053(4)	71(2)
F(6)	4153(2)	1928(8)	938(4)	88(2)
F(8)	6776(2)	1620(7)	−25(4)	76(2)
F(9)	7745(2)	−573(8)	143(4)	86(2)
F(10)	7875(2)	−2828(8)	1585(4)	88(2)
F(11)	7023(3)	−2913(7)	2870(4)	78(2)
F(12)	6056(2)	−696(7)	2718(3)	72(2)
C(1)	4879(4)	4115(11)	1181(5)	50(2)
C(2)	5507(5)	4561(11)	1325(6)	56(2)
C(3)	5995(4)	3459(11)	1375(6)	50(2)
C(4)	5866(4)	1762(12)	1294(5)	51(2)
C(5)	5242(4)	1304(14)	1154(6)	60(2)
C(6)	4759(4)	2405(13)	1094(6)	59(3)
C(7)	6392(4)	524(10)	1353(6)	49(2)
C(8)	6828(4)	482(11)	708(6)	53(2)
C(9)	7320(4)	−615(11)	775(6)	52(2)
C(10)	7392(4)	−1744(13)	1504(7)	63(3)
C(11)	6959(4)	−1801(12)	2152(6)	59(2)
C(12)	6473(4)	−681(12)	2066(6)	55(2)
H(1)	4340	6645	571	122

[11]. Coordinates of H atom were initially defined from a difference synthesis of the electronic density, and the synthesis has been calculated with the use of 538 reflexes at $\theta \le 18°$. By virtue of the fact that the structure refinement with these coordinates occurred inconsistently, the final model of the structure has been determined with the values of H coordinates that have been calculated by means of geometry. In so doing, the last-mentioned appeared to be close to the data that have been received previously.

As a consequence of this, it has been found that the H atom is localized near to the bond that connects S(1) and C(3) atoms, the distance between them being equal to 3.589(9) Å. The final parameters of the refinement: $R1 = 0.0581$, $wR2 = 0.1676$ for 786 reflections with $I \ge 2\sigma(I)$; GOOF = 0.937, $R1 = 0.1179$, $wR2 = 0.2342$ throughout the reflections (201 is the adjusted parameter). The maximum and the

TABLE 2

Basic interatomic distances (d), valence angles (ω) and intermolecular contacts in the structure of $C_6F_5C_6F_4SH$

Bonds	d, Å	Bonds	d, Å	Intermolecular contacts	
S(1)−C(1)	1.754(8)	C(1)−C(6)	1.40(1)	S(1)−C(2)	3.559(9)
S(1)−H(1)	1.2000	C(2)−C(3)	1.36(1)	S(1)−C(3)	3.589(9)
F(2)−C(2)	1.360(9)	C(3)−C(4)	1.39(1)	S(1)−C(2)'	3.610(9)
F(3)−C(3)	1.325(9)	C(4)−C(5)	1.37(1)	S(1)−F(9)	3.474(5)
F(5)−C(5)	1.35(1)	C(4)−C(7)	1.49(1)	S(1)−F(8)	3.394(6)
F(6)−C(6)	1.334(9)	C(5)−C(6)	1.35(1)	S(1)−F(11)	3.434(7)
F(8)−C(8)	1.368(9)	C(7)−C(8)	1.37(1)	S(1)−F(2)'	3.490(6)
F(9)−C(9)	1.344(9)	C(7)−C(12)	1.39(1)	S(1)−F(12)	3.495(6)
F(10)−C(10)	1.339(9)	C(8)−C(9)	1.36(1)	F(2)−C(12)	3.12(1)
F(11)−C(11)	1.339(9)	C(9)−C(10)	1.36(1)	F(2)−C(11)	3.247(9)
F(12)−C(12)	1.350(9)	C(10)−C(11)	1.37(1)	F(3)−C(10)	3.352(9)
F(3)−F(8)	2.914(8)	C(11)−C(12)	1.36(1)	F(5)−C(5)	3.180(9)
F(5)−F(12)	2.926(6)	C(1)−C(2)	1.37(1)	F(9)−C(9)	3.31(1)
	ω, degrees		ω, degrees		
C(1)−S(1)−H(1)	109.5	C(8)−C(7)−C(12)	115.2(8)	F(9)−C(10)	3.14(1)
C(2)−C(1)−C(6)	115.6(8)	C(8)−C(7)−C(4)	122.9(8)	F(10)−C(12)	3.17(1)
C(2)−C(1)−S(1)	122.5(7)	C(12)−C(7)−C(4)	122.0(7)	F(10)−C(7)	3.373(9)
C(6)−C(1)−S(1)	121.8(7)	C(9)−C(8)−F(8)	118.1(8)	F(11)−C(8)	3.218(9)
C(3)−C(2)−F(2)	116.6(8)	C(9)−C(8)−C(7)	123.1(8)	F(11)−C(9)	3.096(9)
C(3)−C(2)−C(1)	124.0(8)	F(8)−C(8)−C(7)	118.7(8)	F(11)−C(10)	3.39(1)
F(2)−C(2)−C(1)	119.3(8)	F(9)−C(9)−C(10)	119.4(8)	F(2)−F(5)	3.053(8)
F(3)−C(3)−C(2)	121.4(8)	F(9)−C(9)−C(8)	120.9(8)	F(2)−F(12)	3.164(7)
F(3)−C(3)−C(4)	119.1(8)	C(10)−C(9)−C(8)	119.7(8)	F(3)−F(9)	3.128(8)
C(2)−C(3)−C(4)	119.6(8)	F(10)−C(10)−C(9)	120.6(9)	F(3)−F(10)	3.123(8)
C(5)−C(4)−C(3)	116.8(9)	F(10)−C(10)−C(11)	119.5(9)	F(3)−F(11)	3.214(8)
C(5)−C(4)−C(7)	122.4(9)	C(9)−C(10)−C(11)	119.9(9)	F(5)−F(5)'	2.974(8)
C(3)−C(4)−C(7)	120.8(7)	F(11)−C(11)−C(12)	120.7(8)	F(5)−F(12)	3.162(7)
C(6)−C(5)−F(5)	117.0(8)	F(11)−C(11)−C(10)	120.4(9)	F(6)−F(10)	2.976(7)
C(6)−C(5)−C(4)	123(1)	C(12)−C(11)−C(10)	118.9(9)	F(6)−F(12)	2.897(8)
F(5)−C(5)−C(4)	119.7(9)	F(12)−C(12)−C(11)	119.2(8)	F(8)−F(11)	3.233(8)
F(6)−C(6)−C(5)	122.1(9)	F(12)−C(12)−C(7)	117.6(8)	F(9)−F(9)'	3.272(9)
F(6)−C(6)−C(1)	117.2(9)	C(11)−C(12)−C(7)	123.2(8)	F(9)−F(10)	2.905(8)
C(5)−C(6)−C(1)	120.6(8)				

minimum of the residual electronic density comprise 0.331 and −0.374 $e/Å^3$, respectively; the extinction coefficient is equal to 0.0001(7).

Final values of positional and equivalent isotropic heat parameters of the basis atoms are given in Table 1, and the basic interatomic distances and valence angles, in Table 2*.

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*The tables of the anisotropic heat parameters and the values of the structure factors can be obtained from the authors.

The curves of a thermal analysis (TA) were obtained in the air atmosphere in the Paulik−Paulik−Erdey derivatograph, the temperature increase rate was 2.5 °C/min, quartz crucible, and Al_2O_3 comparison standard. Thermolysis of samples of the compounds I−IV in the atmosphere of argon of high cleanliness (the feed rate was 4−5 l/h) was conducted in a vertical furnace with the use of crucible from porcelain, pyrex glass, and nickel. The weighted

samples of the compounds were 0.15−0.20 g. Two regimes of the thermolysis have been used. Under the regime 1, a crucible with a sample was placed in a beaker from pyrex glass, filled with argon, put in the furnace that was previously blown through with argon, and covered with another beaker. The furnace temperature was raised up to reach the required one at a rate of 3 °C /min for the compounds I, II (up to ~340 °C) and 4 °C /min for the compounds III, IV (up to ~440 °C). Then isothermal ageing was conducted over the course of 1.5 h for the compounds I, II and 1 h for the compounds III, IV (the necessary time for ageing has been found on the basis of prior experiments). Under the regime 2, a crucible with a sample was put in a vertical furnace that was heated up to the required temperature, and then isothermal ageing was conducted. The isothermal regime was provided by means of a PIT-3 precision isodromic thermoregulator.

X-ray diffraction analysis (XRD) of thermolysis products was conducted in DRON-3M and DRON-SEIFERT-RM4 diffractometers ($R = 192$ mm, CuK_{α} radiation, Ni-filter, a scintillation counter, Bragg−Brentano focusing). Spectra have been taken in DRON-3M diffractometer at a rate of 1°/min at ambient temperature in the range of angles $2\theta = 5−70°$. Samples for X-ray diffractometric study were prepared as follows. Solid products of thermolysis were grinded in an agate mortar in the presence of heptane; the produced suspension was spread onto a glazed side of a standard quartz sample pan. Upon heptane dried, the sample represented a thin smooth layer, ~100 μm in thickness. The quantitative XRD was conducted by application of the Chang method. To do this, intensities of (111) lines for Pd were measured and (100), for PdO; next, a mass fraction of both phases was calculated with allowance made for corundum number ($K_{Pd} = 4.1$, $K_{PdO} = 12.94$).

RESULTS AND DISCUSSION

Previously synthesized $HL^1−HL^5$ reagents [7−9] were characterized by melting point T_{melt} and IR spectra. The structure of HL^3 compound was determined by the procedure of XRD anal-
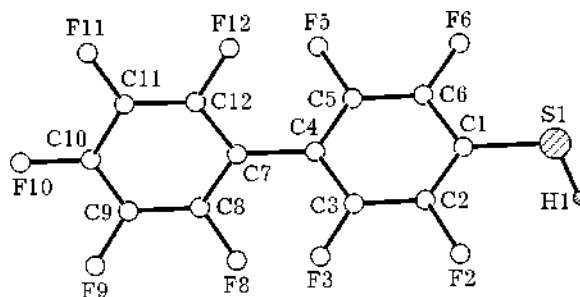

Fig. 1. Molecular structure of $C_6F_5C_6F_4SH$ with the numbering scheme of atoms.

ysis. It has been found that it is constructed of the discrete molecules that contain practically planar C_6F_4 and C_6F_5 rings. F atoms lie practically in the plane of phenyl rings; average deviations from their statistically average planes comprise 0.013 and 0.010 Å. The dihedral angle between the planes of two perfluorophenyl rings of the molecule is 61.9°. At such turn angle, the distance between the nearest F atoms $F(3)−F(8)$ and $F(5)−F(12)$ in orthopositions are equal to 2.914(8) and 2.925(6) Å, respectively. These values exceed the total of two Van der Waals radii of F atom ($R_F = 1.40$ Å) [12], which makes lower the steric strain in the adjacent perfluorophenyl fragments (Fig. 1). The C−S bond length is 1.754(8) Å and it is somewhat shorter than the length of a typical ordinary covalent C−S bond (1.81 Å), the C−S−H angle being 109.5°. The C−C bond length in the rings varies in the range of 1.35−1.40 Å, and the bond length $C(4)−C(7)$ between phenylic rings is much greater and it is equal to 1.49(1) Å. The C−F bond length varies in the range of 1.325−1.368 Å.

The in-depth examination of intermolecular distances has demonstrated that only Van der Waals interactions exist in the studied structure (see Table 2). The shortest contacts have been revealed between F and C atoms of C_6F_4 rings and S atoms that are bonded to it, Å: S(1)...C(2) 3.559(9), S(1)...C(3) 3.589(9), F(5)...F(5)' 2.974(8), F(5)...C(5) 3.180(9). These contacts link the pairs of parallel root-mean-square planes that are multiplied by the centres of symmetry and the rotary axes 2. The resulting is that continuous columns are formed along the c axis. By way of the short contacts S(1)...F(8) = 3.394(6), F(2)...F(5) = 3.053(8), F(2)...C(12) = 3.12(1) Å, the described above columns form layers that are parallel to the (100)
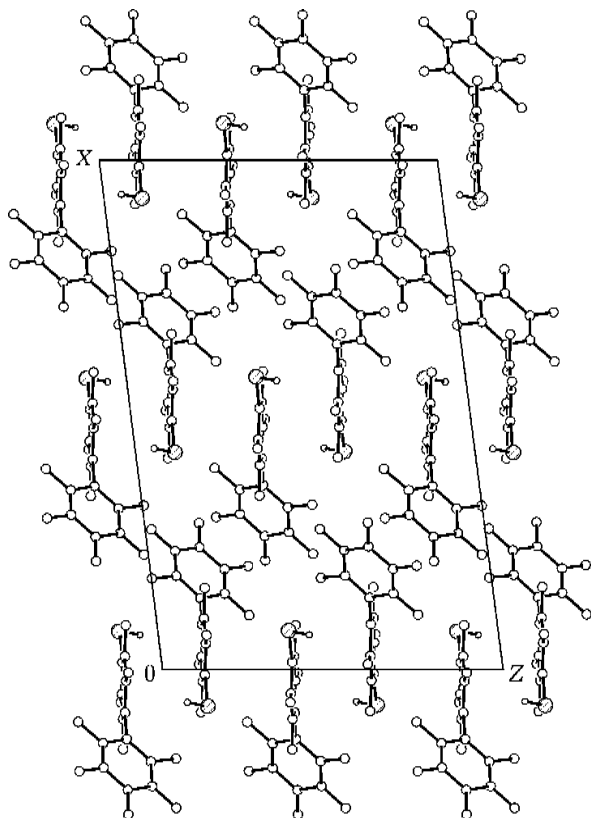
Fig. 2. Molecular packing of the $C_6F_5C_6F_4SH$ structure that is projected onto the plane (010).

plane at the level of $x = 0$ and $x = 1/2$ (Fig. 2). Besides the described above contacts, the shortest intermolecular contacts have also been revealed in packing of the structure under discussion, Å: F(9)...F(10) 2.905(8), F(6)...F(10) 2.976(7), F(6)...F(12) 2.897(8), F(11)...C(9) 3.096(9) (see Table 2). Hence, all the considered contacts in the structure combine HL^3 molecules in a three-dimensional skeleton.

Similarly to pentafluorobenzenethiol, HL^1–HL^4 and HL^5 reagents interact with Pd^{2+} ions to form the products with PdL_2 formulation. There is no band $v(S–H) \approx 2600$ cm^{-1} in the IR spectra of compounds I–V that is present in the spectra of HL^1–HL^5 (2600, 2610, 2590, 2575, 2555 cm^{-1}, respectively). This is suggestive of the replacement of H atom by Pd^{2+} ion, which is accompanied by Pd–S bonding. The presence of Bi–S bond was proved earlier for $Bi(4-CF_3C_6F_4S)_3$ by the procedure of XRD analysis [13].

Compounds III and IV are slightly soluble in organic solvents, which can be indicative of their polynuclear structure [14]. On the contrary, freshly prepared compounds I and II with anions of HL^1 and HL^2 reagents that contain a single benzene ring dissolve in a number of organic solvents. Molecular mass of the compound II in acetone bears witness to its mononuclear structure in this solvent. Molecular mass of the compound V in $CHCl_3$ fits a dimer composition.

Table 3 supplies TA data for the compounds I–IV in the air atmosphere. According to thermogravimetry (TG) data, a mass loss is evidenced for all compounds starting with temperatures 40–50 °C. There are two steps in the TG curves: on the first one, a smooth decrease of mass occurs; the second one is characterized by a sharp mass loss. Only the curve TG of the compound I contains a plateau in an interval of temperatures of 245–290 °C. Upon reaching 245 °C, the mass loss amounts to 7 % for the compound I, which may formally correspond to the loss of two CF_3 groups. The TG curve for the compound II over the range of

TABLE 3

Data of thermal analysis for the compounds I–IV in the air atmosphere

Compound	ΔT of the mass loss in the TG curve, °C	T_{max} of the effect in the DTG curve, °C	T_{max} of an exothermic effect in the DTA curve, °C	Mass of the residue, % from the mass of the weighted sample	Calculated Pd content in the compound, %
I	40–245 290–350	335	345	12	17.6
II	40–170 270–340	300	325	5	14.3
III	50–340 340–385	360	375	0 (an outburst)	13.3
IV	40–340 340–405	380	390	10	15.7

170−270 ºC has a slanted appearance. Temperature ranges of a mass loss for the compounds III and IV are the closest ones. Temperature of effects in the curves of differential thermogravimetry (DTG) and differential thermal analysis (DTA) is the highest for the compound IV that contains a perfluoronaphthalene fragment. Decomposition of the compounds in a crucible of the derivatograph proceeds vigorously and it is followed by the loss of decomposition products. In the case of the compound III, an outburst of the entire solid phase has occurred, which has made difficult to obtain the information about the yield and the composition of solid products of the thermolysis. In this connection, we investigated solid products of the thermolysis that has been conducted in an inert atmosphere (argon) under the conditions that rule out the loss of these products.

Table 4 gives the results of the thermolysis of the compounds I−IV in argon. At first, we have studied the features of the process using the thermolysis of the compound III as an example. The decomposition of this compound (see Table 4, exp. III-4) had the effect that the mass of the residue in a porcelain crucible was equal to only 8.5 % from the mass of the weighted

sample, if the initial mass of the crucible is used for the computation as it is done usually. It is evident that the mass of the residue is much less than the amount of Pd in the compound. The apparent mass loss might be caused by the fugitiveness of the compound III and palladium-containing decomposition products. We have conducted an assessment of possible fugitiveness of this compound. A batch (0.025 g) of the compound III was placed in a glass (pyrex glass) test tube ($d \sim 5$ mm, $l \sim 180$ mm) that was then filled with argon. The test tube was lowered in a vertical furnace, the top of the furnace was screened, and the open part of the test tube (~120−130 mm) was located in the air. The temperature of the furnace was raised starting from the room temperature at a rate of ~4 ºC/min until a film, white in colour, appeared in a cold part of the test tube (380 ºC). Then the test tube was taken out from the furnace and cooled. The mass of the solid phase amounted to 98.4 % from the mass of the initial batch. Next, the test tube was placed in the hot furnace again (380 ºC). Upon the temperature of ~410−420 ºC was reached, vigorous evolving of a gas phase was evidenced, and in so doing, a precipitation of solid products occurred in a cold part of the test tube. Heating was

TABLE 4

Results of thermal decomposition of the compounds I−IV in the atmosphere of argon

Compound	Regime of the thermolysis	Experiment No.	Holding temperature T, ºC	Holding time τ, h	Material of the crucible	Mass of the residue, % from the mass of the weighted sample	Calculated Pd content in the compound, %	Pd (PdO) content, mass % (on evidence of XRD)
I	1	1	340	1.5	Pyrex glass	21.2	17.6	>95 (<5)
	1	2	380	0.5	« «	17.6	17.6	95 (5)
	2	3	340	1.5	Porcelain	21.0	17.6	100
II	1	1	340	1.5	Pyrex glass	15.3	15.1	>95 (<5)
	1	2	380	0.5	« «	15.2	15.1	95 (5)
	2	3	340	1.5	Porcelain	16.1	15.1	100
III	1	1	440	1	Pyrex glass	13.4	13.3	95 (5)
	1	2	540	0.25	« «	13.5	13.3	95 (5)
	1	3	440	1	Nickel	12.4*	13.3	100
	2	4	440	1	Porcelain	13.3	13.3	>95 (<5)
IV	1	1	440	1	Pyrex glass	15.7	15.7	>95 (<5)
	1	2	440	1	Nickel	14.1*	15.7	100

*It has been obtained by emptying the products from nickel crucible.

TABLE 5

Position of most intensive peaks in the diffractograms of the thermolysis products ($2\theta^{\circ}$)

Thermolysis product	hkl	I-1	I-2	I-3	II-1	II-2	II-3	III-1	III-2	III-3	III-4	IV-1	IV-2
Pd	111	40.20	40.20	40.15	40.20	40.20	40.20	40.20	40.20	40.15	40.20	40.15	40.20
	200	46.75	46.75	46.70	46.75	46.75	46.75	46.75	46.75	46.70	46.75	46.75	46.75
	220	68.20	68.20	68.15	68.25	68.20	68.20	68.20	68.20	68.15	68.25	68.25	68.20
PdO	002	33.60	33.60	–	33.60	33.60	–	33.60	33.65	–	33.60	33.60	–
	101	33.95	33.95	–	33.95	33.95	–	33.95	33.95	–	33.95	33.90	–

Note. Roman numerals are used to designate initial substances, and Arabic numerals are used to designate the experiment number.

stopped; the test tube was taken out 15 min later. After cooling, the mass of the solid phase comprised 94 % from the mass of the initial batch.

It appears that the compound III and possible products of its partial decomposition that contain palladium do not possess noticeable fugitiveness at atmospheric pressure and 420 °C. Consequently, an assumption can be made that the mass loss of the crucible (porcelain, pyrex glass) stems from pickling during the decomposition of the compound III containing F atoms (SiF_4 evolving). Indeed, after the products of the thermolysis were completely removed, the mass of the porcelain crucible appeared to be less than the initial. The mass of the residue in the experiment III-4 was equal to 13.3 % with allowance for a mass loss of the crucible (see Table 4), which is close to the calculated Pd content of the compound III. Therefore, masses of solid products of the thermolysis of the compounds I–IV that are given in Table 4 (except for the experiments III-3 and IV-2) were determined as the ratio of the difference between the mass of the melting-pot with the decomposition product and the mass of the crucible that was washed from the decomposition products, to the mass of the weighted sample of the compound. It is evident that the residue mass data and those on the calculated Pd content during the thermolysis of the compounds I (exp. 2), II (exp. 1, 2), III (exp. 1, 2, 4), and IV (exp. 1) are comparable. Mat marks of pickling are well noticeable on crucible from pyrex glass after washing out from thermolysis products, especially those upon the thermolysis of the compounds III and IV.

XRD results (see Tables 4, 5) have suggested that PdO is formed along with the main thermolysis product of Pd during the decomposition of compounds I–IV in argon in crucibles from pyrex glass and porcelain (the compounds I and II, the temperature 340 °C, regime 1; III, IV – the temperature 440 °C, regimes 1, 2). Its formation may proceed both by way of oxygen that is present in argon, and by way of oxygen of the material of the crucibles. To reveal the reason, decomposition of the compounds III (exp. 3) and IV (exp. 2) in nickel crucibles has been performed. According to XRD, only Pd is the thermolysis product in these experiments (see Table 5). This bears witness to the fact that the formation of PdO proceeds by way of oxygen from porcelain and pyrex glass. Disperse Pd is also formed during decomposition of the compounds I and II in a porcelain crucible at a temperature of 340 °C, but when the regime 2 is used (see Tables 4, 5).

CONCLUSION

The investigation has demonstrated that HL^1–HL^4 perfluorothiols and HL^5 thiol represent a group of reagents that hold promise to perform synthesis of compounds of metals with thiols, and there is no necessity of creating special conditions to perform the synthesis. The resulting is that new Pd(II) compounds with aromatic thiols have been obtained. Study of thermolysis processes for the compounds I–IV has demonstrated for the first time that when the thermolysis is conducted in argon atmosphere in porcelain and nickel crucibles, compounds of Pd(II) with perfluorinated aromatic thiols constitute precursors of disperse palladium.

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