Supplementary Material (ESI) for Chemical Communications

Synthesis and Characterization of the High-Nuclearity Osmium-Silver Mixed-Metal Clusters

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Electronic Supplementary Information

Experimental Procedures

Solvents used were distilled from appropriate drying agents and prepared freshly before used. Routine separations of products were performed by thin-layer chromatography using 20 cm X 20 cm glass plates, coated with 0.7 mm thickness of Merck Keiselgel 60 PF_{254}. Infrared spectra were recorded as dichloromethane solution on a Bio-Rad FTS-165 IR spectrometer unless otherwise stated. ^{1}H NMR spectra were recorded on Bruker DPX-400 NMR spectrometer using CD_2Cl_2 solvent unless otherwise stated. Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, using 3-nitrobenzyl alcohol as the matrix solvent.

$[AgPF_6]$ (35 mg, 0.1384 mmol) was allowed to stir with the Vaska's complex, $[Ir(PPh_3)_2(CO)Cl]$ (30 mg, 0.0384 mmol), in THF (10 mL) at room temperature until white precipitate was observed. Then the filtrate was transferred to another flask containing $[Os_3(\mu\text{-}H)(CO)_{11}][PPN]$ (200 mg, 0.1358 mmol) via cannula. The mixture was allowed to stir for another 15 mins and was filtered to remove any insoluble residues. It was then separated by thin layer chromatography using the eluent of 7:3 dichloromethane: hexane mixture. $[Os_{13}Ag_9(CO)_{48}][PPN]$ (**1**), $[Os_9Ag_9(\mu_3\text{-}O)_2(CO)_{30}][PPN]$ (**2**) and an iridium complex, $[Ir(PPh_3)_2(CO)Cl(O_2)]$ (**3**) were isolated with R_f = 0.35, 0.6, 0.75, respectively.

X-Ray Crystallography: Single crystals of **1** were obtained by slow diffusion of its solution of dichloromethane/methanol/diethyl ether. Single-crystal X-ray data were collected on a Bruker SMART CCD area detector with graphite monochromated Mo-Kα radiation (λ= 0.71073Å), operated at 50 kV and 30 mA. The structure was solved by direct method (SIR92) and expanded by difference Fourier. All Os, Ag, P, N and O(1)-O(48) atoms were refined anisotropically, while O(25) and other C atoms were refined isotropically only. The atoms of the solvent molecules, including C(85), Cl(1) Cl(2), O(49) and O(50), were refined isotropically with fixed position and thermal parameters due to their high thermal motion inside the lattice. The refinement of these atoms was unsuccessful and will lead to a high shift/error ratio. Attempts were made to refine the carbon atoms on carbonyl ligands and the phenyl rings anisotropically but were unsuccessful. Hydrogen atoms were all placed at geometrical positions with C-H = 0.95 Å and refined using riding model with U_{iso} (H) = 1.2 U_{eq} (C). The hydrogen atoms on O(49) and O(50) were unable to locate. The two hydrogen atoms of the dichloromethane molecules (H(31) and H(32)) were placed at fixed positions.

Single crystals of **2** were obtained by slow diffusion of its solution of dichloromethane/methanol. Single-crystal X-ray data were collected on a Bruker SMART CCD area detector with graphite monochromated Mo-Kα radiation (λ= 0.71073 Å), operated at 50 kV and 30 mA. The structure was solved by Patterson method (DIRDIF99 PATTY) and expanded by difference Fourier. All Os, Ag, P, N atoms were refined anisotropically, while other O and C atoms were refined isotropically only. Attempts were made to refine the carbonyl ligands and the phenyl rings anisotropically but were unsuccessful. Hydrogen atoms were all placed at geometrical positions with C-H = 0.95 Å and refined using riding model with U_{iso} (H) = 1.2 U_{eq} (C). A dichloromethane molecule was observed inside the crystal lattice as the solvent of crystallization.

Single crystals of **3** were obtained by slow diffusion of its solution of dichloromethane/methanol. Single-crystal X-ray data were collected on a Bruker SMART CCD area detector with graphite monochromated Mo-Kα radiation (λ= 0.71073Å), operated at 50 kV and 30 mA. The structure was solved by Patterson method (DIRDIF99 PATTY) and expanded by difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, except C(37), C(38), O(1) and O(2) were refined isotropically. Hydrogen atoms were all placed at geometrical positions with C-H = 0.95 Å and refined using riding model with U_{iso} (H) = 1.2 U_{eq} (C). Disorder was observed for the chlorine atom and the carbonyl group, in which the occupancy was refined and found to be at 0.59 and 0.41 for the two positions. Subsequent refinements were performed using fixed occupancy factors as found.

Table 1. Crystallographic data and data collection parameters for complexes **1-3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{85}H_{30}Ag_9NOs_{13}O_{48}P_2 \cdot CH_2Cl_2 \cdot 2H_2O$	$C_{66}H_{30}Ag_9NOs_9O_{32}P_2 \cdot CH_2Cl_2$	$C_{37}H_{30}Cl\,IrO_3P_2$
Formula weight	5447.46	4178.44	812.26
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1 (#2)	P-1 (#2)	P-1 (#2)
a (Å)	19.240(3)	14.587(2)	9.7904(13)
b (Å)	19.413(3)	18.744(3)	9.9440(13)
c (Å)	19.787(3)	19.042(3)	17.248(2)
α (∘)	99.230(3)	63.828(3)	96.101(2)
β (∘)	94.512(3)	69.540(3)	91.039(2)
γ (∘)	109.734(4)	85.295(3)	93.565(2)
Volume ($Å^3$)	6795.7(18)	4361.8(12)	1666.0(4)
Z	2	2	2
Density (caculated) (Mg/m^3)	2.662	3.181	1.619
F (000)	4856.00	3736.00	800.00
Crystal size (mm^3)	0.05 x 0.12 x 0.20	0.10 x 0. 15 x 0.20	0.01 x 0.07 x 0.20
Reflections observed [$I>2.00\sigma(I)$]	13629	10869	6122
[R_{int}]	0.067	0.070	0.0313
Max. and min. transmission	0.376, 0.510	0.159, 0.219	0.717, 0.959
Goodness of fit on F^2	1.027	1.017	1.085
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0520, wR_2 = 0.0594	R_1 = 0.0664, wR_2 = 0.1019	R_1 = 0.032, wR_2 = 0.036
Residual Extrema in the Final ΔF Map/$eÅ^{-3}$	2.08, -1.86	5.83, -3.55	2.03, -0.58

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Ag(1)-Ag(2)	2.697(2)	Ag(1)-Ag(3)	2.792(3)
Ag(1)-Ag(4)	2.807(2)	Ag(1)-Ag(6)	2.851(2)
Ag(2)-Ag(4)	3.187(3)	Ag(2)-Ag(5)	2.868(3)
Ag(3)-Ag(5)	2.887(2)	Ag(3)-Ag(6)	2.817(3)
Ag(4)-Ag(5)	2.716(3)	Ag(4)-Ag(6)	2.886(2)
Ag(4)-Ag(8)	2.875(2)	Ag(4)-Ag(9)	2.882(2)
Ag(5)-Ag(6)	2.880(2)	Ag(5)-Ag(7)	2.819(3)
Ag(5)-Ag(8)	3.149(3)	Ag(6)-Ag(7)	2.850(2)
Ag(6)-Ag(9)	2.821(3)	Ag(7)-Ag(8)	2.696(3)
Ag(7)-Ag(9)	2.784(3)	Os(1)-Os(2)	2.9146(16)
Os(1)-Os(3)	2.8659(14)	Os(2)-Ag(2)	2.933(2)
Os(2)-Os(3)	2.9964(16)	Os(3)-Ag(1)	2.855(2)
Os(3)-Ag(2)	2.897(2)	Os(3)-Ag(3)	2.841(2)
Os(4)-Ag(1)	2.888(2)	Os(4)-Ag(4)	2.957(2)
Os(4)-Ag(6)	2.907(2)	Os(4)-Ag(9)	2.979(2)
Os(4)-Os(5)	2.8784(16)	Os(4)-Os(6)	3.0353(15)
Os(5)-Os(6)	2.9057(18)	Os(6)-Ag(9)	2.885(2)
Os(7)-Ag(2)	2.816(2)	Os(7)-Ag(4)	2.988(2)
Os(7)-Ag(5)	2.963(2)	Os(7)-Ag(8)	2.811(2)
Os(8)-Ag(3)	2.958(2)	Os(8)-Os(10)	2.9009(18)
Os(8)-Os(9)	3.0206(14)	Os(9)-Ag(3)	2.955(2)
Os(9)-Ag(5)	2.942(2)	Os(9)-Ag(6)	2.912(2)
Os(9)-Ag(7)	2.881(2)	Os(9)-Os(10)	2.879(2)
Os(11)-Ag(7)	2.858(2)	Os(11)-Ag(8)	2.890(2)
Os(11)-Ag(9)	2.834(2)	Os(11)-Os(12)	2.9890(16)
Os(11)-Os(13)	2.8610(13)	Os(12)-Ag(8)	2.948(2)
Os(12)-Os(13)	2.9101(18)		
Ag(1)-Ag(2)-Ag(4)	56.24(6)	Ag(1)-Ag(2)-Ag(5)	76.45(7)
Ag(1)-Ag(3)-Ag(5)	74.70(8)	Ag(1)-Ag(3)-Ag(6)	61.11(8)
Ag(1)-Ag(4)-Ag(2)	53.02(6)	Ag(1)-Ag(4)-Ag(5)	77.19(9)
Ag(1)-Ag(4)-Ag(6)	60.09(7)	Ag(1)-Ag(4)-Ag(8)	145.67(12)
Ag(1)-Ag(4)-Ag(9)	109.60(7)	Ag(1)-Ag(6)-Ag(3)	59.01(8)
Ag(1)-Ag(6)-Ag(4)	58.58(7)	Ag(1)-Ag(6)-Ag(5)	73.92(7)
Ag(1)-Ag(6)-Ag(7)	126.73(8)	Ag(1)-Ag(6)-Ag(9)	110.10(10)
Ag(1)-Os(3)-Ag(2)	55.93(5)	Ag(1)-Os(3)-Ag(3)	58.70(7)
Ag(1)-Os(4)-Ag(4)	57.40(5)	Ag(1)-Os(4)-Ag(6)	58.95(6)

Ag(1)-Os(4)-Ag(9)	104.82(6)	Ag(2)-Ag(1)-Ag(3)	81.95(9)
Ag(2)-Ag(1)-Ag(4)	70.74(7)	Ag(2)-Ag(1)-Ag(6)	107.29(8)
Ag(2)-Ag(4)-Ag(5)	57.47(8)	Ag(2)-Ag(4)-Ag(6)	94.64(8)
Ag(2)-Ag(4)-Ag(8)	105.62(9)	Ag(2)-Ag(4)-Ag(9)	152.66(11)
Ag(2)-Ag(5)-Ag(3)	77.44(7)	Ag(2)-Ag(5)-Ag(4)	69.55(9)
Ag(2)-Ag(5)-Ag(6)	102.07(8)	Ag(2)-Ag(5)-Ag(7)	147.18(13)
Ag(2)-Ag(5)-Ag(8)	106.79(9)	Ag(2)-Os(3)-Ag(3)	77.71(6)
Ag(2)-Os(7)-Ag(4)	66.55(6)	Ag(2)-Os(7)-Ag(5)	59.45(6)
Ag(2)-Os(7)-Ag(8)	118.42(6)	Ag(3)-Ag(1)-Ag(4)	101.33(9)
Ag(3)-Ag(1)-Ag(6)	59.88(7)	Ag(3)-Ag(5)-Ag(4)	101.18(9)
Ag(3)-Ag(5)-Ag(6)	58.48(6)	Ag(3)-Ag(5)-Ag(7)	109.03(8)
Ag(3)-Ag(5)-Ag(8)	153.25(10)	Ag(3)-Ag(6)-Ag(4)	98.80(8)
Ag(3)-Ag(6)-Ag(5)	60.88(6)	Ag(3)-Ag(6)-Ag(7)	110.16(9)
Ag(3)-Ag(6)-Ag(9)	157.86(8)	Ag(3)-Os(9)-Ag(5)	58.62(6)
Ag(3)-Os(9)-Ag(6)	57.39(6)	Ag(3)-Os(9)-Ag(7)	105.53(8)
Ag(4)-Ag(1)-Ag(6)	61.33(7)	Ag(4)-Ag(2)-Ag(5)	52.98(7)
Ag(4)-Ag(5)-Ag(6)	62.01(7)	Ag(4)-Ag(5)-Ag(7)	77.64(9)
Ag(4)-Ag(5)-Ag(8)	58.15(8)	Ag(4)-Ag(6)-Ag(5)	56.20(7)
Ag(4)-Ag(6)-Ag(7)	74.47(7)	Ag(4)-Ag(6)-Ag(9)	60.66(7)
Ag(4)-Ag(8)-Ag(5)	53.36(7)	Ag(4)-Ag(8)-Ag(7)	77.01(7)
Ag(4)-Ag(9)-Ag(6)	60.79(7)	Ag(4)-Ag(9)-Ag(7)	75.52(8)
Ag(4)-Os(4)-Ag(6)	58.96(6)	Ag(4)-Os(4)-Ag(9)	58.10(5)
Ag(4)-Os(7)-Ag(5)	54.32(7)	Ag(4)-Os(7)-Ag(8)	59.36(6)
Ag(5)-Ag(3)-Ag(6)	60.64(7)	Ag(5)-Ag(4)-Ag(6)	61.79(7)
Ag(5)-Ag(4)-Ag(8)	68.49(8)	Ag(5)-Ag(4)-Ag(9)	100.82(10)
Ag(5)-Ag(6)-Ag(7)	58.94(6)	Ag(5)-Ag(6)-Ag(9)	98.40(7)
Ag(5)-Ag(7)-Ag(6)	61.07(6)	Ag(5)-Ag(7)-Ag(8)	69.61(8)
Ag(5)-Ag(7)-Ag(9)	100.75(10)	Ag(5)-Ag(8)-Ag(7)	57.04(7)
Ag(5)-Os(7)-Ag(8)	66.05(6)	Ag(5)-Os(9)-Ag(6)	58.94(6)
Ag(5)-Os(9)-Ag(7)	57.90(6)	Ag(6)-Ag(4)-Ag(8)	101.25(9)
Ag(6)-Ag(4)-Ag(9)	58.55(7)	Ag(6)-Ag(5)-Ag(7)	59.99(6)
Ag(6)-Ag(5)-Ag(8)	95.13(8)	Ag(6)-Ag(7)-Ag(8)	106.83(10)
Ag(6)-Ag(7)-Ag(9)	60.08(7)	Ag(6)-Ag(9)-Ag(7)	61.11(7)
Ag(6)-Os(4)-Ag(9)	57.25(6)	Ag(6)-Os(9)-Ag(7)	58.93(6)
Ag(7)-Ag(5)-Ag(8)	53.35(7)	Ag(7)-Ag(6)-Ag(9)	58.81(7)
Ag(7)-Os(11)-Ag(8)	55.93(6)	Ag(7)-Os(11)-Ag(9)	58.57(7)
Ag(8)-Ag(4)-Ag(9)	77.29(7)	Ag(8)-Ag(7)-Ag(9)	82.00(10)
Ag(8)-Os(11)-Ag(9)	77.82(6)	Os(1)-Os(2)-Ag(2)	113.21(6)

Os(1)-Os(2)-Os(3)	57.98(3)	Os(1)-Os(3)-Ag(1)	140.57(7)
Os(1)-Os(3)-Ag(2)	115.84(5)	Os(1)-Os(3)-Ag(3)	160.10(7)
Os(1)-Os(3)-Os(2)	59.58(3)	Os(2)-Ag(2)-Ag(1)	95.27(7)
Os(2)-Ag(2)-Ag(4)	133.54(10)	Os(2)-Ag(2)-Ag(5)	163.34(9)
Os(2)-Ag(2)-Os(3)	61.86(4)	Os(2)-Ag(2)-Os(7)	133.53(8)
Os(2)-Os(1)-Os(3)	62.44(3)	Os(2)-Os(3)-Ag(1)	90.68(6)
Os(2)-Os(3)-Ag(2)	59.67(5)	Os(2)-Os(3)-Ag(3)	137.08(5)
Os(3)-Ag(1)-Ag(2)	62.82(6)	Os(3)-Ag(1)-Ag(3)	60.40(7)
Os(3)-Ag(1)-Ag(4)	131.57(8)	Os(3)-Ag(1)-Ag(6)	120.27(10)
Os(3)-Ag(1)-Os(4)	165.60(7)	Os(3)-Ag(2)-Ag(1)	61.25(6)
Os(3)-Ag(2)-Ag(4)	116.07(7)	Os(3)-Ag(2)-Ag(5)	101.56(8)
Os(3)-Ag(2)-Os(7)	163.77(10)	Os(3)-Ag(3)-Ag(1)	60.90(7)
Os(3)-Ag(3)-Ag(5)	102.46(8)	Os(3)-Ag(3)-Ag(6)	121.99(10)
Os(3)-Ag(3)-Os(8)	133.73(7)	Os(3)-Ag(3)-Os(9)	160.28(7)
Os(3)-Os(2)-Ag(2)	58.47(5)	Os(4)-Ag(1)-Ag(2)	131.51(8)
Os(4)-Ag(1)-Ag(3)	118.33(8)	Os(4)-Ag(1)-Ag(4)	62.54(6)
Os(4)-Ag(1)-Ag(6)	60.86(6)	Os(4)-Ag(4)-Ag(1)	60.07(5)
Os(4)-Ag(4)-Ag(2)	111.91(7)	Os(4)-Ag(4)-Ag(5)	118.91(8)
Os(4)-Ag(4)-Ag(6)	59.66(5)	Os(4)-Ag(4)-Ag(8)	138.59(9)
Os(4)-Ag(4)-Ag(9)	61.34(5)	Os(4)-Ag(4)-Os(7)	164.16(8)
Os(4)-Ag(6)-Ag(1)	60.19(6)	Os(4)-Ag(6)-Ag(3)	116.86(8)
Os(4)-Ag(6)-Ag(4)	61.38(6)	Os(4)-Ag(6)-Ag(5)	115.24(8)
Os(4)-Ag(6)-Ag(7)	118.38(9)	Os(4)-Ag(6)-Ag(9)	62.67(6)
Os(4)-Ag(6)-Os(9)	176.29(7)	Os(4)-Ag(9)-Ag(4)	60.56(6)
Os(4)-Ag(9)-Ag(6)	60.08(6)	Os(4)-Ag(9)-Ag(7)	118.11(8)
Os(4)-Ag(9)-Os(11)	160.56(8)	Os(4)-Ag(9)-Os(6)	62.32(4)
Os(4)-Os(5)-Os(6)	63.30(4)	Os(4)-Os(6)-Ag(9)	60.37(4)
Os(4)-Os(6)-Os(5)	57.91(3)	Os(5)-Os(4)-Ag(1)	140.98(5)
Os(5)-Os(4)-Ag(4)	158.36(7)	Os(5)-Os(4)-Ag(6)	135.13(6)
Os(5)-Os(4)-Ag(9)	112.03(5)	Os(5)-Os(4)-Os(6)	58.79(4)
Os(5)-Os(6)-Ag(9)	114.04(6)	Os(6)-Ag(9)-Ag(4)	122.87(8)
Os(6)-Ag(9)-Ag(6)	90.27(6)	Os(6)-Ag(9)-Ag(7)	134.41(9)
Os(6)-Ag(9)-Os(11)	133.79(8)	Os(6)-Os(4)-Ag(1)	143.08(7)
Os(6)-Os(4)-Ag(4)	115.40(5)	Os(6)-Os(4)-Ag(6)	85.75(5)
Os(6)-Os(4)-Ag(9)	57.31(4)	Os(7)-Ag(2)-Ag(1)	115.44(9)
Os(7)-Ag(2)-Ag(4)	59.31(5)	Os(7)-Ag(2)-Ag(5)	62.83(6)
Os(7)-Ag(4)-Ag(1)	107.07(8)	Os(7)-Ag(4)-Ag(2)	54.14(5)
Os(7)-Ag(4)-Ag(5)	62.38(6)	Os(7)-Ag(4)-Ag(6)	124.17(10)

Os(7)-Ag(4)-Ag(8)	57.25(5)	Os(7)-Ag(4)-Ag(9)	134.47(8)
Os(7)-Ag(5)-Ag(2)	57.72(6)	Os(7)-Ag(5)-Ag(3)	135.11(9)
Os(7)-Ag(5)-Ag(4)	63.30(7)	Os(7)-Ag(5)-Ag(6)	125.31(10)
Os(7)-Ag(5)-Ag(7)	107.93(9)	Os(7)-Ag(5)-Ag(8)	54.65(5)
Os(7)-Ag(5)-Os(9)	163.97(8)	Os(7)-Ag(8)-Ag(4)	63.38(6)
Os(7)-Ag(8)-Ag(5)	59.30(6)	Os(7)-Ag(8)-Ag(7)	116.26(9)
Os(7)-Ag(8)-Os(11)	163.82(10)	Os(7)-Ag(8)-Os(12)	133.44(7)
Os(8)-Ag(3)-Ag(1)	139.42(8)	Os(8)-Ag(3)-Ag(5)	121.83(8)
Os(8)-Ag(3)-Ag(6)	93.19(7)	Os(8)-Ag(3)-Os(9)	61.44(5)
Os(8)-Os(10)-Os(9)	63.02(4)	Os(8)-Os(9)-Ag(3)	59.33(5)
Os(8)-Os(9)-Ag(5)	117.88(5)	Os(8)-Os(9)-Ag(6)	90.02(5)
Os(8)-Os(9)-Ag(7)	146.97(7)	Os(8)-Os(9)-Os(10)	58.85(4)
Os(9)-Ag(3)-Ag(1)	118.18(9)	Os(9)-Ag(3)-Ag(5)	60.47(6)
Os(9)-Ag(3)-Ag(6)	60.54(6)	Os(9)-Ag(5)-Ag(2)	138.20(8)
Os(9)-Ag(5)-Ag(3)	60.90(6)	Os(9)-Ag(5)-Ag(4)	119.53(8)
Os(9)-Ag(5)-Ag(6)	60.00(6)	Os(9)-Ag(5)-Ag(7)	59.96(7)
Os(9)-Ag(5)-Ag(8)	111.94(8)	Os(9)-Ag(6)-Ag(1)	117.65(8)
Os(9)-Ag(6)-Ag(3)	62.07(7)	Os(9)-Ag(6)-Ag(4)	115.00(7)
Os(9)-Ag(6)-Ag(5)	61.06(6)	Os(9)-Ag(6)-Ag(7)	59.99(7)
Os(9)-Ag(6)-Ag(9)	116.80(7)	Os(9)-Ag(7)-Ag(5)	62.14(7)
Os(9)-Ag(7)-Ag(6)	61.08(6)	Os(9)-Ag(7)-Ag(8)	129.75(9)
Os(9)-Ag(7)-Ag(9)	119.06(7)	Os(9)-Ag(7)-Os(11)	167.50(9)
Os(9)-Os(8)-Ag(3)	59.23(4)	Os(9)-Os(8)-Os(10)	58.13(4)
Os(10)-Os(8)-Ag(3)	112.37(5)	Os(10)-Os(9)-Ag(3)	113.11(6)
Os(10)-Os(9)-Ag(5)	153.74(7)	Os(10)-Os(9)-Ag(6)	141.30(5)
Os(10)-Os(9)-Ag(7)	140.72(6)	Os(11)-Ag(7)-Ag(5)	130.16(10)
Os(11)-Ag(7)-Ag(6)	120.32(10)	Os(11)-Ag(7)-Ag(8)	62.64(7)
Os(11)-Ag(7)-Ag(9)	60.28(7)	Os(11)-Ag(8)-Ag(4)	101.27(8)
Os(11)-Ag(8)-Ag(5)	116.91(7)	Os(11)-Ag(8)-Ag(7)	61.43(6)
Os(11)-Ag(8)-Os(12)	61.59(5)	Os(11)-Ag(9)-Ag(4)	102.47(6)
Os(11)-Ag(9)-Ag(6)	122.22(9)	Os(11)-Ag(9)-Ag(7)	61.15(6)
Os(11)-Os(12)-Ag(8)	58.25(5)	Os(11)-Os(12)-Os(13)	58.00(3)
Os(11)-Os(13)-Os(12)	62.38(3)	Os(12)-Ag(8)-Ag(4)	162.76(10)
Os(12)-Ag(8)-Ag(5)	133.90(11)	Os(12)-Ag(8)-Ag(7)	94.76(8)
Os(12)-Os(11)-Ag(7)	90.58(6)	Os(12)-Os(11)-Ag(8)	60.16(5)
Os(12)-Os(11)-Ag(9)	137.57(6)	Os(12)-Os(11)-Os(13)	59.61(4)
Os(13)-Os(11)-Ag(7)	141.23(7)	Os(13)-Os(11)-Ag(8)	115.85(5)
Os(13)-Os(11)-Ag(9)	159.62(7)	Os(13)-Os(12)-Ag(8)	112.58(6)

Table 3. Selected bond lengths (Å) and angles (°) for **2**

Ag(1)-Ag(2)	3.082(3)	Ag(1)-Ag(3)	3.118(3)
Ag(1)-Ag(5)	2.939(3)	Ag(1)-Ag(6)	2.922(4)
Ag(2)-Ag(3)	3.159(5)	Ag(2)-Ag(4)	2.938(4)
Ag(2)-Ag(5)	2.869(3)	Ag(3)-Ag(4)	2.898(3)
Ag(3)-Ag(6)	2.953(3)	Ag(4)-Ag(5)	2.787(3)
Ag(4)-Ag(6)	2.791(3)	Ag(4)-Ag(8)	2.934(3)
Ag(4)-Ag(9)	2.949(4)	Ag(5)-Ag(6)	2.785(4)
Ag(5)-Ag(7)	2.870(4)	Ag(5)-Ag(8)	2.937(3)
Ag(6)-Ag(7)	2.937(3)	Ag(6)-Ag(9)	2.894(3)
Ag(7)-Ag(8)	3.136(3)	Ag(7)-Ag(9)	3.136(3)
Ag(8)-Ag(9)	3.106(4)	Os(1)-Ag(1)	2.822(3)
Os(1)-Ag(2)	2.836(3)	Os(1)-O(31)	2.06(2)
Os(1)-Os(2)	2.856(2)	Os(1)-Os(3)	2.858(2)
Os(2)-Ag(1)	2.835(2)	Os(2)-Ag(3)	2.825(3)
Os(2)-O(31)	2.06(2)	Os(2)-Os(3)	2.8535(19)
Os(3)-Ag(2)	2.799(2)	Os(3)-Ag(3)	2.868(3)
Os(3)-O(31)	2.03(2)	Os(4)-Ag(1)	2.828(2)
Os(4)-Ag(5)	2.959(2)	Os(4)-Ag(6)	2.903(2)
Os(4)-Ag(7)	2.842(2)	Os(5)-Ag(2)	2.828(2)
Os(5)-Ag(4)	2.902(3)	Os(5)-Ag(5)	2.942(2)
Os(5)-Ag(8)	2.833(3)	Os(6)-Ag(3)	2.841(3)
Os(6)-Ag(4)	2.910(3)	Os(6)-Ag(6)	2.904(2)
Os(6)-Ag(9)	2.852(2)	Os(7)-Ag(8)	2.861(3)
Os(7)-Ag(9)	2.838(2)	Os(7)-O(32)	2.061(19)
Os(7)-Os(8)	2.8395(18)	Os(7)-Os(9)	2.8596(17)
Os(8)-Ag(7)	2.838(2)	Os(8)-Ag(8)	2.850(2)
Os(8)-O(32)	2.05(3)	Os(8)-Os(9)	2.854(2)
Os(9)-Ag(7)	2.824(3)	Os(9)-Ag(9)	2.839(2)
Os(9)-O(32)	2.03(2)		
Ag(1)-Ag(2)-Ag(3)	59.93(9)	Ag(1)-Ag(2)-Ag(4)	86.79(11)
Ag(1)-Ag(2)-Ag(5)	59.07(8)	Ag(1)-Ag(3)-Ag(2)	58.80(9)
Ag(1)-Ag(3)-Ag(4)	86.83(9)	Ag(1)-Ag(3)-Ag(6)	57.47(8)
Ag(1)-Ag(5)-Ag(2)	64.07(8)	Ag(1)-Ag(5)-Ag(4)	92.49(10)
Ag(1)-Ag(5)-Ag(6)	61.32(10)	Ag(1)-Ag(5)-Ag(7)	108.50(12)
Ag(1)-Ag(5)-Ag(8)	151.38(14)	Ag(1)-Ag(6)-Ag(3)	64.10(9)
Ag(1)-Ag(6)-Ag(4)	92.77(12)	Ag(1)-Ag(6)-Ag(5)	61.94(10)

Ag(1)-Ag(6)-Ag(7)	107.18(12)	Ag(1)-Ag(6)-Ag(9)	152.23(14)
Ag(1)-Os(1)-Ag(2)	66.00(8)	Ag(1)-Os(2)-Ag(3)	66.86(8)
Ag(1)-Os(4)-Ag(5)	61.00(7)	Ag(1)-Os(4)-Ag(6)	61.30(8)
Ag(1)-Os(4)-Ag(7)	112.52(7)	Ag(2)-Ag(1)-Ag(3)	61.27(9)
Ag(2)-Ag(1)-Ag(5)	56.86(8)	Ag(2)-Ag(1)-Ag(6)	87.48(10)
Ag(2)-Ag(3)-Ag(4)	57.85(10)	Ag(2)-Ag(3)-Ag(6)	85.52(10)
Ag(2)-Ag(4)-Ag(3)	65.55(10)	Ag(2)-Ag(4)-Ag(5)	60.08(9)
Ag(2)-Ag(4)-Ag(6)	92.86(10)	Ag(2)-Ag(4)-Ag(8)	106.96(12)
Ag(2)-Ag(4)-Ag(9)	149.52(9)	Ag(2)-Ag(5)-Ag(4)	62.58(9)
Ag(2)-Ag(5)-Ag(6)	94.50(11)	Ag(2)-Ag(5)-Ag(7)	154.82(14)
Ag(2)-Ag(5)-Ag(8)	108.74(8)	Ag(2)-Os(3)-Ag(3)	67.75(9)
Ag(2)-Os(5)-Ag(4)	61.69(9)	Ag(2)-Os(5)-Ag(5)	59.60(7)
Ag(2)-Os(5)-Ag(8)	112.95(9)	Ag(3)-Ag(1)-Ag(5)	86.67(9)
Ag(3)-Ag(1)-Ag(6)	58.43(8)	Ag(3)-Ag(2)-Ag(4)	56.61(9)
Ag(3)-Ag(2)-Ag(5)	87.10(11)	Ag(3)-Ag(4)-Ag(5)	94.02(9)
Ag(3)-Ag(4)-Ag(6)	62.51(8)	Ag(3)-Ag(4)-Ag(8)	152.97(9)
Ag(3)-Ag(4)-Ag(9)	108.64(12)	Ag(3)-Ag(6)-Ag(4)	60.52(8)
Ag(3)-Ag(6)-Ag(5)	92.85(12)	Ag(3)-Ag(6)-Ag(7)	150.58(14)
Ag(3)-Ag(6)-Ag(9)	108.63(9)	Ag(3)-Os(6)-Ag(4)	60.50(8)
Ag(3)-Os(6)-Ag(6)	61.84(7)	Ag(3)-Os(6)-Ag(9)	113.06(10)
Ag(4)-Ag(2)-Ag(5)	57.34(9)	Ag(4)-Ag(3)-Ag(6)	56.98(7)
Ag(4)-Ag(5)-Ag(6)	60.12(9)	Ag(4)-Ag(5)-Ag(7)	95.08(12)
Ag(4)-Ag(5)-Ag(8)	61.60(8)	Ag(4)-Ag(6)-Ag(5)	59.97(9)
Ag(4)-Ag(6)-Ag(7)	93.52(10)	Ag(4)-Ag(6)-Ag(9)	62.46(9)
Ag(4)-Ag(8)-Ag(5)	56.68(7)	Ag(4)-Ag(8)-Ag(7)	86.82(9)
Ag(4)-Ag(8)-Ag(9)	58.38(9)	Ag(4)-Ag(9)-Ag(6)	57.06(8)
Ag(4)-Ag(9)-Ag(7)	86.56(11)	Ag(4)-Ag(9)-Ag(8)	57.90(9)
Ag(4)-Os(5)-Ag(5)	56.96(7)	Ag(4)-Os(5)-Ag(8)	61.52(8)
Ag(4)-Os(6)-Ag(6)	57.38(7)	Ag(4)-Os(6)-Ag(9)	61.56(9)
Ag(5)-Ag(1)-Ag(6)	56.74(10)	Ag(5)-Ag(4)-Ag(6)	59.91(9)
Ag(5)-Ag(4)-Ag(8)	61.71(8)	Ag(5)-Ag(4)-Ag(9)	91.83(9)
Ag(5)-Ag(6)-Ag(7)	60.14(10)	Ag(5)-Ag(6)-Ag(9)	93.04(11)
Ag(5)-Ag(7)-Ag(6)	57.31(9)	Ag(5)-Ag(7)-Ag(8)	58.34(8)
Ag(5)-Ag(7)-Ag(9)	86.54(9)	Ag(5)-Ag(8)-Ag(7)	56.29(8)
Ag(5)-Ag(8)-Ag(9)	85.97(10)	Ag(5)-Os(4)-Ag(6)	56.73(8)
Ag(5)-Os(4)-Ag(7)	59.27(8)	Ag(6)-Ag(4)-Ag(8)	93.19(8)
Ag(6)-Ag(4)-Ag(9)	60.48(9)	Ag(6)-Ag(5)-Ag(7)	62.55(10)
Ag(6)-Ag(5)-Ag(8)	93.24(12)	Ag(6)-Ag(7)-Ag(8)	86.40(8)

Ag(6)-Ag(7)-Ag(9)	56.81(8)	Ag(6)-Ag(9)-Ag(7)	58.12(8)
Ag(6)-Ag(9)-Ag(8)	87.73(12)	Ag(6)-Os(4)-Ag(7)	61.48(7)
Ag(7)-Ag(5)-Ag(8)	65.37(9)	Ag(7)-Ag(6)-Ag(9)	65.07(8)
Ag(7)-Ag(8)-Ag(9)	60.32(9)	Ag(7)-Ag(9)-Ag(8)	60.33(9)
Ag(7)-Os(8)-Ag(8)	66.92(7)	Ag(7)-Os(9)-Ag(9)	67.26(8)
Ag(8)-Ag(4)-Ag(9)	63.73(10)	Ag(8)-Ag(7)-Ag(9)	59.35(8)
Ag(8)-Os(7)-Ag(9)	66.04(9)	Os(1)-Ag(1)-Ag(2)	57.21(8)
Os(1)-Ag(1)-Ag(3)	88.78(8)	Os(1)-Ag(1)-Ag(5)	106.25(12)
Os(1)-Ag(1)-Ag(6)	141.55(9)	Os(1)-Ag(1)-Os(4)	146.96(14)
Os(1)-Ag(2)-Ag(3)	87.73(9)	Os(1)-Ag(1)-Os(2)	60.66(7)
Os(1)-Ag(2)-Ag(1)	56.79(8)	Os(1)-Ag(2)-Ag(4)	139.69(13)
Os(1)-Ag(2)-Ag(5)	107.80(8)	Os(1)-Ag(2)-Os(5)	151.35(13)
Os(1)-Ag(2)-Os(3)	60.97(6)	Os(1)-Os(2)-Ag(1)	59.46(8)
Os(1)-Os(2)-Ag(3)	94.17(9)	Os(1)-Os(2)-Os(3)	60.08(5)
Os(1)-Os(3)-Ag(3)	93.19(7)	Os(1)-Os(3)-Ag(2)	60.15(6)
Os(1)-Os(3)-Os(2)	60.01(5)	Os(2)-Ag(1)-Ag(3)	56.42(7)
Os(2)-Ag(1)-Ag(2)	87.46(7)	Os(2)-Ag(1)-Ag(5)	139.09(9)
Os(2)-Ag(1)-Ag(6)	107.48(12)	Os(2)-Ag(1)-Os(4)	148.89(14)
Os(2)-Ag(3)-Ag(1)	56.72(7)	Os(2)-Ag(3)-Ag(2)	86.13(11)
Os(2)-Ag(3)-Ag(4)	139.58(14)	Os(2)-Ag(3)-Ag(6)	106.90(8)
Os(2)-Ag(3)-Os(3)	60.16(7)	Os(2)-Ag(3)-Os(6)	148.41(13)
Os(2)-Os(1)-Ag(1)	59.89(7)	Os(2)-Os(1)-Ag(2)	91.97(9)
Os(2)-Os(1)-Os(3)	59.91(5)	Os(2)-Os(3)-Ag(2)	92.81(6)
Os(2)-Os(3)-Ag(3)	59.16(7)	Os(3)-Ag(2)-Ag(1)	87.90(9)
Os(3)-Ag(2)-Ag(3)	57.17(8)	Os(3)-Ag(2)-Ag(4)	105.38(12)
Os(3)-Ag(2)-Ag(5)	141.35(14)	Os(3)-Ag(2)-Os(5)	144.07(9)
Os(3)-Ag(3)-Ag(1)	85.99(11)	Os(3)-Ag(3)-Ag(2)	55.07(8)
Os(3)-Ag(3)-Ag(4)	104.65(12)	Os(3)-Ag(3)-Ag(6)	137.54(14)
Os(3)-Ag(3)-Os(6)	149.48(9)	Os(3)-Os(1)-Ag(1)	91.99(8)
Os(3)-Os(1)-Ag(2)	58.88(6)	Os(3)-Os(2)-Ag(1)	91.84(7)
Os(3)-Os(2)-Ag(3)	60.68(7)	Os(4)-Ag(1)-Ag(2)	118.49(10)
Os(4)-Ag(1)-Ag(3)	119.00(13)	Os(4)-Ag(1)-Ag(5)	61.71(7)
Os(4)-Ag(1)-Ag(6)	60.61(8)	Os(4)-Ag(5)-Ag(2)	121.28(10)
Os(4)-Ag(5)-Ag(1)	57.29(6)	Os(4)-Ag(5)-Ag(4)	120.71(12)
Os(4)-Ag(5)-Ag(6)	60.61(7)	Os(4)-Ag(5)-Ag(7)	58.34(7)
Os(4)-Ag(5)-Ag(8)	123.70(12)	Os(4)-Ag(5)-Os(5)	178.23(13)
Os(4)-Ag(6)-Ag(1)	58.09(7)	Os(4)-Ag(6)-Ag(3)	122.14(12)
Os(4)-Ag(6)-Ag(4)	122.61(13)	Os(4)-Ag(6)-Ag(5)	62.66(8)

Os(4)-Ag(6)-Ag(9)	123.19(9)	Os(4)-Ag(6)-Ag(7)	58.25(7)
Os(4)-Ag(6)-Os(6)	175.84(11)	Os(4)-Ag(7)-Ag(5)	62.39(8)
Os(4)-Ag(7)-Ag(6)	60.27(7)	Os(4)-Ag(7)-Ag(9)	116.96(9)
Os(4)-Ag(7)-Ag(8)	120.72(11)	Os(4)-Ag(7)-Os(8)	151.93(14)
Os(4)-Ag(7)-Os(9)	144.47(13)	Os(5)-Ag(2)-Ag(1)	121.25(9)
Os(5)-Ag(2)-Ag(3)	116.85(13)	Os(5)-Ag(2)-Ag(4)	60.39(8)
Os(5)-Ag(2)-Ag(5)	62.19(7)	Os(5)-Ag(4)-Ag(2)	57.91(8)
Os(5)-Ag(4)-Ag(3)	123.28(13)	Os(5)-Ag(4)-Ag(5)	62.25(8)
Os(5)-Ag(4)-Ag(6)	122.16(10)	Os(5)-Ag(4)-Ag(8)	58.09(8)
Os(5)-Ag(4)-Ag(9)	121.81(10)	Os(5)-Ag(4)-Os(6)	176.48(8)
Os(5)-Ag(5)-Ag(1)	122.28(9)	Os(5)-Ag(5)-Ag(4)	60.79(7)
Os(5)-Ag(5)-Ag(7)	122.94(10)	Os(5)-Ag(5)-Ag(2)	58.22(7)
Os(5)-Ag(5)-Ag(6)	120.91(9)	Os(5)-Ag(5)-Ag(8)	57.62(7)
Os(5)-Ag(8)-Ag(4)	60.39(8)	Os(5)-Ag(8)-Ag(5)	61.29(8)
Os(5)-Ag(8)-Ag(7)	117.53(10)	Os(5)-Ag(8)-Ag(9)	118.76(9)
Os(5)-Ag(8)-Os(7)	150.13(8)	Os(5)-Ag(8)-Os(8)	147.66(12)
Os(6)-Ag(3)-Ag(1)	117.55(9)	Os(6)-Ag(3)-Ag(2)	118.76(10)
Os(6)-Ag(3)-Ag(4)	60.92(9)	Os(6)-Ag(3)-Ag(6)	60.13(8)
Os(6)-Ag(4)-Ag(2)	124.12(10)	Os(6)-Ag(4)-Ag(3)	58.58(9)
Os(6)-Ag(4)-Ag(5)	121.12(10)	Os(6)-Ag(4)-Ag(6)	61.21(8)
Os(6)-Ag(4)-Ag(8)	121.91(12)	Os(6)-Ag(4)-Ag(9)	58.25(8)
Os(6)-Ag(6)-Ag(1)	122.08(9)	Os(6)-Ag(6)-Ag(3)	58.03(8)
Os(6)-Ag(6)-Ag(4)	61.41(7)	Os(6)-Ag(6)-Ag(5)	121.38(9)
Os(6)-Ag(6)-Ag(7)	124.00(10)	Os(6)-Ag(6)-Ag(9)	58.92(7)
Os(6)-Ag(9)-Ag(4)	60.19(8)	Os(6)-Ag(9)-Ag(6)	60.72(7)
Os(6)-Ag(9)-Ag(7)	118.84(10)	Os(6)-Ag(9)-Ag(8)	118.01(12)
Os(6)-Ag(9)-Os(7)	148.30(8)	Os(6)-Ag(9)-Os(9)	148.21(12)
Os(7)-Ag(8)-Ag(4)	107.71(12)	Os(7)-Ag(8)-Ag(5)	138.34(13)
Os(7)-Ag(8)-Ag(7)	86.90(10)	Os(7)-Ag(8)-Ag(9)	56.62(8)
Os(7)-Ag(8)-Os(8)	59.62(7)	Os(7)-Ag(9)-Ag(4)	107.92(12)
Os(7)-Ag(9)-Ag(6)	141.00(14)	Os(7)-Ag(9)-Ag(7)	87.31(8)
Os(7)-Ag(9)-Ag(8)	57.34(8)	Os(7)-Ag(9)-Os(9)	60.50(6)
Os(7)-Os(8)-Ag(7)	93.33(7)	Os(7)-Os(8)-Ag(8)	60.37(7)
Os(7)-Os(8)-Os(9)	60.29(5)	Os(7)-Os(9)-Ag(7)	93.18(7)
Os(7)-Os(9)-Ag(9)	59.73(6)	Os(7)-Os(9)-Os(8)	59.59(5)
Os(8)-Ag(7)-Ag(5)	107.40(11)	Os(8)-Ag(7)-Ag(6)	139.02(8)
Os(8)-Ag(7)-Ag(8)	56.73(6)	Os(8)-Ag(7)-Ag(9)	86.69(8)
Os(8)-Ag(7)-Os(9)	60.54(7)	Os(8)-Ag(8)-Ag(4)	139.84(12)

Os(8)-Ag(8)-Ag(5)	105.29(7)	Os(8)-Ag(8)-Ag(7)	56.35(6)
Os(8)-Ag(8)-Ag(9)	87.07(10)	Os(8)-Os(7)-Ag(8)	60.00(5)
Os(8)-Os(7)-Ag(9)	92.67(6)	Os(8)-Os(7)-Os(9)	60.11(5)
Os(8)-Os(9)-Ag(7)	59.96(7)	Os(8)-Os(9)-Ag(9)	92.33(9)
Os(9)-Ag(7)-Ag(5)	140.20(9)	Os(9)-Ag(7)-Ag(6)	104.94(12)
Os(9)-Ag(7)-Ag(8)	87.51(9)	Os(9)-Ag(7)-Ag(9)	56.59(8)
Os(9)-Ag(9)-Ag(4)	139.76(13)	Os(9)-Ag(9)-Ag(6)	105.71(8)
Os(9)-Ag(9)-Ag(7)	56.16(7)	Os(9)-Ag(9)-Ag(8)	87.87(9)
Os(9)-Os(7)-Ag(8)	92.39(6)	Os(9)-Os(7)-Ag(9)	59.77(5)
Os(9)-Os(8)-Ag(7)	59.49(8)	Os(9)-Os(8)-Ag(8)	92.72(8)

Table 4. Selected bond lengths (Å) and angles (°) for **3**

Ir(1)-Cl(1)	2.356(3)	Ir(1)-Cl(2)	2.405(7)
Ir(1)-P(1)	2.366(1)	Ir(1)-P(2)	2.368(1)
Ir(1)-C(37)	1.88(1)	Ir(1)-C(38)	1.83(2)
Ir(1)-O(3)	2.025(4)	Ir(1)-O(4)	2.070(4)
Cl(2)-Ir(1)-Cl(1)	100.6(2)	P(1)-Ir(1)-Cl(1)	92.29(8)
P(2)-Ir(1)-Cl(1)	88.59(8)	Ir(1)-Cl(1)-O(2)	165(1)
O(3)-Ir(1)-Cl(1)	108.5(1)	O(4)-Ir(1)-Cl(1)	150.5(1)
C(37)-Ir(1)-Cl(1)	94.7(4)	P(1)-Ir(1)-Cl(2)	90.2(2)
O(4)-Ir(1)-O(3)	42.2(2)		