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Synthesis and Structure of Osmium Complexes: $[Ph_3PR]_2^+[OsBr_6]^{2-}$ (R = *cyclo*-C_3H_5, *n*-C_4H_9, *cyclo*-C_6H_{11}, $CH_2C(O)Ph$), $[Ph_3PPr]_2^+[OsBr_6]^{2-} \cdot DMSO$, and $[Ph_3P(CH_2)_3PPh_3]^{2+}[OsBr_6]^{2-} \cdot DMSO$

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Abstract—The complexes $[Ph_3PR]_2[OsBr_6]$, R = *cyclo*-C_3H_5 (**I**), *n*-C_4H_9 (**II**), *cyclo*-C_6H_{11} (**III**), $CH_2C(O)Ph$ (**IV**), $[Ph_3PPr]_2[OsBr_6] \cdot DMSO$ (**V**), and $[Ph_3P(CH_2)_3PPh_3][OsBr_6] \cdot DMSO$ (**VI**) (CIF files CCDC nos. 1000171, 1000148, 1000172, 1000173, 1000147, and 1000149 for structures **I**–**VI**, respectively) were prepared by reactions of sodium hexabromoosmate with phosphonium bromides in dimethyl sulfoxide. According to X-ray diffraction data, phosphorus atoms in the cations have slightly distorted tetrahedral coordination (CPC angles, 105.2(3)°–115.5(3)°; P–C, 1.773(6)–1.814(6) Å). In the octahedral $[OsBr_6]^{2-}$ anions, the Os–Br bond lengths are 2.4734(8)–2.5203(5) Å and the *cis*-BrOsBr and *trans*-BrOsBr angles are 88.38(2)°–91.53(3)° and 177.276(18)°–180°, respectively. The structural organization in the crystals is formed by H···Br (2.74–3.04 Å) and H···O_{DMSO} (2.28–2.63 Å) ion–ion hydrogen bonds.

Keywords: synthesis, ionic complexes, alkyltriphenylphosphonium cation, hexabromoosmate anion, dimethyl sulfoxide, structure, X-ray diffraction

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INTRODUCTION

Osmium complexes with mononuclear $[OsBr_6]^{2-}$ anions are represented in the literature by few examples [1–5]. However, recent data attest to antitumor activities of some ionic osmium halide complexes. For example, complexes of the general formula $Cat^+[OsCl_5L]^-$, where L is 1*H*-pyrazole (HPz), 1*H*-imidazole (HIm), or 1*H*,2,4-triazole (HTrz); Cat^+ is Na^+, H_2Pz^+, H_2Trz^+, or H_2Ind^+ (protonated 1*H*-indazole) possess a moderate antiproliferative activity against cancer cells in vitro (ovarian carcinoma, non-small cells lung cancer, and colon adenocarcinoma). The replacement of azolium cations by sodium cations results in a considerable increase in the cytotoxicity of the complexes [6]. Here we describe the synthesis of previously unknown complexes with phosphonium cations and hexabromoosmate anions and consider their structural features.

EXPERIMENTAL

Synthesis of $[Ph_3PC_3H_5$-*cyclo*$]_2^+[OsBr_6]^{2-}$ (I). A mixture of triphenyl(cyclopropyl)phosphonium bromide (0.032 g, 0.08 mmol) and sodium hexabromoosmate(IV) (0.030 g, 0.04 mmol) was dissolved with stirring in 2 mL of dimethyl sulfoxide. When the solution volume was decreased to 0.5 mL, brown crystals were formed. The crystals were separated and dried. The yield of complex **I** was 0.033 g (62%), T_{dec} = 293°C.

IR (ν, cm^{-1}): 3076, 3053, 3036, 2982, 2909, 2849, 1672, 1585, 1481, 1437 (P–C_{Ph}), 1115, 1026, 997 (P–C_{Ph}), 893, 791, 748, 729, 718, 692, 662, 529, 507, 419. ^{1}H NMR (δ, ppm; *J*, Hz): 7.92 (m, 3H, *p*-H); 7.86 (dm, 6H, $^3J_{H,P}$ = 12.6, *o*-H); 7.77 (dm, 6H, $^4J_{H,P}$ = 3.5, *m*-H); 2.81 (dm, 1H, $^2J_{H,P}$ = 16.4, H-1); 1.53 (dm, 2H, $^3J_{H,P}$ = 12.2, H-2a); 0.65 (dm, 2H, $^3J_{H,P}$ = 17.1, H-2b). ^{13}C NMR (δ, ppm; *J*, Hz): 135.1 (d, $^4J_{C,P}$ = 2.8, 3**p*-C); 133.9 (d, $^2J_{C,P}$ = 10.0, 6**o*-C); 130.2 (d, $^3J_{C,P}$ = 12.5, 6**m*-C); 118.2 (d, $^1J_{C,P}$ = 89.4, 3**ipso*-C); 4.6 (d, $^2J_{C,P}$ = 4.7, C-2,3); 0.3 (d, $^1J_{C,P}$ = 87.2, C-1). ^{31}P NMR (δ, ppm): 28.6.

For $C_{42}H_{40}P_2Br_6Os$		
anal. calcd., %:	C, 39.51;	H, 3.14.
Found, %:	C, 39.42;	H, 3.58.

The other complexes were prepared by a similar procedure.

$[Ph_3P\text{-}n\text{-}C_4H_9]_2^+[OsBr_6]^{2-}$ (II): (54%), T_{dec} = 280°C. IR (ν, cm^{-1}): 3076, 3055, 2959, 2928, 2887, 2868, 1585, 1483, 1437 (P–C_{Ph}), 1188, 1163, 1113, 995 (P–C_{Ph}), 895, 746, 723, 691, 530, 509, 498, 419. ^{1}H NMR (δ, ppm; *J*, Hz): 7.92–7.88 (m, 3H, *p*-H); 7.83–7.75 (m, 12H, *m*-H, *o*-H); 3.55 (m, 2H, H-1); 1.56–1.45 (m, 4H, H-2, H-3); 0.89 (t, 3H, $^3J_{H,H}$ = 7.0, H-4). ^{13}C NMR (δ, ppm; *J*, Hz): 134.9 (d, $^4J_{C,P}$ = 3.1, 3**p*-C); 133.6 (d, $^2J_{C,P}$ = 10.1, 6**o*-C); 130.3 (d, $^3J_{C,P}$ = 12.4, 6**m*-C); 118.4 (d, $^1J_{C,P}$ = 85.6, 3**ipso*-C); 23.7 (d, $^2J_{C,P}$ = 4.5, C-2); 23.1 (d, $^3J_{C,P}$ = 17.2, C-3); 20.3 (d, $^1J_{C,P}$ = 50.1, C-1); 13.2 (s, C-4).

For $C_{44}H_{40}P_2Br_6Os$

anal. calcd., %:	C, 40.38;	H, 3.67
Found, %:	C, 40.26;	H, 3.71.

$[Ph_3PC_6H_{11}\text{-}cyclo]_2^+[OsBr_6]^{2-}$ (III): (61%), T_{dec} = 305°C. IR (ν, cm^{-1}): 3078, 3051, 2943, 2857, 1585, 1483, 1437 (P–C_{Ph}), 1107, 995 (P–C_{Ph}), 918, 885, 850, 820, 754, 743, 723, 689, 546, 523, 471, 419. ^{1}H NMR (δ, ppm; *J*, Hz): 7.92–7.87 (m, 9H, *o*-H, *p*-H); 7.78 (ddd, 6H, $J_{H,H}$ = 8.2, 7.4, $^4J_{H,P}$ = 3.2, *m*-H); 4.18 (m, 1H, H-1); 2.03 (m, 2H, *cyclo*-CH-ring); 1.78 (m, 2H, *cyclo*-CH); 1.71–1.55 (m, 3H, *cyclo*-CH); 1.11–1.02 (m, 3H, *cyclo*-CH). ^{13}C NMR (δ, ppm; *J*, Hz): 134.8 (d, $^4J_{C,P}$ = 3.0, 3**p*-C); 133.8 (d, $^2J_{C,P}$ = 9.4, 6**o*-C); 130.4 (d, $^3J_{C,P}$ = 12.1, 6**m*-C); 117.2 (d, $^1J_{C,P}$ = 83.1, 3**ipso*-C); 28.9 (d, $^1J_{C,P}$ = 46.8, C-1); 25.8 (d, $^2J_{C,P}$ = 2.9, C-2,6); 25.2 (d, $^3J_{C,P}$ = 14.1, C-3,5); 24.8 (d, $^4J_{C,P}$ = 1.6, C-4).

For $C_{48}H_{52}P_2Br_6Os$

anal. calcd., %:	C, 42.37;	H, 3.82.
Found, %:	C, 42.30;	H, 3.90.

$[Ph_3PCH_2C(O)Ph]_2^+[OsBr_6]^{2-}$ (IV): (66%), T_{dec} = 298°C. IR (ν, cm^{-1}): 3057, 2909, 2849, 1672 ν(C=O), 1597, 1584, 1481, 1447, 1437 (P–C_{Ph}), 1325, 1313, 1300, 1204, 1107, 995 (P–C_{Ph}), 986, 856, 745, 718, 684, 507, 445, 434, 419. ^{1}H NMR (δ, ppm; *J*, Hz): 8.09 (dd, 2H, $J_{H,H}$ = 8.2, 1.1, *o*-H); 7.90–7.83 (m, 9H, H_{Ar}); 7.78–7.74 (m, 7H, H_{Ar}); 7.61 (dd, 2H, $J_{H,H}$ = 8.2, 7.6, *m*-H); 6.17 (d, 2H, $^2J_{H,P}$ = 13.0, CH_2). ^{13}C NMR (δ, ppm; *J*, Hz): 192.2 (d, $^2J_{C,P}$ = 6.3, CO); 135.0 (d, $^3J_{C,P}$ = 6.3, *ipso*-C); 134.8 (s, *p*-C); 134.7 (d, $^4J_{C,P}$ = 2.8, 3**p*-C); 133.6 (d, $^2J_{C,P}$ = 10.8, 6**o*-C); 130.0 (d, $^3J_{C,P}$ = 12.8, 6**m*-C); 129.0 (s, *o*-C); 128.9 (s, *m*-C); 118.9 (d, $^1J_{C,P}$ = 89.0, 3**ipso*-C); 35.4 (d, $^1J_{C,P}$ = 61.8, CH_2).

For $C_{52}H_{44}O_2P_2Br_6Os$

anal calcd., %:	C, 43.59;	H, 3.07.
Found, %:	C, 43.49;	H, 3.11.

$[Ph_3PPr]_2[OsBr_6]$ · DMSO (V): (52%), T_{dec} = 215°C. IR (ν, cm^{-1}): 3075, 3055, 3013, 2987, 2967, 2924, 2887, 1585, 1483, 1437 (P–C_{Ph}), 1192, 1161, 1111, 1026 ν(S=O), 995 (P–C_{Ph}), 748, 729, 721, 689, 529, 507, 457, 440, 419. ^{1}H NMR (δ, ppm; *J*, Hz): 7.92–7.89 (m, 3H, *p*-H); 7.83–7.75 (m, 12H, *m*-H, *o*-H); 3.53 (m, 2H, H-1); 1.58 (m, 2H, H-2); 1.08 (td, 3H, $J_{H,H}$ = 7.3, $^4J_{H,P}$ = 1.8, H-3). ^{13}C NMR (δ, ppm; *J*, Hz): 134.9 (d, $^4J_{C,P}$ = 3.1, 3**p*-C); 133.5 (d, $^2J_{C,P}$ = 10.0, 6**o*-C); 130.3 (d, $^3J_{C,P}$ = 12.4, 6**m*-C); 118.3 (d, $^1J_{C,P}$ = 85.5, 3* *ipso*-C); 22.4 (d, $^1J_{C,P}$ = 49.6, C-1); 15.7 (d, $^2J_{C,P}$ = 4.2, C-2); 15.0 (d, $^3J_{C,P}$ = 18.0, C-3).

For $C_{44}H_{50}OSP_2Br_6Os$

anal. calcd., %:	C, 38.89;	H, 3.68.
Found, %:	C, 38.79;	H, 3.72.

$[Ph_3P(CH_2)_3PPh_3]_2^+[OsBr6]^2$ · DMSO (VI): (70%), T_{dec} = 337°C. IR (ν, cm^{-1}): 3075, 3052, 2990, 2930, 2907, 2893, 1585, 1483, 1437 (P–C_{Ph}), 1339, 1317, 1113, 1028 ν(S=O), 995 (P–C_{Ph}), 961, 756, 741, 731, 723, 689, 540, 527, 515, 507, 498, 419. ^{1}H NMR (δ, ppm; *J*, Hz): 7.89 (m, 6H, *p*-H); 7.79–7.72 (m, 24H, *m*-H, *o*-H); 3.65 (m, 4H, H-1, H-3); 1.88 (m, 2H, H-2).

For $C_{41}H_{42}OSP_2Br_6Os$

anal. calcd., %:	C, 37.45;	H, 3.20.
Found, %:	C, 37.34;	H, 3.31.

The IR spectra of compounds **I**–**VI** were measured on a Shimadzu IRAffinity-1S FT IR spectrometer; the samples were prepared as KBr pellets (4000–400 cm^{-1} range). The ^{1}H, ^{31}P, and ^{13}C NMR spectra of compounds **I**–**VI** in DMSO-d_6 were recorded on a Bruker AVANCE 500 spectrometer (500, 202, and 126 MHz, respectively). The chemical shifts were referred to internal TMS for ^{1}H, external H_3PO_4 for ^{31}P, and to the solvent signal for ^{13}C (δ_C 39.5 ppm).

X-ray diffraction analysis for crystals **I**–**VI** was carried out at 296(2) K on a D8 QUEST Bruker diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The data were collected and edited, the unit cell parameters were refined, and the absorption corrections were applied using the SMART and SAINT-Plus program packages [7]. All calculations

Table 1. Crystallographic data and X-ray experiment and structure refinement details for **I–VI**

Parameter	Value					
	I	**II**	**III**	**IV**	**V**	**VI**
M	1276.34	1308.42	1360.50	1432.48	1436.62	1314.41
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	18.8159(5)	11.5972(5)	10.8333(4)	9.8434(3)	9.5158(3)	15.7572(6)
b, Å	14.6456(3)	16.2031(6)	14.9902(6)	10.5709(4)	18.9960(6)	15.6757(6)
c, Å	15.8749(4)	12.6915(5)	14.6100(6)	12.6165(4)	14.8884(5)	18.3535(8)
α, deg	90	90	90	94.3720(10)	90	90
β, deg	90	98.9230(10)	93.3300(10)	91.7530(10)	95.4130(10)	92.9780(10)
γ, deg	90	90	90	107.0790(10)	90	90
V, Å^3	4374.65(18)	2356.00(16)	2368.56(16)	1249.31(7)	2679.26(15)	4527.3(3)
Z	4	4	4	2	4	4
ρ(calcd), g/cm^3	1.938	1.844	1.908	1.904	1.781	1.928
μ, mm^{-1}	8.497	7.891	7.853	7.453	7.025	8.259
F(000)	2432.0	1256.0	1312.0	688.0	1392.0	2512.0
Crystal size, mm	0.17 × 0.15 × 0.11	0.68 × 0.42 × 0.32	0.2 × 0.03 × 0.03	0.34 × 0.14 × 0.09	0.52 × 0.46 × 0.21	0.48 × 0.29 × 0.11
Data collection range of θ, deg	5.76–52.92	5.98–52.84	6.62–52.14	6–52.16	5.9–52.84	5.8–52.86
Ranges of reflection indices	$-23 \le h \le 23$, $-18 \le k \le 18$, $-19 \le l \le 19$	$-14 \le h \le 14$, $-20 \le k \le 20$, $-15 \le l \le 15$	$-13 \le h \le 12$, $-18 \le k \le 18$, $-18 \le l \le 18$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-23 \le k \le 23$, $-18 \le l \le 18$	$-19 \le h \le 19$, $-19 \le k \le 19$, $-22 \le l \le 22$
Reflections measured	111062	35044	67995	28525	33664	77618
Reflections unique (R_{int})	8966 (0.0543)	4829 (0.0394)	4631 (0.1332)	4934 (0.0314)	5477 (0.0440)	9269 (0.0629)
Reflections with $I > 2\sigma(I)$	8966	4829	4631	4934	5477	9269
Number of refinement parameters	460	242	259	286	271	471
GOOF	1.024	1.029	1.046	1.037	0.860	1.057
R-factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0267$, $wR_2 = 0.0570$	$R_1 = 0.0252$, $wR_2 = 0.0506$	$R_1 = 0.0364$, $wR_2 = 0.0539$	$R_1 = 0.0194$, $wR_2 = 0.0418$	$R_1 = 0.0312$, $wR_2 = 0.0967$	$R_1 = 0.0323$, $wR_2 = 0.0577$
R-factors for all reflections	$R_1 = 0.0344$, $wR_2 = 0.0599$	$R_1 = 0.0331$, $wR_2 = 0.0535$	$R_1 = 0.0865$, $wR_2 = 0.0654$	$R_1 = 0.0262$, $wR_2 = 0.0439$	$R_1 = 0.0469$, $wR_2 = 0.1132$	$R_1 = 0.0533$, $wR_2 = 0.0636$
Residual electron density (max/min/), e/Å^3	0.41/–0.31	0.98/–0.95	0.93/–1.58	0.56/–0.35	1.21/–0.81	1.01/–0.94

Table 2. Bond lengths (*d*) and bond angles (ω) in structures **I**–**VI**

Bond	*d*, Å	Angle	ω, deg
		I	
Os(1)–Br(1)	2.4801(7)	Br(1)Os(1)Br(2)	89.93(3)
Os(1)–Br(2)	2.5033(6)	Br(1)Os(1)Br(4)	89.00(2)
Os(1)–Br(3)	2.4865(6)	Br(1)Os(1)Br(5)	179.06(3)
Os(1)–Br(4)	2.4976(6)	Br(1)Os(1)Br(6)	89.36(2)
Os(1)–Br(5)	2.4825(7)	Br(2)Os(1)Br(3)	91.26(2)
Os(1)–Br(6)	2.4865(6)	Br(2)Os(1)Br(4)	178.88(3)
P(1)–C(1)	1.793(6)	Br(2)Os(1)Br(5)	89.54(2)
P(1)–C(11)	1.792(6)	Br(3)Os(1)Br(4)	88.38(2)
P(1)–C(21)	1.800(6)	Br(3)Os(1)Br(5)	90.93(3)
P(1)–C(31)	1.778(6)	Br(3)Os(1)Br(6)	179.18(3)
P(2)–C(41)	1.798(6)	Br(4)Os(1)Br(5)	91.53(3)
P(2)–C(51)	1.788(6)	Br(5)Os(1)Br(6)	89.86(2)
P(2)–C(61)	1.791(6)	C(1)P(1)C(11)	111.5(3)
P(2)–C(71)	1.773(6)	C(11)P(1)C(21)	108.0(3)
		II	
Os(1)–Br(1)	2.4924(3)	Br(1)Os(1)Br(2)	89.333(13)
Os(1)–Br(2)	2.4872(4)	Br(1)Os(1)Br(3)	89.015(13)
Os(1)–Br(3)	2.4825(4)	Br(2)Os(1)Br(3)	89.383(16)
P(1)–C(1)	1.787(4)	C(1)P(1)C(31)	108.54(19)
P(1)–C(11)	1.795(4)	C(1)P(1)C(21)	110.35(18)
		III	
Os(1)–Br(1)	2.4970(5)	Br(1)Os(1)Br(2)	90.72(2)
Os(1)–Br(2)	2.4734(8)	Br(1)Os(1)Br(3)	90.65(2)
Os(1)–Br(3)	2.4741(6)	Br(2)Os(1)Br(3)	90.15(3)
P(1)–C(1)	1.788(6)	C(1)P(1)C(21)	105.2(3)
P(1)–C(31)	1.814(6)	C(1)P(1)C(11)	115.5(3)
		IV	
Os(1)–Br(1)	2.4889(3)	Br(1)Os(1)Br(2)	89.895(11)
Os(1)–Br(2)	2.4746(3)	Br(1)Os(1)Br(3)	89.153(10)
Os(1)–Br(3)	2.5031(3)	Br(2)Os(1)Br(3)	89.984(10)
P(1)–C(1)	1.793(3)	C(1)P(1)C(21)	106.44(12)
C(31)–C(37)	1.487(3)	C(21)P(1)C(38)	113.75(13)
C(37)–C(38)	1.518(3)		
P(1)–C(38)	1.803(2)		
O(1)–C(37)	1.212(3)		
		V	
Os(1)–Br(1)	2.5037(4)	Br(1)Os(1)Br(2)	90.447(17)
Os(1)–Br(2)	2.4864(5)	Br(1)Os(1)Br(3)	90.533(18)
Os(1)–Br(3)	2.4816(5)	Br(2)Os(1)Br(3)	90.44(2)
P(1)–C(1)	1.790(5)	C(21)P(1)C(31)	108.1(2)
P(1)–C(11)	1.802(5)	C(1)P(1)C(31)	112.0(2)
S(1)–C(34)	1.757(8)		
S(1)–C(35)	1.756(9)		
S(1)–O(1)	1.493(5)		

Table 2. (Contd.)

Bond	*d*, Å	Angle	ω, deg
		VI	
Os(1)–Br(1)	2.4838(5)	Br(1)Os(1)Br(2)	89.356(19)
Os(1)–Br(2)	2.4802(5)	Br(1)Os(1)Br(3)	91.321(18)
Os(1)–Br(3)	2.4785(5)	Br(1)Os(1)Br(4)	88.452(17)
Os(1)–Br(4)	2.5203(5)	Br(1)Os(1)Br(5)	177.276(18)
Os(1)–Br(5)	2.4883(5)	Br(1)Os(1)Br(6)	90.268(19)
Os(1)–Br(6)	2.4819(5)	Br(2)Os(1)Br(3)	90.57(2)
P(1)–C(1)	1.801(5)	Br(2)Os(1)Br(4)	90.435(18)
P(1)–C(11)	1.799(4)	Br(2)Os(1)Br(5)	90.197(19)
P(1)–C(21)	1.793(4)	Br(2)Os(1)Br(6)	179.50(2)
P(1)–C(27)	1.803(4)	Br(3)Os(1)Br(4)	178.97(2)
P(2)–C(29)	1.800(4)	Br(3)Os(1)Br(5)	91.370(18)
P(2)–C(31)	1.791(4)	Br(3)Os(1)Br(6)	89.76(2)
P(2)–C(41)	1.799(5)	Br(4)Os(1)Br(5)	88.864(16)
P(2)–C(51)	1.793(5)	Br(4)Os(1)Br(6)	89.231(18)
S(1)–O(1)	1.487(5)	Br(5)Os(1)Br(6)	90.164(19)
S(1)–C(7)	1.709(8)	C(21)P(1)C(27)	105.7(2)
S(1)–C(1a)	1.677(9)	C(11)P(1)C(21)	111.6(2)

on structure solution and refinement were done using the SHELXL/PC [8] and OLEX2 [9] program packages. The structures were solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and refinement details for structures **I**–**VI** are summarized in Table 1, and selected bond lengths and bond angles are in Table 2.

Full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (nos. 1000171, 1000148, 1000172, 1000173, 1000147, and 1000149 for structures **I**–**VI**, respectively, deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

A known specific feature of $[OsX_6]^{2-}$ ions is high kinetic inertness. Nevertheless, under certain conditions, they can undergo transformations associated with a decrease in osmium oxidation state to +3 and +2. Indeed, potassium hexabromoosmate(IV) reacts with dimethyl sulfoxide at room temperature with successive displacement of bromide ions by dimethyl sulfoxide molecules and partial reduction of osmium to give *trans*-$[Os^{+2}Br_2(DMSO\text{-}S)_4]$; however, this reaction is very slow (over a period of 2 years) [10].

In order to elucidate specific structural features of phosphonium complexes containing hexabromoosmate anions and the effect of the nature of phosphonium cations on the kinetic stability of hexabromoosmate anions in dimethyl sulfoxide solution, we carried out reactions of sodium hexabromoosmate with tetraorganylphosphonium bromides in dimethyl sulfoxide.

We found that slow evaporation of the solvent from solutions of tetraorganylphosphonium bromide and sodium hexabromoosmate(IV) in DMSO (2 : 1 molar ratio) without heating the reaction mixture results in precipitation of air-stable dark brown crystals of $[Ph_3PR]_2^+[OsBr_6]^{2-}$ in up to 70% yield:

$$2[Ph_3PR]^+Br + Na_2[OsBr_6] \xrightarrow{DMSO} [Ph_3PR]_2^+[OsBr_6]^{2-} + 2NaBr$$

R = *cyclo*-C_3H_5 (**I**), *n*-C_4H_9 (**II**), *cyclo*-C_6H_{11} (**III**), $CH_2C(O)Ph$ (**IV**)

Similar reactions with triphenyl-*n*-propylphosphonium bromide (1 : 2 molar ratio) and trimethylene-bis-triphenylphosphonium dibromide (1 : 1 molar ratio) afford complexes that contain a solvent molecule according to X-ray diffraction data: $[Ph_3PPr\text{-}n]_2^+[OsBr_6]^{2-} \cdot DMSO$ (**V**) and $[Ph_3P(CH_2)_3PPh_3]^{2+}[OsBr_6]^{2-} \cdot DMSO$ (**VI**).

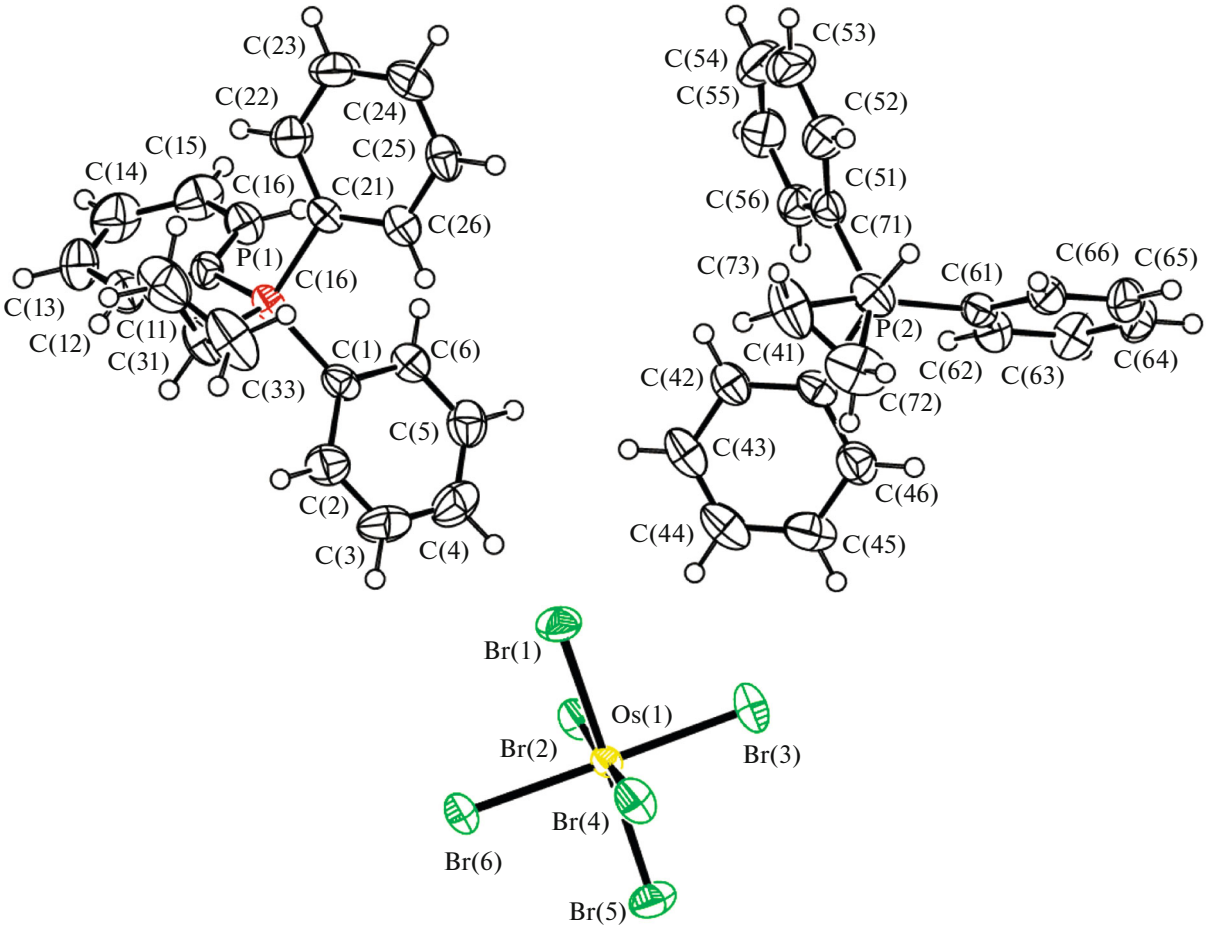

Fig. 1. Structure of complex **I**.

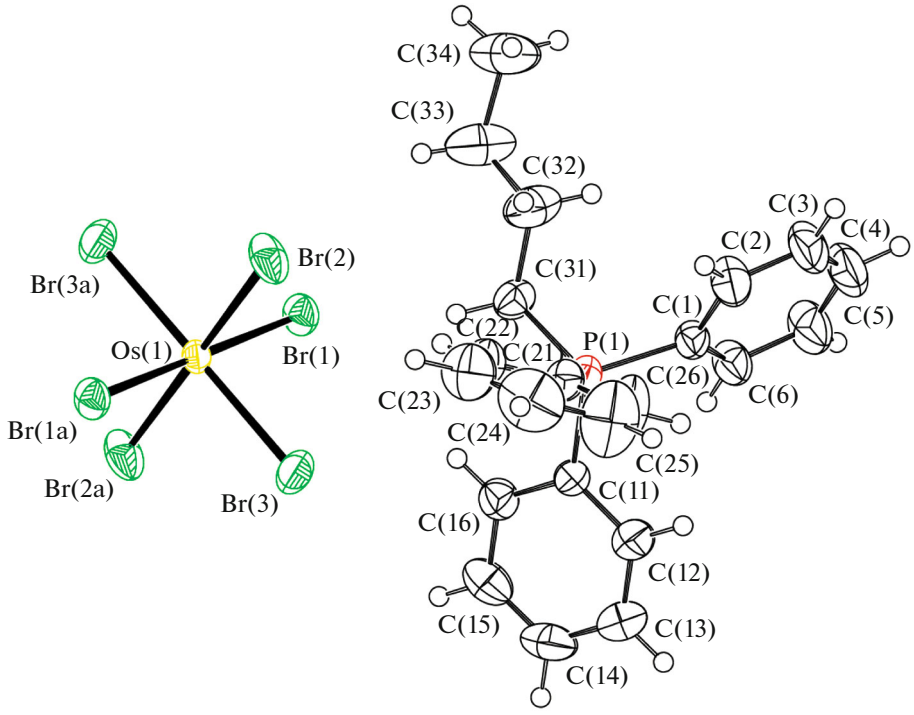

Fig. 2. Structure of complex **II**.

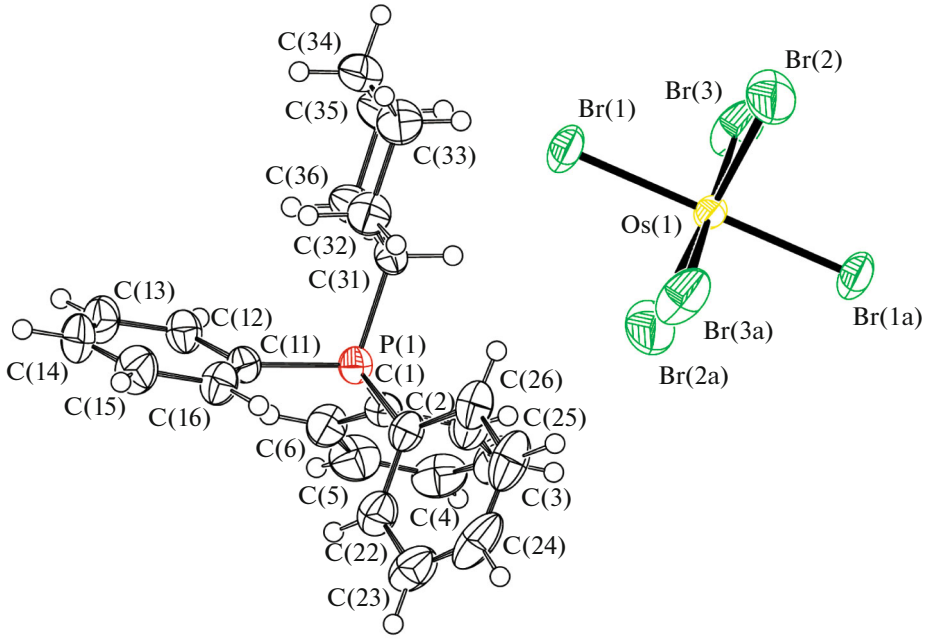

Fig. 3. Structure of complex **III**.

Complexes **I**–**VI** are formed by tetraorganylphosphonium cations with almost undistorted tetrahedral coordination of phosphorus and octahedral mononuclear hexabromoosmate anions (Figs. 1–6).

The CPC angles in the cations of **I**–**V** vary in the ranges 108.0(3)°–111.5(3)°, 108.5(2)°–110.3(2)°, 105.2(3)°–112.9(3)°, 106.4(1)°–113.7(1)°, and 108.1(2)°– 112.0(2)°, respectively; the P–C distances (1.773(6)–1.800(6), 1.787(4)–1.795(4), 1.795(6)–1.814(6), 1.793(3)–1.803(2), 1.790(5)–1.802(5) Å in **I**, **II**, **III**, **IV**, and **V**, respectively) are shorter than the sum of the phosphorus and carbon covalent radii (1.88 Å [11]). In the binuclear cation of **VI**, the P(1)–C (1.793(4)–1.803(4) Å) and P(2)–C (1.791(4)–1.801(5) Å) distances are almost equal; the same is true for the CP(1)C (105.7(2)°–111.6(2)°) and CP(2)C (106.9(2)°–111.2(2)°) angles.

The octahedral $[OsBr_6]^{2-}$ anions in **II**–**V** are centrosymmetric. In **I** and **VI**, the anion configuration is somewhat distorted: the *trans*-BrOsBr angles vary in

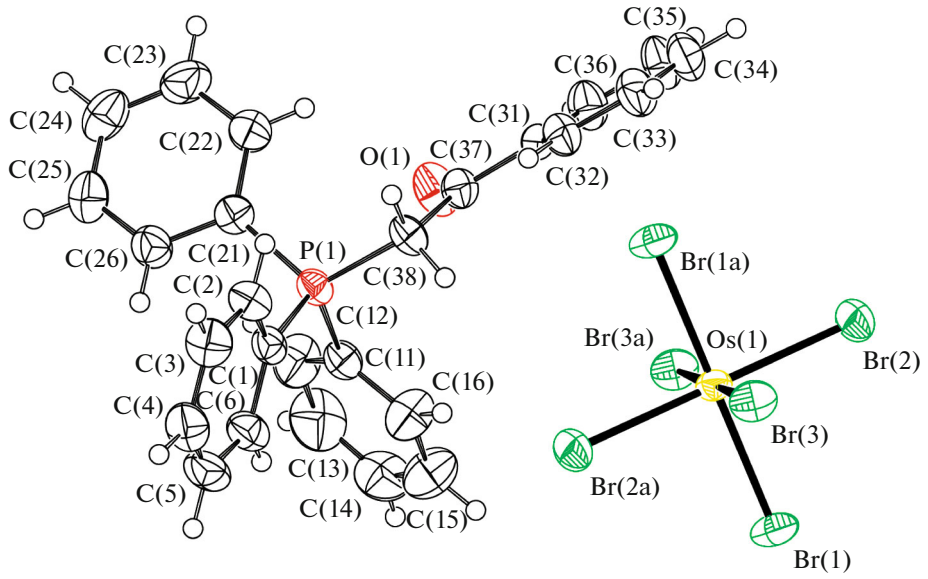

Fig. 4. Structure of complex **IV**.

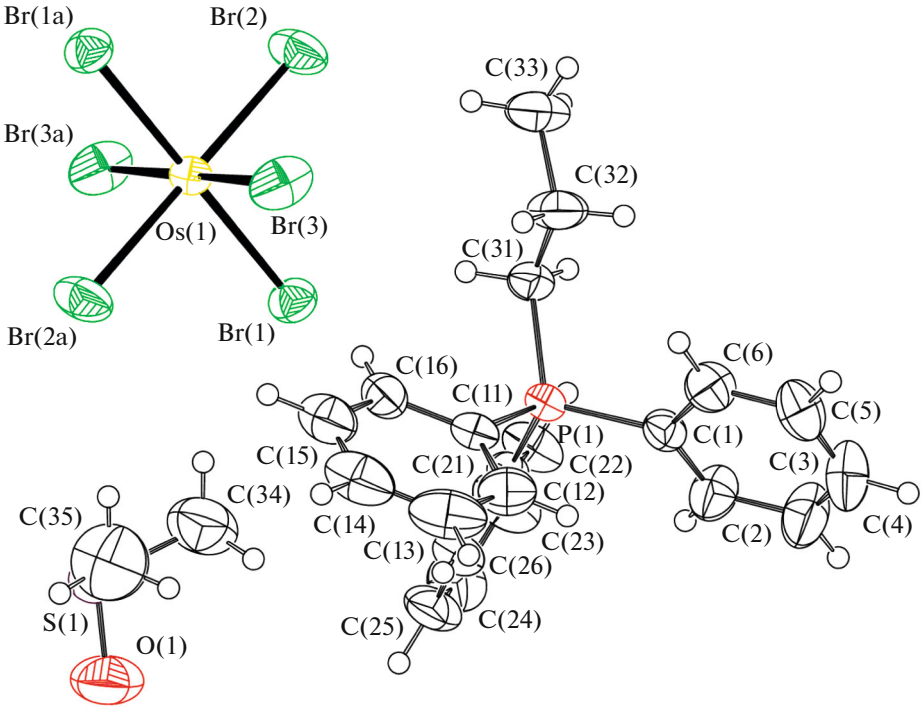

Fig. 5. Structure of complex **V**.

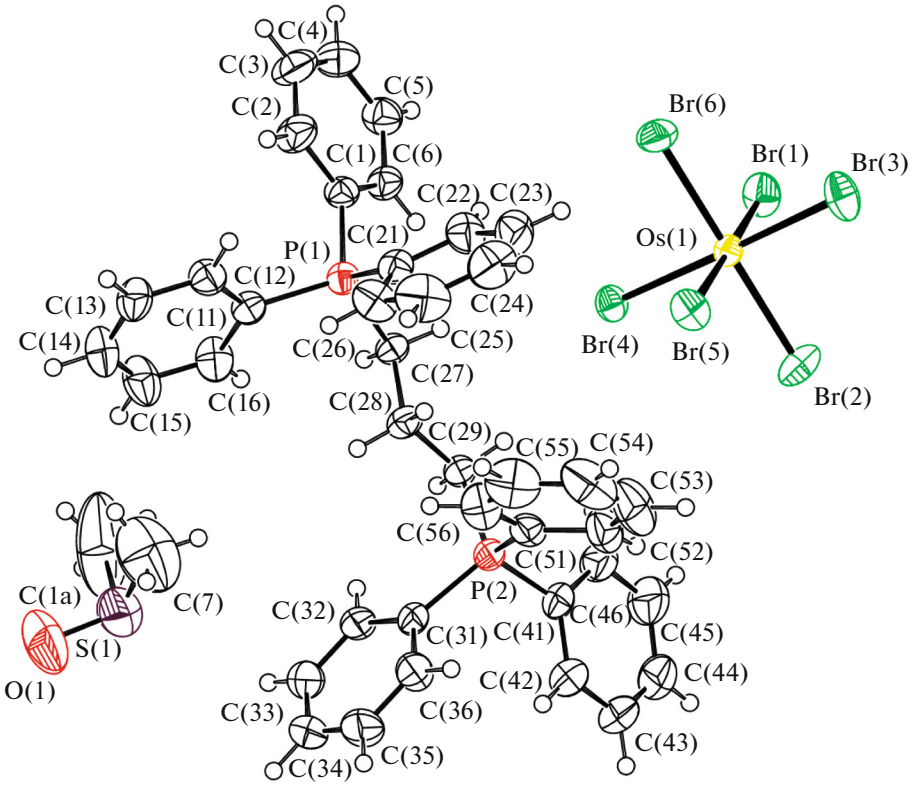

Fig. 6. Structure of complex **VI**.

the range of 177.276(18)°–179.50(2)°. The Os–Br bond lengths (2.4734(8)–2.5203(5) Å) are shorter than the sum of osmium and bromine covalent radii (2.56 Å [11]).

The structural organization in crystals **I**–**VI** is formed by weak ion–ion hydrogen bonds (H···Br 2.74–3.04 Å), the strongest one being in complex **IV** (H···Br 2.74 Å). Apart from this, in **V** and **VI**, the oxygen atoms of the dimethyl sulfoxide solvate molecules form O···H bonds (2.28–2.63 Å) with the hydrogen atoms of the triphenyl-*n*-propylphosphonium and trimethylene-bis-triphenylphosphonium cations.

Thus, the reactions of tetraorganylphosphonium bromides with sodium hexabromoosmate in a dimethyl sulfoxide solution give complexes containing tetraorganylphosphonium cations and mononuclear $[OsBr_6]^{2-}$ anions. The complexes are stable in solution and in air, the dimethyl sulfoxide molecules are not incorporated in the coordination spheres of the anions, but are present in the crystal lattice of **V** and **VI**.

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