Electronic Supplementary Material (ESI) for Dalton Transactions.

Phosphine and Isocyanide Substitution and Alkyne Coordination and C≡C Activation at Pentanuclear Molybdenum/Tungsten-Iridium Clusters

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Supplementary Information

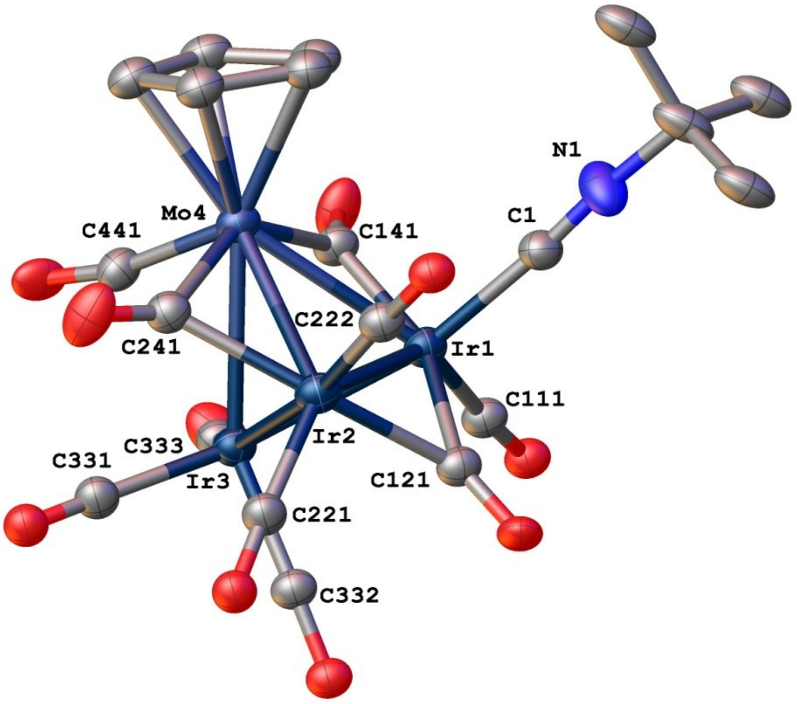
EXPERIMENTAL DETAILS

General Conditions and Reagents. Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, the extent of reaction being monitored regularly by IR spectroscopy. Product clusters proved indefinitely stable in air as solids and for at least short periods of time in solution, and thus no special precautions were taken to exclude air in their work-up. Solvents used in reactions were AR grade and distilled under nitrogen using standard methods: CH_2Cl_2 over CaH_2, toluene and THF over sodium benzophenone ketyl. All other solvents and other reagents were obtained commercially and were used as received. Petrol refers to a fraction of boiling range 60 – 80 °C. Cluster products were purified by preparative thin-layer chromatography (TLC) on 20 × 20 cm glass plates coated with Merck GF_{254} silica gel (0.5 mm). Analytical TLC was conducted on aluminum sheets coated with 0.25 mm Merck GF_{254} silica gel.

Instrumentation. Infrared spectra were recorded on PerkinElmer System 2000 and PerkinElmer Spectrum One FT-IR spectrometers using a CaF_2 solution cell and AR grade cyclohexane or CH_2Cl_2 solvent; spectral features are reported in cm^{-1}. ^1H NMR spectra were recorded on a Varian Gemini-300 spectrometer at 300 MHz in $CDCl_3$ (Cambridge Isotope Laboratories) and referenced to residual solvent (δ 7.26). ^{31}P NMR spectra were recorded on a Varian Gemini-300 spectrometer at 121 MHz in $CDCl_3$ and referenced to external 85% H_3PO_4. Unit resolution and high-resolution ESI mass spectra were recorded on a Micromass-Waters LC-ZMD single quadrupole liquid chromatograph-MS instrument, and are reported in the form: *m*/*z* (assignment, relative intensity). Microanalyses were carried out by the Microanalysis Service Unit in the Research School of Chemistry, ANU, or at the School of Human Sciences, Science Centre, London Metropolitan University, UK.

Synthesis of $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_5(CN^tBu)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (3b). CN^tBu (3 μL, 2.2 mg, 27 μmol) was added to a brown solution of $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (**1a**) (10.4 mg, 8.0 μmol) in CH_2Cl_2 (7 mL) and the resultant mixture was heated at reflux for 48 h. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (4:1) afforded two bands. The contents of the first ($R_f = 0.3$ brown) band were extracted into CH_2Cl_2, which was then reduced in volume to afford a brown solid identified as unreacted $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (**1a**) (6.2 mg, 60%) by IR spectral comparison to an authentic sample.[S1] The contents of the second band ($R_f = 0.1$, brown) were extracted into CH_2Cl_2, and then reduced in volume to afford a brown solid identified as **3b** (2.6 mg, 24%). IR (CH_2Cl_2): ν(NC) 2146 m, ν(CO) 2000 s, 1963 sh, 1948 br s, 1868 w sh, 1817 br m cm^{-1}. ^1H NMR: δ 5.15 (s, 5H, Cp), 4.97 (s, 5H, Cp), 1.91 (s, 15H, C_5Me_5), 1.48 (s, 9H, ^tBu). MS (ESI): calc., $C_{33}H_{34}Ir_3Mo_2NO_8$, 1346.9281 ($[M]^+$); found, 1346.9310 ($[M]^+$). The small amount of material precluded microanalysis.

Reaction of $MoIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (2a) with $CNBu^t$. $CNBu^t$ (3.5 μL, 30.6 μmol) was added to a brown solution of $MoIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2a**) (13.7 mg, 10.2 μmol) in CH_2Cl_2 (10 mL) and the resultant mixture was stirred for 5 min. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:2) afforded three bands. The contents of the first (R_f = 0.7, yellow) and second (R_f = 0.5, yellow) bands were in trace amounts and were not isolated. The contents of the third band (R_f = 0.3, yellow) were extracted into CH_2Cl_2, which was then reduced in volume to afford a yellow compound (10.2 mg, 9.2 μmol). A crystal suitable for a single-crystal X-ray diffraction study was obtained from slow diffusion of ethanol into a dichloromethane solution. Although the crystal structure of $MoIr_3(\mu\text{-}CO)_3(CNBu^t)(CO)_7(\eta^5\text{-}C_5H_5)$ was unequivocally determined (see below), the data were of poor quality, so metrical parameters cannot be discussed and the crystal structure is provided solely to display the connectivity of the cluster. With respect to the plane of bridging carbonyl ligands, the cluster from the present study has a diaxial (η^5-C_5H_5, Bu^tNC) ligand disposition. A structural study of an isomer with the axial (η^5-C_5H_5), apical (Bu^tNC) ligand disposition has been reported previously.[S2]



Molecular structure of $MoIr_3(\mu\text{-}CO)_3(CNBu^t)(CO)_7(\eta^5\text{-}C_5H_5)$ with displacement ellipsoids set at the 40 % probability level. Hydrogen atoms have been omitted for clarity. $C_{20}H_{14}Ir_3MoNO_{10}$, triclinic, *P*-1, a = 9.4392(9), b = 11.6292(11), c = 16.7753(16) Å, α = 93.783(3), β = 91.474(3), γ = 110.044(3)°, V = 1723.8(3) Å^3.

Reaction of $MoIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (2a) with $CNC_6H_3Me_2$-2,6. $CNC_6H_3Me_2$-2,6 (5.0 mg, 38.1 μmol) was added to a brown solution of $MoIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2a**) (9.9 mg, 7.36 μmol) in CH_2Cl_2 (10 mL) and the resultant mixture was stirred for 30 min. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:2) afforded three bands. The contents of the first (R_f = 0.6, yellow) and third (R_f = 0.3, yellow) bands were in trace amounts and were not isolated. The contents of the second band (R_f = 0.4, yellow) were extracted into CH_2Cl_2, which was then reduced in volume to afford a yellow compound identified as $MoIr_3(\mu\text{-}CO)_3(CNC_6H_3Me_2\text{-}2,6)(CO)_7(\eta^5\text{-}C_5H_5)$ (9.8 mg, 8.5 μmol) by IR spectroscopic comparison to an authentic sample.[S2]

Synthesis of $W_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (4b). PPh_3 (8.2 mg, 31.3 µmol) was added to a dark red solution of $W_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (**1c**) (9.5 mg, 6.5 µmol) in CH_2Cl_2 (20 mL) and the resultant mixture was refluxed for 14 h. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (9:1) afforded three bands. The contents of the first band (R_f = 0.7, red) and the third band (R_f = 0.4, red) were in trace amounts and consequently were not isolated. The contents of the second band (R_f = 0.6, red) were extracted into CH_2Cl_2, which was then reduced in volume to afford a dark red solid, identified as **4b** (8.3 mg, 75%). IR (CH_2Cl_2): ν(CO) 2005 s, 1949 s, 1888 w, 1770 m, 1708 m cm^{-1}. ^1H NMR: δ 7.40-7.51 (m, 15H, C_6H_5), 4.98 (s, 5H, C_5H_5), 4.83 (s, 5H, C_5H_5), 1.74 (s, 15H, C_5Me_5). ^{31}P NMR: δ 14.0 (s, PPh_3). MS (ESI): calculated, $C_{46}H_{40}Ir_3O_8PW_2$, 1698.0368 ($[M]^+$); found, 1698.0333 ($[M]^+$); $C_{46}H_{40}Ir_3NaO_8PW_2$, 1721.0266 ($[M + Na]^+$); found, 1721.0239 ($[M + Na]^+$). Anal: calc. for $C_{46}H_{40}Ir_3O_8PW_2$: C 32.57, H 2.37%: found C 32.69, H 2.40 %.

Synthesis of $Mo_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (4c). PPh_3 (9.5 mg, 36.2 µmol) was added to a dark red solution of $Mo_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**1b**) (13.3 mg, 10.4 µmol) in THF (25 mL) and the resultant mixture was refluxed for 14 h. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a preparative silica TLC plate. Elution with CH_2Cl_2 afforded 1 band (R_f = 0.9, red). Extraction with CH_2Cl_2 and reduction of the solvent volume afforded a brown solid identified as **4c** (10.8 mg, 69%). IR (CH_2Cl_2): ν(CO) 2004 s, 1954 s, 1874 w, 1771 m, 1721 m cm^{-1}. ^1H NMR: δ 7.40-7.53 (m, 15H, C_6H_5), 5.53 (s, 1H, C_5Me_4H), 4.82 (s, 10H, C_5H_5), 1.77 (s, 12H, C_5Me_4H). ^{31}P NMR: δ 29.0 (s, PPh_3). MS (ESI): calculated, $C_{45}H_{38}Ir_3Mo_2O_8P$, 1511.9301 ($[M]^+$); found, 1511.9319 ($[M]^+$, 25). Anal: calc. for $C_{45}H_{38}Ir_3Mo_2O_8P$: C 35.88, H 2.54%: found C 36.16, H 2.53 %.

Synthesis of $W_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (4d). *Method A:* PPh_3 (9.8 mg, 37.4 µmol) was added to a dark red solution of $W_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**1d**) (13.5 mg, 9.22 µmol) in THF (25 mL) and the resultant mixture was refluxed for 14 h, the extent of reaction being monitored by IR spectroscopy. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (9:1) afforded two bands. The contents of the first band (R_f = 0.5, red) were extracted with CH_2Cl_2 and reduced in volume to afford a dark red solid identified as unreacted $W_2Ir_3(\mu\text{-}CO)_3(CO)_6(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**1d**) (3.8 mg, 28%).[S1] The contents of the second band (R_f = 0.4, red) were extracted into CH_2Cl_2, which was then reduced in volume to afford a brown solid identified as **4d** (8.6 mg, 55%). IR (CH_2Cl_2): ν(CO) 2005 s, 1950 s, 1880 w, 1771 m, 1711 m cm^{-1}. ^1H NMR: δ 7.41-7.51 (m, 15H, C_6H_5), 5.52 (s, 1H, C_5Me_4H), 5.07 (s, 5H, C_5H_5), 4.81 (s, 5H, C_5H_5), 1.67 (s, 12H, C_5Me_4H). ^{31}P NMR: δ 18.0 (s, PPh_3). MS (ESI): calc., $C_{45}H_{38}Ir_3O_8PW_2$, 1684.0200 ($[M]^+$); found, 1684.0037 ($[M]^+$, 40). Anal: calc. for $C_{45}H_{38}Ir_3O_8PW_2$: C 32.13, H 2.28%: found C 32.75, H 2.21 %.

Method B: PPh_3 (8.3 mg, 31.6 µmol) was added to a dark red solution of $W_2Ir_3(\mu\text{-}CO)_4(CO)_5(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**1d**) (10.2 mg, 6.97 µmol) in THF (20 mL) and the resultant mixture was refluxed for 14 h, the extent of reaction being monitored by IR spectroscopy. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (9:1) afforded a single band ($R_f = 0.8$, red) that was extracted into CH_2Cl_2 and the extract then reduced in volume, to afford a dark red solid identified as **4d** (9.7 mg, 82%).

Synthesis of $WIr_4(\mu\text{-}CO)_3(CO)_6(PPh_3)(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (5b). PPh_3 (0.8 mg, 3.1 μmol) was added to a solution of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2b**) (4.5 mg, 3.1 μmol) in CH_2Cl_2 (5 mL), and the resultant solution stirred at room temperature for 16 h. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:2) afforded at least six bands. Bands appearing in trace amounts were not isolated. The contents of the third band ($R_f = 0.3$, purple) were extracted into CH_2Cl_2, which was then reduced in volume to afford a purple solid, identified crystallographically as **5b** (2.1 mg, 40%). IR (*n*-hexane): ν(CO) 2028 m, 1997 s, 1979 s, 1965 m, 1943 w, 1932 w, 1832 w sh, 1821 m, 1784 m, 1775 w sh, 1727 m cm^{-1}. ^1H NMR: δ 7.38-7.36 (m, 15H, PPh_3), 5.18 (s, 5H, C_5H_5), 1.84 (s, 15H, C_5Me_5). ^{31}P NMR: δ 13.0 (PPh_3). MS (ESI): calc., $C_{42}H_{35}Ir_4O_9PW$, 1670.0022 ($[M]^+$); found, 1670.0066 ($[M]^+$). Anal: calc. for $C_{42}H_{35}Ir_4O_9PW$: C 30.25, H 2.12%: found C 30.60, H 2.33%.

Reaction of $MoIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4H)$ (2c) with PPh_3. PPh_3 (6.3 mg, 24.0 μmol) was added to a brown solution of $MoIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4H)$ (**2c**) (12.0 mg, 8.99 μmol) in CH_2Cl_2 (15 mL) and the resultant mixture was stirred for 1 h. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (8:1) afforded four bands. The contents of the second ($R_f = 0.6$, green) and fourth ($R_f = 0.4$, red) bands were in trace amounts and were not isolated. The contents of the first band ($R_f = 0.8$, yellow) were extracted into CH_2Cl_2, which was then reduced in volume to afford a yellow compound identified as $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ (3.4 mg, 9.19 μmol) by IR spectroscopic comparison to an authentic sample.[S1] The contents of the third band ($R_f = 0.5$, orange) were extracted into CH_2Cl_2, which was then reduced in volume to afford an orange solid, identified as $IrCl(CO)(PPh_3)_2$ (2.5 mg, 3.2 μmol) by comparison of single-crystal X-ray diffraction-derived unit cell data and IR spectral data to the literature values.[S3,S4]

Reaction of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4H)$ (2d) with PPh_3. PPh_3 (23.5 mg, 89.7 μmol) was added to a brown solution of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_4H)$ (**2d**) (13.5 mg, 9.50 μmol) in CH_2Cl_2 (15 mL) and the resultant mixture was stirred for 1 h. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (8:1) afforded four bands. The contents of the third ($R_f = 0.6$, dark red) and fourth ($R_f = 0.4$, red) bands were in trace amounts and were not isolated. The contents of the first band ($R_f = 0.8$, yellow) were extracted into CH_2Cl_2, which was then reduced in volume to afford a compound identified as $Ir(CO)_2(\eta^5\text{-}C_5Me_4H)$ (4.2 mg, 11.3 μmol) by IR spectroscopic comparison to an authentic sample.[S1] The contents of the second band ($R_f = 0.7$, orange) were extracted into CH_2Cl_2, which was then reduced in volume to afford an orange solid, identified as $IrCl(CO)(PPh_3)_2$ (2.8 mg, 3.59 μmol) by IR spectroscopic comparison to the literature data.[S4]

Synthesis of $WIr_4(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu_3\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (8b). Diphenylacetylene (2.0 mg, 11.1 μmol) was added to a solution of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2b**) (10.0 mg, 7.0 μmol) in CH_2Cl_2, and the resultant solution was heated at reflux for 20 h, the extent of reaction being monitoring by IR spectroscopy. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:1) afforded at least six bands. Bands appearing in trace amounts were not isolated. The contents of the sixth band ($R_f = 0.3$, green) were extracted with CH_2Cl_2 and the extracts were reduced in volume to afford a green solid, identified crystallographically as **8b** (5.4 mg, 50%). IR (*n*-hexane): ν(CO) 2041 w, 2025 s, 2005 s, 1982 m, 1951 w, 1690 w, 1673 w cm^{-1}. ^1H NMR: δ 7.08-6.82 (m, 10H, C_2Ph_2), 5.60 (s, 5H, C_5H_5), 1.89 (s, 15H, C_5Me_5). MS (ESI): calc., $C_{37}H_{31}Ir_4O_8W$, 1559.0046 ($[M + H]^+$); found, 1559.0052 ($[M + H]^+$). Anal: calc. for $C_{37}H_{30}Ir_4O_8W$: C 28.57, H 1.94%: found C 28.59, H 1.92%.

Synthesis of $WIr_4(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(CO)_8(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (8c). Phenylacetylene (10 μL, 9.3 mg, 0.090 mol) was added to a solution of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2b**) (11.5 mg, 8.0 μmol) in CH_2Cl_2 (15 mL), and the resultant solution heated at reflux for 17 h, the extent of reaction being monitored by IR spectroscopy. The solution was taken to dryness in vacuo, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:1) afforded at least eight bands; bands appearing in trace amounts were not isolated. The contents of the eighth band ($R_f = 0.2$, green) were extracted with CH_2Cl_2 and the extracts reduced in volume to afford a green solid, identified as **8c** (2.8 mg, 24%). IR (*n*-hexane ν(CO) 2039 m, 2020 vs, 2005 vs, 1982 s, 1952 m, 1691 m, 1673 m cm^{-1}. ^1H NMR: δ 9.84 (s, 1H, HC_2), 7.23-7.09 (m, 5H, Ph), 5.57 (s, 5H, C_5H_5), 1.89 (s, 15H, C_5Me_5). MS (ESI): calc., $C_{31}H_{26}Ir_4O_8W$, 1481.9655 ($[M]^+$); found, 1481.9648 ($[M]^+$). The small amount of material precluded microanalysis.

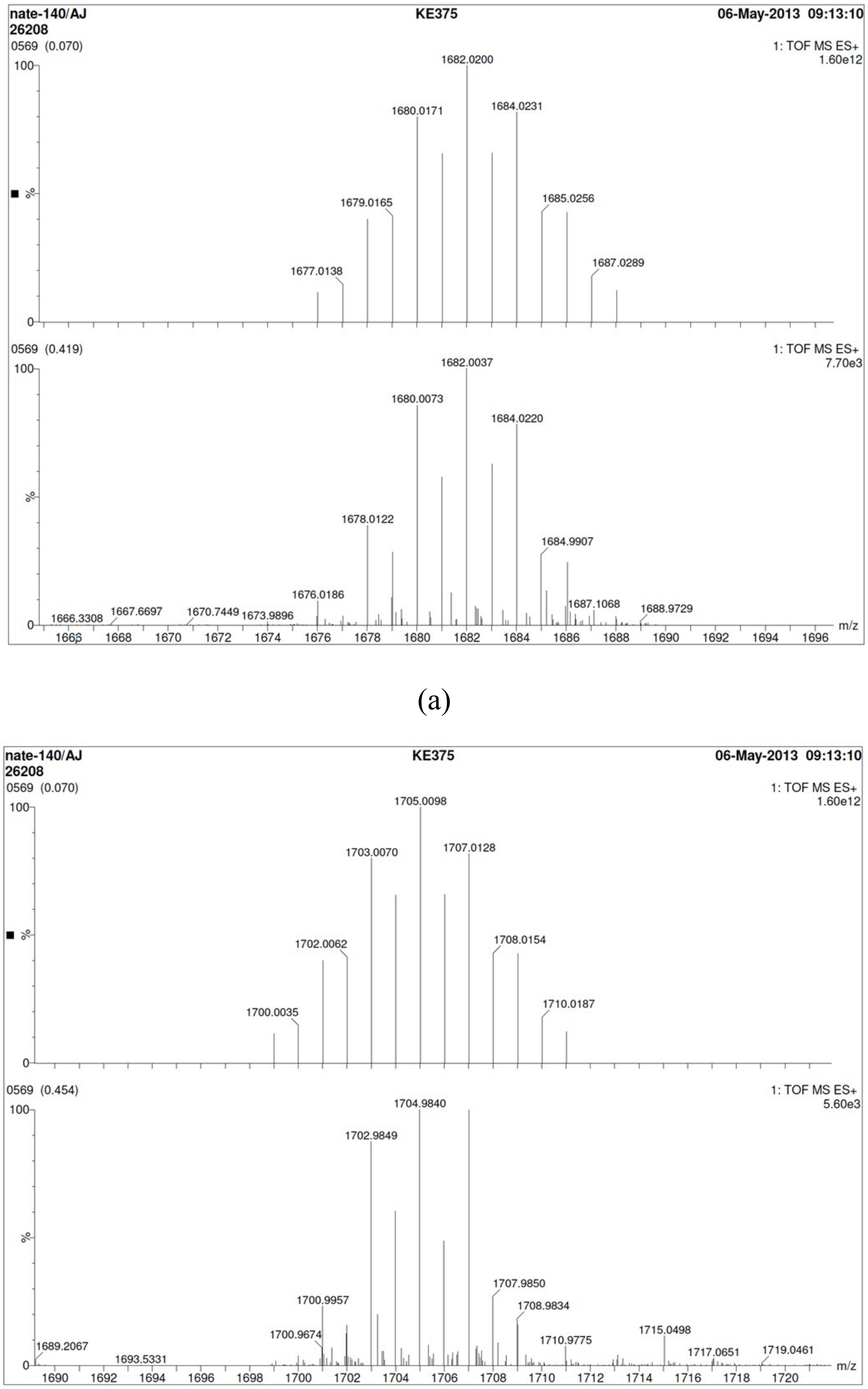
Synthesis of $WIr_4\{\mu_3\text{-}\eta^2\text{-}PhC_2C_6H_4(C{\equiv}CPh)\text{-}4\}(\mu_3\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (9b). 1,4–Bis(phenylethynyl)benzene (2.0 mg, 7.2 μmol) was added to a solution of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2b**) (10 mg, 7.0 μmol) in CH_2Cl_2 (15 mL), and the resultant solution heated at reflux for 17 h, the extent of reaction being monitored by IR spectroscopy. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:1) afforded at least six bands; bands appearing in trace amounts were not isolated. The contents of the fifth band ($R_f = 0.2$, green) were extracted with CH_2Cl_2 and the extracts reduced in volume to afford a green solid, identified as **9b** (4.5 mg, 39%). IR (*n*-hexane): ν(CO) 2040 w, 2025 vs, 2006 s, 1983 m, 1952 w, 1692 w, 1673 m cm^{-1}. ^1H NMR: δ 7.47-6.80 (m, 14H, phenyl), 5.60 (s, 5H, C_5H_5), 1.89 (s, 15H, C_5Me_5). MS (ESI): calculated, $C_{45}H_{35}Ir_4O_8W$, 1659.0359 ($[M + H]^+$); found, 1659.0360 ($[M + H]^+$). Slow decomposition of **9b** precluded elemental analysis.

Synthesis of $[WIr_4(\mu_3\text{-}CO)_2(CO)_6(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)]_2(\mu_6\text{-}\eta^4\text{-}PhC_2C_6H_4(C_2Ph)\text{-}4)$ (10b). 1,4–Bis(phenylethynyl)benzene (1.0 mg, 3.6 μmol) was added to a solution of $WIr_4(\mu\text{-}CO)_3(CO)_7(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)$ (**2b**) (10.0 mg, 7.0 μmol) in CH_2Cl_2 (15 mL), and the resultant solution heated at reflux for 20 h, the extent of reaction being monitored by IR spectroscopy. The solution was taken to dryness *in vacuo*, and the crude residue dissolved in the minimum amount of CH_2Cl_2 and applied to a silica preparative TLC plate. Elution with CH_2Cl_2/petrol (3:1) afforded at least 6 bands; bands appearing in trace amounts were not isolated. The contents of the fifth band (R_f = 0.2, green) were extracted with CH_2Cl_2 and the extracts reduced in volume to afford a green solid, identified as **9b** (3.3 mg, 29%) by IR spectral comparison with an authentic sample. The baseline was collected, extracted with CH_2Cl_2 and re-applied to a silica preparative TLC plate. Elution with acetone/petrol (2:3) afforded one band, (R_f = 0.53, green), the contents of which were extracted with CH_2Cl_2 and the extracts reduced in volume to afford a green solid, identified as **10b** (1.9 mg, 9%). IR (CH_2Cl_2): ν(CO) 2035 w sh, 2015 s, 2002 s, 1976 m, 1945 w, 1682 w, 1664 w br cm^{-1}. MS (ESI): calculated, $C_{68}H_{54}Ir_8O_{16}W_2$, 3037.9466 ($[M]^+$); found, 3037.9512 ($[M]^+$). The low yield precluded NMR spectroscopic and microanalytical analysis.

Table S1: Crystal data for **3a**, **4a – 4c**, **5b**, **6**, **7a**, **8a**, **8b**, and **9a**

	3a.CH_2Cl_2	**4a**	**4b**	**4c**	**4b**.$CHCl_3$	**6**.1.5(CH_2Cl_2)	**7a**	**8a**.CH_2Cl_2	**8b**.CH_2Cl_2	**9a**
Formula	$C_{38}H_{36}Cl_2Ir_3Mo_2NO_8$	$C_{46}H_{40}Ir_3Mo_2O_8P$	$C_{46}H_{40}Ir_3O_8PW_2$	$C_{45}H_{38}Ir_3Mo_2O_8P$	$C_{43}H_{36}Cl_3Ir_4O_9PW$	$C_{60.5}H_{53}Cl_3Ir_4Mo_1O_8P_2$	$C_{52}H_{45}Ir_3Mo_2O_4$	$C_{38}H_{32}Cl_2Ir_4MoO_8$	$C_{38}H_{32}Cl_2Ir_4O_8W$	$C_{45}H_{34}Ir_4O_8W$
FW	1474.06	1520.23	1696.05	1506.20	1786.69	1941.21	1502.36	1552.28	1640.19	1655.37
Size (mm)	0.12x0.09x0.02	0.17×0.13×0.02	0.09x0.08x0.02	0.11x0.10x0.08	0.14x0.09x0.09	0.13x0.09x0.02	0.38x0.08x0.03	0.23×0.05×0.04	0.27×0.23×0.02	0.10x0.08x0.02
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	$P2_1/c$	$P2_12_12_1$	$Pca2_1$	*Pnma*	$P2_1/c$	$C2/c$	*P*-1
a (Å)	11.6744(2)	9.9426(2)	9.889(2)	17.343(4)	10.79590(10)	20.3569(3)	34.0170(2)	9.30850(10)	28.5670(5)	9.6277(19)
b (Å)	13.4649(3)	10.4797(2)	10.453(2)	13.899(3)	14.6502(2)	13.29420(10)	35.8002(3)	37.3217(5)	10.11050(10)	14.429(3)
c (Å)	14.0805(3)	22.5472(4)	22.590(5)	17.040(3)	28.7210(4)	43.3524(5)	12.72950(10)	11.8641(2)	28.6713(4)	17.748(4)
α (°)	73.3974(11)	77.4385(11)	77.38(3)	90	90	90	90	90	90	79.44(3)
β (°)	67.3962(10)	89.2173(9)	88.45(3)	97.84(3)	90	90	90	109.0667(5)	105.2678(7)	75.44(3)
γ (°)	82.4596(11)	73.4475(11)	73.38(3)	90	90	90	90	90	90	90.36(3)
V (Å^3)	1957.60(6)	2195.12(7)	2181.9(8)	4069.1(14)	4542.57(10)	11732.4(2)	15502.2(2)	3895.57(9)	7988.8(2)	2342.4(8)
Z	2	2	2	4	4	8	12	4	8	2
D_{calc} (g cm^{-3})	2.501	2.300	2.582	2.459	2.612	2.198	1.931	2.647	2.727	2.347
μ (mm^{-1})	10.972	9.706	14.458	10.470	14.463	9.495	8.210	14.116	16.33	13.815
θ_{min} (°)	2.8	2.8	2.6	2.8	2.7	2.6	2.6	2.6	2.7	2.6

θ_{max} (°)	27.5	27.5	27.5	28.7	27.5	27.5	27.5	27.5	27.5	26.0
$N_{collected}$	45073	42982	36504	86619	53801	136483	167090	75384	75950	40808
N_{unique}	8977	10048	9868	10405	10384	25863	18064	8942	9169	35293
$N_{observed}$	7800 ($I > 2\sigma(I)$)	9088 ($I > 2\sigma(I)$)	8883 ($I > 2\sigma(I)$)	8898 ($I > 2\sigma(I)$)	9194 ($I > 2\sigma(I)$)	14579 ($I > 2\sigma(I)$)	14693 ($I > 2\sigma(I)$)	7077 ($I > 2\sigma(I)$)	6581 ($I > 2\sigma(I)$)	28729 ($I > 2\sigma(I)$)
No. of parameters	494	546	546	536	550	1402	852	457	459	199
R_1	0.032	0.032	0.061	0.039	0.037	0.043	0.032	0.042	0.039	0.107
wR_2	0.066	0.084	0.170	0.094	0.085	0.080	0.082	0.088	0.080	0.268
S	1.04	1.08	1.07	1.05	1.02	0.93	1.03	1.16	1.04	1.11
$(\Delta/\rho)_{min}$ (e Å^{-3})	-1.61	–1.61	–6.34	–4.32	-2.00	-2.14	–1.26	–1.87	-1.71	-3.79
$(\Delta/\rho)_{max}$ (e Å^{-3})	4.75	1.52	5.65	3.19	1.25	3.63	1.57	1.86	2.01	4.85



(a)

(b)

Figure S1. (a) Calculated (top) and experimental ESI MS (bottom) molecular ion for $W_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**4d**). (b) Calculated (top) and experimental ESI MS (bottom) $[M + Na]^+$ ion for $W_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**4d**).

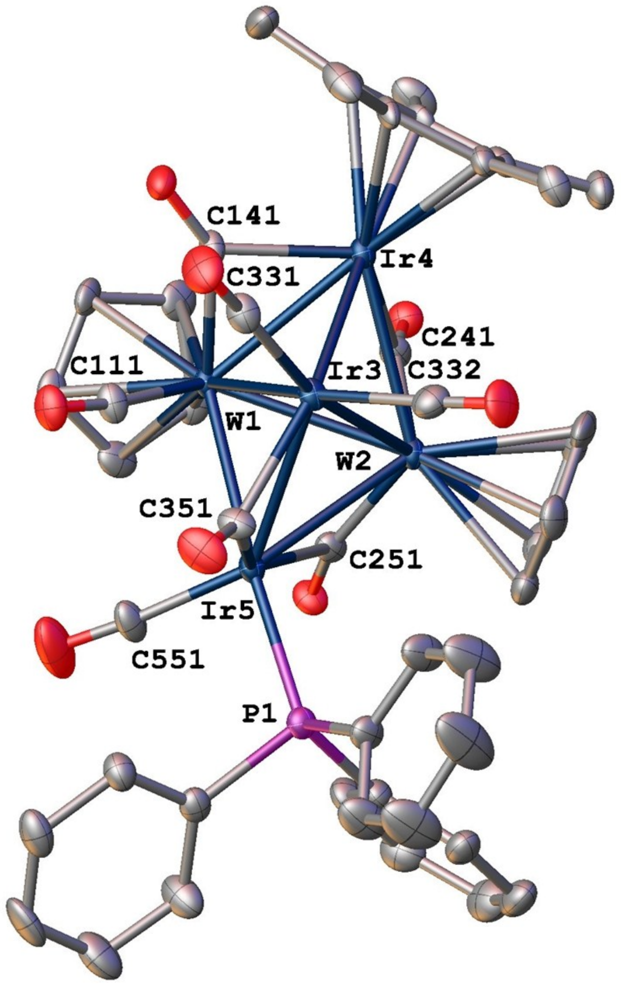


Figure S2. ORTEP plot and atom numbering scheme for $W_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (**4b**). Displacement ellipsoids are shown at the 40% probability level. Hydrogen atoms have been omitted for clarity.

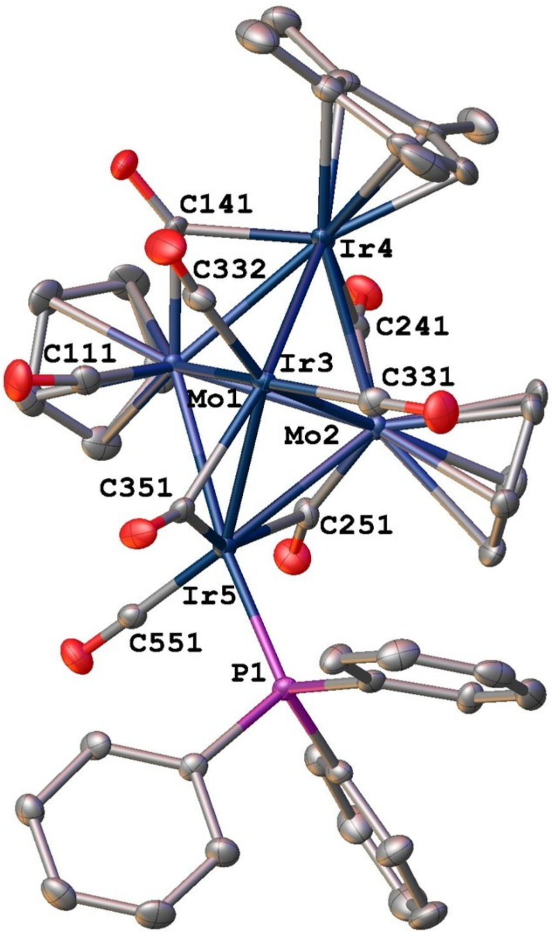


Figure S3. ORTEP plot and atom numbering scheme for $Mo_2Ir_3(\mu\text{-}CO)_4(CO)_4(PPh_3)(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_4H)$ (**4c**). Displacement ellipsoids are shown at the 40% probability level. Hydrogen atoms have been omitted for clarity.

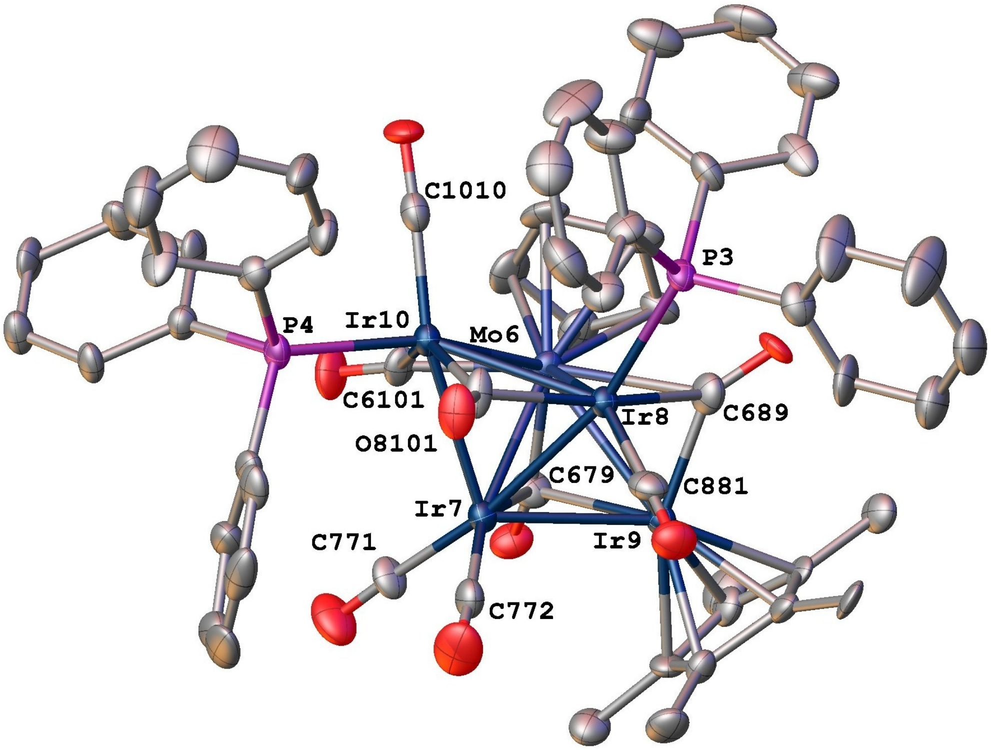


Figure S4. ORTEP plot and atom numbering scheme for one of the two crystallographically distinct molecules of $\mathrm{MoIr_4(\mu_3\text{-}CO)_2(\mu\text{-}CO)_2(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)}$ (**6**). Displacement ellipsoids are shown at the 40% probability level. Hydrogen atoms and lattice dichloromethane molecules have been omitted for clarity. Selected bond lengths: Mo6-Ir7 2.7666(14), Mo6-Ir8 2.9281(13), Mo6-Ir9 2.8371(13), Mo6-Ir10 2.7894(14), Ir7-Ir8 2.7204(8), Ir7-Ir9 2.6744(8), Ir7-Ir10 2.7425(8), Ir8-Ir9 2.7760(8), Ir8-Ir10 2.7608(8), Mo6-C679 1.980(16), Mo6-C689 2.631(18), Mo6-C6101 2.115(16), Ir7-C679 2.495(17), Ir7-C771 1.857(15), Ir7-C772 1.875(17), Ir8-C689 2.161(15), Ir8-C881 1.843(17), Ir8-C8101 2.150(14), Ir8-P3 2.365(4), Ir9-C679 2.502(17), Ir9-C689 1.993(18), Ir10-C1010 1.845(18), Ir10-C6101 2.164(16), Ir10-C8101 2.062(15), Ir10-P4 2.324(4) Å.

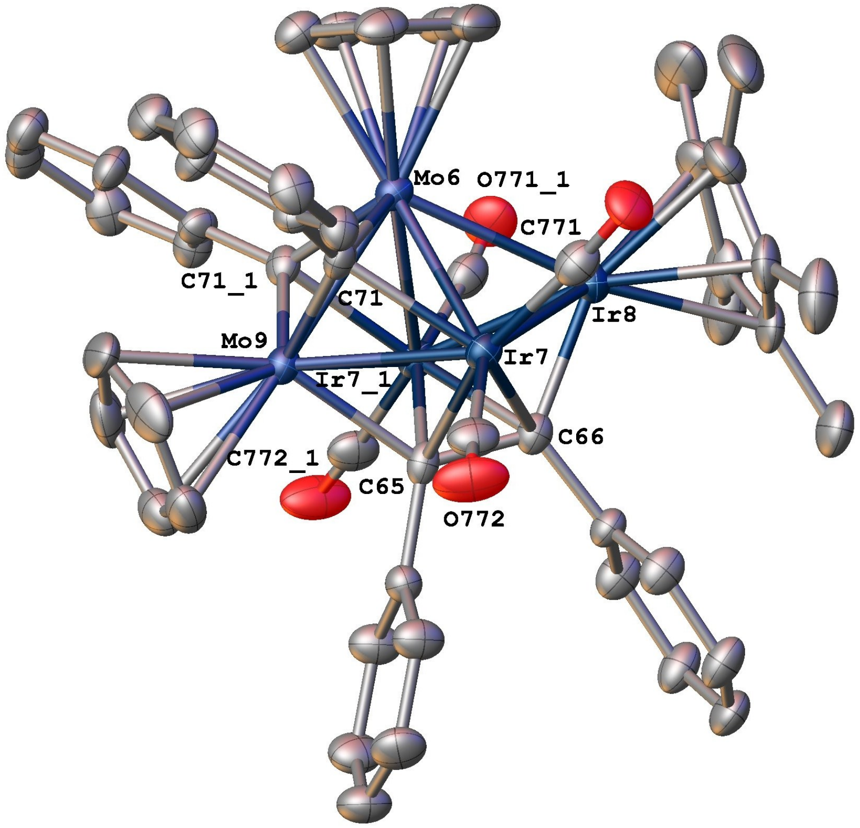


Figure S5. ORTEP plot and atom numbering scheme for one of the two crystallographically distinct molecules of $Mo_2Ir_3(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)(\mu_3\text{-}CPh)_2(CO)_4(\eta^5\text{-}C_5H_5)_2(\eta^5\text{-}C_5Me_5)$ (**7a**) (the cluster molecule that is generated through a mirror plane passing through Mo6, Ir8 and Mo9: see Experimental). Displacement ellipsoids are shown at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths: Mo6-Ir7 2.8374(5), Mo6-Ir7_1 2.8374(5), Mo6-Ir8 2.7764(7), Mo6-Mo9 2.6026(9), Ir7-Ir8 2.7485(3), Ir7-Mo9 2.8325(5), Ir7_1-Ir8 2.7485(3), Ir7_1-Mo9 2.8325(5), Mo6-C71 2.072(5), Mo6-C71_1 2.072(5), Ir7-C771 1.847(6), Ir7-C772 1.873(6), Ir7-C65 2.306(4), Ir7-C66 2.343(4), Ir7-C71 2.145(5), Ir7_1-C65 2.306(4), Ir7_1-C66 2.343(4), Ir8-C66 2.033(7), Mo9-C65 2.176(6), Mo9-C71 2.046(5), Mo9-C71_1 2.046(5), C65-C66 1.482(9) Å. Symmetry operation used to generate equivalent atoms: _1: x, -y + ½, z.

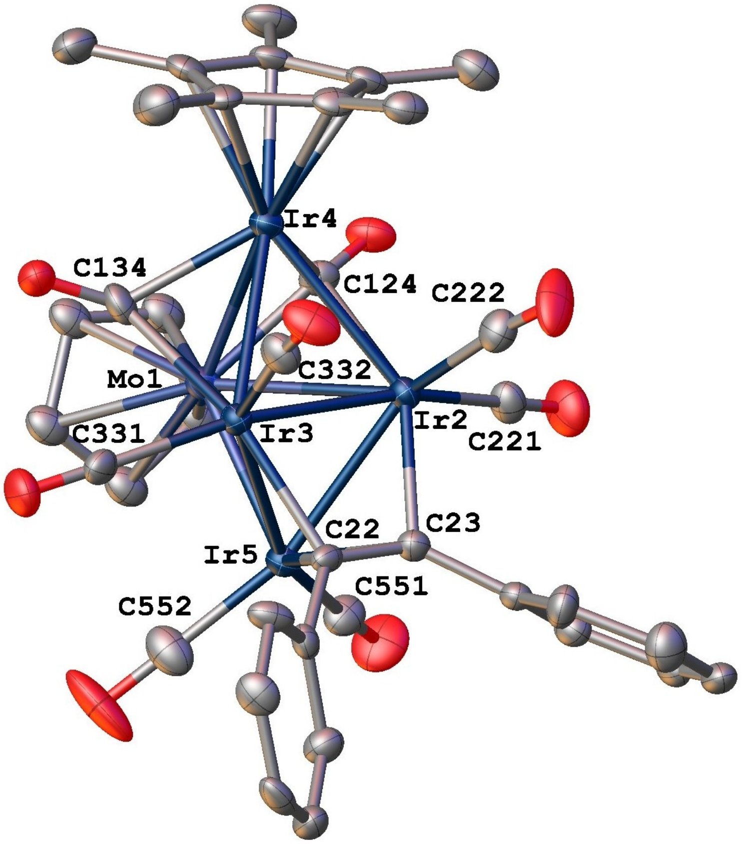


Figure S6. ORTEP plot and atom numbering scheme for $MoIr_4(\mu_3-\eta^2-PhC_2Ph)(\mu_3-CO)_2(CO)_6(\eta^5-C_5H_5)(\eta^5-C_5Me_5)$ (**8a**). Displacement ellipsoids are shown at the 40% probability level. Hydrogen atoms and the lattice dichloromethane molecule have been omitted for clarity.

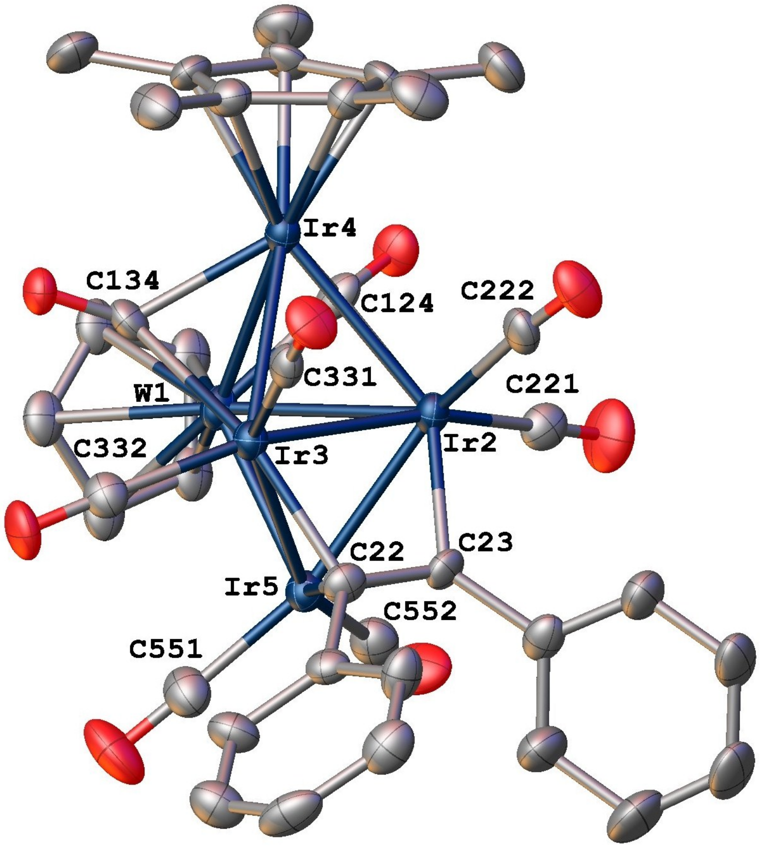


Figure S7. ORTEP plot and atom numbering scheme for $WIr_4(\mu_3-\eta^2-PhC_2Ph)(\mu_3-CO)_2(CO)_6(\eta^5-C_5H_5)(\eta^5-C_5Me_5)$ (**8b**). Displacement ellipsoids are shown at the 40% probability level. Hydrogen atoms and the lattice dichloromethane molecule have been omitted for clarity.

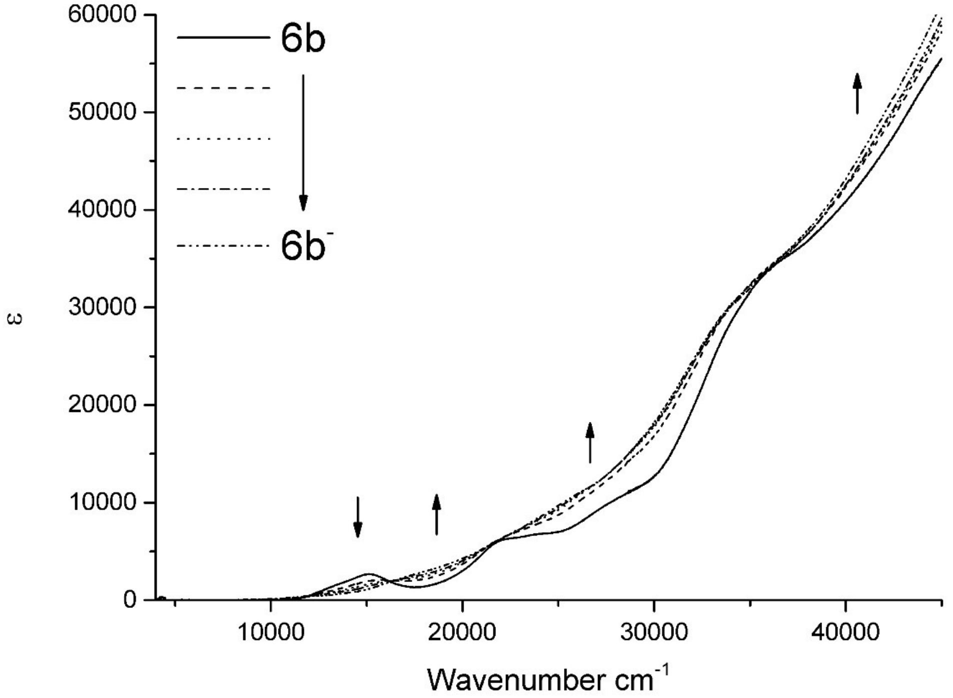


Figure S8. UV-Vis spectral changes accompanying the reduction of **8b** when a voltage of *ca.* -1.2 V is applied to the OTTLE cell (0.3 M $(NBu^n_4)PF_6$ supporting electrolyte, CH_2Cl_2 solvent, 298 K).

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