The Palladium Complexes $[Ph_3(cyclo\text{-}C_3H_5)P]_2^+ [PdBr_4]^{2-}$, $[Ph_3(cyclo\text{-}C_3H_5)P]_2^+ [Pd_2Br_6]^{2-}$, and $[Ph_3(cyclo\text{-}C_3H_5)P]^+[PdBr_3(DMSO)]^-$: Synthesis and Structures

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Received December 15, 2014

Abstract—A reaction of palladium dibromide with HBr and (cyclopropyl)(triphenyl)phosphonium bromide in water followed by recrystallization from acetonitrile or DMF afforded the complexes $[Ph_3(cyclo\text{-}C_3H_5)P]_2^+ [PdBr_4]^{2-}$ (**I**) and $[Ph_3(cyclo\text{-}C_3H_5)P]_2^+ [Pd_2Br_6]^{2-}$ (**II**). Recrystallization of complexes **I** and **II** from DMSO gave $[Ph_3(cyclo\text{-}C_3H_5)P]^+[PdBr_3(DMSO)]^-$ (**III**). According to X-ray diffraction data, the P−C bond lengths in the tetrahedral (cyclopropyl)(triphenyl)phosphonium cations of complexes **I**–**III** are 1.773(5)−1.802(5) (**I**), 1.778(5)−1.802(5) (**II**), 1.767(5)−1.797(5) Å (**III**); the angles CPC are 107.4(2)°−111.1(2)° (**I**), 107.2(2)°−111.2(2)° (**II**), and 108.4(2)°−110.5(2)° (**III**), and (CIF file CCDC no. 999905 (**I**), 1035313 (**II**), 999907 (**III**)). In the square anions $[PdBr_4]^{2-}$, the Pd−Br bond length is 2.4333(5)−2.4459(5) Å. In the planar centrosymmetric dinuclear anions $[Pd_2Br_6]^{2-}$, the bond lengths Pd−Br$_{brid}$ and Pd−Br$_{term}$ are 2.4559(7), 2.4600(7) and 2.3952(7), 2.4045(8) Å; the angles PdBrPd and Br$_{term}$PdBr$_{term}$ are 92.57(2)° and 91.98(3)°, respectively. In the square anions $[PdBr_3(DMSO)]^-$, the DMSO molecule is coordinated by the Pd atom through the sulfur atom (Pd−Br, 2.3986(7)−2.4288(6) Å; Pd−S, 2.2633(13) Å).

INTRODUCTION

Reactions of PdI_2 with (alkyl)(triphenyl)phosphonium iodides in the presence of HI are known to yield ionic palladium complexes $[Ph_3P(Alk)]_2^+[Pd_2I_6]^{2-}$ (Alk = C_2H_5 or C_5H_{11}); their recrystallization from DMSO does not result in reconstruction of the dinuclear anion [1]. However, recrystallization of bromine-containing palladium complexes of this type, $[Ph_3P(Alk)]_2^+[Pd_2Br_6]^{2-}$ (Alk = $cyclo\text{-}C_5H_9$, C_4H_9, or C_5H_{11}), from DMSO is accompanied by transformation of the dinuclear anions $[Pd_2Br_6]^{2-}$ into the mononuclear anions $[PdBr_3(DMSO)]^-$ containing a solvent molecule in the coordination sphere of the Pd atom [2].

Continuing our investigations of reactions between palladium halides and onium compounds of Group 15 elements, here we studied a reaction of $PdBr_2$ with (cyclopropyl)(triphenyl)phosphonium bromide in water in the presence of HBr and determined the structures of the complexes obtained upon recrystallization of the reaction product from acetonitrile, DMF, and DMSO.

EXPERIMENTAL

Synthesis of $[Ph_3(cyclo\text{-}C_3H_5)P]_2^+ [PdBr_4]^{2-}$ (I). Palladium dibromide (0.15 g, 0.56 mmol) was dissolved in 48% HBr (2 mL). Then a solution of (cyclopropyl)(triphenyl)phosphonium bromide (0.431 g, 1.12 mmol) in hot water (20 mL) was added with stirring. The red-brown precipitate that formed was collected by filtration, dried, and recrystallized from acetonitrile to give red-brown crystals of complex **I**. The yield was 0.58 g (99%), $T_{decomp} = 233°C$.

For $C_{42}H_{40}P_2Br_4Pd$

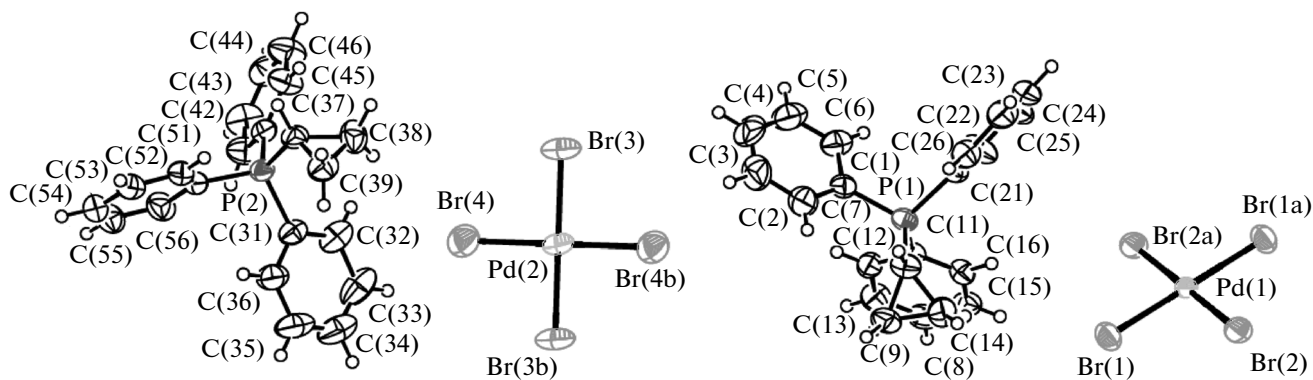|		
anal. calcd., %:	C, 48.82;	H, 3.87.
Found, %:	C, 48.76;	H, 3.94.

Fig. 1. Structure **I**.

IR (ν, cm^{-1}): 3076, 3050, 3020, 2994, 1585, 1479, 1436, 1338, 1314, 1297, 1191, 1160, 1114, 1077, 1055, 1023, 995, 894,865, 842, 797, 787, 772, 750, 726, 689, 662, 525, 498.

Synthesis of [Ph$_3$(*cyclo*-C$_3$H$_5$)P]$_2^+$[Pd$_2$Br$_6$]$^{2-}$ (II). Palladium dibromide (0.15 g, 0.56 mmol) was dissolved in 48% HBr (2 mL). Then a solution of (cyclopropyl)(triphenyl)phosphonium bromide (0.431 g, 1.12 mmol) in hot water (20 mL) was added with stirring. The red-brown precipitate that formed was collected by filtration, dried, and recrystallized from DMF to give red-brown crystals of complex **I** (0.313 g, 54%) with T_{decomp} = 233°C and red crystals of complex **II** (0.167 g, 46%) with T_{decomp} = 239°C.

For C$_{42}$H$_{40}$P$_2$Br$_6$Pd$_2$

anal. calcd., %:	C, 38.82;	H, 3.08.
Found, %:	C, 39.57;	H, 3.14.

IR (ν, cm^{-1}): 3075, 3051, 3020, 2993, 1586, 1479, 1437, 1337, 1315, 1298, 1192, 1161, 1115, 1078, 1055, 1024, 996, 895,865, 843, 798, 787, 773, 752, 726, 688, 663, 526, 497.

Synthesis of [Ph$_3$(*cyclo*-C$_3$H$_5$)P]$^+$[PdBr$_3$(DMSO)]$^-$ (III). Complexes **I** and **II** were dissolved in DMSO. Removal of the solvent from both solutions resulted in the formation of red-brown crystals of complex **III** (T_{decomp} = 129°C).

For C$_{23}$H$_{26}$OSPBr$_3$Pd

anal. calcd., %:	C, 37.94;	H, 3.57.
Found, %:	C, 37.87;	H, 3.64.

IR (ν, cm^{-1}): 3053, 2984, 1587, 1482, 1437, 1340, 1316, 1292, 1193, 1163, 1115, 1072, 1051, 1020, 996, 964, 928, 894, 864, 835, 791, 748, 724, 690, 662, 527, 494, 460, 421.

The IR spectra of complexes **I**–**III** were recorded on a Bruker Tensor 27 spectrometer (KBr pellets) in the 4000–400 cm^{-1} range.

Single-crystal X-ray diffraction study of complexes **I**–**III** was carried out on a D8 QUEST automated four-circle diffractometer (Bruker) (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Crystallographic data were collected and edited, the unit cell parameters were refined, and an absorption correction was applied with the SMART and SAINT-Plus programs [3]. All calculations for structure determination and refinement were performed with the SHELXL/PC [4] and OLEX2 programs [5]. Structures **I**–**III** were determined by the direct methods and refined anisotropically (for non-hydrogen atoms) by the least-squares method.

Crystallographic parameters and the data collection and refinement statistics for structures **I**–**III** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. Structures **I**–**III** are shown in Figs. 1–3, respectively.

Comprehensive tables of the atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Structural Database (nos. 999905 (**I**), 1035313 (**II**), and 999907 (**III**); deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

We found that PdBr$_2$ reacts with HBr and (cyclopropyl)(triphenyl)phosphonium bromide in water to give a finely divided red-brown precipitate. The latter was recrystallized from different solvents.
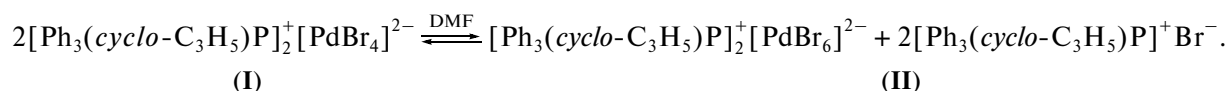
Recrystallization from acetonitrile afforded red-brown crystals of complex **I**.

The use of *N,N*-dimethylformamide resulted in simultaneous formation of red-brown crystals of complex **I** (54%) and red crystals of complex **II** containing a dinuclear anion, [Ph$_3$(*cyclo*-C$_3$H$_5$)P]$_2^+$[Pd$_2$Br$_6$]$^{2-}$ (46%).

Table 1. Crystallographic parameters and the data collection and refinement statistics for structures **I–III**

Parameter	Value		
	I	**II**	**III**
M	1032.72	649.47	727.60
T, K	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	16.9473(7)	9.8998(3)	7.8468(3)
b, Å	14.6610(6)	13.5984(5)	11.9501(5)
c, Å	18.2161(8)	16.5995(6)	14.4043(5)
α, deg	90.00	90.00	85.1730(10)
β, deg	117.0800(10)	94.0650(10)	88.6780(10)
γ, deg	90.00	90.00	78.0520(10)
V, Å^3	4029.9(3)	2229.03(13)	1316.72(9)
Z	4	4	2
ρ_{calcd}, g/cm^3	1.702	1.935	1.835
μ, mm^{-1}	4.535	6.285	5.410
$F(000)$	2032.0	1248.0	708.0
Crystal dimensions, mm	$0.47 \times 0.38 \times 0.17$	$0.29 \times 0.28 \times 0.12$	$0.75 \times 0.56 \times 0.47$
θ scan range, deg	6.08–52.88	5.54–53.6	6.24–52.98
Ranges of h, k, and l indices	$-21 \leq h \leq 21$, $-18 \leq k \leq 18$, $-22 \leq l \leq 22$	$-12 \leq h \leq 12$, $-17 \leq k \leq 17$, $-21 \leq l \leq 21$	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$
Number of measured reflections	73 900	41 015	17 215
Number of unique reflections (R_{int})	8271 (0.0636)	4755 (0.0384)	4930 (0.0270)
Number of parameters refined	445	235	273
GOOF	1.017	1.043	1.034
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0433$, $wR_2 = 0.1063$	$R_1 = 0.0425$, $wR_2 = 0.1155$	$R_1 = 0.0423$, $wR_2 = 0.1059$
R factors for all reflections	$R_1 = 0.0661$, $wR_2 = 0.1184$	$R_1 = 0.0602$, $wR_2 = 0.1303$	$R_1 = 0.0525$, $wR_2 = 0.1132$
Residual electron density (min/max), e/A^3	1.96/−0.99	2.58/−0.68	0.90/−1.11

Complexes **I** and **II** can be assumed to be in dynamic equilibrium in solutions:

$$2[Ph_3(cyclo\text{-}C_3H_5)P]_2^+[PdBr_4]^{2-} \xrightleftharpoons{DMF} [Ph_3(cyclo\text{-}C_3H_5)P]_2^+[PdBr_6]^{2-} + 2[Ph_3(cyclo\text{-}C_3H_5)P]^+Br^-.$$

$$\textbf{(I)} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{(II)}$$

Shift of the equilibrium toward complex **I** or **II** depends on the solvent. For instance, complex **I** dominates in acetonitrile.

We found that dissolution of complexes **I** and **II** in DMSO is accompanied by ligand exchange resulting in transformation of the anions and introduction of a DMSO molecule into the coordination sphere of the Pd atom, ultimately giving complex **III**.
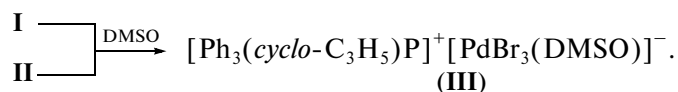
$$\begin{matrix} \textbf{I} \\ \textbf{II} \end{matrix} \xrightarrow{DMSO} [Ph_3(cyclo\text{-}C_3H_5)P]^+[PdBr_3(DMSO)]^-.$$
$$\textbf{(III)}$$

Table 2. Selected bond lengths d and bond angles ω in structures **I–III***

Bond	d, Å	Angle	ω, deg
		I	
P(1)–C(1)	1.793(5)	C(1)P(1)C(21)	107.6(2)
P(1)–C(11)	1.791(4)	C(11)P(1)C(1)	109.7(2)
P(1)–C(7)	1.766(5)	C(11)P(1)C(21)	110.2(2)
P(1)–C(21)	1.798(5)	C(7)P(1)C(1)	109.4(2)
P(2)–C(31)	1.802(5)	C(7)P(1)C(11)	109.1(2)
P(2)–C(51)	1.795(5)	C(7)P(1)C(21)	110.9(2)
P(2)–C(37)	1.773(5)	C(51)P(2)C(31)	107.4(2)
P(2)–C(41)	1.795(5)	C(51)P(2)C(41)	111.1(2)
Pd(1)–Br(1)	2.4459(5)	C(37)P(2)C(31)	110.6(2)
Pd(1)–Br(2)	2.4333(5)	C(37)P(2)C(51)	108.9(2)
Pd(2)–Br(3)	2.4362(5)	C(37)P(2)C(41)	109.6(2)
Pd(2)–Br(4)	2.4431(7)	C(41)P(2)C(31)	109.2(2)
		II	
Pd(1)–Br(1)	2.4559(7)	Br(1)Pd(1)Br(1a)	87.43(2)
Pd(1)–Br(2)	2.4045(8)	Br(2)Pd(1)Br(1)	90.86(3)
Pd(1)–Br(3)	2.3952(7)	Br(3)Pd(1)Br(1)	176.28(3)
P(1)–C(1)	1.794(5)	Br(3)Pd(1)Br(2)	91.98(3)
P(1)–C(21)	1.802(5)	C(1)P(1)C(21)	107.2(2)
P(1)–C(11)	1.786(5)	C(11)P(1)C(1)	110.7(2)
P(1)–C(31)	1.778(5)	C(11)P(1)C(21)	110.1(2)
		C(31)P(1)C(1)	111.2(2)
		C(31)P(1)C(21)	108.9(2)

* The symmetry operation codes are (a) $1 - x$, $1 - y$, $-z$.

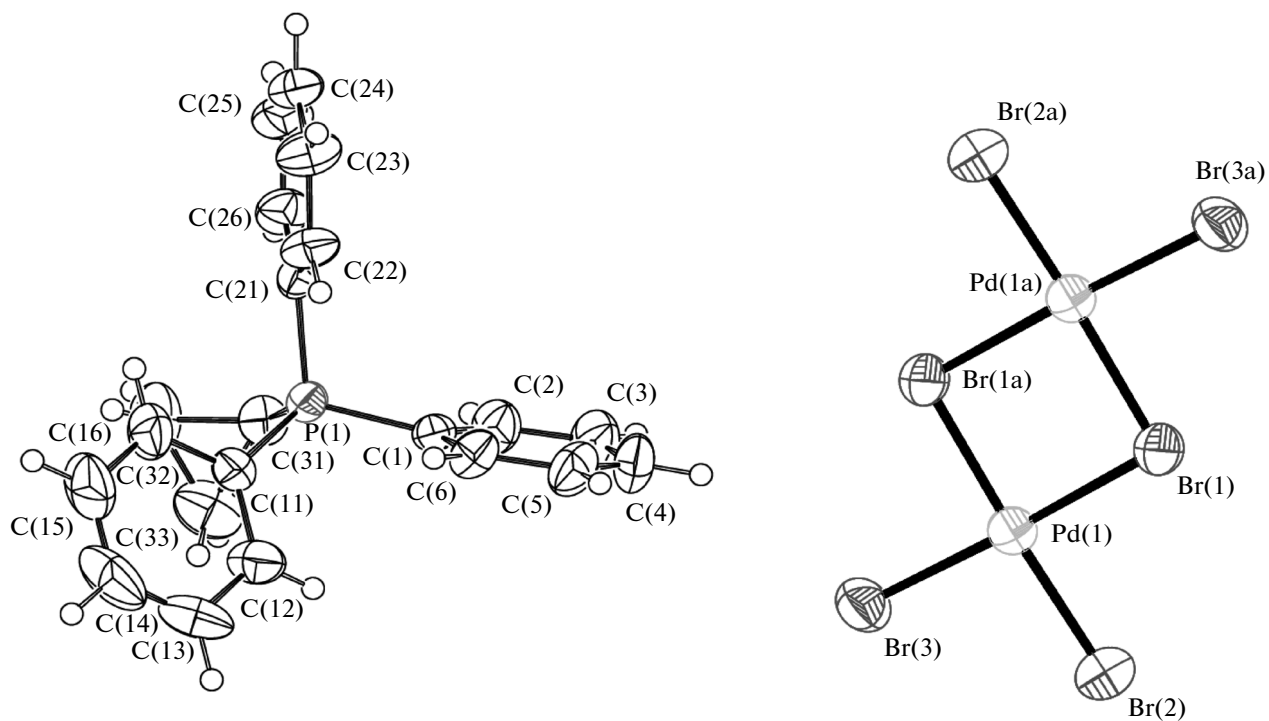| Bond	d, Å	Angle	ω, deg
		III	
P(1)–C(1)	1.797(5)	C(11)P(1)C(1)	109.7(2)
P(1)–C(11)	1.791(5)	C(17)P(1)C(1)	109.8(3)
P(1)–C(17)	1.767(5)	C(17)P(1)C(11)	108.4(2)
P(1)–C(21)	1.791(4)	C(17)P(1)C(21)	110.5(2)
Pd(1)–Br(1)	2.4288(6)	C(21)P(1)C(1)	108.5(2)
Pd(1)–Br(2)	2.3986(7)	C(21)P(1)C(11)	109.9(2)
Pd(1)–S(1)	2.2633(13)	Br(2)Pd(1)Br(1)	89.07(3)
Pd(1)–Br(3)	2.4222(7)	Br(2)Pd(1)Br(3)	176.61(4)
S(1)–C(8)	1.732(9)	S(1)Pd(1)Br(1)	179.22(4)
S(1)–O(1)	1.410(5)	S(1)Pd(1)Br(2)	90.36(4)
S(1)–C(7)	1.706(10)	Br(3)Pd(1)Br(1)	89.86(3)

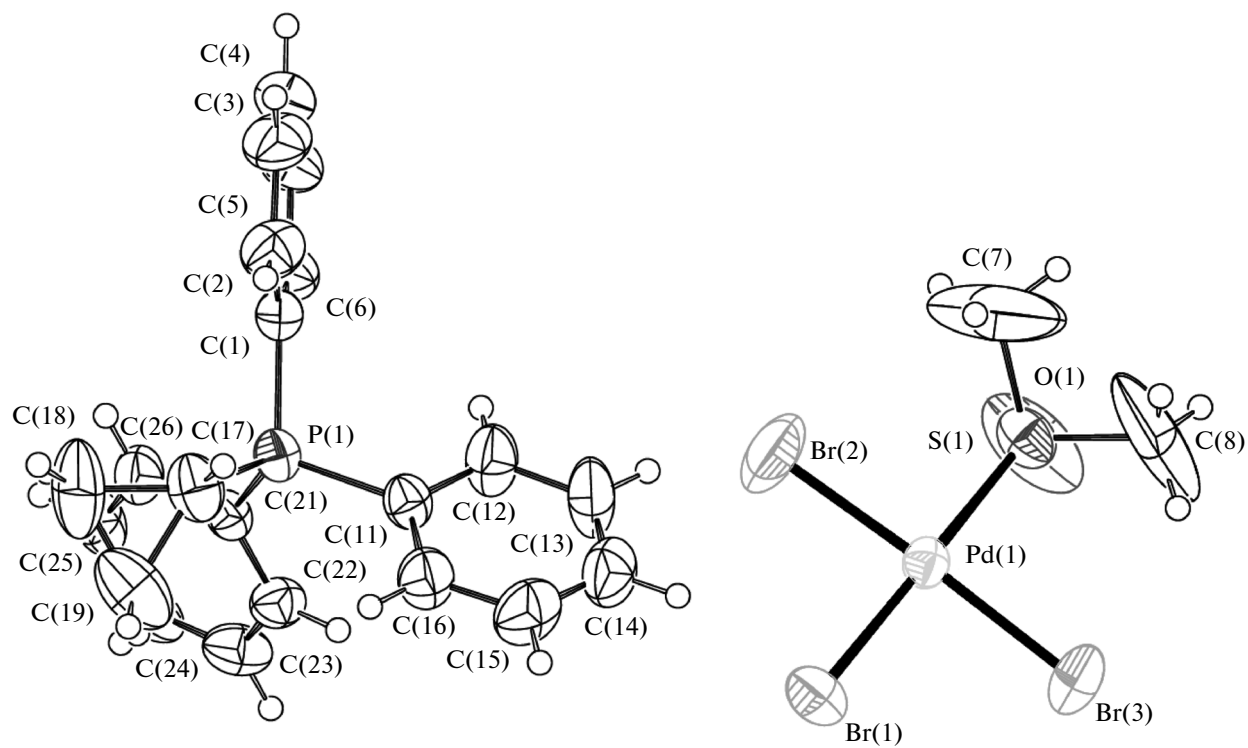**Fig. 2.** Structure **II**.

Fig. 3. Structure **III**.
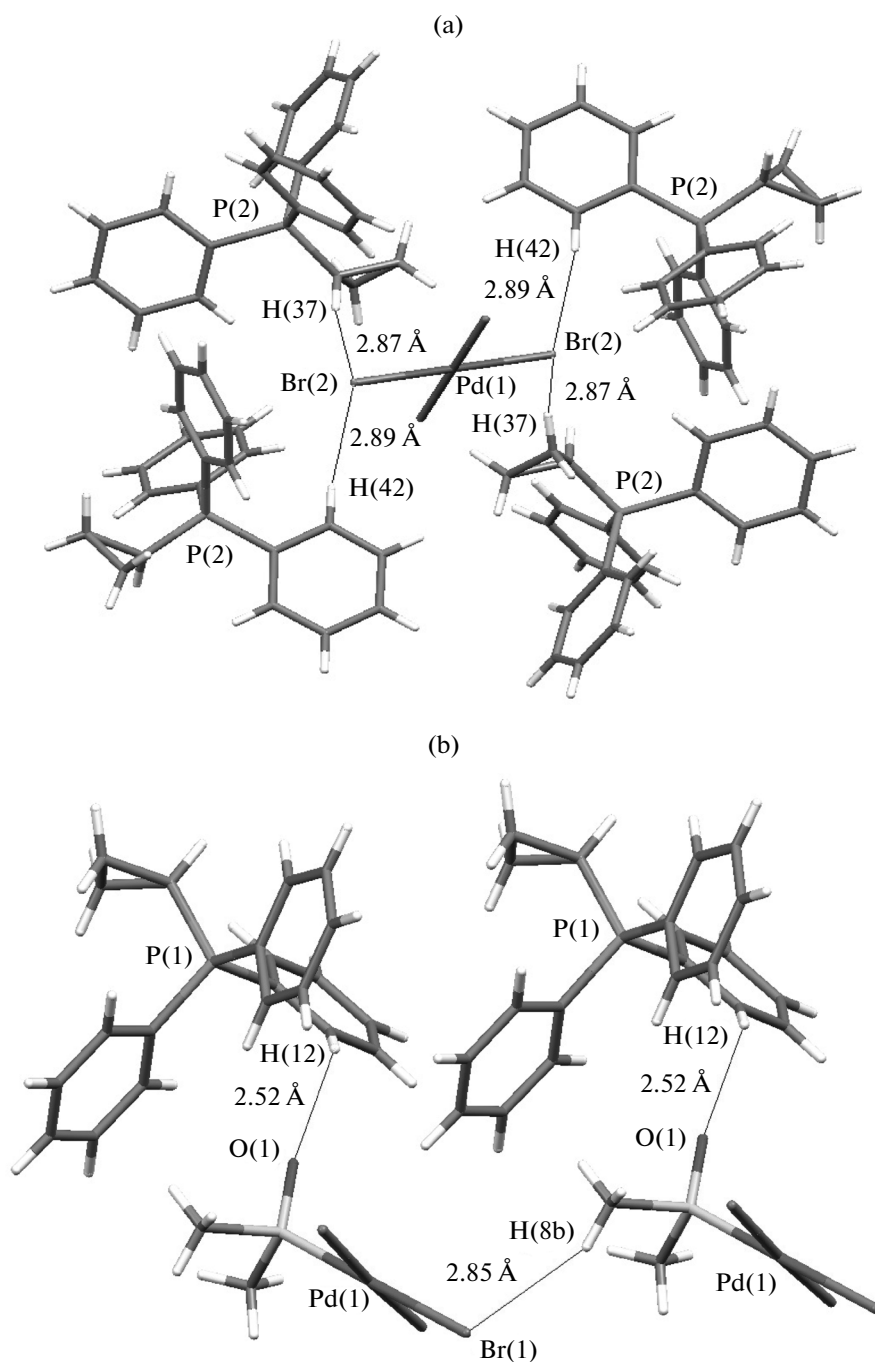
(a)

(b)

Fig. 4. Hydrogen bonding patterns in the crystals of complexes **I** (a) and **III** (b).

The crystals of complex **I** consist of two types of crystallographically independent cations and anions, both with only slightly differing geometrical parameters. The tetrahedral configuration of the cations in structures **I**–**III** is virtually undistorted. The bond angles CPC (107.4(2)°–111.1(2)° in 107.2(2)°–111.2(2)° in **II**, and 108.4(2)°–110.5(2)° in **III**) differ little from the theoretical value. The P–C bond

lengths are close to each other (1.773(5)–1.802(5) Å in **I**, 1.706(10)–1.797(5) Å in **II**, and 1.767(5)–1.797(5) Å in **III**). In all the cations, the P–C(*cyclo*-C_3H_5) bonds are shorter than the P–C(Ph) bonds. In the centrosymmetric square anions $[PdBr_4]^{2-}$, the Pd(1)–Br(1,2) (2.4459(5) and 2.4333(5) Å) and Pd(2)–Br(3,4) bond lengths (2.4362(5) and 2.4431(7) Å) are close to each other. The *cis*-angles BrPd(1)Br

$(89.642(18)°, 90.358(18)°)$ and $BrPd(2)Br$ $(90.46(2)°,$ $89.54(2)°)$ approximate to a theoretical value of $90°$. In the planar centrosymmetric dinuclear anions $[Pd_2Br_6]^{2-}$, the $Pd-Br_{brid}$ and $Pd-Br_{term}$ bond lengths are $2.4559(7)$, $2.4600(7)$ and $2.3952(7)$, $2.4045(8)$ Å; the angles $PdBrPd$ and $Br_{term}PdBr_{term}$ are $92.57(2)°$ and $91.98(3)°$, respectively. In the anions $[PdBr_3(DMSO)]^-$, the angles $BrPdBr$ $(89.07(3)°$ and $89.86(3)°)$ are somewhat smaller than the angles $SPdBr$ $(90.36(4)°$ and $90.67(4)°)$. The $Pd-Br$ bond lengths are $2.4288(6)$, $2.3986(7)$, and $2.4222(7)$ Å. The DMSO ligands are coordinated to the Pd atom through the sulfur atom. The $Pd-S$ bond length $(2.2633(13)$ Å$)$ is shorter than the sum of the covalent radii of the Pd and S atoms $(2.34$ Å $[6])$. The plane of the square $[Br_3S]$ is rotated in such a way that the substituents at the $Pd-S$ bond adopt the most favorable "staggered" conformation.

Structure **I** in the crystal is stabilized by interionic hydrogen bonds involving the Br atoms and the H atoms of the cyclopropyl and phenyl substituents (Fig. 4a).

The crystal of complex **II** shows supporting contacts between the phenyl and cyclopropyl H atoms in the cations and the Br atoms of the anions ($H\cdots Br$ $2.96-3.00$ Å). In the crystal of complex **III**, the hydrogen bonds $C-H\cdots Br$ and $C-H\cdots O$ involve the DMSO ligands and the phenyl H atoms of the cations (Fig. 4b).

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Translated by D. Tolkachev