Electronic Supplementary Information

Structure-Activity Relationships for Organometallic Osmium Arene Phenylazopyridine Complexes with Potent Anticancer Activity

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Contents

Synthesis and Characterization

[Os(η^6-bip)(1-CF_3-4-Cl-azpy)I]PF_6 (1). [Os(η^6-bip)I_2]$_2$ (50.0 mg, 0.042 mmol) was dissolved in methanol (40 mL) at 353 K. 1-CF_3-4-Cl-azpy (24.0 mg, 0.084 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 16 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (27.7 mg, 0.17 mmol) was added. The solution was then left in a freezer at 253 K for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 43.1 mg (57.1 %). ESI-MS Calcd for $C_{24}H_{17}ClF_3IN_3Os$: m/z 758.0, found 757.8. ^{1}H NMR($(CD_3)_2CO$): δ 9.80 (s, 1H), 8.71 (d, 1H, J = 2 Hz), 7.96 (d, 2H, J = 8 Hz), 7.72 (t, 1H, J = 8 Hz), 7.56-7.44 (m, 6H), 7.42-7.38 (m, 2H), 7.27 (t, 1H, J = 6 Hz), 7.22 (d, 1H, J = 6 Hz), 6.98 (t, 1H, J = 6 Hz), 6.88 (d, 1H, J = 6 Hz), 6.77 (t, 1H, J = 6 Hz), CHN analysis: Found: C, 31.98%; H, 2.08%; N, 4.34%. Calcd for $C_{24}H_{17}ClF_9IN_3OsP$: C, 31.96% H, 1.90% N, 4.66%.

[Os(η^6-*p*-cym)(1-CF_3-4-Cl-azpy)I]PF_6 (2). [Os(η^6-*p*-cym)I_2]$_2$ (50.0 mg, 0.043 mmol) was dissolved in methanol (40 mL). 1-CF_3-4-Cl-azpy (24.6 mg, 0.086 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from yellow to red brown immediately. The solution was stirred at ambient temperature for 72 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (28.0 mg. 0.17 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured crystals formed which were collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 54.4 mg (71.7 %). ESI-MS Calcd for $C_{22}H_{21}ClF_3IN_3Os$: m/z 738.0, found 737.8. ^{1}H MR($(CD_3)_2CO$): δ 8.91 (s, 1H), 8.41 (d, 2H, , J = 6 Hz), 8.06-7.79 (m, 6H), 7.07 (d, 2H, , J = 6 Hz), 6.46-6.40 (m, 3H), 6.16 (d, 2H, , J = 6 Hz), 2.77 (s, 3H), 2.62-2.52 (m, 1H), 0.91 (d of d, 6H). CHN analysis: Found: C, 29.91%; H, 2.38%; N, 4.83%. Calcd for $C_{22}H_{21}ClF_9IN_3OsP$: C, 29.96%; H, 2.40%; N, 4.76%.

[Os(η^6-bip)(1-CF$_3$-4-Cl-azpy)Cl]PF$_6$ (3). [Os(η^6-bip)Cl$_2$]$_2$ (50.0 mg, 0.06 mmol) was dissolved in methanol (40 mL) at 353 K. 1-CF$_3$-4-Cl-azpy (34.3 mg, 0.12 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 2 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (39.1 mg, 0.24 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 71.9 mg (88.7 %). ESI-MS Calcd for $C_{24}H_{17}Cl_2F_3N_3Os$: m/z 666.0, found 666.0. ^{1}H NMR((CD$_3$)$_2$CO): δ 9.55 (s, 1H), 8.84 (d, 1H, J = 2 Hz), 7.99 (d, 2H, J = 8 Hz), 7.76 (t, 1H, J = 8 Hz), 7.66-7.54 (m, 6H), 7.50-7.47(m, 2H), 7.07 (d, 1H, J = 6 Hz), 6.98-6.92 (m, 3H), 6.54-6.49 (m, 1H). CHN analysis: Found: C, 36.43%; H, 2.07%; N, 5.17%. Calcd for $C_{24}H_{17}Cl_2F_9N_3OsP$: C, 35.56%; H, 2.11%; N, 5.18%.

[Os(η^6-*p*-cym)(1-CF$_3$-4-Cl-azpy)Cl]PF$_6$ (4). [Os(η^6-*p*-cym)Cl$_2$]$_2$ (50.0 mg, 0.063 mmol) was dissolved in methanol (40 mL). 1-CF$_3$-4-Cl-azpy (36.1 mg, 0.126 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from yellow to red brown immediately. The solution was stirred at ambient temperature for 12 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (41.2 mg, 0.25 mmol) was added. The solution was then left in the freezer (253 K) for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 69.2 mg (69.5 %). ESI-MS Calcd for $C_{22}H_{21}Cl_2F_3N_3Os$: m/z 646.1, found 646.0. ^{1}H NMR((CD$_3$)$_2$CO): δ 9.80 (s, 1H), 8.88 (s, 1H), 8.18 (m, 2H), 7.96-7.81 (m, 3H), 7.03 (d, 1H, J = 8 Hz), 6.68 (d, 1H, J = 8 Hz), 6.56 (m, 2H), 2.80 (s, 3H), 2.58-2.49 (m, 1H), 0.98 (d of d, 6H). CHN analysis: Found: C, 33.26%; H, 2.59%; N, 5.24%. Calcd for $C_{22}H_{21}Cl_2F_9N_3OsP$: C, 33.43%; H, 2.68%; N, 5.32%.

[Os(η^6-*p*-cym)(1-Cl-azpy)I]PF$_6$ (5). [Os(η^6-*p*-cym)I$_2$]$_2$ (50.0 mg, 0.043 mmol) was dissolved in methanol (30 mL). 1-Cl-azpy (18.7 mg, 0.086 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 4 h. The volume was reduced to about 10

mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (28.0 mg, 0.17 mmol) was added. The solution was then left in the freezer (253 K) for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 28.0 mg (40.0 %). ESI-MS Calcd for $C_{21}H_{22}ClIN_3Os$: m/z 670.0, found 669.9. ^{1}H NMR($(CD_3)_2CO$): δ 9.01 (d, 1H, J = 6 Hz), 8.20 (d, 1H, J = 8 Hz), 8.14-8.02 (m, 3H), 7.81 (m, 1H), 7.14 (d, 2H, J = 9 Hz), 6.61 (m, 2H), 6.46 (d, 1H, J = 6 Hz), 6.16 (m, 4H), 2.39 (s, 3H), 2.69-2.64 (m, 1H), 1.03 (d of d, 6H). CHN analysis: Found: C, 30.38%; H, 2.62%; N, 5.11%. Calcd for $C_{21}H_{22}ClF_6IN_3OsP$: C, 30.99%; H, 2.72%; N, 5.16%.

[Os(η^6-bip)(1-Cl-azpy)I]PF$_6$ (6). [Os(η^6-bip)I_2]$_2$ (30.0 mg, 0.025 mmol) was dissolved in methanol (40 mL) at 353 K. 1-Cl-azpy (10.8 mg, 0.050 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 2 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (16.3 mg, 0.10 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 22.0 mg (52.8 %). ESI-MS Calcd for $C_{23}H_{18}ClIN_3Os$: m/z 690.0, found 689.9. ^{1}H NMR($(CD_3)_2CO$): δ 8.56 (d, 1H, J = 6 Hz), 8.33 (t, 1H, J = 8 Hz), 8,19 (d, 1H, J = 6 Hz), 7.87 (d, 2H, J = 8 Hz), 7.66 (t, 1H, J = 8 Hz), 7.52-7.39 (m, 7H), 7.19 (d, 1H, J = 6 Hz), 7.00 (t, 2H, J = 6 Hz), 6.99-6.78 (m, 2H). CHN analysis: Found: C, 32.82%; H, 2.08%; N, 4.75%. Calcd for $C_{23}H_{18}ClF_6IN_3OsP$: C, 33.12%; H, 2.18%; N, 5.04%.

[Os(η^6-*p*-cym)(1-Cl-azpy)Cl]PF$_6$ (7). [Os(η^6-*p*-cym)Cl_2]$_2$ (50.0 mg, 0.063 mmol) was dissolved in methanol (30 mL). 1-Cl-azpy (27.4 mg, 0.126 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from yellow to red immediately. The solution was stirred at ambient temperature for 4 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (41.2 mg, 0.25 mmol) was added. The solution was then left in the freezer (253 K) for 24 h. The dark coloured precipitate which was collected by filtration, washed with cold ethanol and diethyl

ether, then finally dried *in vacuo*. Yield: 86.3 mg (94.8 %). ESI-MS Calcd for $C_{21}H_{22}Cl_2N_3Os$: m/z 578.1, found 578.1. ^{1}H NMR($(CD_3)_2CO$): δ 8.94 (d, 1H, J = 8 Hz), 8.41 (t, 1H, J = 8 Hz), 8.30(d, 1H, J = 8 Hz), 8.13(d, 2H, J = 8 Hz), 7.76 (m, 3H), 7.06 (d, 1H, J = 6 Hz), 6.42 (d, 1H, J = 6 Hz), 6.37 (d, 1H, J = 6 Hz), 6.16 (d, 1H, J = 6 Hz), 2.62-2.54 (m, 1H), 2.46 (s, 3H), 0.99 (d of d, 6H). CHN analysis: Found: C, 34.91%; H, 3.02%; N, 5.75%. Calcd for $C_{21}H_{22}Cl_2F_6N_3OsP$: C, 34.91%; H, 3.07%; N, 5.82%.

[Os(η^6-bip)(1-Cl-azpy)Cl]PF$_6$ (8). [Os(η^6-bip)Cl_2]$_2$ (50.0 mg, 0.060 mmol) was dissolved in methanol (40 mL) at 353 K. 1-Cl-azpy (26.1 mg, 0.12 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 1 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (39.1 mg, 0.24 mmol) was added. The solution was then left in the freezer (253K) for 24 h. Dark coloured powder was precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 27.8 mg (31.2 %). ESI-MS Calcd for $C_{23}H_{18}Cl_2N_3Os$: m/z 598.0, found 598.0. ^{1}H NMR($(CD_3)_2CO$): ^{1}H NMR($(CD_3)_2CO$): δ 8.92 (d, 1H, J = 6 Hz), 8.43 (t, 1H, J = 8 Hz), 8,26 (d, 1H, J = 6 Hz), 7.94 (d, 2H, J = 8 Hz), 7.72 (t, 1H, J = 8 Hz), 7.62-7.35 (m, 7H), 7.06 (t, 11H, J = 6 Hz), 6.94 (t, 2H, J = 6 Hz), 6.74 (t, 1H, J = 6 Hz), 6.50 (t, 1H, J = 6 Hz), CHN analysis: Found: C, 36.95%; H, 2.39%; N, 5.59%. Calcd for $C_{23}H_{18}Cl_2F_6N_3OsP$: C, 37.20%; H, 2.44% ; N, 5.66%.

[Os(η^6-bip)(2-F-azpy)I]PF$_6$ (9). [Os(η^6-bip)I_2]$_2$ (25.0 mg, 0.021 mmol) was dissolved in methanol (20 mL) at 313 K. 2-F-Azpy (8.4 mg, 0.042 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from yellow to brown immediately. The solution was heated under reflux (353K) for 12 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (13.7 mg, 0.084 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured powder precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 15.5 mg (45.0 %). ESI-MS Calcd for $C_{23}H_{18}FIN_3Os$: m/z 674.0, found 674.1. ^{1}H NMR($(CD_3)_2CO$): δ 9.50 (t, 1H, J = 2 Hz), 8.88 (d of d, 1H), 8,91 (d of d, 2H), 8,32(d of t, 1H), 8,02 (d of d, 1H), 7.95-7.92 (m, 2H), 7.73-7.41 (m, 5H), 7.13-

7.09 (m, 2H), 6.96 (t, 1H, J = 7 Hz). 6.79 (d, 1H, J = 7 Hz), 6.65 (t, 1H, J = 7 Hz). CHN analysis: Found: C, 34.17%; H, 2.28%; N, 5.04%. Calcd for $C_{23}H_{18}F_7IN_3OsP$: C, 33.79%; H, 2.22%; N, 5.14%.

[Os(η^6-bip)(2-F-Azpy)Cl]PF$_6$ (10) [Os(η^6-bip)Cl$_2$]$_2$ (50.0 mg, 0.06 mmol) was dissolved in methanol (40 mL) and water (10 mL) mixture at 353 K. 2-F-Azpy (24.1 mg, 0.12 mmol) in methanol (10 mL) was added drop-wise. The solution was heated under reflux (353K) for 4 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (97.8mg, 0.6 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured powder precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 37.5 mg (86.1 %). ESI-MS Calcd for $C_{23}H_{18}ClFN_3Os$: m/z 582.1, found 582.0. ^{1}H NMR($(CD_3)_2CO$): δ 9.53 (t, 1H, J = 2 Hz), 9.08 (d of d, 1H), 8,40 (d of t, 2H), 7.94 (d, 2H J = 8 Hz), 7.73 (t, 1H, J = 8 Hz), 7.63-7.48 (m, 7H), 7.97-7.32 (m, 2H), 6.87 (t, 1H, J = 6 Hz). 6.78 (d, 1H, J = 6 Hz), 6.47 (t, 1H, J = 6 Hz). CHN analysis: Found: C, 37.69%; H, 2.33%; N, 5.87%. Calcd for $C_{23}H_{18}ClF_7N_3OsP$: C, 38.05%; H, 2.50%; N, 5.79%.

[Os(η^6-*p*-cym)(2-F-azpy)I]PF$_6$ (11). [Os(η^6-*p*-cym)I$_2$]$_2$ (50.0 mg, 0.043 mmol) was dissolved in methanol (40 mL) at 313 K. 2-F-azpy (34.8 mg, 0.17 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 313 K for 4 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (70.0 mg, 0.43 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured powder precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 38.7 mg (48.5 %). ESI-MS Calcd for $C_{21}H_{22}FIN_3Os$: m/z 654.0, found 654.0. ^{1}H NMR($(CD_3)_2CO$): δ 9.70 (s, 1H), 9.13 (d, 1H, J = 6 Hz), 8.34 (t, 1H, J = 6 Hz), 8.17 (d, 2H, J = 6 Hz), 7.82-7.73 (m, 3H), 6.84 (d, 1H, J = 6 Hz), 6.52 (d, 1H, J = 6 Hz), 6.45 (d, 1H, J = 6 Hz), 6.35 (d, 1H, J = 6 Hz), 2.83 (s, 3H), 2.65-2.61 (m, 1H), 1.02 (dd, 6H). CHN analysis: Found: C, 32.27%; H, 2.81%; N, 5.21%. Calcd for $C_{21}H_{22}F_7IN_3OsP$: C, 31.63%; H, 2.78%; N, 5.27%.

[Os(η^6-*p*-cym)(2-F-Azpy)Cl]PF_6 (12). [Os(η^6-*p*-cym)Cl_2]$_2$ (25.0 mg, 0.032 mmol) was dissolved in methanol (20 mL) at 313 K. 2-F-azpy (12.7 mg, 0.063 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at ambient temperature for 4 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (20.5 mg, 0.13 mmol) was added. The solution was then left in the freezer (253 K) for 24 h. Dark coloured powder was precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 11.9 mg (52.7 %). ESI-MS Calcd for $C_{21}H_{22}ClFN_3Os$: m/z 561.1, found 561.0. ^{1}H NMR($(CD_3)_2CO$): δ 9.70 (s, 1H), 9.12 (d, 1H, J = 6 Hz), 8.43 (t, 1H, J = 6 Hz), 8.17 (d, 2H, J = 6 Hz), 7.65-7.58 (m, 3H), 6.87 (d, 1H, J = 6 Hz), 6.80 (d, 1H, J = 6 Hz), 6.51 (d, 1H, J = 6 Hz), 6.42 (d, 1H, J = 6 Hz), 2.81 (s, 3H), 2.53-2.49 (m, 1H), 0.97 (dd, 6H). CHN analysis: Found: C, 35.07%; H, 2.98%; N, 5.71%. Calcd for $C_{21}H_{22}ClF_7N_3OsP$: C, 35.72%; H, 3.14%; N, 5.95%.

[Os(η^6-bip)(2-Cl-azpy)I]PF_6 (13). [Os(η^6-bip)I_2]$_2$ (30.0 mg, 0.025 mmol) was dissolved in methanol (10 mL) at 353 K and heated under reflux for 1 h. 2-Cl-azpy (10.8mg, 0.050 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 2 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (16.3 mg, 0.10 mmol) was added. The solution was then left in the freezer (253 K) for 24 h. The dark coloured crystalline precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 24.5 mg (29.3 %). ESI-MS Calcd for $C_{23}H_{18}ClIN_3Os$: m/z 690.0, found 689.9. ^{1}H NMR($(CD_3)_2CO$): δ 9.46 (d, 1H, J = 3 Hz), 8.99 (d, 1H, J = 9 Hz), 8,40 (d of d, 1H), 7.91 (d, 2H, J = 8 Hz), 7.69 (t, 1H, J = 8 Hz), 7.55-7.47 (m, 3H), 7.44-7.39(m, 4H), 7.13 (d, 1H, J = 6 Hz), 7.09 (t, 1H, J = 6 Hz), 6.89 (t, 1H, J = 6 Hz), 6.82 (d, 1H, J = 6 Hz), 6.72 (t, 1H, J = 6 Hz). CHN analysis: Found: C, 32.92%; H, 2.06%; N, 5.03%. Calcd for $C_{23}H_{18}ClF_6IN_3OsP$: C, 33.21%; H, 2.18%; N, 5.04%.

[Os(η^6-*p*-cym)(2-Cl-azpy)I]PF_6 (14). [Os(η^6-*p*-cym)I_2]$_2$ (50.0 mg, 0.043 mmol) was dissolved in methanol (40 mL) at 313 K. 2-Cl-azpy (18.8 mg, 0.0865 mmol) in methanol (10

mL) was added drop-wise, the solution-colour changed from yellow to red immediately. The solution was stirred at ambient temperature for 3 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (28.2 mg, 0.173 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 45.7 mg (64.8 %). ESI-MS Calcd for $C_{21}H_{22}ClIN_3Os$: m/z 670.0, found 669.9. ^{1}H NMR($(CD_3)_2CO$): δ 9.71 (s, 1H), 9.05 (d, 1H, J = 9 Hz), 8.45 (d, 1H, J = 6 Hz), 8.16 (d, 2H, J = 6 Hz), 7.83-7.71 (m, 3H), 6.88 (d, 1H, J = 6 Hz), 6.57 (d, 1H, J = 6 Hz), 6.47 (d, 1H, J = 6 Hz), 6.35 (d, 1H, J = 6 Hz), 2.78 (s, 3H), 2.69-2.65 (m, 1H), 1.00 (d of d, 6H). CHN analysis: Found: C, 30.95%; H, 2.60%; N, 5.12%. Calcd for $C_{21}H_{22}ClF_6IN_3OsP$: C, 30.99%; H, 2.72%; N, 5.16%.

[Os(η^6-bip)(2-Cl-azpy)Cl]PF$_6$ (15). [Os(η^6-bip)$Cl_2]_2$ (50.0 mg, 0.060 mmol) was dissolved in methanol (20 mL) at 353 K and heated under reflux and N_2 for 1 h. 2-Cl-azpy (26.1 mg, 0.120 mmol) in methanol (10 mL) was added drop-wise. The solution was stirred at 353 K for 1 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (39.1 mg, 0.24 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured crystals formed which were collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 41.3 mg (46.3 %). ESI-MS Calcd for $C_{23}H_{18}Cl_2N_3Os$: m/z 598.0, found 598.0. ^{1}H NMR($(CD_3)_2CO$): δ 9.49 (d, 1H, J = 3 Hz), 8.97 (d, 1H, J = 9 Hz), 8,48 (d of d, 1H), 7.92 (d, 2H, J = 8 Hz), 7.70 (t, 1H, J = 8 Hz), 7.61-7.46 (m, 3H), 7.44-7.38(m, 4H), 6.96 (d, 1H, J = 6 Hz), 6.89 (d, 1H, J = 6 Hz), 6.85 (t, 1H, J = 6 Hz), 6.79 (t, 1H, J = 6 Hz), 6.46 (t, 1H, J = 6 Hz). CHN analysis: Found: C, 36.92%; H, 2.32%; N, 5.56%. Calcd for $C_{23}H_{18}Cl_2F_6N_3OsP$: C, 37.20%; H, 2.44%; N, 5.66%.

[Os(η^6-*p*-cym)(2-Cl-azpy)Cl]PF$_6$ (16). [Os(η^6-*p*-cym)$Cl_2]_2$ (50.0 mg, 0.063 mmol) was dissolved in methanol (40 mL) at 313 K. 2-Cl-azpy (27.5 mg, 0.126 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from yellow to red immediately. The solution was stirred at ambient temperature for 24 h. The volume was reduced to about 10

mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (41.2 mg, 0.253 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured crystals formed which were collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 41.2 mg (45.2 %). ESI-MS Calcd for $C_{21}H_{22}Cl_2N_3Os$: m/z 578.1, found 578.0. ^{1}H NMR($(CD_3)_2CO$): δ 9.68 (s, 1H), 9.01 (d, 1H, J = 9 Hz), 8.45 (d of d, 1H), 8.13 (d, 2H, J = 6 Hz), 7.83-7.51 (m, 3H), 6.89 (d, 1H, J = 6 Hz), 6.52 (d, 1H, J = 6 Hz), 6.39-6,34 (m, 2H), 2.80 (s, 3H), 2.54-2.46 (m, 1H), 0.98 (d of d, 6H). CHN analysis: Found: C, 34.80%; H, 2.98%; N, 5.78%. Calcd for $C_{21}H_{22}Cl_2F_6N_3OsP$: C, 34.91%; H, 3.07% N, 5.82%.

[Os(bip)(2-Br-azpy)I]PF_6 (17). $[Os(bip)I_2]_2$ (30.0 mg, 0.025 mmol) was dissolved in methanol (30 mL) and water (10 mL), and the solution was heated under reflux (T=353 K) for 1.5 h. 2-Br-azpy (13.1 mg, 0.05 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from orange to brown immediately. The solution was stirred and heated under reflux for 1.5 h further. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (16.4 mg, 0.2 mmol) was added. The solution was then left in a fridge for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 22.5 mg (51.2 %). ESI-MS Calcd for $C_{23}H_{18}BrIN_3Os$: m/z 733.9, found 733.7. ^{1}H NMR($(CD_3)_2CO$): δ 9.50 (d, 1H, J = 2 Hz), 8.91 (d, 1H, J = 9 Hz), 8,52 (d of d, 1H), 7.92 (d, 2H, J = 8 Hz), 7.69 (t, 1H, J = 8 Hz), 7.55-7.44 (m, 2H), 7.43-7.39 (m, 5H), 7.16-7.19 (m, 2H), 6.87 (t, 1H, J = 6 Hz), 6.81 (d, 1H, J = 6 Hz), 6.71 (t, 1H, J = 6 Hz). CHN analysis: Found: C, 31.94%; H, 1.97%; N, 4.74%. Calcd for $C_{23}H_{18}BrF_6IN_3OsP$: C, 31.45%; H, 2.07% N, 4.78%.

[Os(η^6-*p*-cym)(2-Br-Azpy)I]PF_6 (18). $[Os(\eta^6\text{-}p\text{-cym})I_2]_2$ (20.0 mg, 0.017 mmol) was dissolved in methanol (40 mL). 2-Br-Azpy (9.3 mg, 0.035 mmol) in methanol (10 mL) was added drop-wise. The solution colour changed from yellow to dark red immediately, it was stirred at ambient temperature for 16 h. The volume was reduced to ca 5 mL by removal of methanol on a rotary evaporator and ammonium hexafluorophosphate (11.3 mg, 0.069 mmol)

was added. Then the solution was left in a freezer (253 K) for 24 h. A dark coloured solid precipitated, which was filtered off, washed with diethyl ether, dried *in vacuo*. Yield: 16.2 mg (54.7%). Anal. ESI-MS Calcd for $C_{21}H_{22}BrIN_3Os$: m/z 714.0, found 713.9. ^{1}H NMR($(CD_3)_2CO$) δ 9.79 (s, 1H), 8.95 (d, 1H, J = 9 Hz), 8.67 (d, 1H, J = 6 Hz), 8.16 (d, 1H, J = 7 Hz), 7.86-7.78 (m, 3H), 6.93 (d, 1H, J = 6 Hz), 6.57 (d, 1H, J = 6 Hz), 6.39 (m, 2H), 2.56-2.53 (m, 1H), 2.46 (s, 3H), 1.00 (d of d, 6H). CHN analysis Found: C, 29.98%; H, 2.85%; N, 4.72%, Calcd for $C_{21}H_{22}BrIF_6N_3OsP$: C, 29.38%; H, 2.58%; N, 4.90%.

[Os(bip)(2-Br-azpy)Cl]PF_6 (19). $[Os(bip)Cl_2]_2$ (30.0 mg, 0.036 mmol) was dissolved in methanol (30 mL) and water (10 mL), and the solution was heated under reflux (T=353 K) for 1 h. 2-Br-azpy (18.9 mg, 0.072 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from orange to brown immediately. The solution was stirred and heated under reflux for 1 h further. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (59.0 mg, 0.36 mmol) was added. The solution was then left in a fridge for 24 h. The dark coloured precipitate was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 19.2 mg (33.8 %). ESI-MS Calcd for $C_{23}H_{18}BrClN_3Os$: m/z 642.0, found 641.9. ^{1}H NMR($(CD_3)_2CO$): δ 9.54 (d, 1H, J = 2 Hz), 8.88 (d, 1H, J = 9 Hz), 8,61 (d of d, 1H), 7.72 (d, 2H, J = 8 Hz), 7.61 (t, 1H, J = 8 Hz), 7.50-7.44 (m, 2H), 7.43-7.36 (m, 5H), 6.98 (d, 1H, J = 6 Hz), 7.89-7.80 (m, 3H), 6.47 (t, 1H, J = 6 Hz). CHN analysis: Found: C, 34.84%; H, 2.15%; N, 5.29%. Calcd for $C_{23}H_{18}BrClF_6N_3OsP$: C, 35.10%; H, 2.31% N, 5.34%.

[Os(η^6-*p*-cym)(2-Br-Azpy)Cl]PF_6 (20). $[Os(\eta^6\text{-}p\text{-cym})Cl_2]_2$ (30.0 mg, 0.038 mmol) was dissolved in methanol (20 mL) ; 2-Br-Azpy (20.0 mg, 0.076 mmol) in methanol (10 mL) was added drop-wise, the solution colour changed from yellow to dark red immediately. The solution was stirred at ambient temperature for 3 h. The volume was reduced to ca. 5 mL by removal of methanol on a rotary evaporator and ammonium hexafluorophosphate (24.7 mg, 0.15 mmol) was added. Then the solution was left in the freezer (253 K) for 24 h; A dark colour crystalline precipitated which was filtered off and washed with diethyl ether, then dried *in vacuo*. Yield: 39.2 mg (67.3%). Anal. ESI-MS Calcd for $C_{21}H_{22}BrClN_3Os$: m/z

622.0, found 622.1. ^{1}H NMR($(CD_3)_2CO$) δ 9.83 (s, 1H), 9.00 (d, 1H, J = 9 Hz), 8.61 (d, 1H, J = 6 Hz), 8.22 (d, 1H, J = 6 Hz), 7.80-7.78 (m, 3H), 6.94 (d, 1H, J = 6 Hz), 6.63 (d, 1H, J = 6 Hz), 6.41 (d, 1H, J = 6 Hz), 6.39 (d, 1H, J = 6 Hz), 2.80 (s, 3H), 2.67-2.64 (m, 1H), 1.02 (d of d, 6H). CHN analysis Found: C, 32.85%; H, 2.82%; N, 5.39%, Calcd for $C_{21}H_{22}BrClF_6N_3OsP$: C, 32.89%; H, 2.89%; N, 5.48%.

[Os(η^6-bip)(2-I-azpy)I]PF$_6$ (21). [Os(η^6-bip)I_2]$_2$ (26.0 mg, 0.022 mmol) was dissolved in methanol (20 mL) and water (5 mL), and the solution was heated under reflux (T=353 K) for 1 h. 2-Br-azpy (13.4 mg, 0.043 mmol) in methanol (5 mL) was added drop-wise, the solution-colour changed from orange to brown immediately. The solution was stirred and heated under reflux for 1 h further. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (14.3 mg, 0.088 mmol) was added. The solution was then left in a fridge (253 K) for 24 h. Dark coloured powder precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 19.2 mg (52.0 %). ESI-MS Calcd for $C_{23}H_{18}F_6IN_3Os$: m/z 781.9, found 781.8. ^{1}H NMR($(CD_3)_2CO$): δ 9.54 (d, 1H, J = 2 Hz), 8.74 (d, 1H, J = 9 Hz), 8,64 (d of d, 1H), 7.92 (d, 2H, J = 8 Hz), 7.70 (t, 1H, J = 8 Hz), 7.52-7.46 (m, 3H), 7.44-7.41(m, 4H), 7.15 (d, 1H, J = 6 Hz), 7.09 (d, 1H, J = 6 Hz), 6.83-6.78 (m, 2H), 6.69 (t, 1H, J = 6 Hz). CHN analysis: Found: C, 29.90%; H, 1.87%; N, 4.51%. Calcd for $C_{23}H_{18}F_6I_2N_3OsP$: C, 29.85%; H, 1.96% N, 4.54%.

[Os(η^6-*p*-cym)(2-I-azpy)I]PF$_6$ (22). [Os(η^6-*p*-cym)I_2]$_2$ (25.0 mg, 0.022 mmol) was dissolved in methanol (40 mL) at 313 K. 2-I-Azpy (13.4 mg, 0.043 mmol) in methanol (10 mL) was added drop-wise, the solution-colour changed from orange to blue immediately. The solution was stirred at ambient temperature for 4 h. The volume was reduced to about 10 mL by removal of methanol on a rotary evaporator, and ammonium hexafluorophosphate (14.0 mg, 0.086 mmol) was added. The solution was then left in a freezer (253 K) for 24 h. Dark coloured powder precipitated which was collected by filtration, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 27.4 mg (70.4 %). ESI-MS Calcd for $C_{21}H_{22}F_6IN_3Os$: m/z 762.0, found 761.8. ^{1}H NMR($(CD_3)_2CO$): δ 9.89 (s, 1H), 9.13 (m, 1H),

8.71 (d of d, 1H), 8.18 (m, 2H), 7.82-7.73 (m, 2H), 6.91 (d, 1H, J = 6 Hz), 6.59 (d, 1H, J = 6 Hz), 6.41 (d, 1H, J = 6 Hz), 6.35 (d, 1H, J = 6 Hz), 2.83 (s, 3H), 2.65-2.61 (m, 1H), 1.02 (d of d, 6H). CHN analysis: Found: C, 27.62%; H, 2.27%; N, 4.64%. Calcd for $C_{21}H_{22}F_6I_2N_3OsP$: C, 27.86%; H, 2.45% N, 4.64%.

[Os(η^6-bip)(3-Cl-Azpy)I]PF$_6$ (23). [Os(η^6-bip)I$_2$]$_2$ (30.0 mg, 0.025 mmol) in methanol (30 mL) and water (10 mL) was heated under refluxed (T=348 K) for 1.5 h. 3-Cl-Azpy (11.2 mg, 0.052 mmol) in methanol (10 mL) was added drop-wise. The solution colour changed from orange to dark red immediately, it was stirred at 348 K for 1.5 h. The volume was reduced to ca. 10 mL by removal of methanol on a rotary evaporator and ammonium hexafluorophosphate (41.0 mg, 0.25 mmol) was added. Then the solution was left in a fridge for 24 h. A dark colour powder precipitated, which was filtered off, washed with cold methanol and diethyl ether, dried *in vacuo*. Yield: 28.4 mg (68.1%). Anal. ESI-MS Calcd for $C_{23}H_{18}ClIN_3Os$: m/z 690.0, found 689.9. ^{1}H NMR((CD$_3$)$_2$CO) δ 9.41 (d, 1H, J = 6 Hz), 9.14 (d, 1H, J = 2 Hz), 7.96-7.90 (m, 3H), 7.74 (t, 1H, J = 5 Hz), 7.59-7.41 (m, 7H), 7.13 (d, 1H, J = 6 Hz), 7.05 (t, 1H, J = 6 Hz), 6.92-6.85 (m, 2H), 6.74 (t, 1H, J = 6 Hz). CHN analysis Found: C, 33.12%; H 2.18%; N 5.04%, Calcd for $C_{23}H_{18}ClF_6IN_3OsP$: C, 32.89%; H, 2.89%; N, 5.48%.

[Os(η^6-*p*-cym)(3-Cl-Azpy)I]PF$_6$ (24). [Os(η^6-*p*-cym)I$_2$]$_2$ (30.0 mg, 0.026 mmol) was dissolved in methanol (50 mL) . 3-Cl-Azpy (12.5 mg, 0.058 mmol) in methanol (10 mL) was added drop-wise. The solution colour changed from yellow to dark red immediately. It was then stirred at ambient temperature for 5 h. The volume was reduced to ca. 10 mL by removal of methanol on a rotary evaporator and ammonium hexafluorophosphate (41.8 mg, 0.26 mmol) was added. Then the solution was left in a freezer (253 K) for 24 h. Dark coloured crystals formed, which were filtered off, washed with diethyl ether, finally dried *in vacuo*. Yield: 28.4 mg (67.1%). Anal. ESI-MS Calcd for $C_{21}H_{22}ClIN_3Os$: m/z 670.0, found 670.0. ^{1}H NMR((CD$_3$)$_2$CO) δ 9.59 (d, 1H, J = 6 Hz), 9.16 (s, 1H), 8.18 (m, 2H), 7.96 (m, 1H), 7.84 (s, 1H), 7.76 (t, 3H), 6.82 (d, 1H, J = 6 Hz), 6.48-6.45 (m, 2H), 6.36 (d, 1H, J = 6 Hz), 2.73 (s, 3H), 2.66 (m, 1H), 1.03 (d of d, 6H). CHN analysis Found: C, 30.94%; H, 2.60%; N, 5.12%;

Calcd for $C_{21}H_{22}ClF_6IN_3OsP$: C, 30.99%; H, 2.72%; N, 5.16%. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution of complex 10 at 277 K.

[Os(η^6-bip)(3-Cl-Azpy)Cl]PF$_6$ (25). [Os(η^6-bip)Cl$_2$]$_2$ (30.0 mg, 0.036 mmol) in methanol (30 mL) and water (10 mL) was heated under reflux (T=348 K) for 1 h. 3-Cl-Azpy (16.1 mg, 0.073 mmol) in methanol (10 mL) was added drop-wise, the solution colour changed from orange to dark red immediately. The solution was stirred at 348 K for 2 h. The volume was reduced to ca. 10 mL by removal of methanol on a rotary evaporator and ammonium hexafluorophosphate (59.0 mg, 0.36 mmol) was added. Then the solution was left in the fridge for 24 h; A dark coloured powder precipitated, which was filtered off and washed with cold methanol and diethyl ether, then dried *in vacuo*. Yield: 31.0 mg (57.9%). Anal. ESI-MS Calcd for $C_{23}H_{18}Cl_2N_3Os$: m/z 597.6, found 598.0. ^{1}H NMR($(CD_3)_2CO$) δ 9.05 (d, 1H, J = 6 Hz), 8.87 (s, 1H), 7.73 (d, 1H, J = 6 Hz), 7.39 (d, 2H, J = 6 Hz), 7.28 (m, 1H), 7.17 (t, 2H, J = 6 Hz), 7.08-7.02 (m, 5H), 6.49 (d, 1H, J = 6 Hz), 6.46 (d, 1H, J = 6 Hz), 6.33 (t, 1H, J = 6 Hz), 6.18 (t, 1H, J = 6 Hz), 5.86 (t, 1H, J = 6 Hz). CHN analysis Found: C, 37.06%; H, 2.38%; N, 5.58%, Calcd for $C_{23}H_{18}Cl_2F_6N_3OsP$: C, 37.20%; H, 2.44%; N, 5.66%.

[Os(η^6-*p*-cym)(3-Cl-Azpy)Cl]PF$_6$ (26). [Os(η^6-*p*-cym)Cl$_2$]$_2$ (30.0 mg, 0.038 mmol) was dissolved in methanol (20 mL); 3-Cl-Azpy (16.7 mg, 0.077 mmol) in methanol (10 mL) was added drop-wise, the solution colour changed from yellow to dark red immediately. The solution was stirred at ambient temperature for 3 h. The volume was reduced to ca. 5 mL by removal of methanol on a rotary evaporator and ammonium hexafluorophosphate (25.0 mg, 0.15 mmol) was added. Then the solution was left in the freezer (253 K) for 24h; Dark coloured crystals formed which were filtered off and washed with diethyl ether, dried *in vacuo*. Yield: 39.1 mg (71.2%). Anal. ESI-MS Calcd for $C_{21}H_{22}Cl_2N_3Os$ [M] m/z 578.1, found 578.1. ^{1}H NMR($(CD_3)_2CO$) δ 9.60 (d, 1H, J = 6 Hz), 9.13 (s, 1H), 8.15 (d, 2H, J = 7 Hz), 8.11 (m, 1H), 7.86-7.79 (m, 3H), 6.84 (d, 1H, J = 6 Hz), 6.46 (d, 1H, J = 6 Hz), 6.38 (s, 2H), 2.56-2.53 (m, 1H), 2.43 (s, 3H), 1.00 (d of d, 6H). CHN analysis Found: C, 34.80%; H, 2.96%; N, 5.79%, Calcd for $C_{21}H_{22}Cl_2F_6N_3OsP$: C, 34.91%; H, 3.07%; N, 5.82%.

[Os(η^6-bip)(Abpy)I]PF$_6$ (27). [Os(η^6-bip)I$_2$]$_2$ (50.1 mg, 0.0418 mmol) and Abpy (19.5 mg, 0.105 mmol) were dissolved methanol (30 mL) and heated under reflux at 353 K for 3 h. The volume was reduced to ca. 10 mL by removal of methanol on a rotary evaporator. Ammonium hexafluorophosphate (29.3 mg, 0.16 mmol) was added. Then the solution was left in a freezer (253 K) for 24 h. A dark coloured precipitate formed, which was filtered off, washed with cold ethanol and diethyl ether, finally dried *in vacuo*. Yield: 48.2 mg (72.0%). Anal. ESI-MS Calcd for $C_{22}H_{18}IN_4Os$: m/z 657.0, found 656.9. ^{1}H NMR($(CD_3)_2CO$) δ 9.44 (d, 1H J = 6 Hz), 9.07 (m, 1H), 8.76 (d, 1H J = 6 Hz), 8.38 (t, 1H, J = 8 Hz), 8.14 (m, 2H), 7.76 (m, 2H), 7.61 (m, 2H), 7.45 (m, 3H). 7.25 (d, 1H, J = 6 Hz), 7.13 (d, 1H, J = 6 Hz), 7.03 (t, 1H, J = 6 Hz), 6.95 (t, 1H, J = 6 Hz), 6.82 (t, 1H, J = 6 Hz). CHN analysis Found: C, 32.59%; H, 2.17%; N, 7.07%, Calcd for $C_{20}H_{22}F_6IN_4OsP$: C, 33.01%; H, 2.27%; N, 7.00%.

[Os(η^6-*p*-cym)(Abpy)I]PF$_6$ (28). [Os(η^6-*p*-cym) I$_2$]$_2$ (40.0 mg, 0.035 mmol) was dissolved in 50 mL of methanol at 313 K; Abpy (16.1 mg, 0.087 mmol) in methanol (5 mL) was added drop-wise, the solution colour changed from orange to pink immediately; and was stirred at ambient temperature for 16 h. The volume was reduced to ca. 10 mL by removal of methanol on a rotary evaporator. Ammonium hexafluorophosphate (56.2 mg, 0.35 mmol) was added. Then the solution was left in a freezer (253 K) for 24 h. A dark coloured precipitate formed, which was filtered off, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 35.2 mg (64.5%). Anal. ESI-MS Calcd for $C_{20}H_{22}IN_4Os$: m/z 637.0, found 637.0. H NMR($(CD_3)_2CO$) δ 9.74 (d, 1H, J = 6 Hz), 9.12 (m, 1H), 8.90 (d, 1H, J = 5 Hz), 8.41 (m, 1H), 8.22 (m, 2H), 7.86 (m, 2H), 6.78 (d, 1H, J = 6 Hz), 6.72 (d, 1H, J = 6 Hz), 6.57 (d, 1H, J = 6 Hz), 6.51 (d, 1H, J = 6 Hz), 2.72 (s, 3H), 2.39 (m, 1H), 0.93 (d of d, 6H). CHN analysis Found: C, 30.91%; H, 2.74%; N, 7.28%, Calcd for $C_{20}H_{22}F_6IN_4OsP$: C, 30.78%; H, 2.84%; N, 7.18%.

[Os(η^6-bip)(Abpy)Cl]PF$_6$ (29). [Os(η^6-bip)Cl$_2$]$_2$ (51.0 mg, 0.064 mmol) and Abpy (32.0 mg, 0.17 mmol) were dissolved in methanol (30 mL) and heated under refluxed (T = 348 K) for 4 h. The solution colour changed from orange to pink immediately. The volume was reduced to ca. 10 mL by removal of methanol on a rotary evaporator and ammonium

hexafluorophosphate (40.0 mg, 0.24 mmol) was added. Then the solution was left in a freezer (253 K) for 24 h. A black crystalline product precipitated, which filtered off and washed with cold methanol and diethyl ether, then dried *in vacuo*. Yield: 56.4 mg (62.6%). Anal. ^{1}H NMR($(CD_3)_2CO$) δ 9.49 (d, 1H, J = 6 Hz), 9.05 (m, 1H), 8.80 (d, 1H, J = 8 Hz), 8.46 (t, 1H, , J = 8 Hz), 8.17 (m, 2H), 7.82 (m, 2H), 7.66 (d, 2H, J = 6 Hz), 7.48 (m, 3H). 7.14 (d, 1H, J = 6 Hz), 6.97 (d, 2H, J = 3 Hz), 6.82 (t, 1H, J = 6 Hz), 6.53 (m, 1H). CHN analysis Found: C, 36.91%; H, 2.42%; N, 8.25%, Calcd for $C_{20}H_{22}ClF_6N_4OsP$: C, 37.27%; H, 2.56%; N, 7.90%.

[Os(η^6-*p*-cym)(Abpy)Cl]PF$_6$ (30). [Os(η^6-*p*-cym)$Cl_2]_2$ (35.2 mg, 0.0445 mmol) was dissolved in methanol (25 mL) at RT. Abpy (20.4 mg, 0.11 mmol) in methanol (5 mL) was added drop-wise, the solution colour changed from orange to pink immediately. The solution was stirred at RT for 1 h. The volume was reduced to ca 10 mL by removal of methanol on a rotary evaporator. Ammonium hexafluorophosphate (73.0 mg, 0.45 mmol) was added. Then the solution was left in the freezer (253 K) for 24 h. The dark coloured precipitate was filtered off and washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 41.5 mg (67.7%). Anal. ESI-MS Calcd for $C_{20}H_{22}ClN_4Os$: m/z 545.1, found 545.0. ^{1}H NMR($(CD_3)_2CO$) δ 9.72 (d, 1H, J = 5 Hz), 9.07 (m, 1H), 8.94 (d, 1H, J = 4 Hz), 8.49 (t, 1H, J = 8 Hz), 8.25 (m, 2H), 7.88 (m, 2H), 6.93 (d, 1H, J = 6 Hz), 6.74 (d, 1H, J = 6 Hz), 6.49 (d, 1H, J = 6 Hz), 6.40 (d, 1H, J = 6 Hz), 2.58 (m, 1H), 2.39 (s, 3H), 0.95 (d of d, 6H). CHN analysis Found: C, 34.69%; H, 3.08%; N, 8.20%, Calcd for $C_{20}H_{22}ClPN_4OsF_6$: C, 34.86%; H, 3.22%; N, 8.13%.

[Os(η^6-*p*-cym)(OH-Azpy-NO$_2$)I]PF$_6$ (31). [Os(η^6-*p*-cym)$I_2]_2$ (23.8 mg, 0.020 mmol) was dissolved in methanol (30 mL) . OH-Azpy-NO_2 (10.5mg, 0.043 mmol) in methanol (5 mL) was added drop-wise. The solution was stirred at ambient temperature for 48 h with 7 drops of HCl (1 M). The volume was reduced to ca. 2 mL by removal of methanol on a rotary evaporator. The complex was purified by chromatography on a Sephadex LH20 column. Ammonium hexafluorophosphate (10.0 mg, 0.61 mmol) was added. Then the solution was left in the fridge for 0.5 h. The dark coloured precipitate was filtered off, washed with cold ethanol and diethyl ether, then finally dried *in vacuo*. Yield: 12.7 mg (37.8%). Anal. ESI-MS

Calcd for $C_{21}H_{22}IN_4O_3Os$: m/z 697.0, found 696.9. ^{1}H NMR($(CD_3)_2CO$) δ 9.87 (d, 1H, J = 2 Hz), 9.68 (d, 1H, J = 9 Hz), 9.39 (d, 2H, J = 9 Hz), 9.73 (d, 2H, J = 9 Hz), 8.57 (m, 1H), 7.38 (d, 1H, J = 8 Hz), 7.04 (d, 1H, J = 8 Hz), 6.57 (s, 1H), 4.50 (m, 1H), 3.60 (s, 3H), 1.86 (d of d, 6H). CHN analysis Found: C, 31.06%; H, 2.83%; N, 6.44%, Calcd for $C_{21}H_{22}F_6IN_4O_3OsP$: C, 30.01%; H, 2.64%; N, 6.67%.

[Os(η^6-*p*-cym)(OH-Azpy-NO_2)Cl]PF_6 (32). [Os(η^6-*p*-cym) Cl_2]$_2$ (31.5 mg, 0.040 mmol) was dissolved in methanol (30 mL). OH-Azpy-NO_2 (19.7 mg, 0.081 mmol) in methanol (10 mL) was added drop-wise, the solution colour changed from yellow to brown immediately. The solution was stirred at ambient temperature for 4 h. The volume was reduced to about 2 mL by removal of methanol on a rotary evaporator. The complex was purified by chromatography on a Sephadex LH20 column. Ammonium hexafluorophosphate (26.2 mg, 0.16 mmol) was added. Then the solution was left in the freezer (253 K) for 1 h. The dark coloured precipitate was filtered off, washed with diethyl ether, and finally dried *in vacuo*. Yield: 25.1 mg (41.8%). Anal. ESI-MS Calcd for $C_{21}H_{22}ClN_4O_3Os$: 605.1, found 605.1. ^{1}H NMR($(CD_3)_2CO$) δ 9.06 (d, 1H, J = 2 Hz), 8.79 (d, 1H, J = 9 Hz), 8.56 (d, 2H, J = 9 Hz), 8.33 (d, 2H, J = 9 Hz), 7.80 (d, 1H, J = 8 Hz), 6.74 (d, 1H, J = 8 Hz), 6.36 (d, 2H, J = 8 Hz), 6.22 (d, 1H, J = 8 Hz), 2.57-2.52 (m, 1H), 2.47 (s, 3H), 1.00 (d of d, 6H). CHN analysis Found: C, 34.35%; H, 2.95%; N, 7.35%, Calcd for $C_{21}H_{22}ClF_6N_4O_3OsP$: C, 33.67%; H, 2.96%; N, 7.48%.

Table S1

(A) X-ray crystallographic data for compounds **7**, **10**, **13** and **14**.

	7	**10**	**13**	**14**
Formula	$C_{23}H_{18}Cl_2F_6N_3OsP$	$C_{23}H_{18}ClF_7N_3OsP$	$C_{23}H_{18}ClF_6IN_3OsP$	$C_{21}H_{22}ClF_6IN_3OsP$
Molar mass	742.47	726.02	833.92	813.94
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Crystal size /mm	0.35 x 0.25 x 0.08	0.40 x 0.16 x 0.16	0.25 x 0.10 x 0.10	0.50 x 0.40 x 0.08
Space group	P2(1)/c	P-1	P2(1)/n	P-1
Crystal	black block	brown block	black block	purple block
a / Å	7.6240(5)	7.4624(2)	6.9574(2)	7.6626(5)
b / Å	28.9718(19)	10.8856(4)	16.7829(6)	11.9693(8)
c / Å	11.0421(14)	14.5449(5	20.7297(7	13.6120(6)
α / deg	90	81.182(3)	90	99.966(5)
β / deg	94.240(8)	84.223(2)	93.182(3)	102.906(5)
γ / deg	90	82.970(3)	90	91.374(5)
T / K	298(2)	100(2)	100(2)	100(2)
Z	4	2	4	2
R [F > 4σ (F)][a]	0.0654	0.0249	0.023	0.0323
R_w[b]	0.1996	0.0569	0.0484	0.0779
GOF[c]	1.044	0.998	1.008	1.018
Δρ max and min/ eÅ^{-3}	3.453 and -4.967	1.152 and -1.411	0.718 and -0.747	1.683 and -1.828

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2)]^{1/2}$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$. Where n = number of reflections and p = number of parameters

(B) X-ray crystallographic data for compounds **16**, **18** and **19**.

	16	**18**	**19**
Formula	$C_{21}H_{22}Cl_2F_6N_3OsP$	$C_{21}H_{22}BrF_6IN_3OsP$	$C_{23}H_{18}BrClF_6N_3OsP$
Molar mass	722.49	858.4	786.93
Crystal system	Triclinic	Triclinic	Triclinic
Crystal size /mm	0.22 x 0.18 x 0.16	0.20 x 0.14 x 0.12	0.40 x 0.18 x 0.05
Space group	P-1	P-1	P-1
Crystal	green block	black block	brown block
a / Å	9.1784(2)	7.8035(3)	8.8866(5)
b / Å	10.6711(3)	11.9630(5)	10.0428(4)
c / Å	12.2921(4)	13.6394(6)	14.1695(7
α / deg	93.579(2)	100.216(4)	103.452(4)
β / deg	93.460(2)	102.863(4)	94.374(4)
γ / deg	96.430(2)	90.779(3)	100.802(4)
T / K	100(2)	100(2)	100(2)
Z	2	2	2
R [F > 4σ (F)][a]	0.0214	0.0264	0.0257
R_w[b]	0.0424	0.0608	0.0567
GOF[c]	0.977	1.034	0.99
Δρ max and min/ eÅ^{-3}	0.800 and -0.759	2.450 and -0.866	1.113 and -1.144

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2)]^{1/2}$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$. Where n = number of reflections and p = number of parameters

(C) X-ray crystallographic data for compounds **20**, **24** and **25**

	20	**24**	**26**
Formula	$C_{21}H_{22}BrClF_6N_3OsP$	$C_{22}H_{27}ClF_6IN_3O_{1.50}Os$	$C_{21}H_{22}Cl_2F_6N_3OsP$
Molar mass	766.95	854.99	722.49
Crystal system	Monoclinic	Orthorhombic	Triclinic
Crystal size /mm	0.30 x 0.10 x 0.05	0.32 x 0.32 x 0.18	0.20 x 0.12 x 0.05
Space group	P2(1)/n	Pbca	P-1
Crystal	black block	black block	black block
a / Å	16.6936(5)	19.4975(4)	7.2224(2)
b / Å	9.0505(3)	14.2729(3)	10.6661(4)
c / Å	16.9583(5)	20.3022(3)	15.8327(6)
α / deg	90	90	79.383(3)
β / deg	107.970(3)	90	78.400(3)
γ / deg	90	90	85.931(3)
T / K	100(2)	173(2)	100(2)
Z	2	2	2
$R\ [F > 4\sigma\ (F)]$[a]	0.0292	0.0324	0.0221
R_w[b]	0.0524	0.073	0.045
GOF[c]	0.926	0.921	0.984
Δρ max and min/ eÅ^{-3}	2.010 and -1.610	1.734 and -1.466	1.287 and -0.795

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2)]^{1/2}$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$. Where n = number of reflections and p = number of parameters

Table S2. Selected bond lengths (Å) and angles (°). (A) Iodido complexes [Os(η^6-bip)(2-Cl-Azpy)I]PF_6 (**13**), [Os(η^6-*p*-cym)(2-Cl-Azpy)I]PF_6 (**14**), [Os(η^6-*p*-cym)(2-Br-Azpy)I]PF_6 (**18**) and [Os(η^6-*p*-cym)(3-Cl-Azpy)I]PF_6 (**24**). (B) Chlorido complexes [Os(η^6-bip)(1-Cl-Azpy)Cl]PF_6 (**7**), [Os(η^6-bip)(2-F-Azpy)Cl]PF_6 (**10**), [Os(η^6-*p*-cym)(2-Cl-azpy)Cl]PF_6 **(16)**, [Os(η^6-bip)(2-Br-Azpy)Cl]PF_6 (**19**), [Os(η^6-*p*-cym)(2-Br-Azpy)Cl]PF_6 (**20**) and [Os(η^6-*p*-cym)(3-Cl-Azpy)Cl]PF_6 (**26**).

(A) Iodido complexes

bond length/angle	**13**	**14**	**18**	**24**
Os(1)-N(8)	2.006(3)	2.033(4)	2.033(3)	2.009(3)
Os(1)-N(1)	2.057(3)	2.065(4)	2.051(3)	2.053(3)
Os(1)-C(15)	2.219(3)	2.213(5)	2.210(4)	2.228(4)
Os(1)-C(19)	2.261(3)	2.230(5)	2.220(4)	2.245(4)
Os(1)-C(18)	2.172(3)	2.240(5)	2.245(4)	2.190(4)
Os(1)-C(16)	2.221(3)	2.239(5)	2.243(4)	2.226(4)
Os(1)-C(20)	2.313(3)	2.219(5)	2.216(4)	2.284(4)
Os(1)-C(17)	2.203(3)	2.260(5)	2.268(4)	2.247(4)
Os(1)-I(1)	2.7063(2)	2.7002(4)	2.7056(3)	2.7007(3)
N(7)-N(8)	1.293(4)	1.296(5)	1.290(5)	1.284(4)
N(8)-Os(1)-N(1)	74.94(10)	75.47(16)	75.15(13)	74.41(13)
N1-Os-I	84.72(7)	84.98(11)	84.91(9)	82.36(9)
I-Os-N8	87.31(7)	88.76(11)	89.49(9)	87.76(9)

(B) Chlorido complexes

bond length/angle	**7**	**10**	**16**	**19**	**20**	**26**
Os(1)-N(8)	2.007(7)	2.023(3)	2.012(2)	2.039(3)	2.024(2)	2.0067(17)
Os(1)-N(1)	2.124(9)	2.053(3)	2.059(2)	2.055(3)	2.047(2)	2.0638(18)
Os(1)-C(15)	2.173(10)	2.233(3)	2.227(3)	2.242(4)	2.238(3)	2.246(2)
Os(1)-C(19)	2.227(9)	2.233(3)	2.218(3)	2.181(4)	2.208(3)	2.217(2)
Os(1)-C(18)	2.225(12)	2.239(3)	2.227(3)	2.204(4)	2.228(3)	2.221(2)
Os(1)-C(16)	2.255(10)	2.212(3)	2.173(3)	2.215(4)	2.187(3)	2.177(2)
Os(1)-C(20)	2.230(10)	2.233(3)	2.263(3)	2.278(4)	2.259(3)	2.286(2)
Os(1)-C(17)	2.257(11)	2.242(4)	2.226(3)	2.215(4)	2.238(3)	2.231(2)
Os(1)-Cl(1)	2.387(3)	2.3727(8)	2.3954(6)	2.3896(9)	2.3880(7)	2.3915(5)
N(7)-N(8)	1.276(11)	1.287(4)	1.295(3)	1.283(5)	1.295(3)	1.292(2)
N(8)-Os(1)-N(1)	73.8(3)	74.52(11)	74.96(9)	74.32(13)	74.88(10)	74.68(7)
N1-Os-Cl	83.5(3)	82.24(8)	84.88(6)	84.69(9)	85.11(7)	84.45(5)
Cl-Os-N8	89.6(2)	88.36(8)	87.82(6)	88.86(9)	86.44(7)	89.63(5)

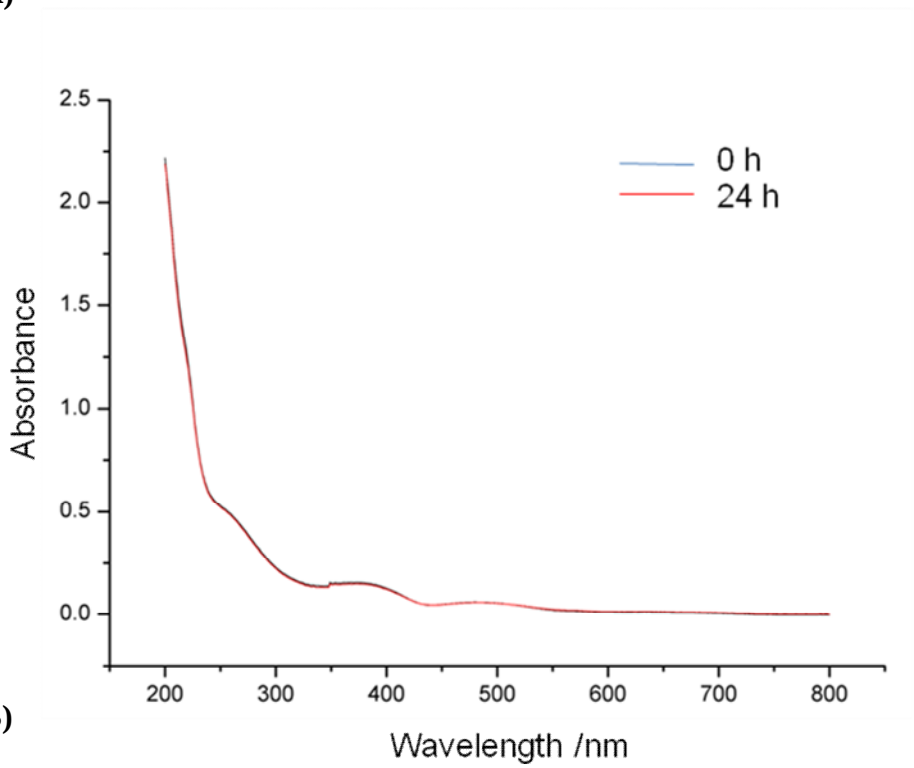
Table. S3. Comparison of octanol/water partition coefficients (log P values) and cytotoxicity towards A2780 cells. Data are the mean of three experiments and are reported as mean ± standard error of the mean (SEM)

Complex	Log P	IC_{50}/μM
9	-0.99 (± 0.28)	0.63 (±0.1)
13	-0.09 (± 0.06)	1.0 (±0.1)
17	0.08 (± 0.07)	0.59 (±0.02)
19	0.13 (± 0.06)	>50
23	-0.59 (± 0.32)	22.0 (±2.0)
25	-1.45 (± 0.37)	>100

Table S4. Time dependent accumulation of Os from complexes **9** and **23** in A2780 human ovarian cancer cells.

Time / h	**9** ppt Os/10^4 cells	**23** ppt Os/10^4 cells
0.5	40.6 (±1.6)	64.8 (±5.6)
1	51.8 (±2.8)	67.4 (±0.3)
4	263.8 (±12.7)	67.9 (±1.8)
24	399.4 (±20.9)	35.1 (±2.2)

(A)



(B)

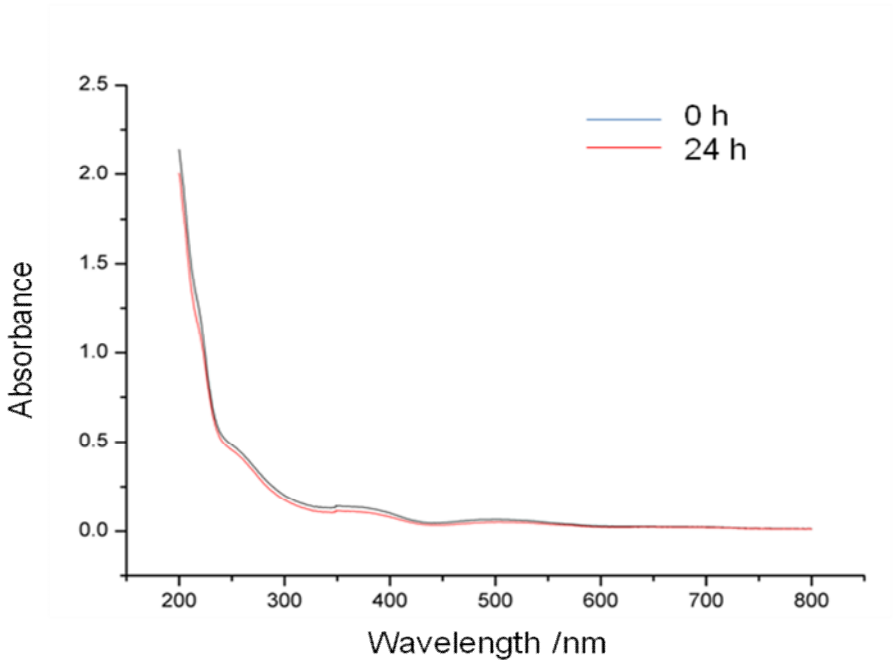


Figure S1. Electronic absorption spectra for compounds **9** (A) and **23** (B) before and after incubation for 24 h at 310 K in a solution of methanol and water (5:95 v/v).

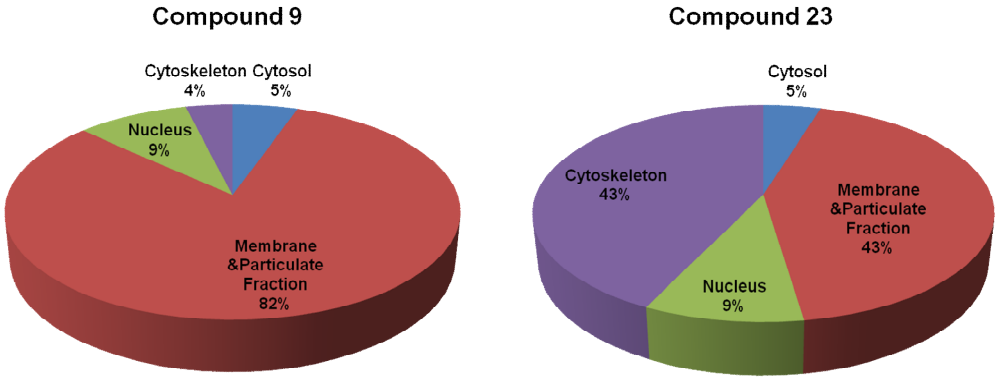


Fig. S2 Distribution of osmium in A2780 cells as a percentage of total osmium for compounds **9** and **23**. All data are the mean of three experiments and are reported as mean ± standard error of the mean (SEM)