P,S-Ligands. Complexes of *P,P,P′,P′*-tetraphenylethylenediphosphine monosulfide with $PdCl_2$

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1 : 1 and 1 : 2 complexes of $Ph_2P(CH_2)_2P(S)Ph_2$ with $PdCl_2$ were synthesized. Their structures were established by ^{31}P NMR and IR spectroscopy and X-ray diffraction analysis. In the crystals, the 1 : 1 complex has a chelate structure. In CH_2Cl_2, this complex partially dissociates at the Pd...S=P bond. According to the X-ray diffraction data, only the P^{III} atoms in the 1 : 2 complex are coordinated. The reaction of the 1 : 2 complex with $AgNO_3$ afforded the cationic chelate complex $[Pd(Ph_2P(CH_2)_2P(S)Ph_2)_2]^{2+}$ $2NO_3^-$.

Key words: palladium complexes, phosphinophosphine sulfides; ^{31}P NMR and IR spectroscopy; X-ray diffraction analysis.

Complexes of different metals with diphosphine ligands $R_2P(CH_2)_nPR_2$ have been studied comprehensively. Structures of neutral and cationic complexes both of the open and chelate types have been described. The structures of 1 : 1 neutral chelate complexes[1] and 1 : 2 cationic chelate complexes[2,3] of divalent palladium with ethylenediphosphines were also reported; 1 : 1 and 1 : 2 open complexes of palladium with methylenediphosphines were obtained, both the dimeric[4] and trimeric[5] structures being typical of the 1 : 1 complexes. When one PR_2 group in the diphosphine ligand $R_2P(CH_2)_nPR_2$ is replaced by the phosphoryl group $P(O)R_2$ (or by the thiophosphoryl group $P(S)R_2$), the ligand can be coordinated to the metal atom through either the O (S) or P atom. The number of known complexes of this type is substantially smaller than that of complexes with the diphosphine ligands. Thus, only 13 complexes of Co, W, Re, Mo, Fe, and some other metals with the $R_2P(CH_2)_nP(O)R_2$ ligands are documented.[6] In most of these complexes, the ligand is coordinated to the metal atom through the P atom of the phosphine group. Note that the chelate five-membered metallacycles in which the coordination occurs through both donor atoms, *viz.*, through the P atom of the phosphine group and the O atom of the phosphoryl group, were observed only in the halide complexes. Two palladium complexes of this type are known, *viz.*, the $PdCl_2(PPh_2CH_2CHP(O)Ph_2)_2$[7] and $PdCl_2(Me_2PCH_2P(O)Me_2)_2$[8] open complexes. The $\{PdCl_2P_2\}$ coordination squares in these complexes are formed by the Cl and P atoms of the phosphine groups and have planar *trans* structures.

The structures of complexes in which one or both PR_2 groups are replaced by the thiophosphoryl group $P(S)R_2$ are also poorly studied. For monosubstituted ligands, mercury complex $HgI_2[Ph_2PCH_2P(S)Ph_2]$,[9] rhodium complex $[RhCl(CO)(Ph_2PCH_2P(S)Ph_2)$,[10] silver complex $Ag_2(NO_3)_2(Ph_2PCH_2CH_2P(S)Ph_2)_2$,[11] and palladium complex $PdCl_2(Ph_2PCH_2P(S)Ph_2)$[6] were reported.

Further studies of such structures are topical. It should also be noted that the mixed bidentate ligands $Ph_2P(CH_2)_nX$, where n = 1 or 2 and X = NR_2, SR, or $R_2P(O)$, have attracted growing interest in recent years because their complexes with "soft" transition metals Rh^I, Pt^{II}, and Ru^{II} exhibit catalytic activity.[12–16] In particular, the rhodium complexes are used as homogeneous catalysts of hydroformylation of alkenes[15] and aldehydes[13] as well as of carbonylation of methanol.[14–16]

In the present work, we synthesized complexes of $PdCl_2$ with the $Ph_2P(CH_2)_2P(S)Ph_2(L)$ ligand with compositions metal : ligand = 1 : 1 (**1**) and 1 : 2 (**2**). Their structures in solutions and crystals were established by ^{31}P NMR and IR spectroscopy and X-ray diffraction analysis.

Results and Discussion

The structure of the $Pd(L)Cl_2$ complex (1) (Figs. 1 and 2, Tables 1 and 2). According to data from X-ray diffraction analysis, the ligand in complex **1** is coordinated to the Pd atom through the P and S atoms to form a six-membered metallacycle. The $\{PdCl_2PS\}$ coordination square is substantially distorted. The S(1) atom deviates from the plane through the remaining atoms by 0.662(2) Å. On the whole, the distortion of the square can be described as tetrahedral, *viz.*, the pairs of the *trans* P(2) and Cl(1) atoms and the *trans* S(1) and Cl(2)

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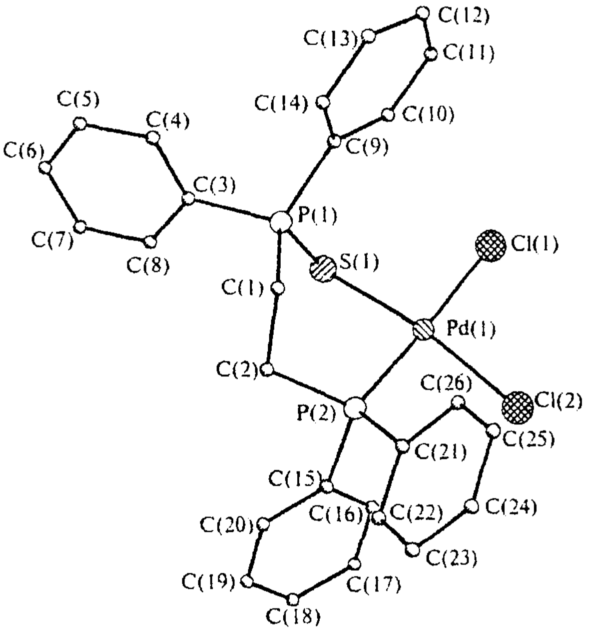


Fig. 1. Structure of the complex $Pd[Ph_2P(CH_2)_2P(S)Ph_2]Cl_2$ (**1**).

atoms deviate from the mean plane in opposite directions by 0.18 Å. The Pd(1)—P(2) bond length (2.238(1) Å) is substantially smaller (by 0.074 Å) than the corresponding bond length in open *trans*-complex **2** (see below), whereas the Pd—Cl bonds (the average length is 2.346 Å) are, on the contrary, substantially elongated (by 0.038 Å). These changes in the Pd—Cl and Pd—P bond lengths are attributable to the *trans* effect, which is evident from the comparison of the Pd—Cl bond lengths. Thus the Pd(1)—Cl(1) bond (2.367(1) Å) in the *trans* position with respect to the P(2) atom is substantially longer than the Pd(1)—Cl(2) bond (2.325(1) Å) in the *trans* position with respect to the S(1) atom. The Pd(1)—S(1) (2.306(1) Å) and P=S (2.003(2) Å) bond lengths in complex **1** are smaller than the Pd—S (2.334 and 2.350 Å) and P=S (2.014 and 2.013 Å) bond lengths in the known open *trans* complexes $PdCl_2(R_3P{=}S)_2$,

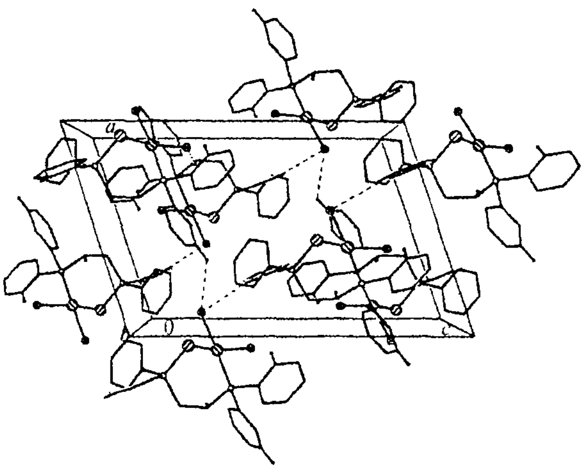


Fig. 2. Molecular packing in the crystals of **1**.

Table 1. Crystallographic data and details of refinement of the structures of **1**, **2**, and **2a**

Parameter	**1**	**2**	**2a**
Molecular formula	$C_{26}H_{24}Cl_2P_2PdS$	$C_{56}H_{52}Cl_{14}P_4PdS_2$	$C_{56}H_{52}Cl_{14}P_4PdS_2$
M	607.75	1515.68	1515.68
Space group	$P2_1/n$	$P2_1/n$	$P2_1$
T/K	293(2)	193(2)	153(2)
a/Å	11.150(1)	9.245(4)	9.206(3)
b/Å	14.010(5)	21.613(9)	21.537(7)
c/Å	16.955(4)	16.226(7)	32.326(11)
α/deg	90	90	90
β/deg	108.73(1)	92.82(4)	92.87(3)
γ/deg	90	90	90
V/Å^3	2508(1)	3238(2)	6401
Z	4	2	4
d_{calc}/g cm^{-3}	1.609	1.554	1.573
Diffractometer	CAD4	Syntex $P2_1$	Siemens $P3/PC$
Radiation	Mo-Kα (γ = 0.71073 Å)		
μ/cm^{-1}	11.77	10.64	10.77
Scan mode	θ—5/3θ	θ—2θ	θ—2θ
2θ$_{max}$/deg	50	46	46
Number of independent reflections	4375	3919	8985
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0384 (3486 refl.)	0.0623 (3098 refl.)	0.0484 (3763 refl.)
wR_2 (based on F^2 for all reflections)	0.1234	0.1974	0.2410
Number of refinable parameters	385	453	1241
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$		
a	0.0564	0.1031	0.2300
b	5.7381	7.2408	0.00

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structures of **1** and **2**

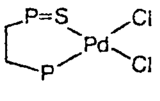
Bond type	Bond	*d*/Å	Bond	*d*/Å
	Complex **1**		Complex **2**	
Pd—P	Pd(1)—P(2)	2.2379(13)	Pd(1)—P(1)	2.321(2)
Pd—S	Pd(1)—S(1)	2.3063(14)	—	
Pd—Cl	Pd(1)—Cl(1)	2.3665(13)	Pd(1)-Cl(1)	2.308(2)
	Pd(1)—Cl(2)	2.3251(14)	—	
P=S	P(1)—S(1)	2.003(2)	P(2)—S(1)	1.960(3)
P—C(Ph)	P(1)—C(3)	1.807(5)	P(1)—C(15)	1.809(8)
	P(1)—C(9)	1.801(5)	P(1)—C(21)	1.815(7)
	P(2)—C(15)	1.828(5)	P(2)—C(3)	1.816(7)
	P(2)—C(21)	1.831(5)	P(2)—C(9)	1.798(8)
P—C(CH_2)	P(1)—C(1)	1.821(5)	P(1)—C(1)	1.840(7)
	P(2)—C(2)	1.843(5)	P(2)—C(2)	1.820(7)
CH_1—CH_2	C(1)—C(2)	1.530(7)	C(1)—C(2)	1.507(12)
Angle type	**Angle**	**ω/deg**	**Angle**	**ω/deg**
	Complex **1**		Complex **2**	
P—Pd—Cl	P(2)—Pd(1)—Cl(1)	175.38(5)	P(1)—Pd(1)—Cl(1)	93.81(7)
	P(2)—Pd(1)—Cl(2)	89.92(5)	P(1)—Pd(1)—Cl(1)'	86.19(7)
P—Pd—S	P(2)—Pd(1)—S(1)	90.17(5)	—	—
Cl—Pd—S	Cl(1)—Pd(1)—S(1)	90.10(5)	—	—
	Cl(2)—Pd(1)—S(1)	166.38(5)	—	—
Cl—Pd—Cl	Cl(1)—Pd(1)—Cl(2)	90.91(5)	—	—
Pd—S—P	Pd(1)—S(1)—P(1)	105.10(7)	—	—
Pd—P—C(CH_2)	Pd(1)—P(2)—C(2)	115.2(2)	Pd(1)—P(1)—C(1)	117.7(2)
Pd—P—C(Ph)	Pd(1)—P(2)—C(15)	114.2(2)	Pd(1)—P(1)—C(15)	111.2(2)
	Pd(1)—P(2)—C(21)	113.2(2)	Pd(1)—P(1)—C(21)	114.0(2)
S—P—C(Ph)	S(1)—P(1)—C(3)	108.2(2)	S(1)—P(2)—C(3)	112.7(3)
	S(1)—P(1)—C(9)	112.1(2)	S(1)—P(2)—C(9)	112.4(2)
S—P—C(CH_2)	S(1)—P(1)—C(1)	110.7(2)	S(1)—P(2)—C(2)	111.3(3)
C(CH_2)—P—C(Ph)	C(2)—P(2)—C(15)	105.5(2)	C(1)—P(1)—C(15)	101.0(3)
	C(2)—P(2)—C(21)	101.4(2)	C(1)—P(1)—C(21)	103.3(3)
	C(1)—P(1)—C(3)	107.5(3)	C(2)—P(2)—C(3)	106.0(3)
	C(1)—P(1)—C(9)	111.0(2)	C(2)—P(2)—C(9)	106.6(4)
C(Ph)—P—C(Ph)	C(3)—P(1)—C(9)	106.6(4)	C(3)—P(2)—C(9)	107.4(3)
	C(15)—P(2)—C(21)	106.2(2)	C(15)—P(1)—C(21)	108.5(3)

where PR_3 = PBu^t [17] or $PPhEt_2$.[18] This shortening of the Pd(1)—S(1) bond may also be attributed to the *trans* effect of the Cl(2) atom. Therefore, the bonds between the Pd atom and both donor atoms of the ligand in chelate complex **1** are stronger than the corresponding bonds in the complexes of the open type.

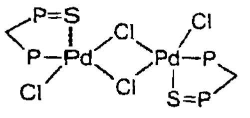
The chelate ring Pd(1)P(2)C(2)C(1)P(1)S(1) is substantially corrugated. The folding angles along the S(1)...P(2) and S(1)...C(2) lines are 28.3° and 47.3°, respectively. The geometric parameters of the organic ligand have standard values.

Apparently, the molecular packing in the crystal (see Fig. 2) is determined by weak interactions involving the Cl atoms, *viz.*, by the Cl...H—C_{Ph} contacts (Cl(1)...H(4') and Cl(1)...H(23")) and the Cl...H—C(sp^3) contact (Cl(2)...H(2)). The Cl...H distances (2.83(7), 2.86(6), and 2.85(6) Å, respectively) are only slightly smaller than the sum of the van der Waals radii of the Cl and H atoms (2.97 Å).[19] In the crystals, the molecules are linked in layers by virtue of these interactions.

It is of interest that the above-mentioned $PdCl_2(Ph_2PCH_2P(S)Ph_2)$ complex whose ligand contains the methylene bridge,[6] unlike monomeric complex **1**, has (according to the data from ^{31}P NMR and IR spectroscopy and mass spectrometry) dimeric bridging structure **3**.



1



3

Unfortunately, this complex has not been studied by X-ray diffraction analysis.

The structure of the Pd(L_2)Cl_2 complex (2) (Figs. 3 and 4, Tables 1 and 2). For complex **2** isolated from $CHCl_3$, two types of crystals (**2** and **2a**) were obtained. According to the data from X-ray diffraction studies, these crystals have the same composition, *viz.*, $Pd(L_2)Cl_2 \cdot 4CHCl_3$, and identical structures. The structures of **2** and **2a** differ in that some $CHCl_3$ molecules of solvation in **2a** are disordered, which leads to the lowering of the crystal symmetry. Probably, this is associated with the fact that crystals of **2a** are nonequilibrium crystals. The subsequent discussion of the geometric parameters will be based mainly on the data for the structure of **2**.

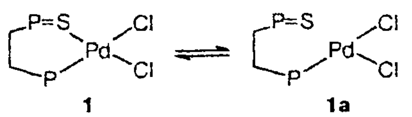
The crystal structure of **2** consists of centrosymmetrical isolated Pd(L_2)Cl_2 molecules. The L ligands are coordinated to the Pd atom through the P(1) and P(1A) atoms of the phosphine groups PPh_2. The {$PdCl_2P_2$} coordination polyhedron is planar. The Pd—P bond length (2.321 Å) is close to the average values for the Pd—PEt_3 and Pd—PPh_3 bond lengths (2.315 and 2.308 Å, respectively).[20] The Pd—Cl bond length (2.308 Å) has a value typical of the planar-square complexes. The similar Pd—P and Pd—Cl bond lengths (2.327 and 2.292 Å, respectively) were found in the structurally similar centrosymmetrical complex $PdCl_2(Ph_2PCH_2CH_2P(O)Ph_2)$[7] and in diphosphine complexes $PdCl_2(PAr_3)_2$, where Ar = p-ClC_6H_4 or p-MeC_6H_4[21] (the average Pd—P and Pd—Cl bond lengths are 2.344 and 2.291 Å, respectively). The geometric parameters of the ligand molecule also have standard values. The P=S bond length (1.960 Å) coincides with the average length of the P=S double bond (1.954 Å).[20]

The molecule of the complex is surrounded by four $CHCl_3$ molecules of solvation, which are linked in isolated associates {$PdCl_2(L_2) \cdot 4CHCl_3$} through hydrogen bonds between the "mobile" H atoms of the $CHCl_3$ molecules and the S atoms (see Fig. 3). The parameters of the hydrogen bonds are as follows: the C(1s)—H(1s) and C(2s)—H(2s) bond lengths are 0.87(8) and 0.99(9) Å, respectively; the C(1s)...S(1), C(2s)...S(1), H(1s)...S(1), and H(2s)...S(1) distances are 3.65(1), 3.683(9), 2.93(8), and 2.87(9) Å, respectively; the C(1s)—H(1s)—S(1) and C(2s)—H(2s)—S(1) angles are 142(6)° and 140(6)°, respectively. In the crystal, the molecules are aligned along the *b* axis (see Fig. 4). The P=S...$(HCCl_3)_2$ hydrogen bonds stabilize complex **2**. This stabilization may be responsible for the fact that attempts to prepare complex **1** in $CHCl_3$ always led to the formation of complex **2**.

Structures of the complexes in solutions. The behavior of complexes **1** and **2** in solutions was studied by ^{31}P NMR and IR spectroscopy.

The IR spectrum of the L ligand has one absorption band at 615 cm^{-1} corresponding to absorption of the free P=S group.[11] In the IR spectrum of solid complex **1**, this band is shifted to the low-frequency region (to 595 cm^{-1}), which is characteristic of the coordinated P=S group of the P=S—Pd^{2+} fragment. When complex **1** was dissolved in CH_2Cl_2, a band at 615 cm^{-1} corresponding to the free P=S groups (Scheme 1) appeared in the spectrum along with the band at 595 cm^{-1}, which is indicative of partial dissociation of the complex at the P=S—Pd^{2+} bond yielding form **1a** (Scheme 1).

Scheme 1



The IR spectrum of solid complex **2** in the region of P=S stretching vibrations has one band at 615 cm^{-1} corresponding to the structure with free P=S groups ($[S=P(CH_2)_2P—Pd—P(CH_2)_2P=S]Cl_2$). In the IR spectrum of this complex in $CHCl_3$, the band of noncoordinated P=S groups is shifted to 610 cm^{-1} due to hydrogen bonding between the P=S groups and the solvent. This is also confirmed by the fact that the IR

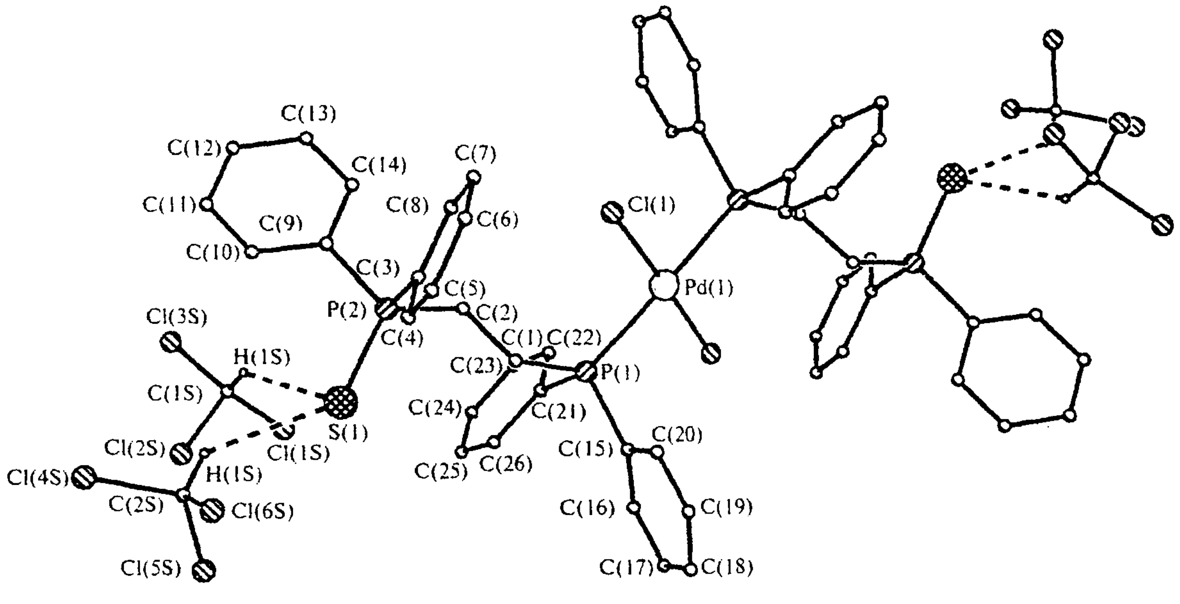


Fig. 3. Structure of the complex $Pd[Ph_2P(CH_2)_2P(S)Ph_2]_2Cl_2 \cdot 4CHCl_3$ (**2**).

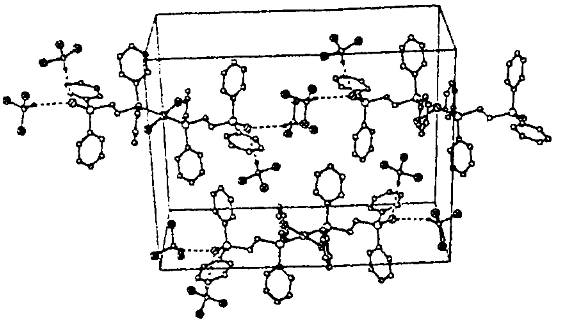


Fig. 4. Molecular packing in the crystals of **2**.

spectrum of the solution of **2** has an intense band at 3020 cm^{-1} in the region of C—H stretching vibrations. This band corresponds to the C—H groups of $CHCl_3$ molecules involved in hydrogen bonding with the P=S groups.[22]

The ^{31}P-{^{1}H} NMR spectrum of the free ligand in CH_2Cl_2 has two doublet signals at δ_P −12.6 (P^{III}) and 44.3 (P^V) with the spin-spin coupling constant J_{PP} = 49.7 Hz (Table 3). The signals for the P^{III} and P^V atoms in the NMR spectra of complexes **1** and **2** are shifted downfield, the shift of the signal for the P^{III} atom directly bound to the palladium atom ($\Delta\delta_P$ = 31.9—32.0) being substantially larger than that for the P^V atom ($\Delta\delta_P$ = 0.7). The shifts of the signals for the P^{III} and P^V atoms in the spectra of complexes **1** and **2** are virtually identical, which. is, apparently, attributable to rapid ligand exchange between the complexes in solution.

The reaction of complex **2** with $AgNO_3$ afforded cationic chelate complex **4**:

$$Pd(L_2)Cl_2 + 2\ AgNO_3 \rightarrow [Pd(L_2)]^{2+}\ 2NO_3^- + 2\ AgCl$$

2 **4**

The ^{31}P NMR spectrum of complex **4** in $CHCl_3$ has two signals for the P^{III} atoms at δ 26.0 and 20.8 (the intensity ratio is 1.5 : 1.0), which can be assigned to *cis* and *trans* isomers **4a** and **4b**, respectively, and one signal for P^V at δ 42.3 ($\Delta\delta_P$ = −2.1). In this spectrum, the splitting of the signals is absent, which may be attributed to the ligand exchange in the complex, which is, in particular, evidenced by broadening of the signals for the P^{III} and P^V atoms.

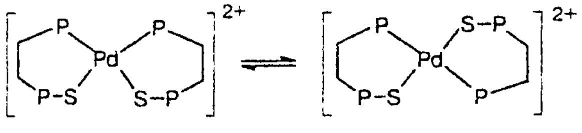
Table 3. ^{31}P-{^{1}H} NMR spectra (δ) of the **L** ligand and complexes **1**, **2**, and **4**

Compound	Solvent	δP^{III}	$\Delta\delta$	δP^V	$\Delta\delta$	J_{PP}/Hz
L	CH_2Cl_2	−12.6	—	44.3	—	49.7
1	CH_2Cl_2	19.3	31.9	45.0	0.7	26.7
2	CH_2Cl_2	19.4	32.0	45.0	0.7	26.8
4a	$CHCl_3$	26.0	38.6	42.3	−2.1	—
4b	$CHCl_3$	20.8	33.4	42.3	−2.1	—

The IR spectrum of solid complex **4** has an absorption band at 580 cm^{-1} corresponding to vibrations of coordinated P=S groups. This band in the spectrum of a solution of complex **4** in $CHCl_3$ is split into two bands at 585 and 575 cm^{-1}, which may also be indicative of the formation of the *cis* and *trans* isomers in the solution. The intense band at 1370 cm^{-1} in the spectra of solid complex **4** and of a solution of **4** in $CHCl_3$ is assigned to the free NO_3 group.[23] Of note is the strong shift of the P=S band to the low-frequency region characteristic of the single P—S bond (560—570 cm^{-1}).[24] In the spectrum of the structurally similar cationic chelate complex with P=O groups,[25] *viz.*, $[Pd(Ph_2P(O)CH_2P(O)Ph_2)_2]^{2+}$ $2PF_6^-$, the bands of the P=O groups are also substantially shifted to the low-frequency region (to 1130—1120 cm^{-1}). The IR spectrum of complex **4** in $CHCl_3$ has an intense band at ~3010 cm^{-1} in the region of CH stretching vibrations. This band may be assigned to the shifted band at 3024 cm^{-1} corresponding to the C—H groups of $CHCl_3$[22] involved in hydrogen bonding with NO_3^-. The IR spectrum of solid complex **4** has a broad band at ~3440 cm^{-1} in the region of OH vibrations and a band $\delta(H_2O)$ at 1640 cm^{-1} of coordinated water molecules.

The data from ^{31}P NMR and IR spectroscopy suggest that an equilibrium between the *cis* and *trans* forms exists in a solution of complex **4** in $CHCl_3$ (Scheme 2).

Scheme 2



4a **4b**

Thus, the reaction of $Ph_2P(CH_2)_2P(S)Ph_2$ with $PdCl_2$ afforded complexes whose structures depend on their compositions and the nature of the anions at the Pd atom. Complex **1** (1 : 1) has a chelate structure. In complex **2** (1 : 2), only the P^{III} atoms are coordinated and the free P—S groups are solvated by $CHCl_3$ molecules. The reaction of complex **2** with $AgNO_3$ gave cationic chelate complex **4**.

Experimental

The $Ph_2P(CH_2)_2P(S)Ph_2$ ligand was synthesized as described earlier.[26] The IR spectra of the complexes in KBr pellets and in solutions in $CHCl_3$ and CH_2Cl_2 (l = 0.07 mm, C = 0.2 mol L^{-1}) were measured on a UR-20 spectrophotometer (400—3700 cm^{-1}). The ^{31}P-{^{1}H} NMR spectra were recorded on Bruker WP-200 SY and Bruker AMX-400 instruments (operating at 81.01 and 162.02 MHz, respectively) with 85% H_3PO_4 as the external standard; the concentrations of the solutions were 0.1—0.2 mol L^{-1}.

Synthesis of the complex palladium {[2-(diphenylphosphino)ethyl]diphenylphosphine sulfide-S,P'}dichloride, $Pd[Ph_2P(CH_2)_2P(S)Ph_2]Cl_2$ (1). The ligand (0.102 g, 0.2369 mmol) was dissolved in MeCN (8 mL) and then $PdCl_2$ (0.042 g, 0.2369 mmol) was added to the solution. After 24 h, $PdCl_2$ dissolved and orange crystals precipitated. The crystals were isolated and dried *in vacuo*. Complex **1** was obtained in a yield of 0.111 g (77%). Found (%): C, 51.2; H, 3.9; P, 9.5. $C_{26}H_{24}Cl_2P_2PdS$. Calculated (%): C, 51.4; H, 3.9; P, 10.2.

Synthesis of the complex palladium bis{[2-(diphenylphosphino)ethyl]diphenylphosphine sulfide-S,P'}dichloride, $Pd[Ph_2P(CH_2)_2P(S)Ph_2]_2Cl_2 \cdot 4CHCl_3$ (2). The ligand (0.102 g, 0.2369 mmol) was dissolved in $CHCl_3$ (8 mL) and then $PdCl_2$ (0.021 g, 0.1184 mmol) was added to the solution. After one day, orange crystals precipitated. These crystals were isolated and dried *in vacuo*. Complex **2** was obtained in a yield of 0.0983 g (80%). The solvate molecules were removed by heating *in vacuo*. Found (%): C, 60.7; H, 5.1; Cl, 7.1. $C_{52}H_{48}Cl_2P_4PdS_2$. Calculated (%): C, 60.2; H, 4.7; Cl, 6.8.

Synthesis of the complex palladium bis{[2-(diphenylphosphino)ethyl]diphenylphosphine sulfide-S,P'}dinitrate, $[Pd(Ph_2P(CH_2)_2P(S)Ph_2)_2]^{2+}\ 2NO_3^- \cdot 4H_2O$ (4). Complex **2** (0.1015 g, 0.0977 mmol) was dissolved in $CHCl_3$ (4 mL) with gentle heating and then a solution of $AgNO_3$ (0.0332 g, 0.1954 mmol) in MeCN (5 mL) was added. The white precipitate of AgCl that formed was filtered off. Anhydrous ether was added to the filtrate until an orange precipitate formed. Complex **4** was obtained in a yield of 0.105 g (78%). Found (%): N, 2.7; P, 10.2. $C_{52}H_{56}N_2O_{10}P_4PdS_2$. Calculated (%): N, 2.4; P, 10.6.

X-ray diffraction studies of complexes 1 and 2. Crystals of complex **1** were prepared by crystallization from acetonitrile. Crystals of complexes **2** and **2a** were isolated from chloroform. The experimental X-ray intensity data sets were collected on four-circle automated diffractometers (see Table 1). The structures were solved by direct methods. All nonhydrogen atoms were located from difference electron density syntheses. The positions of the hydrogen atoms of complexes **1** and **2** were located from difference electron density syntheses. The positions of the hydrogen atoms in complex **2a** were calculated geometrically. The Cl atoms of disordered solvate molecules in the structure of **2a** were refined with occupancies of 0.5. The atomic coordinates and the temperature factors were refined based on F^2_{hkl} by the least-squares method (by the full-matrix method for the structures of **1** and **2** and by the block-diagonal method for **2a**) with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms for complexes **1** and **2** (for **2a**, the H atoms were refined using the riding model). All calculations were carried out with the use of the SHELXTL PLUS 5 program package.[27]

The crystallographic parameters and details of X-ray diffraction studies and structure refinement are given in Table 1. Selected bond lengths and bond angles for complexes **1** and **2** are listed in Table 2.

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