### **Supporting Information for**

### Stoichiometry Effect on the Structure, Coordination and Anticancer Activity of Gold(I/III) Bisphosphine Complexes

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#### **Experimental Section**

#### **General Information**

All the solvents used in the work were purchased from Greenfield Global (ACS grade). Tetrachloroauric(III) acid trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) and iodobenzene were purchased from ACROS Organic, and the Au salt was stored under nitrogen atmosphere. Sodium hexafluorophosphate was purchased from Matrix scientific. Sodium tetrafluoroborate sodium perchlorate, potassium chloride, tetrahydrothiophene was purchased from Alfa Aesar. Clorox bleach was purchased from VWR. 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was purchased from Cayman Chemicals. Nitric acid (trace metal grade) and hydrochloric acid (trace metal grade) were purchased from Thermo Fisher scientific. All biological supplements for media, PBS and trypsin-EDTA were purchased from Corning Inc. and used as purchased. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). <sup>1</sup>H, <sup>13</sup>C (<sup>1</sup>H-decoupled), and <sup>31</sup>P (<sup>1</sup>H-decoupled) NMR spectra were recorded on a 500 MHz JEOL ECZr and Bruker Avance NEO 400 MHz spectrometer and samples calibrated for: <sup>1</sup>H NMR (CDCl<sub>3</sub>  $\delta$  = 7.26 ppm), <sup>13</sup>C NMR (CDCl<sub>3</sub>  $\delta$  = 77.16), <sup>19</sup>F NMR and <sup>31</sup>P NMR externally referenced to H<sub>3</sub>PO<sub>4</sub>  $\delta$  = 0.00). Liquid chromatography mass spectra were obtained by direct flow injection (injection volume =  $10 \mu$ L) using ElectroSpray Ionization (ESI) on an Advion Expression CMS MassExpress 6.7.15.1 mass spectrometer instrument in the positive mode coupled with RP-HPLC using an Agilent Technologies 1100 series HPLC instrument and an Agilent Phase Eclipse Plus C18 column (4.6 mm ' 100 mm; 3.5 µm particle size). All compounds were found to be 97% pure. High-resolution mass spectra (HRMS) were recorded on a Thermo Q Exactive Hybrid Quadrupole-Orbitrap mass spectrometer. Compound was prepared at a concentration of 1 mg/mL in 100% acetonitrile. Solution was directly infused at a rate of 20 µL/min and spectrum was collected for 1 minute in positive ion mode. The source parameters were: capillary voltage = 2.8kV and ion source = 120 °C with a sheath flow pressure of 8 psi. Au content was determined using Varian Spectra AA100Z Atomic Absorption Spectrometer.

#### Synthesis and Characterization

**Synthesis of Iodobenzene dichloride (PhICl<sub>2</sub>)**: To a 250 mL Erlenmeyer flask containing Clorox bleach (30 mL, 6.5 % hypochlorite) at room temperature was added Iodobenzene (0.55 mL, 4.901 mmol) dropwise with vigorous stirring. To the mixture was added conc. HCl (10 mL) dropwise in the dark and yellow precipitate forms. The mixture was stirred in the dark for 30 minutes. The suspension was filtered, washed with water (100 mL) and diethyl ether (30 mL) to give a pale yellow solid. Yield 440 mg, 33 %.

**Synthesis of AuCl(tht)**: In a 10 ml round bottom flask with stir bar was HAuCl<sub>4</sub>•3H<sub>2</sub>O (1.0 g, 2.54 mmol) dissolved in Ethanol/water (4:1) (10 mL) mixture. To this solution was added tetrahydrothiophene (0.5 mL, 5.332 mmol) and the reaction was stirred at room temperature for 30 minutes to give a white precipitate. The precipitate was filtered and washed with excess diethyl ether to give the product as a white solid. Yield: 710 mg, 88 %

**Synthesis of AuCl<sub>3</sub>(tht):** The compound was prepared according to reported procedure. Briefly, AuCl(tht) (120 mg, 0.374 mmol) was dissolved in 10 mL of dichloromethane. To this solution was added PhICl<sub>2</sub> (102.9 mg, 0.374 mmol) and the reaction stirred for 30 minutes. The solvent was evaporated to yield a yellow solid. Yield: 110 mg, 75 %.

# General Procedure A: Synthesis of Bis-[1,2-bis-(diphenylphosphino)benzene]gold(I) complexes.

To a 50 mL round-bottomed flask containing dichloromethane (10 mL) was added HAuCl<sub>4</sub>•3H<sub>2</sub>O (44.1 mg, 0.112 mmol), the light-yellow solution was stirred for 2 mins followed by the addition of 1,2-bis(diphenylphosphino)benzene (50 mg, 0.112 mmol) and the corresponding sodium salt (0.224 mmol). The reaction was stirred for 15 mins, monitored by TLC using 5% MeOH/DCM to ensure consumption of the starting materials. The bright yellow solution was then passed through celite and the solution was evaporated to dryness to give a bright yellow solid.

## General procedure B: Synthesis of Chloro bis-[1,2-bis-(diphenylphosphino) benzene]gold(III) tetrachloroaurates(III)

To a 50 mL round-bottomed flask containing DCM (20 mL) was added HAuCl<sub>4</sub>•3H<sub>2</sub>O (176.42 mg, 0.448 mmol 2 equiv.), the light-yellow solution was stirred for 2 mins followed by the addition

of 1,2-bis(diphenylphosphino)benzene (100 mg, 0.224 mmol). The reaction was stirred for 15 mins, monitored by TLC (5% MeOH/DCM) and the solvent evaporated to give a yellow solid. The crude product was purified via flash chromatography on combiFlashRf + Lumen using 1 - 5% MeOH/DCM as eluent to give the product.

# General Procedure C: Synthesis of chloro bis-[1,2-bis-(diphenylphosphino) benzene]gold(III) complexes

To a 50 mL round-bottomed flask with stirrer was added AuCl<sub>3</sub>(tht) (87.68 mg, 0.224 mmol 2 eq), DPPBz (50 mg, 0.112 mmol 1 eq) and the corresponding sodium salt in dichloromethane. The bright yellow solution was stirred at room temperature for 15 minutes. It was then passed through celite, concentrated, and redissolved in DCM. Diethyl ether was added, and the precipitate was filtered to give a yellow solid.

1-AuCl<sub>4</sub> Prepared as described in general procedure A: Bright yellow solid Yield: 100 mg, 63 %, <sup>1</sup>H NMR (500 MHz, acetonitrile- $d_3$ )  $\delta$  7.60 - 7.52 (m, 5H), 7.46 – 7.42 (m, 5H), 7.38 - 7.35 (m, 3H), 7.34 - 7.30 (m, 6H), 7.14 – 7.09 (m, 29H). <sup>31</sup>P NMR (202 MHz, acetonitrile- $d_3$ )  $\delta$  22.11. <sup>13</sup>CNMR (126 MHz, acetonitrile- $d_3$ )  $\delta$  134.29, 132.29, 131.70, 130.31, 129.02, 128.69. Purity was determined to be > 97% by RP-HPLC: R<sub>f</sub> = 4.81, 5.1(phosphine oxide) minutes using the following method: Flow rate: 1 ml/min;  $\lambda$  = 260 nm; Eluent A = DI. water with 0.1% trifluoroacetic acid; Eluent B = Acetonitrile with 0.05% formic acid; Solvent Gradient: 0 – 4 min (0:100 H<sub>2</sub>O: ACN). 4 – 17 min until end of run (100:0 H<sub>2</sub>O: ACN). 17 min until end of run (50:50 H<sub>2</sub>O: ACN).

**3-AuCl**<sub>4</sub> Prepared as described in general procedure B: Yellow solid. Yield: 80 mg, 17 %, <sup>1</sup>H NMR (500 MHz, acetonitrile- $d_3$ )  $\delta$  7.77 – 7.75 (m, 4H), 7.60- 7.46 (m, 16H), 7.33 – 7.30 (m, 4H), 7.23 – 7.17 (m, 16H), 6.92 – 6.84 (m, 8H) <sup>31</sup>P NMR (202 MHz, acetonitrile- $d_3$ )  $\delta$  57.82. Purity was determined to be > 97% by RP-HPLC: R<sub>f</sub> = 11.0, 12.0 (phosphine oxide) minutes using the following method: Flow rate: 1 ml/min;  $\lambda$  = 260 nm; Eluent A = DI. water with 0.1% trifluoroacetic acid; Eluent B = Acetonitrile with 0.05% formic acid; Solvent Gradient: 0 – 20 min (0:100 H<sub>2</sub>O: ACN). 20 min until end of run (100:0 H<sub>2</sub>O: ACN). Elemental analysis Calc. (C<sub>60</sub>H<sub>48</sub>Au<sub>3</sub>Cl<sub>9</sub>P<sub>4</sub>•CH<sub>2</sub>Cl<sub>2</sub>): %C 38.81, %H 2.67; Found: %C 38.85, %H 2.61. HRMS Calc. for

 $C_{60}H_{48}Au_3Cl_9P_4$ : [M-2AuCl<sub>4</sub><sup>-</sup>]/2 562.10303; Found: 562.10352;  $\Delta$  0.00049; mass error (ppm): 0.871726.

**1-PF**<sub>6</sub> Prepared as described in general procedure A. Yield: 60 mg, 43% <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.55 – 7.51 (m, 4H), 7.47 -7.43 (m, 4H), 7.34 – 7.30 (m, 8H), 7.11 – 7.06 (m, 15H), 7.05 – 7.01 (m, 17H). <sup>31</sup>PNMR (202 MHz, CDCl<sub>3</sub>)  $\delta$  21.84, -136.67, -138.77, -140.19, - 143.71, -147.23, -149.39, -150.75. Purity was determined to be > 97% by RP-HPLC: R<sub>f</sub> = 11.1, minutes using the following method: Flow rate: 1 ml/min;  $\lambda$  = 260 nm; Eluent A = DI. water with 0.1% trifluoroacetic acid; Eluent B = Acetonitrile with 0.05% formic acid; Solvent Gradient: 0 – 20 min (0:100 H<sub>2</sub>O: ACN). 20 min until end of run (100:0 H<sub>2</sub>O: ACN).

**3-PF**<sub>6</sub> Prepared as described in general procedure C Yield: 80 mg, 50.5% <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.74 – 7.71 (m, 3H), 7.65 – 7.59 (m, 3H), 7.57 – 7.44 (m, 16H), 7.43 – 7.36 (m, 26H). <sup>31</sup>P NMR (162 MHz, DMSO)  $\delta$  29.92, -131.02, -135.41, -139.81, -144.20, -148.59, -152.98, -157.37. Purity was determined to be > 97% by RP-HPLC: R<sub>f</sub> = 9.7, 10.4 (phosphine oxide) minutes using the following method: Flow rate: 1 ml/min;  $\lambda$  = 260 nm; Eluent A = DI. water with 0.1% trifluoroacetic acid; Eluent B = Acetonitrile with 0.05% formic acid; Solvent Gradient: 0 – 20 min (0:100 H<sub>2</sub>O: ACN). 20 min until end of run (100:0 H<sub>2</sub>O: ACN).

1-Cl Prepared as described in general procedure A Yield: 60 mg, 24%. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 – 7.51 (m, 4H), 7.47 -7.45 (m, 4H), 7.34 – 7.30 (m, 8H), 7.11 – 7.05 (m, 16H), 7.05 -7.00 (m, 16H). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  21.18. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  134.26, 132.56, 132.44, 132.33, 132.27, 132.23, 132.19, 132.14, 132.11, 131.61, 130.29, 129.03, 129.00, 128.98, 128.95, 128.93, 77.35, 77.04, 76.72. Purity was determined to be > 97% by RP-HPLC: R<sub>f</sub> = 8.6, 10.9 (phosphine oxide) minutes using the following method: Flow rate: 1 ml/min;  $\lambda$  = 260 nm; Eluent A = DI. water with 0.1% trifluoroacetic acid; Eluent B = Acetonitrile with 0.05% formic acid; Solvent Gradient: 0 – 20 min (0:100 H<sub>2</sub>O: ACN). 20 min until end of run (100:0 H<sub>2</sub>O: ACN). Elemental analysis Calc. (C<sub>60</sub>H<sub>48</sub>AuClP<sub>4</sub>•0.7C<sub>4</sub>H<sub>10</sub>O•0.6CH<sub>2</sub>Cl<sub>2</sub>): %C 62.00, %H 4.61; Found: %C 62.01, %H 4.61

**1-BF**<sub>4</sub> Prepared as described in general procedure A. Yield: 50 mg, 37.9% <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 4H), 7.47 – 7.45(m, 4H), 7.35 – 7.28 (m, 7H), 7.10 – 7.07 (m,

16H), 7.05 – 7.01 (m, 16H). <sup>31</sup>PNMR (202 MHz, CHLOROFORM-*D*)  $\delta$  21.82. <sup>19</sup>FNMR (471 MHz, DMSO-*D*<sub>6</sub>)  $\delta$  -148.17. Purity was determined to be > 97% by RP-HPLC: R<sub>f</sub> = 10.6, minutes using the following method: Flow rate: 1 ml/min;  $\lambda$  = 260 nm; Eluent A = DI. water with 0.1% trifluoroacetic acid; Eluent B = Acetonitrile with 0.05% formic acid; Solvent Gradient: 0 – 20 min (0:100 H<sub>2</sub>O: ACN). 20 min until end of run (100:0 H<sub>2</sub>O: ACN).

#### X-ray Crystallography.

Crystal for complexes **3-AuCl**<sub>4</sub> and **3-PF**<sub>6</sub> were grown at room temperature from a vapor diffusion of chloroform into diethylether. After carefully selecting appropriate crystals through microscopic inspection using crossed polarizers, crystals were attached using polyisobutene oil on the end of a glass fiber, cooled through a cold gas stream of liquid nitrogen and diffraction collected using Bruker D8 Venture diffractometer with graded multilayer focused MoK $\alpha$  X-rays ( $\lambda = 0.71073$  Å). APEX3 package<sup>1-5</sup> was used to correct Lorentz-polarization effects by integrating, scaling, merging, and correcting the raw data gotten from the diffractometer. Thereafter, the space group, structure solution and refinement were determined with SHELXT and SHELXL while the ellipsoid plots were drawn using SHELXTL-XP. <sup>6-8</sup> The positioning of hydrogen atoms was determined after calculation and refining using a riding model with their isotropic displacement parameters (U<sub>iso</sub>) determined based on the atom to which they were attached while anisotropic displacement parameters were to refine non-hydrogen atoms. The structures, deposited in the Cambridge Structural Database, were checked for missed symmetry, twinning, and overall quality with PLATON, <sup>9</sup> an R-tensor, <sup>10</sup> and finally validated using CheckCIF. <sup>9</sup>

#### **Biological Characterization**

#### LCMS Stability Studies with DMEM

Stock solution of **3-AuCl**<sub>4</sub> or **1-Cl** (1 mg/mL) was prepared in methanol. 100  $\mu$ L of the stock solution was diluted with DMEM (100  $\mu$ L) to make 0.5 mM equimolar solution. The resulting solution was analyzed at different time points from 0 h to 48 h using an Advion expression CMS mass express 6.7.15.1 coupled with RP-HPLC using an Agilent Technologies 1100 series HPLC instrument and an Agilent Phase Eclipse Plus C18 column (4.6 mm ' 100 mm; 3.5  $\mu$ m particle size). The data was analyzed using Advion data express and Graphpad 9.5.1 software.

#### In Vitro Biological Assay

#### Cell Culture.

MDA-MB-231 (triple negative breast cancer cell) was purchased from ATCC, while BT-333 (glioblastoma cells) was a generous gift from Dr. Gilles Berger. The two cancer cells were grown separately in DMEM supplemented with 10% FBS, 1% amphotericin B and 1% penicillin/streptomycin and kept in an incubator at 37 °C with 5 - 10% CO<sub>2</sub>. All supplements along with PBS and trypsin-EDTA were purchased from Corning Inc. and used as purchased.

#### In vitro Cytotoxicity.

The cytotoxicity of the Au(I/III) diphenyl complexes were performed in MDA-MB-231 and BT-333 cancer cells. The cancer cells were grown and harvested after reaching 80% confluency via trypsinization. The cells were then suspended in 10 mL of DMEM, centrifuged at 2000 rpm for 5 minutes, pellet removed, and the pellets were resuspended in 5 mL of DMEM. Cell plating was carried out at a density of 3000 (MDA-MB-231) or 4,000 (BT-333) cells/well in a 96-well clear bottom plate. The cells were allowed to adhere overnight in an incubator at 37 °C with 5 - 10% CO<sub>2</sub> before treating with the Au complexes. All compounds were prepared fresh as 1 mM stock solution in DMSO and diluted with DMEM to 300  $\mu$ M. The cells were then treated at seven different concentrations with a 3x serial dilution starting at 100  $\mu$ M for the highest concentration and DMSO control. The treated 96-well plates were incubated at 37 °C for 72 h with 5 - 10% CO<sub>2</sub>. After 72 h, the media was pipetted out and replaced with a solution of 100  $\mu$ L of 3-(4,5dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT dye) and incubated for 4 h at 37 °C with 5-10% CO<sub>2</sub>. The dye was removed from each well and replaced DMSO (100  $\mu$ L ) to induce cell lysis. The plates were read using a Biotek Synergy H1 Plate Reader at 570 nm (peak absorbance) and the data plotted as mean  $\pm$  SD using Graphpad 10.1.2.

#### Mitochondrial Metabolism Analysis with Seahorse XF96 Analysis.

For the mitostress experiment, MDA-MB-231 cells (30,000 cells/wells, 100  $\mu$ L) was plated in Seahorse XF96 plates and allowed to adhere overnight at 37 °C with 5 - 10% CO<sub>2</sub>. Stock solutions of 1-Cl and 3-AuCl<sub>4</sub> (1 mM) were prepared in DMSO and diluted to a working concentration of 100  $\mu$ M with Seahorse XF96 assay buffer. The assay was performed using a pneumatic injection of both complexes, with injection concentrations of 10  $\mu$ M, 5  $\mu$ M, and 1  $\mu$ M. This was followed by injection of oligomycin (1.5  $\mu$ M), FCCP (0.6  $\mu$ M) and rotenone/ antimycin A (0.5  $\mu$ M). The metabolic parameters were calculated based on the reading gotten from a minimum of 12 wells and the data plotted as mean± SD using Graphpad 10.1.2.

#### Whole Cellular Uptake.

MDA-MB-231 cells (1 x 10<sup>6</sup> cells/well) were seeded in triplicate in a 6-well clear bottom plate with a final volume of 2.5 mL and allowed to adhere overnight at 37 °C. MDA-MB-231 cells were treated with 1-Cl and 3-AuCl<sub>4</sub> (10  $\mu$ M, 18 h), collected via trypsinization and centrifuged at 2000 rpm for 5 mins. The pellets formed were suspended in 1 ml of DMEM, transferred to a 1.5 ml Eppendorf tube, and recentrifuged at 2000 rpm for 5 minutes. The media was aspirated, and the pellets washed with PBS (1 ml x 2). The pellets were then digested as follows: 200  $\mu$ L of aqua regia was added to the pellets and placed on a heating block at 60 °C for 4 hr to give a golden yellow solution. The solution was cooled to room temperature and diluted appropriately with 1% HNO<sub>3</sub> GFAAS solution before been subjected to analysis with GFAAS. Cellular Au concentration were expressed as nmol of Au per million cells. Data is plotted as mean ± s.e.m (n = 3) using Graphpad Prism 10.1.2.

#### Mitochondrial uptake.

MDA-MB-231 (20 x 10<sup>6</sup>) were seeded in duplicate in a 6-well clear bottom plate with a final volume of 2.5 mL and allowed to adhere overnight at 37 °C. MDA-MB-231 cells were treated with 1-Cl and 3-AuCl<sub>4</sub> (10  $\mu$ M, 18 h) and collected via trypsinization. Extraction of mitochondria was carried out according to the procedures of the mitochondria extraction kit (ThermoFisher Scientific). The pellets were then digested as follows: 200  $\mu$ L of aqua regia was added to the pellets and placed on a heating block at 60 °C for 4 hr to give a golden yellow solution. The solution was cooled to room temperature and diluted appropriately with 1% HNO<sub>3</sub> GFAAS solution before been subjected to analysis with GFAAS. Mitochondria Au concentration was expressed as nmol of Au per million cells. Data is plotted as mean ± s.e.m (n = 2) using Graphpad Prism 10.1.2

X-ray Structural Data and Crystal Refinement			
	3-AuCl <sub>4</sub>	3-PF <sub>6</sub>	
Empirical Formula	$C_{65}H_{60}Au_3Cl_{11}OP_4$	$C_{68}H_{60}AuClF_{12}N_4P_6$	
Molecular Weight (g/mol)	1961.86	1579.43	
Temperature (K)	90.0(2) K	90.0(2) K	
Crystal System, Space Group	Triclinic, P-1	Monoclinic, C2/c	
Unit Cell Dimensions (A),	a = 14.8238(5) A alpha = 74.169 (1) deg.	a = 32.0791(12) A alpha = 90 deg.	
	b = 14.9728(5) A beta = 84.618(1) deg.	b = 9.7153(4) A beta = 109.019(1) deg.	
	c = 17.2596(5) A gamma = 65.137(1) deg.	c = 22.1492(7) A gamma = 90 deg.	
Volume	3342.98(19) A^3	6526.1(4) A^3	
Z, calculated density	2, 1.949 Mg/m^3	4, 1.608 Mg/m^3	
Absorption Coefficient	7.144 mm <sup>-1</sup>	2.522 mm^-1	
F(000)	1884	3160	
Crystal Size (mm)	0.120 x 0.100 x 0.080	0.180 x 0.130 x 0.120	

Table 1. X-ray Parameters of 3-AuCl<sub>4</sub> and 3-PF<sub>6</sub>

Theta Range	1.926 to 27.501 deg	1.971 to 27.528 deg
Completeness to Theta = 25.242	96.8 %	99.9
F <sup>2</sup>	1.027	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1033	R1= 0.0198, wR2 = 0.0467



**Fig. S1.** Crystal structure of **3-AuCl**<sub>4</sub>. Thermal ellipsoids are shown at the 50% probability level. Hydrogen and solvent molecules are omitted for clarity. Only one representative molecule from the asymmetric unit is shown.



Figure S2. <sup>1</sup>HNMR of 1-AuCl<sub>4</sub> in acetonitrile-d<sub>3</sub> at 298K



Figure S3. <sup>31</sup>PNMR of 1-AuCl<sub>4</sub> in acetonitrile-d<sub>3</sub> at 298K



Figure S4. <sup>13</sup>CNMR of 1-AuCl<sub>4</sub> in acetonitrile-d<sub>3</sub> at 298K



Figure S5. <sup>1</sup>HNMR of 3-AuCl<sub>4</sub> in DMSO-d<sub>6</sub> at 298K



Figure S6. <sup>31</sup>PNMR of 3-AuCl<sub>4</sub> in DMSO-d<sub>6</sub> at 298K



Figure S7. <sup>1</sup>HNMR of 1-PF<sub>6</sub> in CDCl<sub>3</sub> at 298K



200 180 160 140 -160 -180 -20 120 100 20 0 f1 (ppm) -100 -120 80 60 40 -20 -80 -140 -40 -60

Figure S8. <sup>31</sup>PNMR of 1-PF<sub>6</sub> in CDCl<sub>3</sub> at 298K



Figure S9. <sup>1</sup>HNMR of 3-PF<sub>6</sub> in DMSO-d<sub>6</sub> at 298K



150 130 110 90 -50 f1 (ppm) -130 -25 70 50 30 10 -10 -30 -70 -110 -150 -170 -190 -210 -230 . -90

Figure S10. <sup>31</sup>PNMR of 3-PF<sub>6</sub> in CDCl<sub>3</sub> at 298K



Figure S11. <sup>1</sup>HNMR of 1-Cl in CDCl<sub>3</sub> at 298K



Figure S12. <sup>31</sup>PNMR of 1-Cl in CDCl<sub>3</sub> at 298K



Figure S13. <sup>13</sup>CNMR of 1-Cl in CDCl<sub>3</sub> at 298K



Figure S14. <sup>1</sup>HNMR of 1-BF<sub>4</sub> in CDCl<sub>3</sub> at 298K



Figure S15. <sup>31</sup>PNMR of 1-BF<sub>4</sub> in CDCl<sub>3</sub> at 298K

HPLC Trace of Complexes



Figure S16. HPLC of 1-AuCl<sub>4</sub> ( $\lambda$  = 260 nm)



Figure S17. HPLC of 3-AuCl<sub>4</sub> ( $\lambda$  = 260 nm)



Figure S18. HPLC of 1-PF<sub>6</sub> ( $\lambda$  = 260 nm)



Figure S19. HPLC of 3-PF<sub>6</sub> ( $\lambda = 260$  nm)



Figure S20. HPLC of 1-Cl ( $\lambda = 260$  nm)



Figure S21. HPLC of 1-BF<sub>4</sub> ( $\lambda$  = 260 nm)



Figure S22. ESI of 1-AuCl<sub>4</sub>



Figure S24. ESI of 1-PF<sub>6</sub>



Figure S25. ESI of 3-PF<sub>6</sub>



Figure S26. ESI of 1-Cl



Figure S27. ESI of 1-BF<sub>4</sub>



Figure S28. HRMS of 3-AuCl<sub>4</sub>

**Cytotoxicity studies** 



Figure S29. Dose response curve for 1-AuCl<sub>4</sub> in MDA-MB-231 and BT-333 cancer cells.



Figure S30. Dose response curve for 3-AuCl<sub>4</sub> in MDA-MB-231 and BT-333 cancer cells.



Figure S31. Dose response curve for 1-PF<sub>6</sub> in MDA-MB-231 and BT-333 cancer cells.



Figure S32. Dose response curve for 3-PF<sub>6</sub> in MDA-MB-231 and BT-333 cancer cells.



Figure S33. Dose response curve for 1-Cl in MDA-MB-231 and BT-333 cancer cells.



Figure S34. Dose response curve for 1-BF4 in MDA-MB-231 and BT-333 cancer cells.



Figure S35. Dose response curve for Au(I)/(III) compounds in MRC5 cells.



Figure S36. Standard curve of GFAAS analysis for Whole cell uptake and mitochondria uptake.

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