SYNTHESIS OF SOME LIGANDS OF THE TRITHIENYLPHOSPHINE SERIES. CRYSTAL AND MOLECULAR STRUCTURES OF trans-DICHLOROBIS[TRI(2-THIENYL)PHOSPHINE]PALLADIUM(II)

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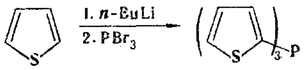
The preparation of some ligands of the trithienylphosphine series is described; Pd(II) complexes were obtained from them. The crystal and molecular structures of trans-dichlorobis[tri(2-thienyl)phosphine]palladium(II) were studied.

During our investigation of complexes that include thiophene derivatives as ligands we encountered the problem as to the degree that the existing concept [1] regarding the analogy of the chemical and even some physical properties of compounds of the benzene and thiophene series can be extended to the complexes formed by the latter. As subjects for the study of this problem we decided to use palladium complexes of trithienylphosphines — analogs of the well-known dichlorobis(triphenylphosphine)palladium(II).

In the present preliminary communication we describe the synthesis of some of the relevant ligands of the thiophene series and the corresponding complexes of divalent palladium, as well as the crystal and molecular structures of one of these complexes, viz., dichlorobis[tri(2-thienyl)phosphine]palladium(II). We hope at some later date to report data pertaining to the chemical properties of the above-mentioned thiophene complexes, as well as similar information for complexes that include β-thienyl groupings.

Trithienylphosphines can be obtained through the corresponding organolithium or organomagnesium compounds. Thus tri(2-thienyl)phosphine (I) and tri(5-methyl-2-thienyl)phosphine were obtained for the first time by means of organomagnesium synthesis [2, 3], while tri(3-thienyl)phosphine (II) was obtained by means of organolithium synthesis [4].

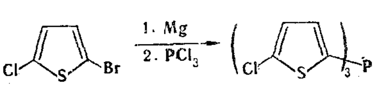
In the present research we have for the first time realized the synthesis of phosphine I by direct metallation of thiophene with n-BuLi and subsequent treatment with PBr_3.



I

It should be noted that the direct metallation of thiophene for such ends has also been previously used but in the preparation of tri(2-thienyl)phosphine oxide (III) by treatment of 2-thienyllithium with $POCl_3$ [5]; the yield of phosphine oxide III is low, and impurities that are difficult to remove are formed in the preparation of tri(4-methyl-2-thienyl)phosphine through metallation of 3-methylthiophene [3].

In the present research we obtained tri(5-chloro-2-thienyl)phosphine (IV) for the first time by means of 5-chloro-2-bromothiophene, which forms an organomagnesium derivative exclusively at the bromine atom [6].



IV

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TABLE 1. Complexes of Palladium with Trithienylphosphines

Compound	Temp. of the onset of decomposition	UV spectrum		Found, %						Empirical formula	Calculated, %						Yield, %
		λmax, nm	lg ε	C	H	Cl	P	Pd	S		C	H	Cl	P	Pd	S	
V	247	238, 309, 370	4,82; 3,94; 4,44	39,4	2,7	9,4	8,6	14,8	25,6	$C_{24}H_{18}Cl_2P_2PdS_6$	39,1	2,5	9,6	8,4	14,4	26,1	79
VI	256—258	227, 244, 287, 350	4,61; 4,58; 3,95; 4,21	39,5	2,6	9,4	8,3	14,3	25,5	$C_{24}H_{18}Cl_2P_2PdS_6$	39,1	2,5	9,6	8,4	14,4	26,1	76
VII	243—245	245, 275, 385	4,66; 4,50; 4,26	44,0	3,7	8,5	7,5	13,0	23,2	$C_{30}H_{30}Cl_2P_2PdS_6$	43,8	3,7	8,6	7,5	12,9	23,4	76
VIII	235	250, 270, 367	4,92; 4,90; 4,05	31,3	1,5	29,6	6,6	11,4	20,0	$C_{24}H_{12}Cl_8P_2PdS_6$	30,5	1,3	30,0	6,6	11,3	20,4	79

TABLE 2. Coordinates of the Nonhydrogen Atoms ($\cdot 10^4$; $\cdot 10^5$ for the Cl Atoms)[a]

Atom	x	y	z
Pd	0	0	0
Cl	22575 (15)	−4334 (7)	18618 (13)
P	3165 (13)	−9873 (6)	−14555 (12)
S(1)[b]	376 (2)	−1004 (1)	−4658 (2)
S(2), C(6)[c]	3781 (2)	−573 (2)	−1418 (2)
S(3), C(10)[c]	−264 (2)	−1970 (1)	903 (2)
C(1)	−705 (5)	−975 (2)	−3433 (4)
C(2)[b]	−2519 (5)	−955 (3)	−4210 (4)
C(3)	−2764 (7)	−929 (3)	−5783 (6)
C(4)	−1328 (8)	−955 (3)	−6118 (6)
C(5)	2435 (5)	−1198 (2)	−1233 (5)
C(6), S(2)[c]	3260 (2)	−2000 (1)	−712 (2)
C(7)	5061 (6)	−1784 (3)	−523 (7)
C(8)	5360 (6)	−1100 (3)	−862 (6)
C(9)	−447 (5)	−1817 (2)	−867 (5)
C(10), S(3)[c]	−1178 (2)	−2517 (1)	−1996 (2)
C(11)	−1430 (6)	−3029 (3)	−764 (7)
C(12)	−981 (6)	−2773 (3)	625 (6)

[a] The parameters of the anisotropic temperature factors can be obtained from the authors. [b] The S(1) and C(2) atoms undergo partial "replacement" by one another, but this disordering was not taken into account in the refinement. [c] These atoms occupy positions one with another with a population of ∿1/2; this was not taken into account in the refinement.

TABLE 3. Coordinates of the Hydrogen Atoms ($\cdot 10^3$)

Atom	x	y	z
H(3)	−412 (8)	−92 (4)	−668 (8)
H(4)	−114 (9)	−94 (4)	−679 (8)
H(7)	590 (9)	−210 (4)	−7 (8)
H(8)	670 (8)	−95 (4)	−61 (7)
H(11)	−184 (8)	−343 (4)	−111 (8)
H(12)	−85 (8)	−301 (4)	141 (8)

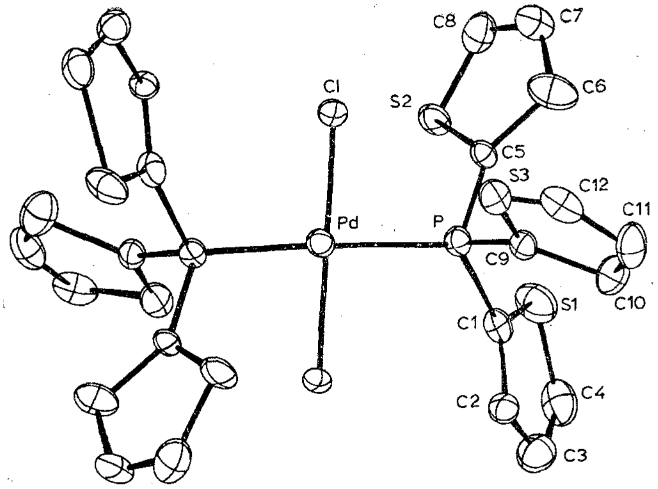


Fig. 1. Molecular structure of trans-dichlorobis[tri(2-thienyl)phosphine]palladium(II).

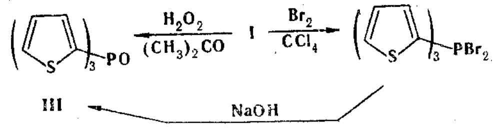
TABLE 4. Bond Lengths

Bond	*d*, Å	Bond	*d*, Å
Pd—Cl	2,292 (1)	S(3)—C(12)	1,570 (6)
Pd—P	2,338 (1)	C(1)—C(2)	1,484 (6)
P—C(1)	1,800 (4)	C(2)—C(3)	1,446 (7)
P—C(5)	1,794 (5)	C(3)—C(4)	1,366 (9)
P—C(9)	1,804 (4)	C(5)—C(6)	1,624 (5)
S(1)—C(1)	1,711 (5)	C(6)—C(7)	1,540 (6)
S(1)—C(4)	1,655 (6)	C(7)—C(8)	1,332 (8)
S(2)—C(5)	1,667 (5)	C(9)—C(10)	1,652 (5)
S(2)—C(8)	1,597 (6)	C(10)—C(11)	1,567 (6)
S(3)—C(9)	1,666 (5)	C(11)—C(12)	1,336 (8)

TABLE 5. Bond Angles

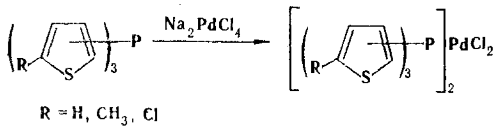
Angle	ω, °	Angle	ω, °
ClPdP	87,94 (4)	C(2)C(3)C(4)	113,9 (5)
PPdCl	92,06 (4)	S(1)C(4)C(3)	114,6 (5)
PdPC(1)	120,1 (1)	PC(5)S(2)	123,1 (3)
PdPC(5)	113,7 (1)	PC(5)C(6)	123,2 (3)
PdPC(9)	109,5 (1)	S(2)C(5)C(6)	113,5 (3)
C(1)PC(5)	104,6 (2)	C(5)C(6)C(7)	97,2 (3)
C(1)PC(9)	103,6 (2)	C(6)C(7)C(8)	118,2 (5)
C(5)PC(9)	103,8 (2)	S(2)C(8)C(7)	115,6 (5)
C(1)S(1)C(4)	92,8 (3)	PC(9)S(3)	122,1 (3)
C(5)S(2)C(8)	95,3 (3)	PC(9)C(10)	122,7 (3)
C(9)S(3)C(12)	94,7 (3)	S(3)C(9)C(10)	114,9 (3)
PC(1)S(1)	122,0 (2)	C(9)C(10)C(11)	94,9 (3)
PC(1)C(2)	126 (3)	C(10)C(11)C(12)	118,0 (5)
S(1)C(1)C(2)	111,7 (3)	S(3)C(12)C(11)	117,4 (4)
C(1)C(2)C(3)	106,9 (4)		

In order to study the chemical properties of the trithienylphosphines we carried out the bromination of phosphine I. Let us point out in this connection that, according to the data in [2], hydrogen bromide is liberated when phosphine I is treated with molecular bromine (the solvent was not indicated); in the opinion of the authors, this constitutes evidence for bromination of the thiophene ring. When we treated phosphine I with molecular bromine in CCl_4 at room temperature, we obtained a substance that fumes in air and forms phosphine oxide III when it is refluxed with aqueous alkali; this very likely indicates the formation of phosphine dibromide as the intermediate rather than product of electrophilic substitution. Phosphine oxide III was found to be identical to the product of oxidation of phosphine I with hydrogen peroxide in acetone.



When the trithienylphosphines obtained in this research are treated with methyl iodide, they form crystalline methyltrithienylphosphonium iodides, while phosphine sulfide was also synthesized in the case of the previously undescribed phosphine IV. The purity of the trithienylphosphines was verified by chromatographic mass spectrometry, by which it was determined that the m/z values of the molecular ions are in agreement with the calculated values; the spectral characteristics of the investigated phosphines (the PMR and UV spectra) were also obtained.

Treatment of the trithienylphosphines with sodium tetrachloropalladate in an aqueous alcohol medium leads to the formation of complexes with the composition $L_2 \cdot PdCl_2$ (where L is the ligand).



In order to determine the mutual orientation of the ligands we made an x-ray diffraction study of dichlorobis[tri(2-thienyl)phosphine]palladium(II) (V). Complexes with tri(2-thienyl)phosphine ligands have not been previously investigated; however, the structure of the V molecule is typical for Pd(II) complexes with other phosphine ligands. Thus, in conformity with location of the Pd atom at the center of symmetry, it has a trans structure, and the palladium atom is coordinated with two chlorine atoms and two tri(2-thienyl)phosphine ligands in the square planar manner that is usual for Pd(II) complexes (Fig. 1). The Pd—Cl [2.292(1) Å] and Pd—P [2.338(1)Å] bond lengths are close to their values in other trans complexes of divalent palladium with chloro and phosphine ligands [7-11] such as Pd—Cl (2.301 Å [7]) and Pd—P (2.331 Å) with a triphenylphosphine ligand in diiodobis(triphenylphosphine)palladium(II), which was investigated in the solvate form $(Ph_3P)_2PdI_2 \cdot 2CH_2Cl_2$ [10].

The phosphorus atoms have the usual tetrahedral configuration of the bonds, but the C—P—C angles are decreased as compared with the ideal value of 109° to 104.0(5)°. On the other hand, the Pd—P—C(1) angle is increased to 120.1(1)° as compared with the other two Pd—P—C angles [113.7(1)° and 109.5(1)°]. This is evidently due to the short intramolecular Cl...C(1) [3.444(3) Å] and Cl...C(2) [3.332(3)Å] contacts (vis-a-vis the sum of the corresponding van der Waals radii of 3.6 Å [12]), which also give rise to inequality of the Cl—Pd—P angles 92.06(4) and 87.94(4)°] and an increase in the P—C(1)—C(2) angle to 126.3(3)°. Let us also note that the P—C(1) bond is closest to the coordination plane of the palladium atom [the Cl—Pd—P—C(1), Cl—Pd—P—C(5), and Cl—Pd—P—C(9) torsion angles are, respectively, −163.8(1), −38.9(1), and 76.6(1)°]. The P—C distances [with an average value of1.799(5) Å] are close to the usual P—C (sp^2) bond lengths in phosphine ligands [11, 13].

In interpreting the structure we found that V molecules that differ with respect to 180° rotation of the S(2)C(5)C(6)C(7)C(8) and S(3)C(9)C(10)C(11)C(12) 2-thienyl substituents about the P—C bonds are present in approximately equal amounts in the crystal. This disordering led to substantial apparent distortion of the bond lengths and angles in both corresponding rings: The bonds with participation of the S(2) and S(3) atoms are shortened, whereas the bonds with participation of the C(6) and C(10) atoms are increased as compared with the bond lengths in the thiophene molecule: S—C 1.718, C=C 1.352, and C—C 1.455 Å [14]. The angles at the S(2) and S(3) atoms are also increased, while the angles at the C(6) and C(10) atoms, which are equal to 91.3 and 111.8°, are decreased. The same disordering, but to a lesser extent, is also observed for the S(1)C(1)C(2)C(3)C(4) ring, in which the deviations of the bond lengths and angles from the values found for the thiophene molecule are not as great as in the two other 2-thienyl substituents. The qualitatively identical inequality of the bond lengths at the sulfur atoms in all three 2-thienyl groups [for example, S(1)—C(1) 1.711(5) is appreciably greater than S(1)—C(4) 1.655(6) Å] is evidently due to disordering of the two α-carbon atoms, viz., to the bond of one of them with the electron-acceptor phosphorus atom of the ligand.

Thus the data from x-ray diffraction analysis constitute evidence for the structural similarity of the trithienylphosphine and triphenylphosphine complexes of halides of divalent palladium.

EXPERIMENTAL*

Chromatographic mass spectrometry was carried out with a Varian MAT-111 spectrometer with a 150 by 0.2 cm column filled with 3% OV-1 on Chromosorb W with helium as the carrier gas at a flow rate of 15 ml/min. The PMR spectra of solutions in $CDCl_3$ were recorded with tetramethylsilane as the internal standard. The UV spectra of solutions in CH_2Cl_2 were recorded with a Specord UV-vis spectrophotometer. The melting points of the trithienylphosphines, phosphonium salts, phosphine oxide III, and phosphine sulfide [sic] IV were determined with a BIT-2 apparatus (Special Design Office, Institute of Organic Chemistry, Academy of Sciences of the USSR), while the temperatures of the onset of decomposition of the complexes were determined with the microscope of a Boetius stage.

Tri(2-thienyl)phosphine (I). A 200-ml sample of an ether solution of n-BuLi (the concentration was 0.0976 g/ml) was added with stirring at 0°C in an argon atmosphere in the course of 30 min to a solution of 25.24 g of thiophene in 115 ml of absolute ether. After 1.5 h, the mixture was cooled to −60°C, and a solution of 19.49 g of PBr_3 in 45 ml of absolute ether was added with stirring. The mixture was then cooled to −30°C and decomposed with a mixture of HCl and NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with ether (three 100-ml portions). The combined organic phases were washed successively with a solution of $NaHCO_3$ and water and dried with $MgSO_4$. The ether was removed, and the residue was chromatographed with a column filled with SiO_2 [40-100 μ, elution with hexane–chloroform (7:1)]. The elutate was evaporated, and distillation of the residue yielded 1.64 g of a fraction with bp 50-165°C (0.32-0.35 hPa) and 13.3 g of a fraction with bp 165-185°C (0.4 hPa) containing phosphine I; the yield was 66.3%. We were unable to obtain a compound in solid form. PMR spectrum: 7.00 (m, 4-H), 7.32 (m, 3-H), and 7.48 ppm (q, 5-H). UV spectrum: λ_{max} 244 nm (log ε 4.36). The compound had an M^+ peak with m/z 280. According to the data in [2], this compound had bp 195-200°C (1.33-2.66 hPa). Methyltri(2-thienyl)phosphonium iodide had mp 184.0-186.5°C (mp 185-186°C [15]).

Tri(2-thienyl)phosphine Oxide (III). A solution of 1.58 g of bromine in 5 ml of absolute CCl_4 was added with stirring at 20°C to a solution of 0.84 g of phosphine I in 10 ml of absolute CCl_4 (a red-orange precipitate formed immediately). After 12 h, the precipitate was removed by filtration, washed with a small amount of warm CCl_4, and dried over P_2O_5 to give 1.38 g of a substance that fumed markedly in air; 0.55 g of this product was refluxed for 3 h with an excess amount of 20% aqueous NaOH solution. The solution was cooled and extracted with ether, the extracts were dried with $MgSO_4$, and the ether was removed to give 0.22 g (60%) of phosphine oxide III with mp 126.5-127.5°C (mp 128°C [2]). Phosphine oxide III was also obtained by oxidation of phosphine I with hydrogen peroxide in acetone by a method similar to that described in [16] and had mp 128°C.

Tri(3-thienyl)phosphine (II). This compound, with mp 68-70°C (mp 69-70°C [4]), was obtained in 50% yield by the method in [4]. PMR spectrum: 6.98 (m, 4-H) and 7.22 ppm (m, 2-H, 5-H). UV spectrum: λ_{max} 230 nm (log ε 4.32). The product had an M^+ peak with m/z 280. Methyltri(3-thienyl)phosphonium iodide had mp 179-182°C (mp 178-179° [15]).

Tri(5-methyl-2-thienyl)phosphine. This compound, with mp 48-49°C (from methanol) (mp 48-49°C [3]), was obtained in 50.6% yield by the method in [3]. PMR spectrum: 2.42 (s, CH_3), 6.65 (sextet, 4-H) and 7.10 ppm (q, 3-H). UV spectrum: λ_{max} 245 nm (log ε 4.32). The product has an M^+ peak with m/z 322. Methyltri(5-methyl-2-thienyl)phosphonium iodide had mp 209-210°C.

Tri(5-chloro-2-thienyl)phosphine. This compound, with mp 82.0-83.5°C (from alcohol), was obtained in 62% yield by a method similar to that described in [3]. Found: C 38.0; H 1.6; Cl 27.6; P 7.7; S 24.9%. $C_{12}H_6Cl_3PS_3$. Calculated: C 37.6; H 1.6; Cl 27.7; P 8.0; S 25.1%. PMR spectrum: 6.85 (q, 4-H) and 7.08 ppm (q, 3-H). UV spectrum: λ_{max} 248 nm (log ε 4.36). The product had an M^+ peak with m/z 382 (Cl^{35}). Tri(5-chloro-2-thienyl)phosphine sulfide had mp 120-122°C. Methyltri(5-chloro-2-thienyl)phosphonium iodide had mp 200-205°C.

The following palladium complexes were obtained: dichlorobis[tri(2-thienyl)phosphine]-

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*With the participation of I. A. Kostenchuk, a graduate student in the Moscow State Pedagogical Institute.

palladium(II) (V), dichlorobis[tri(3-thienyl)phosphine]palladium(II) (VI), dichlorobis[tri(5-methyl-2-thienyl)phosphine]palladium (II) (VII), and dichlorobis[tri(5-chloro-2-thienyl)phosphine]palladium(II) (VIII). These complexes were obtained by the method in [17] by mixing alcohol solutions of the ligands with an aqueous solution of Na_2PdCl_4 (2:1) in an argon atmosphere; the resulting amorphous precipitate was removed by filtration, washed with water, alcohol, and a small amount of ether, dried, and crystallized from benzene or toluene to give crystalline substances. The pertinent data are presented in Table 1.

X-Ray Diffraction Study of Complex V. The crystals of complex V were monoclinic with $a = 8.545(5)$, $b = 18.18(1)$, $c = 9.532(6)$ Å, $\beta = 109.10(4)°$, $d_{calc} = 1.75$ g/cm^3, $Z = 2$, and space group $P2_1/n$ at −120°. The cell parameters and the intensities of 3462 independent reflections with $I \geq 2\sigma$ were measured with a Syntex automatic four-circle diffractometer at −120°C (λ Mo K_α, graphite monochromator, $\theta/2\theta$ scan, and $2\theta \leq 60°$). The Pd atom was placed at the center of symmetry (0,0,0), after which all of the nonhydrogen atoms were found in two successive Fourier syntheses. The disordering was found after refinement by the complete-matrix method of least squares within the anisotropic approximation up to R = 0.090, and further refinement of the S(2), S(3), C(6), and C(10) atoms was accomplished from the arithmetic mean f curves $f = (f_C + f_S)/2$ [18]. Attempts to refine the populations of the positions of these sulfur and carbon atoms gave improbable results. The hydrogen atoms [except for those that were not found because of the disordering at the C(2), C(6), and C(10) atoms] were revealed from differential series and were included in the refinement with fixed $B_{iso} = 5$ Å^2. The final values of the divergence factors were R / 0.045 and $R_\omega = 0.055$. All of the calculations were made with an Eclipse S/200 computer by means of modified EXTL programs.*

The coordinates of the nonhydrogen atoms and their anisotropic temperature factors are presented in Table 2, the coordinates of the hydrogen atoms are presented in Table 3, and the bond lengths and bond angles are presented in Tables 4 and 5, respectively.

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