Palladium(I) and palladium(0) carbonyl bromide complexes

A. V. Kulik,[a]* O. N. Temkin,[a] L. G. Bruk,[a] V. E. Zavodnik,[b] V. K. Belsky,[b] and V. V. Minin[c]

[a]M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation.
E-mail: alkulik@gmail.com
[b]L. Ya. Karpov Institute of Physical Chemistry,
10 ul. Vorontsovo Pole, 105064 Moscow, Russian Federation.
Fax: +7 (095) 975 2450
[c]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 955 4835

New Pd^I and Pd^0 carbonyl bromide complexes co-existing in the same crystal were synthesized and studied by X-ray diffraction analysis. The crystals consist of dimeric complex anions composed of the central $Pd(\mu\text{-}CO)_2Pd$ fragment and four partially disordered terminal ligands (CO and Br^-). The complexes were characterized by IR, ESR, and X-ray photoelectron spectroscopy.

Key words: palladium carbonyl complexes, palladium(0), palladium(I), palladium bromide complexes.

Low-oxidation state palladium carbonyl halide complexes have attracted interest because they serve as catalysts for reactions of carbon monoxide.[1—3]

To our knowledge, the first carbonyl halide compound has been prepared[4] by passing CO saturated with MeOH vapor through a $PdCl_2$ suspension.

Before we started this study, the structures of the palladium(II) carbonyl bromide and chloride complexes, *viz.*, $Bu_4N[PdBr_3CO]$ and $Bu_4N[PdCl_3CO]$,[5] respectively, and palladium(I) carbonyl chloride complexes, $(R_4N)_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ (R = Bu,[6] H [7]) and $Pd_2(\mu\text{-}Cl)_2(CO)_4$,[8] have been studied by X-ray diffraction. The structure of the carbonyl bromide complexes $[Pd_2(\mu\text{-}CO)_2Br_4]^{2-}$ was proposed based on the IR spectroscopic and elemental analysis data.[9,10] The Pd^{II} carbonyl iodide complexes have been characterized only by IR spectroscopy ($\nu(C{=}O) \approx 2112\ cm^{-1}$) and the amount of CO eliminated upon decomposition of the carbonyl complex with triphenylphosphine.[5] Information on the structures of Pd^0 carbonyl halide complexes is lacking.

Since Pd^I bromide complexes exhibit high catalytic activity in carbonylation of acetylene giving rise to succinic and maleic anhydrides and succinic and maleic acid diesters,[11,12] oxidative carbonylation of phenol and acetylene yielding diphenyl carbonate and maleic anhydride, respectively,[13] and coupled oxidation of CO and H_2O to CO_2 and H_2O_2, respectively,[14] and taking into account that the mechanisms of these processes have attracted attention, it was of interest to synthesize a Pd^I carbonyl bromide complex, elucidate its structure, and compare the structural features and catalytic properties of related chloride and bromide complexes. The initial aim of the present study was to synthesize the Pd^I carbonyl bromide complex and investigate its structure.

Carbonylation of tetrahalopalladates in solutions of the corresponding hydrohalic acids is most widely used for the synthesis of Pd^I carbonyl halide complexes.[7,9,10,15] However, in this case, there are difficulties associated with investigation of solutions of complexes in hydrohalic acids by spectroscopic methods and with their use (without isolation) as precursors for the synthesis of catalysts. Of organic solvents, THF is a solvent of choice for the synthesis of Pd^I complexes. In a THF solution, Pd^{II} carbonyl complexes are rapidly produced, and it is convenient to control the reduction rate of these complexes by adding water. Tetrahydrofuran is also suitable for studying the structures of Pd^I carbonyl halide complexes by IR spectroscopy, because is allows the use of salt-optics cells. In addition, THF does not show intense absorption bands in the 1600—2200 cm^{-1} region, where absorption bands of coordinated carbonyl ligands are observed.

The general structural feature of palladium carbonyl halide complexes is the dependence of the coordination mode of the carbonyl group (terminal or bridging) on the oxidation state of the metal atom.[1,2] Terminal coordination is observed in all known Pd^{II} carbonyl halide complexes. Palladium(I) carbonyl halide complexes involve only bridged carbonyl groups. The only exception is the

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$Pd_2(\mu\text{-}Cl)_2(CO)_4$ complex,[8] whose structure was not confirmed in other studies. A consideration of these characteristic features is of great importance for the preliminary discussion of the structures of carbonyl halide complexes based on analysis of their IR spectra.

Results and Discussion

The IR spectra of carbonylation products of THF solutions of lithium tetrachloropalladates show an absorption band belonging to complexes containing terminal carbonyl groups as ligands ($\nu \approx 2108$ cm^{-1}), after which absorption bands assigned to complexes containing bridging carbonyl groups ($\nu \approx 1913$ cm^{-1}) appear, and then the intensity ratio of the bands belonging to carbonyl groups in different coordination modes changes. After 6 h, only complexes with bridging carbonyl groups remain in solution (Fig. 1).

According to the published data[1] and taking into account an increase in the CO_2 concentration in the gas phase over the solution, it can be hypothesized that the change in the intensity ratio of the absorption bands of the bridging and terminal CO groups is associated with reduction of Pd^{II} carbonyl complexes (terminal carbonyl groups) to Pd^{I} complexes (bridging carbonyl groups) (Scheme 1).

After carbonylation of tetrabromopalladates for 20 min, the IR spectrum shows an absorption band belonging to complexes with terminal carbonyl groups ($\nu \approx 2106$ cm^{-1}). Subsequently, absorption bands of the bridging carbonyl group ($\nu \approx 1908$ cm^{-1}) appear, after which the intensity ratio of the bands slowly changes. This IR spectrum, unlike the spectra of chloropalladates, has bands of the bridging and terminal carbonyl groups with comparable intensities regardless of the duration of the reaction. Attempts to prepare solutions containing complexes with carbon monoxide ligands in only one of the possible coordination modes failed. Since palladium carbonyl halide complexes containing both terminal and bridging carbonyl groups were unknown, we initially hypothesized that the bromopalladate system, unlike the chloropalladate system, contains both Pd^{I} and Pd^{II} carbonyl complexes. Hence, we decided to prepare a Pd^{I} carbonyl bromide complex by synthesizing a Pd^{I} carbonyl chloride complex followed by the replacement of the chloride ligands with bromide ligands.

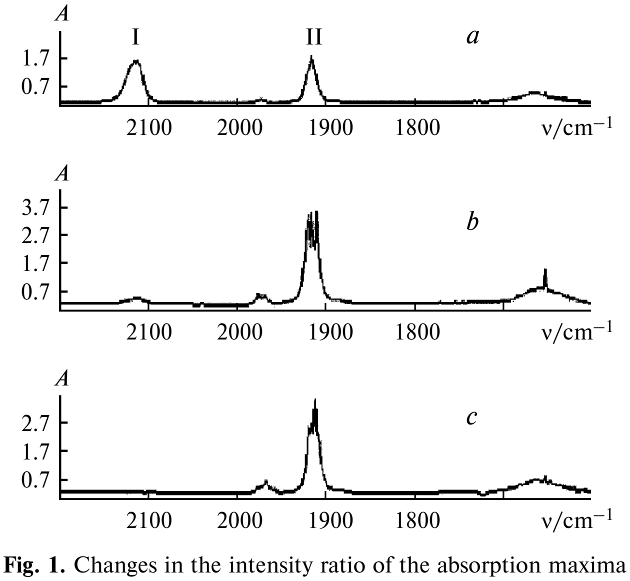
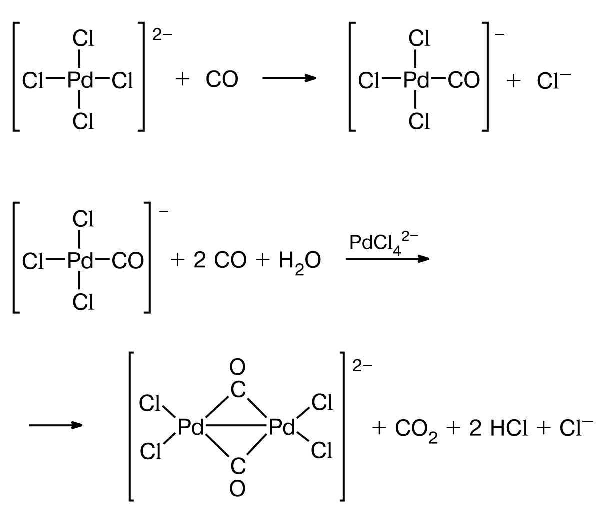


Fig. 1. Changes in the intensity ratio of the absorption maxima of the carbonyl groups in the IR spectra upon reduction of lithium tetrachloropalladate after 10 min (*a*), 4 (*b*), and 6 h (*c*). I is the absorption band assigned to vibrations of the terminal carbonyl group, and II is the absorption band assigned to vibrations of the bridging carbonyl groups.

Scheme 1



We studied the influence of the addition of Br^{-} ions to the presynthesized Pd^{I} carbonyl chloride complex by IR spectroscopy. The results of this study (Table 1) provided evidence that the absorption maxima of the terminal and bridging CO groups are shifted to longer wavelengths, which is generally observed in the spectra of palladium carbonyl bromide complexes compared to the spectra of the corresponding carbonyl chloride complexes.[5] However, this shift is nonmonotonic. After the addition of Br^{-} to $Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$, the absorption maximum is shifted from 1913 to 1905 cm^{-1}, and, after 48 h, it is shifted from 1905 to 1908 cm^{-1}. Upon the addition of Br^{-}, the shape of the absorption band of the coordinated carbonyl groups (Fig. 2) changes substantially with time, which may indicate that the solution contains several types of complexes with bridging ligands.

The change in the intensity ratio of the absorption maxima of the bridging carbonyl groups and the vibrations of the terminal carbonyl groups after the addition of LiBr (Fig. 3) could be attributable to the formation

Table 1. Absorption frequencies of coordinated carbonyl groups

System	Coordination mode			
	bridging		terminal	
	ν/cm^{-1}	A	ν/cm^{-1}	A
$Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$	1913	3.2619	2108	0.6997
$Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ + LiBr	1905	2.3845	2102	0.7259
$Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ + LiBr [a]	1907	3.1598	2105	1.2004
$Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ + LiBr [b]	1908	1.9084	2106	2.8568

[a] Within 24 h after the addition of LiBr.

[b] Within 48 h after the addition of LiBr.

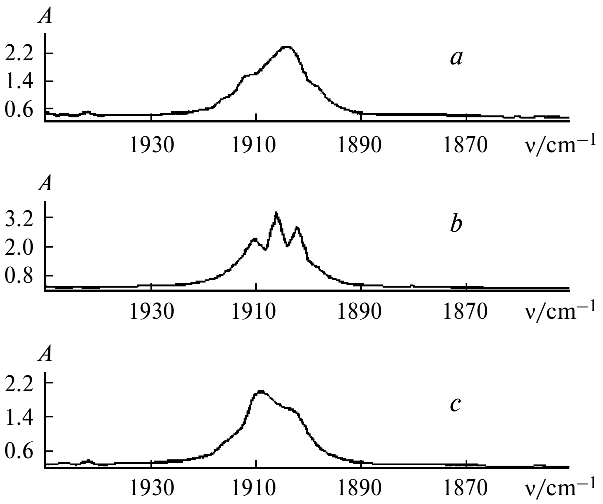


Fig. 2. Dynamics of changes in the peak shape of the vibration of the bridging carbonyl group in the IR spectra after the addition of LiBr to $Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$: after 20 min (*a*), 24 (*b*), and 48 h (*c*).

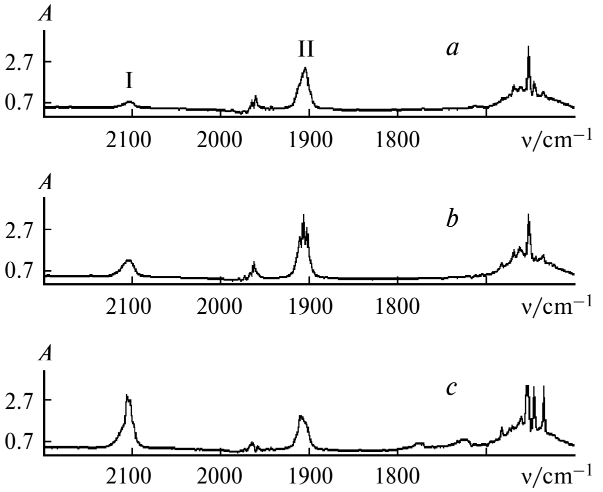


Fig. 3. IR spectra of a $Li_2[Pd_2(\mu\text{-}CO)_2Cl_4]$ solution within 20 min (*a*), 24 (*b*), and 48 h (*c*) after the addition of LiBr. For I and II, see the caption to Fig. 1.

of Pd^{II} carbonyl bromide complexes characterized by the presence of terminal CO groups. However, the formation of Pd^{II} carbonyl bromide complexes in a system, which contains only a Pd^{I} complex in the absence of an oxidizing agent and in which a solution is under an atmosphere of CO, can occur only due to disproportionation of Pd^{I} carbonyl bromide complexes (Scheme 2).

Scheme 2

$$[Pd_2(\mu\text{-}CO)_2Br_4]^{2-} \longrightarrow [PdBr_3CO]^- + Pd^0 + Br^- + CO$$

The formation of palladium black was not observed, which is evidence that Pd^0 is stabilized by the ligands and gives complexes containing terminal carbonyl groups.

Crystalline palladium carbonyl bromide complexes were synthesized according to three procedures, which differ primarily in the Br : Pd ratio and the time of addition of LiBr and bis(triphenylphosphine)iminium chloride (PPN^+Cl^-) (see the Experimental section). All these procedures afforded externally identical yellow crystals **1—3** characterized by different Br : Pd and Br : CO ratios (Table 2), which were determined by X-ray diffraction (see the Experimental section).

Study of the crystal structures of **1—3** by X-ray diffraction revealed the following important fact. All these crystal structures are composed of the dimeric complex anions $Pd_2Br_n(CO)_m{}^{2-}$ ($m + n = 6$) containing the $(Pd_2(\mu\text{-}CO)_2)$ fragment and the PPN^+ cations in a ratio of 1 : 2 regardless of the Br : CO ratio. The complex anion (Fig. 4) contains two palladium atoms, which are linked to each other through two carbonyl bridges, and four partially disordered terminal ligands (Br and CO), whose ratio depends on the conditions of the synthesis (see Table 2 and Fig. 4). The main geometric parameters and occupancies for the partially disordered ligands of the complexes prepared according to methods *1—3* are given in Tables 3 and 4.

Because of disorder of the terminal ligands (Br or CO), whose ratio depends on the conditions of the synthesis (see Table 2 and Fig. 4), it is impossible to unambiguously determine which ligand (Br or CO) occupies a particular terminal position in the coordination sphere of palladium. Attempts to model the Cl/(Br, CO) disorder led to an increase in the *R* factor up to 20%.

Table 2. Atomic ratios in the anions of the palladium carbonyl bromide complexes determined by X-ray diffraction study of single crystals **1—3**

Crystal	Br : Pd	CO : Pd	Br : CO	Br : CO_{term}
1	1.30	1.70	0.76	1.86
2	1.63	1.38	1.18	4.29
3	1.50	1.50	1.00	3.00

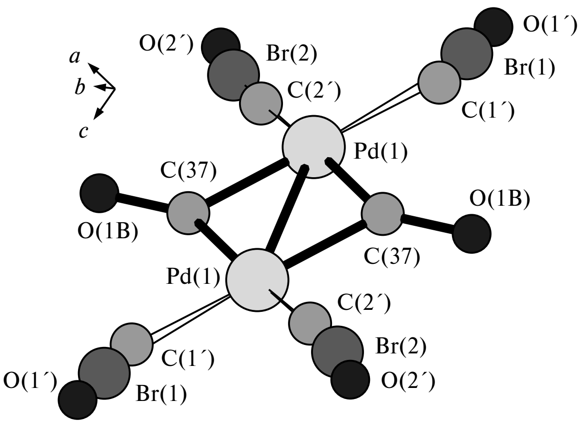


Fig. 4. Structure of the complex anion $Pd_2Br_n(CO)_m^{2-}$ ($m + n = 6$) containing partially disordered ligands.

Table 3. Principal interatomic distances (*d*) and bond angles (ω) in single crystals **1—3**

Parameter	1	2	3
Bond		*d*/Å	
Pd(1)—C(2′)	2.107(1)	2.107(1)	1.922(1)
Pd(1)—C(1′)	1.878(1)	1.890(1)	1.931(1)
Pd(1)—C(37)	1.939(13)	1.944(7)	1.951(5)
Pd(1)—C(37)$^{\#1}$	1.909(14)	1.962(7)	1.969(6)
Pd(1)—Br(1)	2.424(4)	2.444(2)	2.444(1)
Pd(1)—Br(2)	2.474(2)	2.488(1)	2.482(1)
Pd(1)—Pd(1)$^{\#1}$	2.674(2)	2.679(1)	2.681(1)
O(1A)—C(37)	1.20(3)	1.19(1)	1.17(1)
O(1B)—C(37)	1.33(2)	1.25(1)	1.25(1)
O(1′)—C(1′)	1.20(3)	0.87(2)	1.04(1)
O(2′)—C(2′)	1.28(1)	0.84(2)	1.09(1)
Angle		ω/deg	
Br(1)—Pd(1)—Br(2)	93.3(1)	93.27(6)	93.30(3)
Br(2)—Pd(1)—Pd(1)$^{\#1}$	133.6(1)	133.1(1)	133.7(1)
Br(1)—Pd(1)—Pd(1)$^{\#1}$	133.0(1)	133.7(1)	133.0(1)
C(1′)—Pd(1)—C(2′)	93.7(1)	93.7(1)	93.3(2)
C(1′)—Pd(1)—Pd(1)	130.8(1)	130.9(1)	133.2(2)
C(2′)—Pd(1)—Pd(1)	134.42(6)	134.1(1)	131.1(1)
O(1′)—C(1′)—Pd(1)	149.0(2)	164.1(1)	160.5(2)
O(2′)—C(2′)—Pd(1)	111.0(5)	113.0(7)	148.8(2)
C(37)—Pd(1)—Pd(1)$^{\#1}$	46.4(4)	47.0(2)	47.2(2)
C(37)$^{\#1}$—Pd(1)—Pd(1)$^{\#1}$	45.5(4)	46.5(2)	46.6(2)

Note. #1 are the coordinates of the atoms generated by the symmetry operation.

In three types of single crystals, the palladium atom in the anions is in a square-planar environment typical of Pd^I and Pd^{II} complexes.[5—7] On the whole, the geometry of the complex anion is characterized by the following features typical of Pd^I carbonyl chloride complexes:[6,7] the metal atoms are closely spaced, the ligand atoms bound to Pd are in a single plane, and the molecule contains two bridging (carbonyl) and four terminal ligands.

Table 4. Occupancies for the partially disordered ligands in single crystals **1—3** prepared according to the procedures *1—3*

Atom	1	2	3
O(2′)	0.27	0.14	0.18
C(2′)	0.27	0.14	0.18
C(1′)	0.42	0.27	0.32
O(1′)	0.42	0.27	0.32
Br(1)	0.58	0.73	0.68
Br(2)	0.73	0.87	0.82

Each complex anion is surrounded by four cations. Two of them are involved in short contacts between the hydrogen atoms of the Ph rings and the halide terminal ligands (Fig. 5).

As a result of this arrangement, the complex anion is located in the cavity formed by four cations. Each cation is involved in two cavities, resulting in the formation of supramolecular layers (Fig. 6).

The complex anions, which are located in the cavities sharing the cations, differ in the geometric orientation (see Fig. 6). The supramolecular layers are shifted relative to each other. Each cavity is closed from the top and bottom by the PPN^+ cations from the upper and lower layers, respectively. The distance between two adjacent complex anions is 9.52 Å. This gives rise to a cellular supramolecular structure, which apparently contributes substantially to stabilization of the labile complex anions.

The data on the structures and compositions of the complex doubly charged anions can be explained assuming that Pd^I and Pd^0 complexes, which differ in the ratio of the terminal CO and Br ligands, co-exist in solution and co-crystallize in the same crystal form.

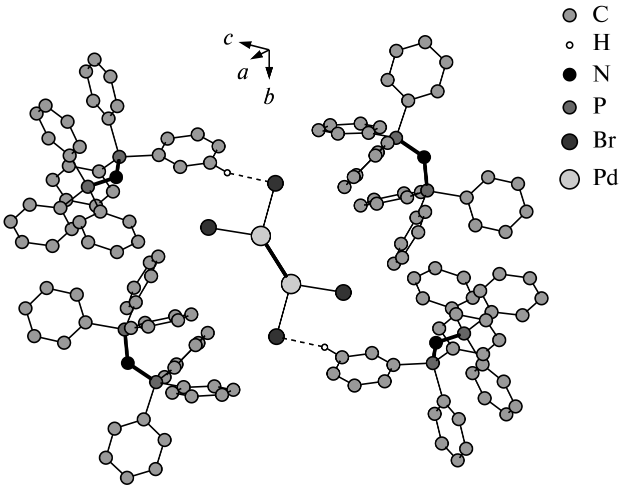


Fig. 5. Complex anion $Pd_2Br_n(CO)_m^{2-}$ ($m + n = 6$) with four cations bound to this anion. The O and C atoms of the anion and the H atoms of the cations, which are not bound to the anion, are omitted.

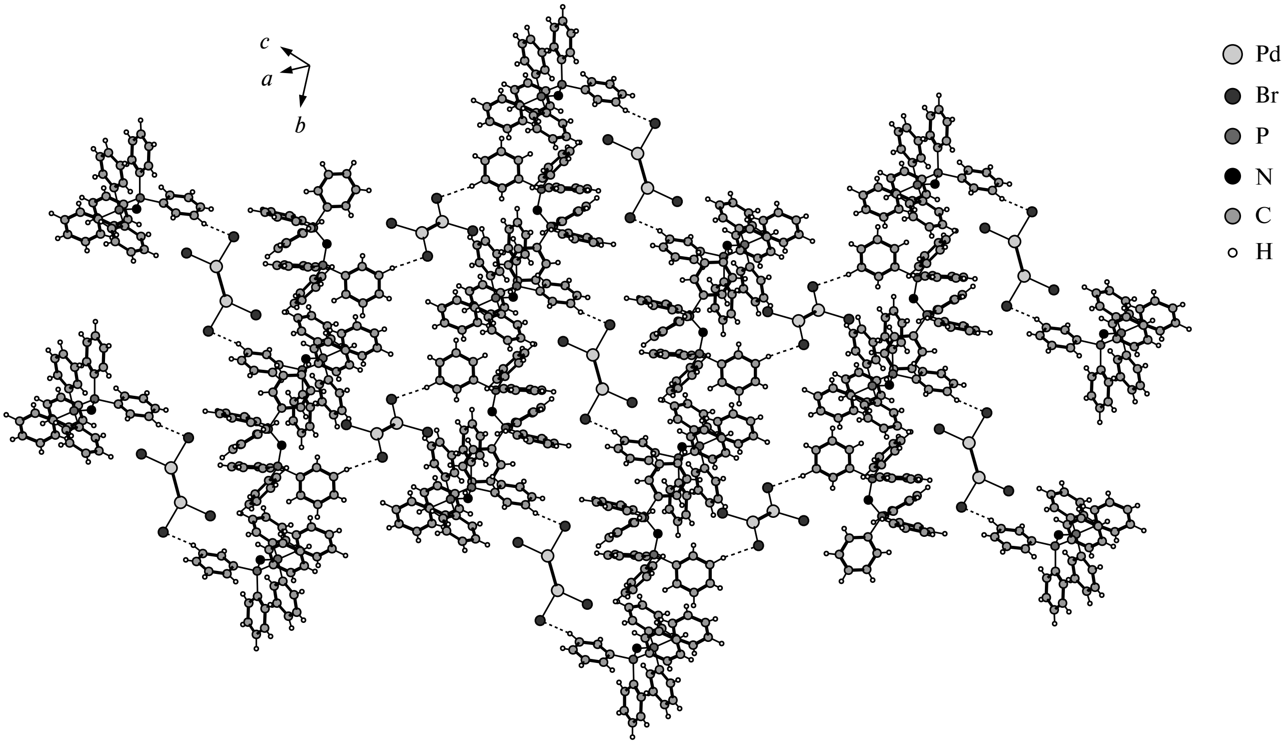
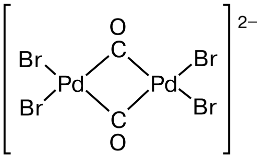
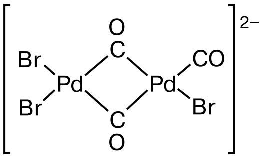


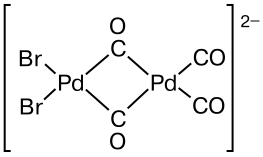
Fig. 6. Supramolecular layers formed by the cations and anions. The carbonyl groups are omitted.



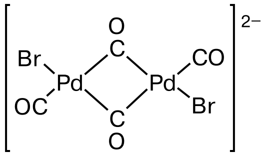
A (Pd^I—Pd^I)



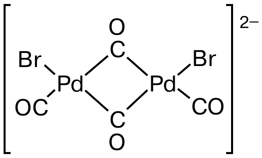
B (Pd^I—Pd^0)



C (Pd^0—Pd^0)



D (Pd^0—Pd^0)



E (Pd^0—Pd^0)

This assumption is consistent with the results of X-ray photoelectron spectroscopy for single crystals **3**, which were prepared according to procedure *3* and are described by the molecular formula $Pd_2(CO)_3Br_3^{2-} \cdot 2PPN^+$.

Binding energy of photoelectrons/eV			Atomic ratios of elements		
Pd ($3d_{5/2}$)	Br (3d)	P (2p)	Br : Pd	P : Pd	P : Br
337.3, 335.6	68.1	132.9	1.6	2.1	1.3

The X-ray photoelectron spectrum has two Pd ($3d_{5/2}$) bands with binding energies of 337.3 and 335.6 eV, which can be assigned to Pd^I and Pd^0, respectively.[1] The Br : Pd, P : Pd, and P : Br ratios evaluated from the XPS data (see above) are in satisfactory agreement with the elemental composition determined from the X-ray diffraction data (see Table 2).

The hypothesis of the possible co-existence of Pd^0 and Pd^I in one complex (see structure **B**) was tested by ESR spectroscopy. Signals of paramagnetic particles were observed neither at room temperature nor at liquid nitrogen temperature.

In the crystal lattice, there are no direct channels for exchange interactions between the Pd_2 fragments separated by a distance of 9.5 Å (see Fig. 6). Hence, the structure **B** containing Pd^I and Pd^0 can be excluded from consideration.

The IR spectrophotometric analysis of a suspension of the crystalline palladium carbonyl bromide complex revealed absorption bands belonging only to the bridging carbonyl group (ν 1985.5 and 1898 cm^{-1}). Unfortunately, this compound partially decomposed during the preparation of the suspension. Apparently, labile Pd^0 complexes undergo decomposition, which can account for the fact that no absorption bands of terminal CO groups are observed in the IR spectrum.

Therefore, the experimental results are not contradictory to the hypothesis that crystals **1—3** (see Table 2) are composed of the complexes **A** along with the complexes **C**, **D**, or **E** in different ratios (**A** : (**C** + **D** + **E**) = 1 : 1 for complex **3**). According to this hypothesis, the absorption bands of terminal CO groups observed in the IR spectra of solutions in the bromide systems should be assigned to terminal CO ligands in the complexes **C**, **D**, and **E**.

The formation of the halide complexes $Pd^0—[PdX_n]^{n-}$ and the halide carbonyl complexes $[Pd(CO)_2(X)_n]^{n-}$ in solutions has been assumed in several studies, where the mechanisms of redox reactions were considered.[3,16—18]

Although the Pd—Pd distance in the presumably zerovalent palladium complexes is sufficient for the formation of the $Pd^0—Pd^0$ bond, the existence of this bond in the dinuclear complex is a debated question. Recently,[19] the Pd^0 phosphine complex $[Pd(R_2PCH_2CH_2PR_2)]_2(\mu\text{-}CO)$ characterized by the rather short Pd—Pd distance (2.714 Å) has been synthesized and characterized. It was hypothesized[20] that the bridging CO group facilitates the close arrangement of the palladium atoms, between which a weak $d^{10}—d^{10}$ interaction occurs. This interaction is called metallophilic attraction. According to the quantum-chemical estimates, the energy of the $Au^I—Au^I$ interaction ($[ClAu(PH_3)]_2$ complex) is 5—12 kcal mol^{-1}.[21] The double excitation involving the 5d electrons is ~90% of the attraction energy. The formation of the Pd=Pd double bond is also possible, but the expected shortening of the Pd—Pd distance was not observed in X-ray diffraction study.

To summarize, three types of single crystals (**1—3**) were prepared by replacing the Cl^- ligand with Br^- in the dimeric Pd^I carbonyl chloride complex in a THF solution. All complexes giving single crystals have the same $Pd_2(\mu\text{-}CO)_2$ fragment. The crystals contain doubly charged anions with four partially disordered terminal ligands (Br and CO). The Br : Pd and CO : Pd ratios in these complexes vary depending on the conditions of the synthesis and crystallization. There are two PPN^+ cations per each complex anion. The results of X-ray diffraction study of single crystals **1—3**, the elemental compositions (X-ray diffraction and XPS data), the presence of Pd^I and Pd^0 atoms in single crystal **3** (XPS data), the absence of paramagnetic particles (ESR data), and the IR spectra of solutions (ν(CO) for the terminal ligand is independent of the reduction time) provide evidence that single crystals **1—3** consist of the anionic Pd^I and Pd^0 carbonyl complexes and differ in their ratio.

Experimental

X-ray diffraction study was carried out on an automated CAD-4 diffractometer (β filter, λ(Mo-Kα), λ = 0.71074 Å, T = 293(2) K, θ/2θ scanning technique). The principal interatomic distances and bond angles are given in Table 3. The crystallographic data and details of X-ray diffraction study are listed in Table 5.

The structures were solved by direct methods. The positional and thermal parameters of the nonhydrogen atoms were refined first isotropically and then anisotropically by the full-matrix least-squares method. The hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. All calculations were carried out with the use of the SHELXS 97 program package.[22]

Table 5. Parameters of X-ray diffraction study for singe crystals **1—3**

Parameter	**1**	**2**	**3**
Formula	$C_{37.70}H_{32}Br_{1.30}NO_{1.70}P_2Pd$	$C_{37.38}H_{30}Br_{1.63}NO_{1.38}P_2Pd$	$C_{37.50}H_{30}Br_{1.50}NO_{1.50}P_2Pd$
Molecular weight	798.47	815.33	806.83
Crystal system		Monoclinic	
Space group	$P(2)1/c$	$P(2)1/c$	P(2)1/c
a/Å	9.469(2)	9.519(2)	9.529(2)
b/Å	15.781(3)	15.762(3)	15.755(3)
c/Å	22.577(5)	22.678(5)	22.661(5)
β/deg	98.24(3)	97.90(3)	98.08(3)
V/Å^3	3338.3(12)	3370.3(12)	3368.3(12)
Z	4	4	4
d_{calc}/g cm^{-3}	1.588	1.607	1.591
μ/cm^{-1}	2.241	2.604	2.458
θ/2θ scanning range/deg	1.58—23.86	1.58—24.98	1.58—24.93
Number of measured/independent reflections	3760/1685	6702/2662	6683/2966
R_{int}	0.016	0.021	0.015
Number of parameter in refinement	407	407	519
R_1 (I > 2σ(I))	0.038	0.028	0.024
wR_2 (based on all reflections)	0.101	0.066	0.063

The X-ray photoelectron spectra were recorded on an LAS-300 OPX-150 RIBER spectrometer (Al-Kα radiation, 1486.6 eV). The spectra were calibrated against the carbon line (C_{1s} = 285 eV). The rms error in the calculated concentrations of the elements is smaller than 10%.

The IR spectra were recorded on a Specord M-80 IR spectrophotometer in KBr cells (0.52 mm) or as Nujol mulls between KBr plates.

A polycrystalline sample was studied by ESR on an SE/X-2542 Radiopan radiospectrometer at 293 and 77 K. The magnetic field was calibrated on an NMR magnetometer in the presence of a standard Mn^{2+} sample in the MgO matrix.

Procedure for the synthesis *1*. Weighed samples of $PdCl_2$ (0.12 g, 0.68 mmol) and LiCl (0.12 g, 2.82 mmol) were placed in a glass reactor and dissolved in THF (10 mL) for 1—2 h. The resulting solution was stirred for 5 h under CO, the reaction being accompanied by a change in the color of the solution from bright red to yellow-green. After 5 h, LiBr (0.12 g, 1.44 mmol) was added, and the reactor was purged with carbon monoxide for 10 min. After the addition of lithium bromide, the color of the solution rapidly changed to red-orange. After stirring, a solution of PPNCl (0.058 mmol mL^{-1}) in acetone (1.5 mL) and hexane (1 mL) were successively added. The solution was cooled to 278 K and kept under CO at this temperature. After 24 h, yellow crystals **1** precipitated.

Procedure for the synthesis *2*. Weighed samples of $PdCl_2$ (0.1 g, 0.56 mmol) and LiCl (0.1 g, 2.35 mmol) were placed in a reactor and dissolved in THF (9 mL) for 1—2 h. The resulting solution was stirred for 5 h under CO, the reaction being accompanied by a change in the color of the solution from bright red to yellow-green. After 5 h, a solution of PPNCl (0.058 mmol mL^{-1}) and LiBr (0.745 mmol mL^{-1}) in acetone (2 mL) was added. The resulting solution was cooled to 278 K and kept under CO at this temperature. After 12 h, yellow crystals **2** precipitated.

Procedure for the synthesis *3*. Weighed samples of $PdCl_2$ (0.1 g, 0.56 mmol) and LiBr (0.1064 g, 1.22 mmol) were placed in a glass reactor and dissolved in THF (9 mL) for 1—2 h. The resulting solution was stirred for 3 h under an atmosphere of carbon monoxide, the reaction being accompanied by a change in the color of the solution from bright red to yellow-orange. Carbonylation was carried out for 3 h, after which hexane (1 mL) was added, the mixture was stirred for 10 min, and PPNCl (0.05 g, 0.087 mmol) was added. The solution was kept without stirring at 293 K under CO. Then hexane (2.5 mL) was added portionwise (0.8 mL) for 3 days, after which crystals **3** precipitated.

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