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Unusual Reactions of Potassium Dihalodicyanoaurates with Organyltriphenylphosphonium Halides

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Abstract—Precipitates synthesized by the reactions of potassium dichloro- and dibromodicyanoaurates with tetraphenylphosphonium, cyanomethyltriphenylphosphonium, and methoxymethyltriphenylphosphonium chlorides are stored in water for several days to give complexes $[Ph_4P][Au(CN)_2]$ (**I**), $[Ph_3PCH_2CN][Au(CN)_2]$ (**II**), and $[Ph_3PCH_2OMe][Au(CN)_2]$ (**III**), respectively, as minor products. The reactions of potassium dichloro-, dibromo-, and diiododicyanoaurates with hydroxymethyltriphenylphosphonium chloride in hot ethanol afford the corresponding (triphenylphosphine)gold(I) halides $(Ph_3P)AuHal$ (Hal = Cl (**IV**), Br (**V**), and I (**VI**)). These reactions carried out in water and followed by recrystallization from ethanol or acetonitrile afford the crystalline product of the ion-exchange interaction $[Ph_3PCH_2OH][Au(CN)_2I_2]$ (**VII**) only in the case of potassium diiododicyanoaurate. Compounds **I**–**VII** are identified by elemental analysis, IR spectroscopy, and X-ray diffraction (XRD) (CIF files CCDC nos. 1978554 (**I**), 1965532 (**II**), 2060230 (**III**), and 2060283 (**VII**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Keywords: organyltriphenylphosphonium dihalodicyanoaurates, organyltriphenylphosphonium dicyanoaurates, (triphenylphosphine)gold(I) halides, redox reaction, XRD

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INTRODUCTION

Cyano-containing compounds of transition metals have a broad range of potentially applicable physicochemical properties and, hence, attract attention of researchers for a long time. In particular, various dicyano- and dihalodicyanoaurate complexes are characterized by luminescence [1–4], birefringence [5–8], negative thermal expansion [9, 10], anticancer activity [11], etc. In addition, $[Au(CN)_2]^-$ and $[Au(CN)_2Hal_2]^-$ anions are excellent building blocks for preparing polynuclear heterometallic ensembles and metal-organic frameworks [12, 13]. Thus, the search for efficient methods for the synthesis of new $[Au(CN)_2]^-$- and $[Au(CN)_2Hal_2]^-$-containing complexes is an urgent task.

It has previously been shown for many examples that the reactions of potassium dihalodicyanoaurates with tetraorganylammonium, tetraorganylphosphonium, and tetraorganylstibonium halides proceed via the classical ion-exchange scheme to form the corresponding dihalodicyanoaurates $[R_4E][Au(CN)_2Hal_2]$ (E = N, P, Sb) [14–19]. It was also demonstrated for some examples that the starting potassium dihalodicyanoaurates and their tetraorganylammonium analogs in the presence of reducing agents (e.g., Me_2S [20]) or under the hydrothermal synthesis conditions can be involved in reductive elimination to form the $[Au(CN)_2]^-$-containing complexes [21].

New unusual examples of the reactions of potassium dihalodicyanoaurates with some organyltriphenylphosphonium chlorides proceeding via both redox and ion-exchange routes are described in this work.

EXPERIMENTAL

Potassium dihalodicyanourates synthesized by the oxidative addition of the corresponding halogen to potassium dicyanoaurate (DCM-Analitica, analytical grade) and commercially available organyltriphenylphosphonium chlorides ($[Ph_4P]Cl$ (Alfa Aesar, 98%), $[Ph_3PCH_2OMe]Cl$ (Alfa Aesar, 98%), $[Ph_3PCH_2CN]Cl$ (Alfa Aesar, 98%), and $[Ph_3PCH_2OH]Cl$ (abcr GmbH, 98%)) were used.

Synthesis of tetraphenylphosphonium dicyanoaurate (I). A solution of tetraphenylphosphonium chloride (104 mg, 0.28 mmol) in water (10 mL) was added with stirring to a solution of potassium dichlorodicyanoaurate (100 mg, 0.28 mmol) in water (10 mL). The formed precipitate was stored in water for several days. After recrystallization from acetotonitrile, colorless crystals of the complex with T_m = 238°C were obtained along with yellow crystals of $[Ph_4P][Au(CN)_2Cl_2]$. The yield of compound **I** was 26 mg (16%).

IR (ν, cm^{-1}): 3057, 3021, 2990, 2139, 1587, 1483, 1435, 1389, 1314, 1186, 1163, 1111, 1070, 1028, 997, 928, 843, 760, 752, 723, 689, 615, 529, 453, 422.

For $C_{26}H_{20}N_2PAu$

Anal. calcd., %	C, 52.98	H, 3.49
Found, %	C, 53.05	H, 3.42

Cyanomethyltriphenylphosphonium $[Ph_3PCH_2CN][Au(CN)_2]$ (**II**) and methoxymethyltriphenylphosphonium $[Ph_3PCH_2OMe][Au(CN)_2]$ (**III**) dicyanoaurates were synthesized by a procedure similar to that for compound **I** using potassium dibromodicyanoaurate and cyanomethyl- and methoxymethyltriphenylphosphonium chlorides, respectively.

The yield of colorless crystals of compound **II** with T_m = 170°C was 20%.

IR (ν, cm^{-1}): 3084, 3061, 2922, 2837, 2741, 2253, 2143, 1587, 1573, 1485, 1437, 1395, 1381, 1341, 1315, 1256, 1200, 1188, 1161, 1115, 1103, 1072, 1028, 997, 926, 839, 775, 756, 745, 725, 689, 615, 550, 505, 498, 463, 446, 430.

For $C_{22}H_{17}N_3PAu$

Anal. calcd., %	C, 47.92	H, 3.11
Found, %	C, 48.01	H, 3.06

The yield of colorless crystals of compound **III** with T_m = 123°C was 16%.

IR (ν, cm^{-1}): 3059, 3011, 2957, 2895, 2832, 2143, 1587, 1483, 1466, 1439, 1314, 1219, 1200, 1184, 1165, 1115, 1099, 1026, 997, 941, 885, 799, 752, 739, 723, 687, 615, 532, 496, 455, 430, 419.

For $C_{22}H_{20}N_2OPAu$

Anal. calcd., %	C, 47.49	H, 3.63
Found, %	C, 47.60	H, 3.55

Synthesis of (triphenylphosphine)gold(I) chloride (IV). Potassium dichlorodicyanoaurate (50 mg, 0.14 mmol) was added with stirring and heating in a water bath to a solution of hydroxymethyltriphenylphosphonium chloride (92 mg, 0.28 mmol) in ethanol (10 mL). A colorless precipitate formed on cooling of the reaction mixture was filtered off, dried, and recrystallized from tetrahydrofuran. Colorless crystals with T_m = 240°C were obtained. The yield of compound **IV** was 55 mg (79%).

IR (ν, cm^{-1}): 3071, 1585, 1479, 1433, 1395, 1329, 1332, 1312, 1294, 1179, 1165, 1157, 1101, 1072, 1026, 999, 932, 748, 714, 692, 615, 546, 501, 446.

For $C_{18}H_{15}PClAu$

Anal. calcd., %	C, 43.70	H, 3.06
Found, %	C, 47.79	H, 3.03

(Triphenylphosphine)gold(I) bromide (**V**) and iodide (**VI**) were synthesized by the procedure similar to that for compound **IV** using potassium dibromo- and diiododicyanoaurates, respectively.

The yield of colorless crystals of compound **V** with T_m = 249°C was 85%.

IR (ν, cm^{-1}): 3071, 1585, 1479, 1433, 1329, 1312, 1292, 1269, 1179, 1165, 1155, 1101, 1072, 1026, 999, 748, 714, 692, 615, 544, 500, 444.

For $C_{18}H_{15}PBrAu$

Anal. calcd., %	C, 40.10	H, 2.81
Found, %	C, 40.19	H, 2.76

The yield of light brown crystals of compound **VI** with T_m = 230°C was 69%.

IR (ν, cm^{-1}): 3071, 3055, 2197, 1585, 1477, 1433, 1387, 1331, 1310, 1292, 1177, 1163, 1153, 1121, 1101, 1069, 1026, 997, 926, 839, 746, 723, 712, 691, 615, 540, 498, 442.

For $C_{18}H_{15}PIAu$

Anal. calcd., %	C, 36.88	H, 2.58
Found, %	C, 37.01	H, 2.52

Synthesis of hydroxymethyltriphenylphosphonium diiododicyanoaurate (VII). A solution of hydroxymethyltriphenylphosphonium chloride (61 mg, 0.28 mmol) in water (10 mL) was added with stirring to a solution of potassium diiododicyanoaurate (100 mg, 0.28 mmol) in water (10 mL). The formed dark red precipitate was filtered off, two times washed with water (by 5-mL portions), dried, and recrystallized from acetonitrile. Dark red crystals with T_m = 125°C were obtained in a yield of 135 mg (92%).

IR (ν, cm^{-1}): 3372, 3057, 2932, 2899, 2180, 1587, 1485, 1439, 1400, 1339, 1315, 1302, 1188, 1163, 1117, 1051, 1028, 1000, 887, 876, 853, 764, 748, 741, 723, 689, 530, 501, 484, 457, 440, 422.

For $C_{21}H_{18}N_2OPI_2Au$

Anal. calcd., %	C, 31.68	H, 2.28
Found, %	C, 31.79	H, 2.26

Elemental analysis was carried out on a Carlo Erba CHNS-O EA 1108 elemental analyzer. Melting points were determined with a Stuart SMP30 instrument.

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds I*–III and VII**

Parameter	Value			
	I	**II**	**III**	**VII**
FW	588.38	551.33	556.34	796.11
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2/n$	$P2_1$	$P2_1/n$	$P2_1/c$
a, Å	10.227(16)	13.689(11)	10.041(6)	10.929(10)
b, Å	7.664(17)	8.444(7)	14.902(10)	10.029(8)
c, Å	14.48(2)	18.058(15)	14.115(9)	21.58(2)
α, deg	90.00	90.00	90.00	90.00
β, deg	90.51(9)	90.04(3)	94.91(2)	95.92(5)
γ, deg	90.00	90.00	90.00	90.00
V, Å^3	1135(4)	2087(3)	2104(2)	2353(4)
Z	2	2	4	4
ρ_{calc}, g/cm^3	1.722	1.754	1.756	2.248
μ, mm^{-1}	6.568	7.135	7.080	8.959
F(000)	568.0	1056.0	1072.0	1464.0
Crystal size, mm	0.15 × 0.11 × 0.05	0.47 × 0.39 × 0.32	0.48 × 0.28 × 0.14	0.65 × 0.38 × 0.23
Range of data collection over θ, deg	7.2–53.22	6.1–66.44	5.8–63.2	5.72–71.62
Ranges of reflection indices	$-9 \le h \le 12$, $-9 \le k \le 9$, $-16 \le l \le 18$	$-21 \le h \le 21$, $-12 \le k \le 12$, $-27 \le l \le 24$	$-14 \le h \le 14$, $-21 \le k \le 21$, $-20 \le l \le 20$	$-17 \le h \le 17$, $-16 \le k \le 16$, $-35 \le l \le 34$
Measured reflections	4091	72703	80453	89547
Independent reflections (R_{int})	2104 (0.0507)	15824 (0.0488)	7042 (0.0657)	10956 (0.0702)
Refinement variables	137	487	245	257
GOOF	1.004	1.027	1.244	1.013
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0595$, $wR_2 = 0.1409$	$R_1 = 0.0426$, $wR_2 = 0.0620$	$R_1 = 0.0583$, $wR_2 = 0.1202$	$R_1 = 0.0432$, $wR_2 = 0.0874$
R factors for all reflections	$R_1 = 0.1440$, $wR_2 = 0.1845$	$R_1 = 0.0998$, $wR_2 = 0.0725$	$R_1 = 0.0858$, $wR_2 = 0.1325$	$R_1 = 0.0894$, $wR_2 = 0.1032$
Residual electron density (max/min), e/Å^3	0.53/–0.92	0.87/–1.51	1.89/–1.93	1.53/–2.38

The IR spectra of compounds **I**–**VII** were recorded on a Shimadzu IRAffinity-1S FT-IR spectrometer for samples pelleted with KBr in an absorption range of 4000–400 cm^{-1}.

XRD for crystals of compounds **I**–**III** and **VII** was carried out on a Bruker D8 QUEST automated four-circle diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [22]. All calculations on structure determination and refinement were performed using the SHELXL/PC [23] and OLEX2 [24] programs. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The crystallographic data and structure refinement results for compounds **I**–**III** and **VII** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge

Table 2. Bond lengths (d) and bond angles (ω) in the structures of compounds **I**–**III** and **VII**

Bond d, Å		Angle ω, deg	
I			
Au(1)–C(7)	1.98(3)	C(7)Au(1)C(7a)	179.5(11)
Au(1)–C(7a)	1.98(3)	C(1)P(1)C(1b)	106.6(7)
P(1)–C(1)	1.783(11)	C(1)P(1)C(11)	110.9(4)
P(1)–C(1b)	1.783(11)	C(1b)P(1)C(11b)	110.9(4)
P(1)–C(11)	1.794(9)	C(11)P(1)C(1b)	111.6(5)
P(1)–C(11b)	1.794(9)	C(1)P(1)C(11b)	111.6(5)
		C(11)P(1)C(11b)	105.4(6)
* Symmetry transforms: (a) $3/2 - x, y, 1/2 - z$; (b) $1/2 - x, y, 1/2 - z$.			
II			
Au(1)–C(7)	2.045(7)	C(7)Au(1)C(8)	177.98(19)
Au(1)–C(8)	2.006(7)	C(37)Au(1)C(38)	177.8(2)
Au(1)–C(37)	1.989(6)	C(11)P(1)C(21)	110.08(19)
Au(1)–C(38)	2.041(6)	C(11)P(1)C(9)	109.8(2)
P(1)–C(11)	1.782(4)	C(11)P(1)C(1)	110.76(19)
P(1)–C(21)	1.794(4)	C(21)P(1)C(9)	109.7(2)
P(1)–C(9)	1.814(4)	C(1)P(1)C(21)	110.2(2)
P(1)–C(1)	1.786(4)	C(1)P(1)C(9)	106.3(2)
P(2)–C(51)	1.783(4)	C(51)P(2)C(31)	110.96(19)
P(2)–C(31)	1.787(4)	C(51)P(2)C(41)	109.9(2)
P(2)–C(41)	1.789(4)	C(51)P(2)C(39)	110.1(2)
P(2)–C(39)	1.811(4)	C(31)P(2)C(41)	110.0(2)
C(9)–C(10)	1.453(7)	C(31)P(2)C(39)	106.3(2)
C(39)–C(40)	1.457(7)	C(41)P(2)C(39)	109.5(2)
III			
Au(1)–C(9)	2.037(9)	C(9)Au(1)C(10)	179.3(3)
Au(1)–C(10)	2.085(9)	C(21)P(1)C(1)	109.0(3)
P(1)–C(21)	1.789(5)	C(21)P(1)C(7)	110.7(3)
P(1)–C(1)	1.791(5)	C(1)P(1)C(7)	106.5(3)
P(1)–C(11)	1.788(5)	C(11)P(1)C(21)	111.3(3)
P(1)–C(7)	1.809(6)	C(11)P(1)C(1)	110.8(2)
O(1)–C(7)	1.412(8)	C(11)P(1)C(7)	108.4(3)
O(1)–C(8)	1.408(8)	C(8)O(1)C(7)	112.4(5)
		O(1)C(7)P(1)	107.6(4)
VII			
Au(1)–I(1)	2.6191(17)	I(1a)Au(1)I(1)	180.000(1)
Au(1)–I(1a)	2.6190(17)	C(8)Au(1)I(1)	91.61(14)
Au(1)–C(8)	1.992(4)	C(8a)Au(1)I(1)	88.39(14)
Au(1)–C(8a)	1.992(4)	I(2b)Au(2)I(2)	180.0
Au(2)–I(2)	2.6015(16)	C(9)Au(2)I(2)	90.00(14)
Au(2)–I(2b)	2.6015(16)	C(9b)Au(2)I(2)	90.00(14)
Au(2)–C(9)	2.084(8)	C(21)P(1)C(1)	111.7(2)
Au(2)–C(9b)	2.084(8)	C(21)P(1)C(7)	108.8(2)
P(1)–C(21)	1.785(4)	C(1)P(1)C(7)	109.0(2)
P(1)–C(11)	1.793(4)	C(11)P(1)C(21)	110.01(19)
P(1)–C(7)	1.778(4)	C(11)P(1)C(1)	108.72(19)
P(1)–C(1)	1.827(5)	C(11)P(1)C(7)	108.6(2)
O(1)–C(7)	1.400(6)	O(1)C(7)P(1)	109.8(3)
** Symmetry transforms: (a) $2 - x, -y, 2 - z$; (b) $2 - x, 1 - y, 2 - z$.			

Crystallographic Data Centre (CIF files CCDC nos. 1978554 (**I**), 1965532 (**II**), 2060230 (**III**), and 2060283 (**VII**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

We have shown for the first time that the prolong storage in an aqueous solution (several days at room temperature and atmospheric pressure) of the precipitated products of the reactions of potassium dihalodicyanoaurates with selected tetraorganylphosphonium salts can be accompanied, in some cases, by the reductive elimination of halogen with the formation of minor amounts of the corresponding $[Au(CN)_2]^-$-containing complexes. For instance, compounds **I**–**III** were synthesized by the reactions of aqueous solutions of potassium dichloro- and dibromodicyanoaurates with tetraphenylphosphonium, cyanomethyltriphenylphosphonium, and methoxymethyltriphenylphosphonium chlorides. The structures of the synthesized complexes were proved by XRD. It should be mentioned that the structure of complex **I** has already been determined earlier but with a lower accuracy (*R* factor was 10.6%) [25].

$$K[Au(CN)_2Hal_2] + [Ph_3PR]Cl \xrightarrow[\text{several days}]{H_2O} [Ph_3PR][Au(CN)_2] + KCl + Hal_2$$

$$Hal = Cl, R = Ph(\mathbf{I});\ Hal = Br, R = CH_2CN(\mathbf{II}),\ CH_2OMe(\mathbf{III}).$$

The results of the reactions of potassium dihalodicyanoaurates with hydroxymethyltriphenylphosphonium chloride also turned out to be rather unusual. For instance, in the cases of the chlorine and bromine derivatives, we failed to obtain complexes of the type $[Ph_3PCH_2OH][Au(CN)_2Hal_2]$ (Hal = Cl, Br). Colorless crystals of the corresponding (triphenylphosphine)gold(I) halides were isolated in minor amounts after the recrystallization of the formed precipitates from ethanol; i.e., the redox reaction occurred. As far as we know, this is the first case of the synthesis of compounds of the $(Ph_3P)AuHal$ type from potassium dihalodicyanoaurates. Unfortunately, attempts to recrystallize products of this reaction from other solvents did not result in the formation of crystals suitable for XRD. Nevertheless, according to the IR spectroscopy data, we can assert that before recrystallization the expected complexes $[Ph_3PCH_2OH][Au(CN)_2Cl_2]$ and $[Ph_3PCH_2OH][Au(CN)_2Br_2]$ were the products of the reactions of potassium dichloro- and dibromodicyanoaurates with hydroxymethyltriphenylphosphonium chloride. In particular, the IR spectra of the formed precipitates contain low-intensity absorption bands of C≡N bonds (2189–2156 cm^{-1}) characteristic of $[Au(CN)_2Hal_2]^-$-containing compounds and absorption bands assigned to vibrations of the O–H and $C{-}H_{aliph}$ bonds of hydroxymethyltriphenylphosphonium cations (in ranges of 3372–3254 and 2932–2826 cm^{-1}, respectively) [26].

At the same time, some optimum conditions for the reduction of potassium dihalodicyanoaurates to (triphenylphosphine)gold(I) halides were experimentally found. For instance, mixing of a phosphonium salt excess with $K[Au(CN)_2Hal_2]$ (2 : 1 mol/mol) in hot ethanol results in a significant increase in the yields of $(Ph_3P)AuHal$. (Triphenylphosphine)gold(I) iodide (**VI**) was also synthesized along with compounds **IV** and **V** using this procedure. Based on the obtained results and the fact that hydroxymethyltriphenylphosphonium chloride can decompose to triphenylphosphine, formaldehyde, and hydrochloric acid [27], we can assume that the reaction course discovered by us is similar to the reduction of chloroauric acid with triphenylphosphine in the presence of water traces [28].

$$[Ph_3PCH_2OH]Cl \xrightarrow{EtOH,\ t} Ph_3P + CH_2O + HCl,$$

$$K[Au(CN)_2Hal_2] + 2Ph_3P \xrightarrow[EtOH,\ t]{H_2O} Ph_3PAuHal + 2HCN + KHal + Ph_3PO$$

$$Hal = Cl(\mathbf{IV}),\ Br(\mathbf{V}),\ I(\mathbf{VI}).$$

In spite of unsuccessful attempts to crystallize hydroxymethyltriphenylphosphonium dichloro- and dibromodicyanoaurates, we obtained stable dark red crystals of their iodine-containing analog $[Ph_3PCH_2OH][Au(CN)_2I_2]$ (**VII**) without any difficulties using the ion-exchange reaction in water followed by recrystallization from ethanol or acetonitrile. The structure of this complex was proved by XRD.

$$K[Au(CN)_2I_2] + [Ph_3PCH_2OH]Cl \xrightarrow{H_2O} \underset{(\mathbf{VII})}{[Ph_3PCH_2OH][Au(CN)_2I_2]} + KCl.$$

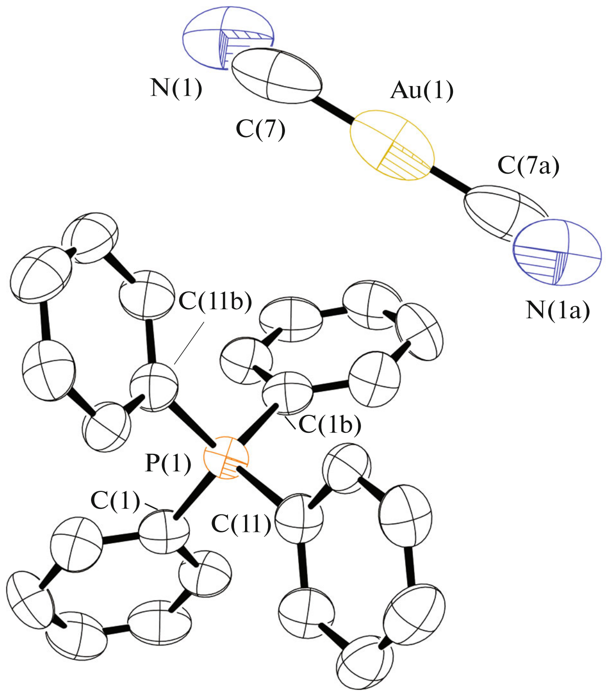

Fig. 1. Structure of complex $[Ph_4P][Au(CN)_2]$ (**I**).

The IR spectra of compounds **I**–**III** and **VII** exhibit characteristic absorption bands of $C\equiv N$ bonds at 2139 (**I**), 2253, 2143 (**II**), 2143 (**III**), and 2181 cm^{-1} (**VII**). For the gold(I) derivatives, these bands are more intense and lie in a longer-wavelength spectral range, which is well consistent with published data. The absorption bands in characteristic ranges of 1450–1435 and 1005–997 cm^{-1} correspond to the $P-C_{Ph}$ bond vibrations: 1435, 997 (**I**), 1437, 997 (**II**), 1439, 997 (**III**), and 1437, 997 cm^{-1} (**VII**). The IR spectrum of complex **VII** also exhibits a broadened absorption band of the O–H bond at 3204 cm^{-1} [26].

According to the XRD data, complexes **I**–**III** and **VII** have ionic structures and consist of weakly distorted tetrahedral organyltriphenylphosphonium cations and dicyanoaurate (**I**–**III**) or dihalodicyanoaurate (**VII**) anions of the linear or planar square geometry, respectively. The structures of compounds **I**, **II**, **III**, and **VII** are shown in Figs. 1–4, respectively (thermal ellipsoids are presented with 50% probability; hydrogen atoms are omitted).

The CPC angles in the cations of compounds **I**–**III** and **VII** vary in ranges of 105.4(6)°–111.6(5)° (**I**), 106.3(2)°–110.96(19)° (**II**), 106.5(3)°–111.3(3)° (**III**), and 108.6(2)°–111.7(2)° (**VII**), respectively. The P–C bond lengths (1.783(11)–1.794(9) Å (**I**), 1.782(4)–1.814(4) Å (**II**), 1.788(5)–1.809(6) Å (**III**), and 1.778(4)–1.827(5) Å (**VII**)) do not exceed the sum of the covalent radii of the phosphorus atom and sp^3-hybridized carbon atom (1.88 Å [29]).

In the centrosymmetric anions $[Au(CN)_2]^-$ and $[Au(CN)_2I_2]^-$, the *trans*-CAuC and *trans*-IAuI angles are 180° or insignificantly deviate from the theoretical value. The *cis*-CAuI angles for complex **VII** range from 88.39(14)° to 91.61(14)°. The Au–C bond lengths (1.98(3) Å (**I**), 1.989(6)–2.045(7) Å (**II**), 2.037(9), 2.085(9) Å (**III**), and 1.992(4), 2.084(8) Å (**VII**)) are close to the sum of covalent radii of the gold atom and *sp*-hybridized carbon atom (2.05 Å [29]). The Au–I distances in complex **VII** do not exceed the sum of covalent radii of the gold and iodine atoms (2.75 Å [29]) and are equal to 2.6015(16) and 2.6191(17) Å.

The spatial organization in the crystals of compounds **II**, **III**, and **VII** is caused by hydrogen bonds $C-H\cdots N\equiv C$ (2.23–2.55 Å (**II**), 2.44 Å (**III**), and

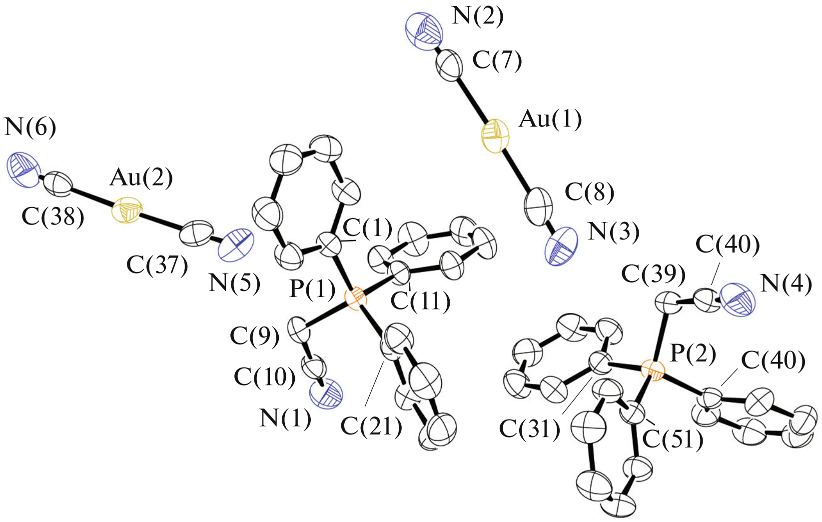

Fig. 2. Structure of complex $[Ph_3PCH_2CN][Au(CN)_2]$ (**II**).

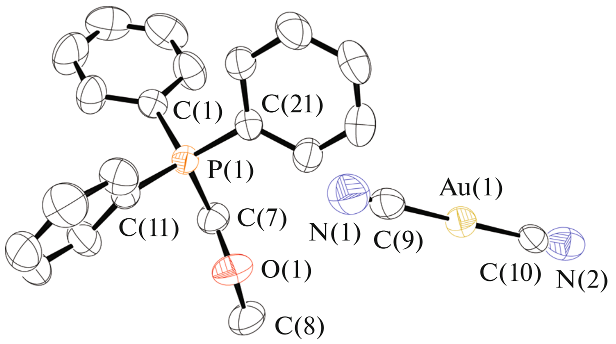

Fig. 3. Structure of complex $[Ph_3PCH_2OMe][Au(CN)_2]$ (**III**).

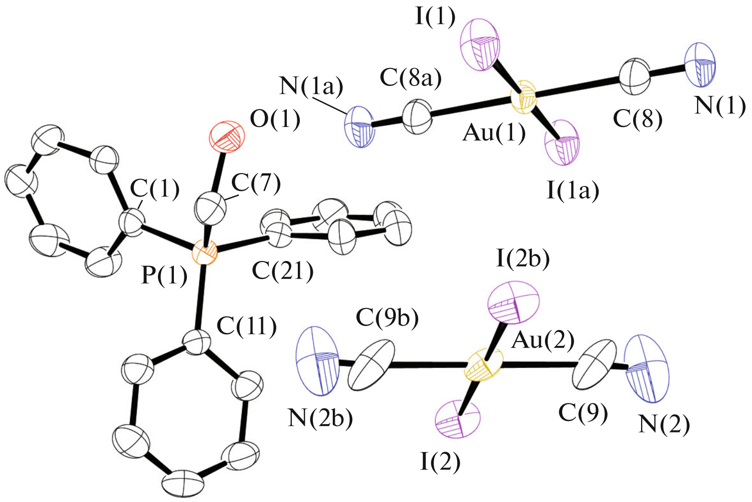

Fig. 4. Structure of complex $[Ph_3PCH_2OH][Au(CN)_2I_2]$ (**VII**).

2.65 Å (**VII**)) and O–H···N≡C (2.05 Å (**VII**)), whose ultimate values do not exceed the sum of the van der Waals radii of the corresponding atoms (H···N 2.65 Å [30]). Complex **II** also contains additional weak C–H···π interactions between the hydrogen atoms of one of the benzene rings of the cation and the electron density of one of the C≡N bonds of the anion, and the distances from the hydrogen atoms to the center of these bonds are equal to 2.80 Å [31]. In turn, the crystals of complex **I** contain no significant interionic contacts.

Thus, we described the unusual examples of the reactions of potassium dihalodicyanoaurates with organyltriphenylphosphonium halides accompanied by the reduction Au(III) → Au(I). It was shown that the storage of precipitates $[Ph_4P][Au(CN)_2Cl_2]$, $[Ph_3PCH_2CN][Au(CN)_2Br_2]$, and $[Ph_3PCH_2OMe]$-$[Au(CN)_2Br_2]$ in water for several days resulted in the formation of the corresponding organyltriphenylphosphonium dicyanoaurates. It was also found that the products of the reactions of potassium dichloro-, dibromo-, and diiododicyanoaurates with hydroxymethyltriphenylphosphonium chloride in hot ethanol were the corresponding (triphenylphosphine)gold(I) halides. These reactions in water at room temperature gave the ion-exchange products $[Ph_3PCH_2OH][Au(CN)_2Hal_2]$, which underwent reduction to $(Ph_3P)AuHal$ upon recrystallization from ethanol in the cases of Hal = Cl and Br. The recrystallization of complex $[Ph_3PCH_2OH][Au(CN)_2I_2]$ occurs without any difficulties and side reactions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

ADDITIONAL INFORMATION

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