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Supporting Information for

Conventional and Unconventional Alkyne Activations by Ru and Os for Unprecedented Dimetalated Quinolizine Complexes

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General Procedures for Synthesis and Characterizations

All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All reagents were used as received, and solvents for reactions were purified by a PureSolv MD5 solvent purification system. *cis*-$[M(dppm)_2Cl_2]$ and *cis*-$[M(bpy)_2Cl_2]$ (M = Ru, Os; dppm = 1,1-bis(diphenylphosphino)methane; bpy = 2,2'-bipyridine) were prepared in accordance with literature methods.[1] ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H–^1H COSY, ^1H–^1H NOESY, ^1H–^{13}C HSQC, ^1H–^{31}P HMBC and ^1H–^{13}C HMBC NMR spectra were recorded on Bruker 600 AVANCE III FT-NMR spectrometer. Peak positions were calibrated with solvent residue peaks as internal standard. The $^{31}P\{^1H\}$ NMR spectra were referenced to external $P(C_6H_5)_3$ (–4.7 ppm).[2] Labeling scheme for H and C atoms in the NMR assignments is shown in Figure S1. Electrospray mass spectrometry was performed on a PE-SCIEX API 3200 triple quadrupole mass spectrometer. Elemental analyses were done on an Elementar Vario Micro Cube carbon-hydrogen-nitrogen elemental microanalyzer.

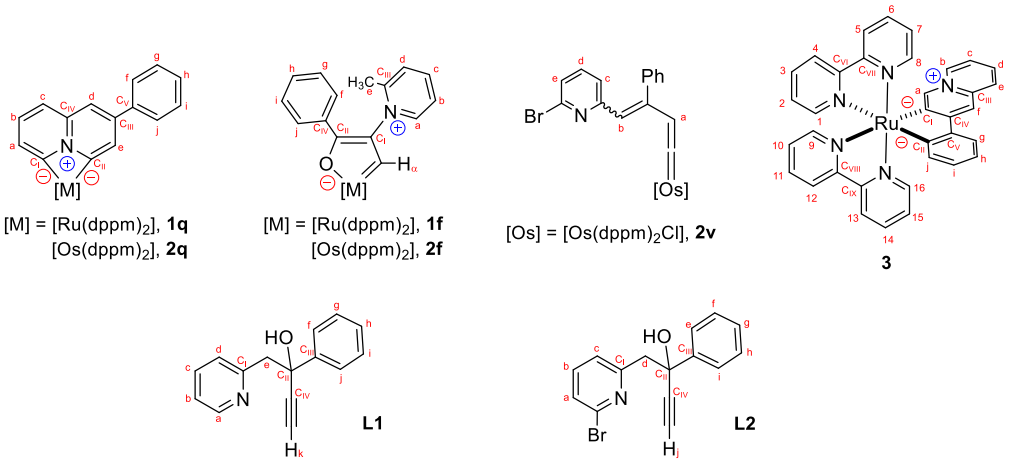


Figure S1. Labeling scheme for H and C atoms in this work.

Synthesis of **L1** and **L2**

This ligand was synthesized according to a modified literature procedure:[3] To a solution of the 2-methylpyridine/6-bromo-2-methylpyridine (1.32 mmol) in THF (20 mL) at -78°C was added lithium diisopropylamide (1.32 mL of a 2.0 M solution in THF/Hexane, 2.64 mmol) in dropwise manner. The reaction mixture was stirred for 30 min at -78°C. Then 1-phenyl-2-propyn-1-one (1.32 mmol) in THF (10 mL) was added dropwisely to the reaction mixture at -78°C and stirred for 30 min. Upon warming up to room temperature, a saturated aqueous NH_4Cl solution (5 mL) was added to the reaction mixture, the aqueous layer was extracted with Et_2O (50 mL × 2) and CH_2Cl_2 (50 mL × 2). The organic phases were combined, washed with brine (50 mL × 2), dried over anhydrous $MgSO_4$, and concentrated to obtain a brown oil. **L1**/**L2** was obtained as yellow oil after silica gel column chromatography (hexane/EtOAc: 4:1 to 7:3 (v/v)).

Synthesis of **1q**(OTf), **1f**$(OTf)_2$, **2q**(OTf), and **2f**$(OTf)_2$

Method 1: A mixture of **L1** (0.45 mmol) and *cis*-$[M(dppm)_2Cl_2]$ (M = Ru/Os, 0.15 mmol) were refluxed in MeOH (50 mL) under argon for 16 hr, during which the metal precursors gradually dissolved and the color of the reaction mixture changed from pale brown to yellowish brown. Upon cooling to room temperature, saturated aqueous NaOTf solution (5 mL) was added into the reaction mixture. The volume of the reaction mixture was concentrated to about 5 mL by reduced pressure, and the resultant brown solids were collected by suction filtration, washed with deionized water (5 mL × 3), EtOH/Et_2O (10 mL × 3), and finally Et_2O (10 mL × 3). The crude product was further purified by basic alumina column and the yellow band (**1q** and **2q**) was eluted with CH_2Cl_2/$(CH_3)_2CO$ 8:2 (v/v) mixture, while the red band (**1f** and **2f**) was eluted with 100% $(CH_3)_2CO$. The collected two bands were concentrated to about 5 mL and added into Et_2O (150 mL) separately to give yellow (**1q** and **2q**) and red (**1f** and **2f**) precipitates. Analytically pure bright yellow (**1q** and **2q**) and deep red (**1f** and **2f**) crystals were obtained by recrystallization of the precipitates (via layering of *n*-hexane onto a CH_2Cl_2 solution of the complexes). Reaction yields provided below are all obtained from Method 1.

Method 2: A mixture of **L1** (0.45 mmol), *cis*-$[M(dppm)_2Cl_2]$ (M = Ru/Os, 0.15 mmol) and 20 equivalent of NaOTf were stirred at room temperature or heat at 40°C/80°C in CH_2Cl_2 (40 mL) under argon for 16 hr, during which the color of the reaction mixture changed from brown to reddish brown. Upon cooling to room temperature, the mixture was filtered and concentrated to about 2 mL by reduced pressure. The crude product was purified by column chromatography as mentioned in the last part of Method 1.

Remark: Two stereoisomers were observed for **1f** and **2f** from both NMR spectroscopy and X-ray crystallography (illustrated in Figure S2).

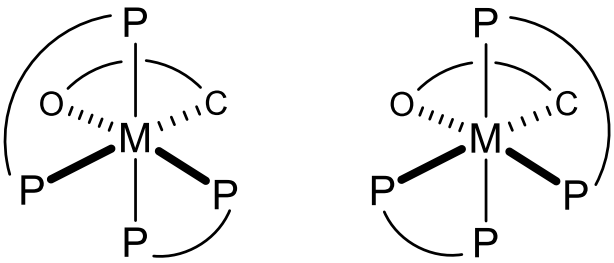


Figure S2. The two stereoisomers observed in **1f** and **2f**.

Synthesis of **2v**(OTf)
A mixture of **L2** (0.45 mmol), *cis*-[Os(dppm)$_2$Cl$_2$] (0.15 mmol) and 20 equivalent of NaOTf were stirred at 40°C (40 mL) under argon for 16 hr, during which the color of the reaction mixture changed from pale yellow to orange red. Upon cooling to room temperature, the mixture was filtered and concentrated to about 2 mL by reduced pressure. The concentrated solution was then added into Et_2O (150 mL) and bright orange solids were collected by suction filtration. Analytically pure bright red crystals were obtained by recrystallization of the precipitates (via layering of *n*-hexane onto a CH_2Cl_2 solution of the complexes).

Remark: The NMR spectra for **2v** suggest that the reaction product is a mixture of isomers where the two dppm auxiliary ligands can be *cis*- and *trans*- to each other, and the alkene moiety on the vinylidene ligand can have *E*- and *Z*-configurations; only the signals from the 2 major species, *E*- & *Z*-form in *cis*-configuration, are clear enough for NMR assignment.

Synthesis of **3**(OTf)
The preparation steps are same as the method 1 for synthesis of **1** and **2,** except for the coloumn chromatography which the crude product was purified by basic alumina column and the purple band was eluted with CH_2Cl_2/$(CH_3)_2CO$ 8:2 to 7:3 (v/v) mixture. The collected band was concentrated to about 5 mL and added to Et_2O (150 mL) separately to give purple precipitates. Analytically pure deep purple crystals were obtained by recrystallization of the precipitates (via layering of *n*-hexane onto a CH_2Cl_2 solution of the complexes).

Synthesis of **Q**(OTf)
A mixture of **L1** (0.45 mmol) and 20 equivalent of CF_3SO_3H were refluxed in MeOH (50 mL) under argon for 16 hr, during which the colour of the reaction mixture changed from yellow to very pale yellow. Upon cooling to room temperature, the solution was removed by rotary evaporator. The remained solids were dissolved by minmium amount of CH_2Cl_2 solution for recrystallization (via layering of *n*-hexane onto a CH_2Cl_2 solution of the compounds) to obtain colourless crystals. The NMR spectra of **Q** obtained from the above synthetic methods are identical to the previous reported data.[4] Product yield for the reaction = 65%.

Liberation of **Q**(OTf) from **1q**(OTf) under high temperature
A mixture of **1q**(OTf) (0.074 mmol) and 2.5 equivalent of CF_3SO_3H in CH_3CN (5 mL) were refluxed in chlorobenzene for 1.5 hr, during which the colour of the reaction mixture changed from pale yellow to colourless. Upon cooling to room temperature, the reaction mixure was neutralized by $NaHCO_3$ solution (0.1M). The solvent was then removed via distillation under negative pressure. The solid residue was dissolved in CH_2Cl_2 for a flash neutral alumina coloum chromatography. The product **Q** was eluted with 100% $(CH_3)_2CO$. Analytically pure colourless crystals were obtained by recrystallization of the precipitates (via layering of *n*-hexane onto a CH_2Cl_2 solution of the compounds). Isolated yield for **Q** = 11%.

Complex 1q(OTf). Yield: 44%. Anal. Calcd for $C_{66}H_{54}SF_3O_3NP_4Ru$: C, 64.81; H, 4.45; N, 1.15. Found: C, 64.82; H, 4.44; N, 1.15. $^1H\{^{31}P\}$ NMR (600 MHz, $(CD_3)_2CO$): δ 4.80–4.90, 5.22–5.39 (m, 4H, 2 CH_2 on dppm), 6.63–6.64 (m, 1H, H_a), 6.77 (s, 1H, H_e), 7.11 (m, 1H, H_c), 7.16–7.18 (m, 1H, H_b), 7.26 (s, 1H, H_d), 7.41–7.44 (m, 2H, H_g & H_i), 7.52–7.55 (m, 1H, H_h), 7.64–7.65 (m, 2H, H_f & H_j), 6.76–6.77, 6.81–6.82, 6.84–6.87, 6.89–6.92, 7.04–7.18, 7.29–7.32, 7.36–7.39, 7.41–7.58, 7.64–7.65, 7.71–7.72 (m, 40H, protons of 4 Ph rings on dppm). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): δ 47.22, 47.05 (CH_2 on dppm), 112.64 (C_d), 115.45 (C_b & C_c), 126.70 (C_e), 127.38 (C_f, C_h & C_j), 128.11 (C_a), 131.77 (C_g & C_i), 133.94 (C_V), 139.79 (C_{III}), 141.40 (C_{IV}), 172.73 (C_I & C_{II}), 128.11, 128.82, 128.99, 129.34, 129.52, 129.69, 129.87, 130.22, 130.40, 130.57, 131.28, 131.80, 132.16, 133.39, 133.74, 137.43, 138.31 (48C of 4 Ph rings on dppm). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -8.19–(-7.39), -1.1652–(-0.7526) (m, 4P on dppm). ESI-MS: m/z 1074.4 [**1q**]$^+$.

Complex 1f(OTf)$_2$. Yield: 64%. Anal. Calcd for $C_{67}H_{57}S_2F_6O_7NP_4Ru$: C, 57.84; H, 4.13; N, 1.01. Found: C, 57.83; H, 4.14; N, 1.00. Isomeric form A: $^1H\{^{31}P\}$ NMR (600 MHz, $(CD_3)_2CO$): δ 4.37–4.40, 4.65–4.68, 4.77–4.80, 5.01–5.03 (m, 4H, 2 CH_2 on dppm), 1.89 (s, 3H, H_e), 6.23–6.25 (m, 2H, H_f & H_j), 6.79 (m, 1H, H_b), 6.88–6.91 (m, 1H, H_g/H_i), 6.98–6.99 (m, 1H, H_a), 7.57–7.59 (m, 1H, H_c), 7.64 (m, 1H, H_g/H_i), 8.08–8.09 (m, 1H, H_d), 8.35–8.39 (m, 1H, H_h), 11.9707 (s, 1H, $H_α$), 8.08–8.09, 7.67–7.71, 7.57–7.60, 7.22–7.25, 6.89–6.91, 6.23–6.25, 7.52–7.57, 7.43–7.50, 7.22–7.25, 7.12–7.15, 7.05–7.07, 6.73–6.75, 6.64–6.65, 7.84–7.85, 7.52–7.57, 7.43–7.47, 7.33–7.37, 6.96–7.01, 7.64–7.67, 6.38–6.39, (m, 40H, protons of 4 Ph rings on dppm). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): δ 45.23, 42.64 (*C*H_2 on dppm), 21.12 (C_e), 126.44 (C_g/C_i), 127.57 (C_a), 129.51 (C_g/C_i), 129.67 (C_c), 130.00 (C_b), 130.48 (C_f & C_j), 131.00 (C_{IV}), 134.65(C_{III}), 134.85 (C_d), 142.44 (C_I), 156.30 (C_{II}), 146.66 (C_h), 195.23 ($C_α$), 134.85, 130.32, 131.78, 129.84, 129.51, 130.48, 132.10, 129.67, 130.00, 131.94, 129.35, 129.78, 131.45, 130.97, 132.42, 132.26, 132.59, 137.12 (48C of 4 Ph rings on dppm). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -26.55–(-26.25), -12.33–(-11.12), 1.44–1.81, 2.73–3.85 (m, 4P on dppm).
Isomeric form B: $^1H\{^{31}P\}$ NMR (600 MHz, $(CD_3)_2CO$): δ 4.21–4.24, 4.49–4.51, 4.30–4.32, 5.04–5.07 (m, 4H, 2 CH_2 on dppm), 1.89 (s, 3H, H_e), 6.86–6.88 (m, 1H, H_a), 7.12–7.13 (m, 2H, H_f & H_j), 7.442 (m, 1H, H_b), 7.48 (m, 1H, H_c), 7.57–7.60 (m, 2H, H_g & H_i), 7.99–8.01 (m, 1H, H_d), 8.35–8.39 (m, 1H, H_h), 11.51 (s, 1H, $H_α$), 7.99–8.02, 7.57–7.60, 7.44–7.50, 7.35–7.38, 6.99–7.06, 6.32–6.33, 7.71–7.74, 7.35–7.38, 7.22–7.25, 7.64–7.74, 7.22, 6.96–7.03, 6.80–6.83, 7.36–7.38, 7.05–7.07, 6.64–6.65 (m, 40H, protons of 4 Ph rings on dppm). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): δ 42.96 (*C*H_2 on dppm), 21.12 (C_e), 126.12 (C_g & C_i), 127.73 (C_a), 129.35 (C_f & C_j), 130.00 (C_b), 132.10 (C_c & C_d), 134.41 (C_{III}), 135.38 (C_{IV}), 140.49(C_I), 146.66 (C_h), 156.06 (C_{II}), 196.44 ($C_α$), 134.20, 129.51, 125.95, 130.00, 132.75, 132.26, 130.64, 127.57, 130.32, 131.78, 130.16, 132.59, 134.69, 127.41, 137.12, 130.97 (48C of 4 Ph rings on dppm). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -23.70–(-23.41), -18.04–(-16.80), -1.42–(-0.30), 3.12–3.38 (m, 4P on dppm).
ESI-MS: m/z 546.8 [**1f**]$^{2+}$.

Complex 2q(OTf). Yield: 58%. Anal. Calcd for $C_{66}H_{54}SF_3O_3NP_4Os$: C, 60.41; H, 4.15; N, 1.07. Found: C, 60.40; H, 4.15; N, 1.08. $^1H\{^{31}P\}$ NMR (600 MHz, $(CD_3)_2CO$): δ 5.26–5.29, 5.36–5.39, 6.07–6.09, 6.21–6.23 (m, 4H, 2 CH_2 on dppm), 6.61–6.62 (m, 1H, H_a), 6.77 (s, 1H, H_e), 7.18–7.20 (m, 1H, H_b), 7.27–7.28 (m, 1H, H_c), 7.40–7.43 (m, 1H, H_h), 7.42 (s, 1H, H_d), 7.45–7.475 (H_g & H_i), 7.72–7.74 (H_f & H_j), 61–6.62, 7.04–7.05, 7.06–7.09, 7.41–7.43, 7.48–7.75, 6.68–6.69, 6.83–6.85, 7.41–7.43, 7.72-7.74, 6.74–6.77, 6.91–6.94, 7.05–7.08, 7.39–7.40, 7.41–7.42, 7.72–7.74 (m, 40H, protons of 4 Ph rings on dppm). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): δ 52.78, 52.86 (*C*H_2 on dppm), 111.25 (C_d), 114.23 (C_c) 123.73 (C_e), 125.14 (C_a), 131.86 (C_g & C_i), 132.03 (C_h), 132.91 ((C_g & C_i), 133.23 (C_b), 138.33 (C_{III}), 139.51 (C_V), 142.74 (C_{IV}), 151.57 (C_I), 151.86 (C_{II}), 125.14, 130.24, 131.82, 133.23, 131.12, 131.47, 132.87, 128.83, 130.41, 132.45, 130.98, 129.36, 129.71, 129.01, 128.30, 123.73, 135.98, 133.62 (48C of 4 Ph rings on dppm). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -52.49–(-52.29), -48.45–(-47.32), -51.91–(-51.71), -50.11–(-48.96), (m, 4P on dppm). ESI-MS: m/z 1164.8 [**2q**]$^+$.

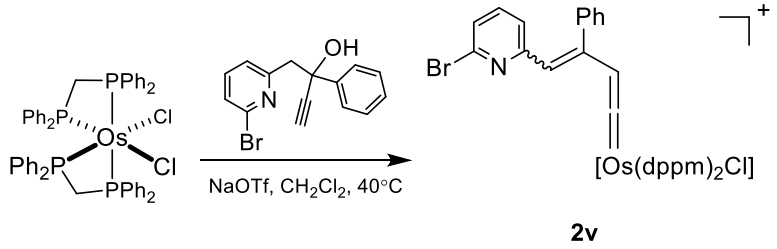
Complex 2f(OTf)$_2$. Yield: 72%. Anal. Calcd for $C_{67}H_{57}S_2F_6O_7NP_4Os$: C, 54.36; H, 3.88; N, 0.95. Found: C, 54.36; H, 3.87; N, 0.94. Isomeric form A: $^1H\{^{31}P\}$ NMR (600 MHz, $(CD_3)_2CO$): δ 4.34–4.37, 5.55–5.57 (m, 4H, 2 CH_2 on dppm), 1.78 (s, 3H, H_e), 6.44–6.45 (m, 1H, H_f/H_j), 6.77–6.78 (m, 1H, H_d), 7.40–7.41 (m, 1H, H_a), 7.70 (m, 1H, H_b), 7.70–7.73 (m, 1H, H_g/H_i), 7.74–7.77 (m, 1H, H_g/H_i), 7.79–7.80 (m, 1H, H_f/H_j), 7.86–7.90 (m, 1H, H_c), 8.43–8.45 (m, 1H, H_h), 12.40 (s, 1H, $H_α$), 8.08–8.10, 7.63–7.69, 7.53–7.58, 7.32–7.34, 6.99–7.04, 6.30–4.32, 7.48–7.51, 7.38–7.41, 7.18–7.22, 7.51–7.58, 7.32–7.36, 7.01–7.04, 6.41–6.43, 7.79–7.80, 7.41–7.46, 7.34–7.37, 6.99–7.00 (m, 40H, protons of 4 Ph rings on dppm). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): δ 48.04, 49.01 (*C*H_2 on dppm), 21.48 (C_e), 122.0897 (C_d), 126.92 (C_g/C_i), 128.69 (C_b), 128.85 (C_g/C_i), 130.14 (C_c), 130.46 (C_a & C_f/C_j), 132.23 (C_f/C_j), 135.71 (C_{III} & C_{IV}), 145.42(C_I), 147.04 (C_h), 156.89 (C_{II}), 196.01 ($C_α$), 134.16, 132.23, 129.49, 131.75, 130.14, 129.82, 130.30, 130.46, 132.71, 132.07, 130.94, 129.66, 125.79 (48C of 4 Ph rings on dppm). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -57.29–(-57.08), -50.95–(-49.93), -54.45–(-54.25), -47.08–(-46.06) (m, 4P on dppm).
Isomeric form B: $^1H\{^{31}P\}$ NMR (600 MHz, $(CD_3)_2CO$): δ 4.93–4.96, 5.52–5.57, 4.34–4.40, 6.03–6.06 (m, 4H, 2 CH_2 on dppm), 2.02 (s, 3H, H_e), 6.81–6.82 (m, 1H, H_d), 7.41–7.44 (m, 1H, H_g/H_i), 7.50–7.51 (m, 1H, H_a), 7.55 (m, 1H, H_f/H_j), 7.70–7.73 (m, 1H, H_b), 7.79–7.80 (m, 1H, H_f/H_j), 7.86–7.90 (m, 1H, H_c), 8.08–8.11 (m, 1H, H_g/H_i), 8.35–8.38 (m, 1H, H_h), 11.93 (s, 1H, $H_α$), 8.18–8.19, 7.78, 7.64–7.69, 7.17–7.22, 6.22–6.23, 6.03–6.06, 7.38–7.58, 7.11–7.17, 6.72–6.74, 7.70–7.73, 6.99–7.01, 6.81–6.82, 7.62–7.63, 7.53–7.56, 7.41–7.45, 7.11–7.15 (m, 40H, protons of 4 Ph rings on dppm). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): δ 48.04, 49.81 (*C*H_2 on dppm), 21.16 (C_e), 122.57 (C_d), 130.14 (C_c & C_f /C_j), 131.43 (C_g/C_i), 132.07 (C_a), 132.23 (C_f /C_j), 132.87 (C_b), 134.16 (C_g/C_i), 135.71(C_{III} & C_{IV}), 143.65 (C_I), 146.88 (C_h), 156.30 (C_{II}), 197.48 ($C_α$), 134.97, 132.23, 129.49, 129.82, 129.33, 130.62, 130.14, 131.75, 129.66, 131.27, 130.46, 132.71, 131.91, 133.36, 130.94, 125.79, 131.59 (48C of 4 Ph rings on dppm). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -61.25–(-61.02), -37.42–(-36.47), -52.63–(-52.42), -40.34–(-39.37) (m, 4P on dppm).
ESI-MS: m/z 602.8 [**2f**]$^{2+}$.

Complex 2v(OTf). Yield: 62%. Anal. Calcd for $C_{66}H_{54}SF_3BrClO_3NP_4Os$: C, 55.52; H, 3.81; N, 0.98. Found: C, 55.53; H, 3.81; N, 0.98. $^1H\{^{31}P\}$ NMR (600 MHz, CD_2Cl_2), *E*- & *Z*-form in *cis*-configuration: δ 5.97, 6.65 (s, 1H, H_a), 6.50, 6.52 (s, 1H, H_b), 7.33–7.35, 7.35–7.37, (m, 1H, H_d), 7.92-7.93, 8.16–8.17 (m, 1H, H_c), 10.01–10.03, 10.06–10.08 (m, 1H, H_e). $^{13}C\{^1H\}$ NMR (150 MHz, $(CD_3)_2CO$): the metalated carbon cannot be resolved, 122.15, 130.42 (C_b), 126.90, 127.43 (C_a), 127.95 (C_d), 131.47, 132.70 (C_c), 122.68 (C_e). $^{31}P\{^1H\}$ NMR (162 MHz, $(CD_3)_2CO$): δ -65.06–(-63.59), -64.62–(-63.13), -61.32–(-59.96), -59.62–(-58.24), -54.23–(-54.05), -53.62–(-53.38), -53.10–(-52.38) (m, 4P on dppm). ESI-MS: m/z 1278.6 [**2v**]$^+$.

Complex 3(OTf). Yield: 42%. Anal. Calcd for $C_{36}H_{26}SF_3O_3N_5Ru$: C, 56.39; H, 3.42; N, 9.13. Found: C, 56.40; H, 3.41; N, 9.14. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.29 (m, 1H, H_j), 6.74–6.76 (m, 1H, H_h), 6.83–6.85 (m, 1H, H_i), 7.13 (s, 1H, H_a), 7.16–7.19 (m, 1H, H_c), 7.36–7.39 (m, 1H, H_d), 7.63–7.65 (m, 1H, H_e), 7.71 (s, 1H, H_f), 7.82–7.83 (m, 1H, H_g), 8.18–8.19 (m, 1H, H_b) 8.35–8.36 (m, 1H, H_1), 7.90–7.93 (m, 1H, H_2), 7.42–7.44 (m, 1H, H_3), 7.75 (m, 1H, H_4), 8.17–8.18 (m, 2H, H_5 & H_9), 7.02–7.03 (m, 1H, H_6), 7.50–7.53 (m, 1H, H_7), 8.05–8.06 (m, 1H, H_8), 7.74–7.75 (m, 2H, H_{10} & H_{12}), 7.20–7.23 (m, 1H, H_{11}), 8.19–8.21 (m, 2H, H_{13} & H_{16}), 6.99–7.02 (m, 1H, H_{14}/H_{15}), 7.59–7.62 (m, 1H, H_{14}/H_{15}). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 108.66 (C_f), 119.21 (C_c), 121.85 (C_h) 123.60 (C_g), 125.61 (C_j & C_v), 125.71 (C_e), 128.00 (C_i & C_{IV}), 129.23 (C_d), 135.74 (C_a), 139.94 (C_{III}), 154.20 (C_b), 169.91 (C_I), C_{II} cannot be resolved, 123.08 (C_1), 135.21 (C_2), 127.47 (C_3), 133.28 (C_4), 121.85 (C_5), 125.36 (C_6), 131.69 (C_7), 122.20 (C_8), 121.85 (C_9), 133.28 (C_{10} & C_{12}), 125.71 (C_{11}), 122.90 (C_{13} & C_{16}), 125.36 (C_{14}/C_{15}), 132.75 (C_{14}/C_{15}), 154.92 (C_{VI}), 156.44 (C_{VII}), 157.31 (C_{VIII} & C_{IX}). ESI-MS: m/z 618.2 [**3**]$^+$.

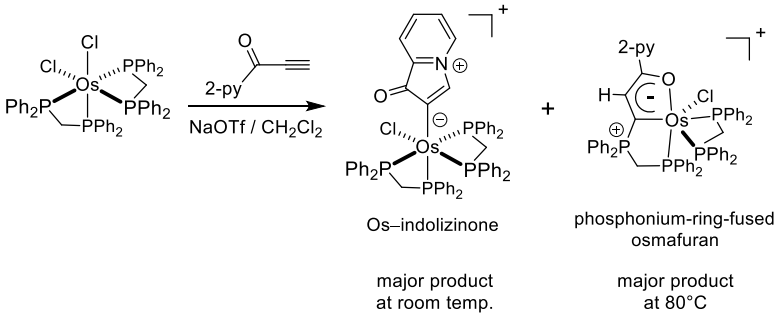
Ligand L1. Yield: 62%. Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.69; H, 5.87; N, 6.28. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.44 (s, 1H, H_k), 3.23–3.25, 3.32–3.34 (m, 2H, H_e), O*H* cannot be resolved, 7.13–7.14 (d, 1H, H_d), 7.20–7.22 (m, 1H, H_b), 7.28–7.31 (m, 1H, H_h), 7.37–7.39 (m, 2H, H_g & H_i), 7.63–7.65 (m, 1H, H_c), 7.75–7.77 (m, 2H, H_f & H_j), 8.52–8.52 (m, 1H, H_a). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 50.69 (C_e), 72.47 (C_{II}), 73.13 (C_k), 86.52 (C_{IV}), 122.20 (C_b), 124.54 (C_d) 125.41 (C_f & C_j), 127.63 (C_h), 128.20 (C_g & C_i), 137.00 (C_c), 144.17 (C_{III}), 148.16 (C_a), 158.37 (C_I).

Ligand L2. Yield: 72%. Anal. Calcd for $C_{15}H_{12}NOBr$: C, 59.62; H, 4.00; N, 4.64. Found: C, 59.63; H, 4.00; N, 4.64. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.49 (s, 1H, H_j), 3.19–3.21, 3.30–3.32 (m, 2H, H_d), 6.10 (br, 1H, O*H*), 7.12–7.13 (d, 1H, H_c), 7.29–7.32 (m, 1H, H_g), 7.37–7.39 (m, 2H, H_f & H_h), 7.41–7.42 (m, 1H, H_a), 7.50–7.52 (s, 1H, H_a), 7.71–7.73 (m, 2H, H_e & H_i). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 51.12 (C_d), 72.55 (C_{III}), 74.82 (C_j), 86.01 (C_V), 123.35 (C_c) 125.30 (C_e & C_i), 126.91 (C_a), 128.05 (C_g), 128.21 (C_f & C_h), 139.37 (C_b), 140.73 (C_{II}), 143.77 (C_{IV}), 159.84 (C_I).



2v

Scheme S1: Synthesis of Os–vinylidene complex **2v**.



Scheme S2: Previous work on the isolation of Os–indolizinone and phosphonium-ring-fused osmafuran complexes.[5]

X-Ray Crystallography

X-ray diffraction data were collected on a Xcalibur, Sapphire3, Gemini ultra, template-Cu, Bruker APEX-II CCD, CCD area detector diffractometer with Cu Kα radiations. Using Olex2,[6] the structures of **1q**$(ClO_4)\cdot CH_2Cl_2$, [**1f**$(CF_3SO_3)_2]_2\cdot 1.5Et_2O\cdot 1.5H_2O$, [**2f**$(CF_3SO_3)_2]_2\cdot Et_2O$, **2v**$(OTf)\cdot CH_2Cl_2$ and **Q**(OTf) were solved with the ShelXT[7] structure solution program using Intrinsic Phasing, **2q**$(ClO_4)\cdot CH_2Cl_2$·with the ShelXS[8] structure solution program using Structure Expansion. Refinements were performed with the ShelXL[9] refinement package using Least Squares minimization.
3$(ClO_4)\cdot H_2O$ with the olex2.solve[7] structure solution program using Charge Flipping. Refinements were performed with the olex2.refine[9] refinement package using Levenberg-Marquardt minimisation.
All non-hydrogen atoms were refined anisotropically, except some solvent molecules CH_2Cl_2 were refined isotropically. CCDC 2001062–2001068 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

1q$(ClO_4)\cdot CH_2Cl_2$: Single crystals of **1q**$(ClO_4)\cdot CH_2Cl_2$ were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of **1q**(ClO_4).
Crystal Data for **1q**$(ClO_4)\cdot CH_2Cl_2$ ($C_{66}H_{56}Cl_3NO_4P_4Ru$; M = 1258.41 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 11.6796(2) Å, b = 19.9722(3) Å, c = 13.1880(2) Å, β = 104.7930(10)°, V = 2974.36(8) Å^3, Z = 2, T = 223.4(8) K, μ(Cu Kα) = 4.781 mm^{-1}, *Dcalc* = 1.405 g/cm^3, 13158 reflections measured (8.226° ≤ 2Θ ≤ 143.71°), 8289 unique (R_{int} = 0.0272, R_{sigma} 0.0391) which were used in all calculations. The final R_1 was 0.0305 (I > 2σ(I)) and wR_2 was 0.0788 (all data).
(CCDC 2001062)

[**1f**$(CF_3SO_3)_2]_2\cdot 1.5Et_2O\cdot 1.5H_2O$: Single crystals of [**1f**$(CF_3SO_3)_2]_2\cdot 1.5Et_2O\cdot 1.5H_2O$ were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of [**1f**$(CF_3SO_3)_2]_2$.
Crystal Data for [**1f**$(CF_3SO_3)_2]_2\cdot 1.5Et_2O\cdot 1.5H_2O$ ($C_{70}H_{66}F_6NO_{8.50}P_4RuS_2$; M = 1460.30 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 22.9780(8) Å, b = 16.4419(6) Å, c = 36.9317(13) Å, β = 104.0000(10)°, V = 13538.4(8) Å^3, Z = 8, T = 173(2) K, μ(Cu Kα) = 3.962 mm^{-1}, *Dcalc* = 1.433 g/cm^3, 203671 reflections measured (5.15° ≤ 2Θ ≤ 149.296°), 27634 unique (R_{int} = 0.0598, R_{sigma} 0.0365) which were used in all calculations. The final R_1 was 0.0939 (I > 2σ(I)) and wR_2 was 0.2635 (all data).
(CCDC 2001065)

2q$(ClO_4)\cdot CH_2Cl_2$: Single crystals of **2q**$(ClO_4)\cdot CH_2Cl_2$ were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of **2a**(ClO_4).
Crystal Data for **2q**$(ClO_4)\cdot CH_2Cl_2$ ($C_{66}H_{56}Cl_3NO_4OsP_4$; M = 1347.54 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 11.6240(2) Å, b = 19.9252(2) Å, c = 13.1753(2) Å, β = 104.8180(10)°, V = 2950.05(8) Å^3, Z = 2, T = 173.00(14) K, μ(Cu Kα) = 6.752 mm^{-1}, *Dcalc* = 1.517 g/cm^3, 11468 reflections measured (6.94° ≤ 2Θ ≤ 136.474°), 7826 unique (R_{int} = 0.0240, R_{sigma} = 0.0341) which were used in all calculations. The final R_1 was 0.0255 (I > 2σ(I)) and wR_2 was 0.0663 (all data).
(CCDC 2001063)

[**2f**$(CF_3SO_3)_2]_2\cdot Et_2O$: Single crystals of [**2f**$(CF_3SO_3)_2]_2\cdot Et_2O$ were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of [**2f**$(CF_3SO_3)_2]_2$.
Crystal Data for [**2f**$(CF_3SO_3)_2]_2\cdot Et_2O$ ($C_{69}H_{62}F_6NO_{7.50}OsP4S_2$; M = 1517.39 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 23.0620(5) Å, b = 16.4101(4) Å, c = 36.9903(9) Å, β = 104.0160(10)°, V = 13582.2(6) Å^3, Z = 8, T = 213(2) K, μ(Cu Kα) = 5.604 mm^{-1}, *Dcalc* = 1.484 g/cm^3, 161466 reflections measured (5.136° ≤ 2Θ ≤ 149.164°), 27913 unique (R_{int} = 0.1004, R_{sigma} = 0.0704) which were used in all calculations. The final R_1 was 0.0801 (I > 2σ(I)) and wR_2 was 0.2526 (all data).
(CCDC 2001066)

2v$(OTf)\cdot CH_2Cl_2$: Single crystals of **2v**$(OTf)\cdot CH_2Cl_2$ were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of **2v**(OTf).
Crystal Data for **2v**$(OTf)\cdot CH_2Cl_2$ ($C_{67}H_{56}BrCl_3F_3NO_3OsP_4S$; M = 1512.52 g/mol): triclinic, space group *P-1* (no. 2), a = 13.0222(4) Å, b = 14.4045(5) Å, c = 19.6691(6) Å, α = 79.1010(10)°, β = 71.4600(10)°, γ = 85.6210(10)°, V = 3434.40(19) Å^3, Z = 2, T = 173(2) K, μ(Cu Kα) = 2.730 mm^{-1}, *Dcalc* = 1.463 g/cm^3, 37106 reflections measured (5° ≤ 2Θ ≤ 52.07°), 13338 unique (R_{int} = 0.0459, R_{sigma} = 0.0517) which were used in all calculations. The final R_1 was 0.0399 (I > 2σ(I)) and wR_2 was 0.1036 (all data).
(CCDC 2001068)

3$(ClO_4)\cdot H_2O$: Single crystals of **3**$(ClO_4)\cdot H_2O$ were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of **3**(ClO_4).
Crystal Data for **3**$(ClO_4)\cdot H_2O$ ($C_{35}H_{28}ClN_5O_5Ru$; M = 735.161 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.9119(1) Å, b = 14.4815(2) Å, c = 21.988(3) Å, β = 97.114(1)°, V = 3131.86(7) Å^3, Z = 4, T = 173.00(14) K, μ(Cu Kα) = 5.274 mm^{-1}, *Dcalc* = 1.559 g/cm^3, 12177 reflections measured (7.32° ≤ 2Θ ≤ 136.48°), 5727 unique (R_{int} = 0.0263, R_{sigma} = 0.0291) which were used in all calculations. The final R_1 was 0.0378 (I > 2u(I)) and wR_2 was 0.0999 (all data).
(CCDC 2001064)

Q(OTf): Single crystals of **Q**(OTf) were obtained by layering of *n*-hexane onto a CH_2Cl_2 solution of **Q**(OTf).
Crystal Data for **Q**(OTf) ($C_{16}H_{12}F_3NO_3S$; M = 355.33 g/mol): orthorhombic, space group $Pna2_1$ (no. 33), a = 13.8910(4) Å, b = 16.2450(4) Å, c = 6.9806(2) Å, V = 1575.24(7) Å^3, Z = 4, T = 173.15 K, μ(Cu Kα) = 2.284 mm^{-1}, *Dcalc* = 1.498 g/cm^3, 16540 reflections measured (8.376° ≤ 2Θ ≤ 148.99°), 3107 unique (R_{int} = 0.0553, R_{sigma} 0.0498) which were used in all calculations. The final R_1 was 0.0362 (I > 2σ(I)) and wR_2 was 0.0955 (all data).
(CCDC 2001067)

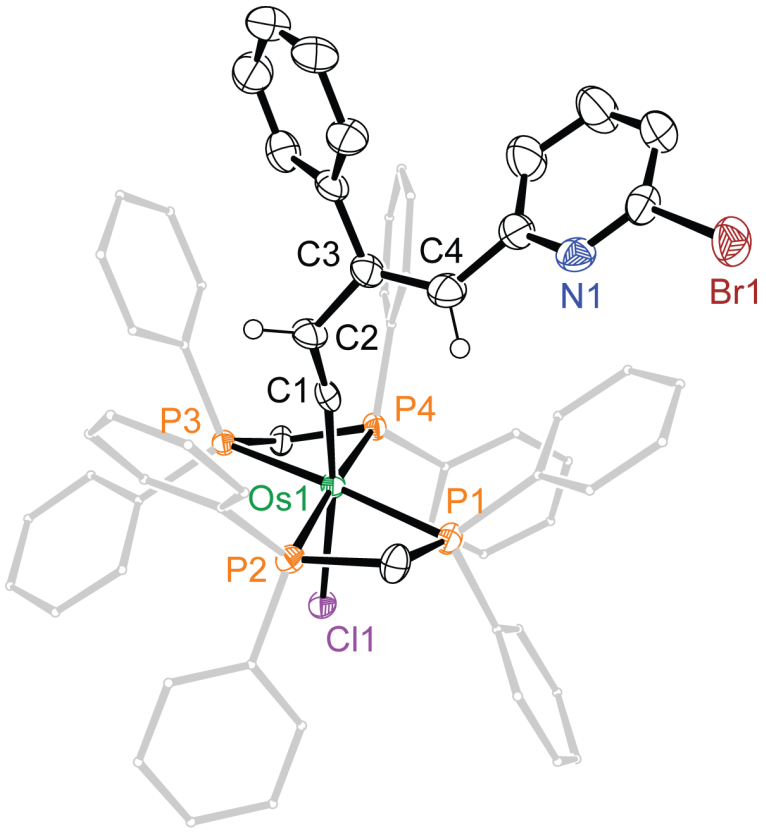


Figure S3. Perspective view of monocation **2v** as represented by 50% probability ellipsoids (hydrogen atoms are omitted and phenyl rings on dppm are represented by gray sticks for clarity).

Table S1. Selected Bond Lengths (Å) and Angles (deg) for **1q**(ClO_4)·CH_2Cl_2 **2q**(ClO_4)·CH_2Cl_2 and **Q**(OTf)

Complex	**1q**(ClO_4)·CH_2Cl_2	**2q**(ClO_4)·CH_2Cl_2	**Q**(OTf)
M–C1	2.087(4)	2.100(5)	-
M–C9	2.075(4)	2.085(5)	-
C1–N1	1.392(5)	1.380(7)	1.381(3)
C9–N1	1.393(5)	1.395(6)	1.382(3)
∠C1–M–C9	64.6(2)	63.7(2)	-
∠M–C1–N1	94.5(2)	95.4(3)	-
∠M–C9–N1	95.0(2)	95.6(3)	-
∠C1–N1–C9	105.9(3)	105.4(4)	119.6(2)
∠P1–M–P2	71.0(1)	70.4(1)	-
∠P3–M–P4	71.0(1)	70.4(1)	-

Table S2. Selected Bond Lengths (Å) and Angles (deg) for [**1f**$(CF_3SO_3)_2]_2 \cdot 1.5Et_2O \cdot 1.5H_2O$ and [**2f**$(CF_3SO_3)_2]_2 \cdot Et_2O$

Complex	[**1f**$(CF_3SO_3)_2]_2 \cdot 1.5Et_2O \cdot 1.5H_2O$[a]	[**2f**$(CF_3SO_3)_2]_2 \cdot Et_2O$[a]
M–C1	2.038(7), 2.016(7)	2.032(8), 2.034(10)
M–O1	2.140(5), 2.168(5)	2.168(7), 2.141(6)
C1–C2	1.372(11), 1.369(10)	1.360(13), 1.351(14)
C2–C3	1.424(12), 1.409(10)	1.429(14), 1.427(15)
C3–O1	1.274(10), 1.284(9)	1.274(11), 1.276(12)
C2–N1	1.467(10), 1.472(9)	1.457(11), 1.459(13)
∠C1–M–O1	76.3(3), 76.1(2)	75.2(3), 75.5(4)

[a] The crystal contains two crystallographically independent cations in the asymmetric unit; structural data are listed in the order of M(1) moiety and then M(2) moiety.

Table S3. Selected Bond Lengths (Å) and Angles (deg) for **3**$(ClO_4) \cdot H_2O$.

Complex	**3**$(ClO_4) \cdot H_2O$
M–C1	2.046(3)
M–C8	2.026(3)
C9–N1	1.389(4)
C10–N1	1.378(5)
∠C1–M–C8	80.61(12)
∠C9–N1–C10	119.3(3)

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