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The significance of phosphoniocarbynes in halocarbyne cross-coupling reactions

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General Considerations

Experimental work was performed using standard Schlenk techniques using dried and pre-purified nitrogen or in an inert atmosphere glovebox charged with an argon atmosphere unless specified otherwise. Reactions employed dried and degassed solvents distilled over sodium and benzophenone (ethers, arenes and paraffins), calcium hydride (CH_2Cl_2, MeCN) or KOH (Et_3N, stored over 4 Å molecular sieves). The compounds [M(≡CBr)(CO)$_2$(Tp*)] (M = Mo **1a**, W **1b**),[1] [Pd(PPh$_3$)$_4$],[3] [Pt(PPh$_3$)$_4$][4] and [Pd$_2$(dba)$_3$][5] were prepared according to published procedures. All other reagents were used as received from commercial suppliers.

NMR spectra were obtained on a Bruker Avance 400 (^{1}H at 400.1 MHz, ^{13}C{^{1}H} at 100.6 MHz, ^{31}P at 162.0 MHz, ^{195}Pt at 85.7), a Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C{^{1}H} at 150.9 MHz) or a Bruker Avance 700 (^{1}H at 700.0 MHz, ^{13}C{^{1}H} at 176.1 MHz, ^{31}P at 283.4 MHz) spectrometers at the temperatures indicated. Chemical shifts (δ) are reported in ppm with coupling constants given in Hz and are referenced to the solvent resonance or external references {$CFCl_3$ for ^{19}F{^{1}H}, 85% H_3PO_4 in H_2O for ^{31}P{^{1}H}, 1.2M Na_2PtCl_6 for ^{195}Pt. The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet), br (broad) and combinations thereof for more highly coupled systems. Where applicable, the stated multiplicity refers to that of the primary resonance exclusive of ^{183}W or ^{195}Pt satellites. In select cases, distinct peaks were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, but to the level of accuracy that is reportable (i.e., 2 decimal places for ^{1}H NMR, 1 decimal place for ^{13}C{^{1}H} NMR) they are reported as having the same chemical shift. ^{13}C{^{1}H} NMR signals for the carbon chain of propargylidyne complexes are designated as M(≡Cα–Cβ≡Cγ R) Compounds such as **2a** and **2b** display an A-B spin coupled system in the ^{31}P{^{1}H} NMR spectrum and these resonances are weighted accordingly to their second order coupling effects consistent with literature procedures. [6]

The abbreviation 'pz' is used to refer to the pyrazolyl rings on the hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) ligand. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. The B*H* protons give rise to very broad signals around 4–5 ppm in the ^{1}H NMR spectra due to coupling to the quadrupolar boron nuclei. These are not listed in the experimental NMR data as their chemical shifts and associated integrals are not determined accurately. The BH unit, being remote from the metal centre of interest is not particularly responsive to variations and accordingly ^{11}B{^{1}H} NMR spectra were not recorded..

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer (liquid) or Perkin Elmer FTIR Spectrum 2 (Solid State ATR, diamond anvil). Signals are denoted according to their absorption strength such as very sharp (vs), strong (s), medium (m), weak (w) or broad (br). Elemental microanalytical data were provided the London Metropolitan University. Solvates evident from data were confirmed where possible by NMR spectroscopy. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or dichloromethane as the matrix.

Data for X-ray crystallography were collected with Enraf Nonius kappa-CCD, Agilent Xcalibur or SuperNova CCD diffractometers using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) employing the CrysAlis PRO software.[7] The structures were solved by direct or Patterson methods and refined by full-matrix least-squares on F^2 using the SHELXS or SHELXT and SHELXL programs.[8-9] Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.[10-11]

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CCDC 1988587-1988594 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

General Procedure – Alkyne-Bromocarbyne Cross-Coupling
Cuprous iodide (10 mg, 53 µmol), [M(≡CBr)(CO)$_2$(Tp*)] (192 µmol) and the mediator complex under investigation (5–10 mol%) were combined under argon. To this was sequentially added, with stirring, triethylamine (10 mL) and the alkyne of choice (210 µmol). The reaction was monitored by thin layer chromatography utilising 1:1 CH_2Cl_2/petroleum ether as eluent. Upon completion, the mixture was freed of volatiles and the residue subjected to anaerobic flash column chromatography (silica gel, CH_2Cl_2/petroleum ether gradient} followed by solvent removal. Recrystallisation by concentration of CH_2Cl_2 into EtOH provided propargylidyne complexes as microcrystalline powders that were collected by vacuum filtration and dried *in vacuo*.

Synthesis of [Mo(≡C–C≡CPh)(CO)$_2$(Tp*)] - Prepared as per the general procedure above employing [Mo_2Pd_2(µ-C)$_2$(µ-Br)$_2$(CO)$_4$(PPh$_3$)$_2$(Tp*)$_2$] (5a: 5 mol%) as a catalyst to a mixture of [Mo(≡CBr)(CO)$_2$(Tp*)] (1a) and ethynylbenzene. The title compound was obtained as a purple powder (68 mg, 121 µmol, 66% isolated yield). IR (CH_2Cl_2, cm^{-1}): 2095 w $\nu_{C\text{-}C}$, 1997 vs ν_{CO}, 1915 vs ν_{CO}. ^{1}H NMR (600 MHz, $CHCl_3$, 25 °C) δ_H = 7.50 (d, 2 H, $^1J_{HH}$ = 7, C_6H_5), 7.36 (t, 1 H, $^1J_{HH}$ = 8, C_6H_5), 7.29 (t, 2 H, $^1J_{HH}$ = 7 Hz, C_6H_5), 5.86 (s, 2 H, pzC*H*), 5.72 (s, 1 H, pzC*H*), 2.59 (s, 6 H, pzCH_3), 2.37 (s, 6 H, pzCH_3), 2.35 (s, 3 H, pzCH_3), 2.33 (s, 3 H, pzCH_3) ppm. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C) δ_C = 253.5 (Cα), 227.8 (CO), 151.5, 151.4 [C^5(pz)] 145.2 144.6 [C^3(pz)], 133.2 [C^{2,6}(C_6H_5)], 129.2 [C^4(C_6H_5)], 128.6 [C^{3,5}(C_6H_5)], 121.4 [C^1(C_6H_5)], 106.5 [C^4(pz)], 100.6 (Cβ), 65.9 (Cγ), 16.0 (2C) 14.7 (1C) 12.8 (3C) (pzCH_3) ppm. MS (ESI, *m/z*): Found: 565.1416. Calcd for $C_{26}H_{28}BMoN_6O_2$ [M+H]$^+$: 565.1416. Data correspond to those previously published.[13]

Synthesis of [Mo(≡C–C≡CSiMe$_3$)(CO)$_2$(Tp*)] - Proof of concept reaction where the title compound has been prepared previously via an alternative route.[13] Prepared by general procedure employing [Mo_2Pd_2(µ-C)$_2$(µ-Br)$_2$(CO)$_4$(PPh$_3$)$_2$(Tp*)$_2$] (5a: 5 mol%) as a catalyst to a mixture of [Mo(≡CBr)(CO)$_2$(Tp*)] (1a) and ethynyltrimethylsilane. The title compound was obtained as a pink powder (78 mg, 140 µmol, 75% isolated yield). IR (THF, cm^{-1}): 2046 w $\nu_{C\text{-}C}$, 1997 vs ν_{CO}, 1916 vs ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H = 5.85 (s, 2 H, pzC*H*), 5.70 (s, 1 H, pzC*H*), 2.54 (s, 6 H, pzCH_3), 2.36 (s, 6 H, pzCH_3), 2.32 (s, 3 H, pzCH_3), 2.31 (s, 3 H, pzCH_3), 0.18 (s, 9 H, $SiCH_3$ ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ_C 255.6 (Cα), 227.5 (CO), 151.6, 151.3 [C^5(pz)], 145.2, 144.5 [C^3(pz)], 113.4 (C$_i$), 106.44 106.42 [C^4(pz)], 75.2 (Cγ), 15.8 14.7 12.8 (pzCH_3), –0.2 ($SiCH_3$) ppm. Data correspond to those previously published.[13]

Synthesis of W(≡C–C≡CPh)(CO)$_2$(Tp*)] - Proof of concept reaction where the title compound has been prepared previously via an alternative route.[13] Prepared as per the general procedure above employing a mixture of [WPt(µ-C)Br(CO)$_2$(PPh$_3$)$_2$(Tp*)] (2b: 100 mol%) and ethynylbenzene for 16 hours. The title compound was obtained as a maroon powder (21 mg, 32 µmol, 43% isolated yield). The only other spectroscopically observable organometallic species present was the precursor 2b such that isolated yields approximate to % conversion. IR (CH_2Cl_2, cm^{-1}): 2100 w $\nu_{C\text{-}C}$, 1982 vs ν_{CO}, 1893 vs $\nu_{C\text{-}C}$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC, δ): 7.48 (d, $^1J_{HH}$ = 7 Hz, PhC*H*), 7.35 (t, $^1J_{HH}$ = 7 Hz, PhC*H*), 7.28 (d, $^1J_{HH}$ = 8 Hz, PhC*H*), 5.91 (s, 2H, pzC*H*), 5.75 (s, 1H, pzC*H*), 2.62 (s, 6H, pzCH_3), 2.39 (s, 3H, pzCH_3), 2.38 (s, 6H, pzCH_3), 2.32 (s, 3H, pzCH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25ºC, δ): 246.4 (s, C$_α$), 226.2 (s, C≡O), 152.3 152.3 145.2 144.4 (s, pzCCH), 132.5 128.4 122.1 (s, Ph), 107.0 (s, C$_β$), 106.65 106.62 (overlapping singlets, pzCH), 70.2 (s, C$_γ$), 16.6 15.2 12.7 12.6 (s, pzCH_3) ppm. Data were consistent with those previously published.[13]

[W(≡C–C≡CSiMe$_3$)(CO)$_2$(Tp*)] - Proof of concept reaction where the title compound has been prepared previously.[13] Prepared as per general procedure employing a mixture of [WPt(µ-C)Br(CO)$_2$(PPh$_3$)$_2$(Tp*)] (2b: 100 mol%) and ethynyltrimethylsilane. The title compound was obtained as a pink powder (17 mg, 26 µmol, 34% isolated yield). The only other spectroscopically observable organometallic species present was the precursor 2b such that isolated yields approximate to % conversion. IR (CH_2Cl_2, cm^{-1}): 2051 w $\nu_{C\text{-}C}$, 1985 vs ν_{CO}, 1895 vs ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 5.90 (s, 2 H, pzC*H*), 5.73 (s, 1 H, pzC*H*), 2.57 (s, 6 H, pzCH_3), 2.36 (s, 9 H, pzCH_3), 2.31 (s, 3 H, pzCH_3), 0.17 (s, 9 H, $SiCH_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ_C = 255.6 (Cα), 227.6 (CO), 151.6 151.3 [C^5(pz)], 145.2 144.5 [C^3(pz)], 113.5 (Cβ), 106.44 106.42 [overlapping singlets, C^4(pz)], 75.2 (Cγ), 15.8 14.7 12.8 (pzCH_3), –0.2 ($SiCH_3$). Data correspond to those previously published.[13]

Synthesis of [MoPt(µ-C)Br(CO)$_2$(PPh$_3$)$_2$] (2a) – This complex was previousl prepared from **1a** and [Pt(η^2-C_2H_4)(PPh$_3$)$_2$] in two steps. Given that [Pt(η^2-C_2H_4)(PPh$_3$)$_2$] is itself prepared in two steps from K_2[$PtCl_4$] while [Pt(PPh$_3$)$_4$] is obtained in a single step, the present methods offers some expedience. [Mo(≡CBr)(CO)$_2$ -(Tp*)] (**1a**: 229 mg, 0.423 mmol) and [Pt(PPh$_3$)$_4$] (408 mg, 0.328 mmol) was stirred in toluene (20 mL) for 16 hours at 60 ºC. Originally a yellow solution, this quickly darkened to provide a brown solution. Solvent was removed under reduced pressure to give a crude orange solid which was purified by flash column chromatography (silica gel, N_2, neat petroleum ether followed by neat CH_2Cl_2) eluting a major yellow compound from which the solvent was removed under reduced pressure. Recrystallisation from a mixture of CH_2Cl_2 and n-hexane afforded an orange microcrystalline powder. This was collected via vacuum filtration and dried *in vacuo* for 1 hour to afford the title compound (232 mg, 0.184 mmol, 56% yield). IR (CH_2Cl_2, cm^{-1}): 1962 vs ν_{CO}, 1873 vs ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H = 7.91 – 7.98 (m, 6 H, C_6H_5), 7.48 – 7.38 (m, 14 H, C_6H_5), 7.21 – 7.12 (m, 4 H, C_6H_5), 7.00 (dt, $^3J_{HH}$ = 8, $^4J_{HH}$ = 4 Hz, C_6H_5), 5.54 (s, 2 H, pzC*H*), 5.49 (s, 1 H, pzC*H*), 2.58 (s, 6 H, pzCH_3), 2.34 (s, 6 H, pzCH_3), 2.20 (s, 3 H, pzCH_3), 1.96 (s, 3 H, pzCH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C) δ_C = 335.7 (m, Mo≡*C*–Pt),

232.8 (*C*≡O), 150.7 (1C), 150.4 (2C), 143.5 (1C) 143.3 [2C, $C^{3,5}$(pz)], 135.4 [d, $C^{2,6}(C_6H_5)$, $^2J_{PC}$ = 11], 135.2 [d, $C^{2,6}(C_6H_5)$, $^2J_{PC}$ = 11], 132.2 [dd,$C^1(C_6H_5)$, $^1J_{PC}$ = 53, $^3J_{PC}$ = 5), 131.1 [dd,$C^1(C_6H_5)$, $^1J_{PC}$ = 53, $^3J_{PC}$ = 5), 130.2, 129.9 [$C^4(C_6H_5)$], 128.1 [d, $C^{3,5}(C_6H_5)$, $^2J_{PC}$ = 11], 127.3 [d, $C^{3,5}(C_6H_5)$, $^2J_{PC}$ = 11], 106.4 105.7 (s, pz*C*H), 16.7 14.3 13.0 12.5 (s, pz*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ_P = Major rotamer: 23.76 (d, $^2J_{PP}$ = 438), 19.38 (d, $^2J_{PP}$ = 438); Minor rotamer: 26.39 (d, $^2J_{PP}$ = 437), 21.00 (d, $^2J_{PP}$ = 437 Hz). $^{195}Pt\{^1H\}$ NMR (85.7 MHz, $CDCl_3$, 25 °C) δ_{Pt} = –3810 (t, $^1J_{PtP}$ = 3200 Hz). MS (ESI, *m/z*): Found: 1262.16794. Calcd for $C_{54}H_{53}BBrMoN_6O_2P_2Pt$ $[M+H]^+$: 1262.16823. NB: Most abundant ion corresponds to $[M-Br]^+$ (100%). Anal. Found: C, 51.33; H, 4.00; N, 6.66 %. Calcd for $C_{54}H_{52}BBroN_6O_2P_2Pt$: C, 51.45; H, 4.16; N, 6.67 %.

Crystal data for $C_{54}H_{52}BBrN_6O_2P_2PtMo.(Et_2O)_3$, M_W = 1483.07, monoclinic, $P2_1/n$, a = 22.4595(4) Å, b = 12.1952(2)Å, c = 24.7641(4) Å, β = 102.5130(10)°, V = 6621.73(19) Å^3, Z = 4, ρ_{calc} = 1.488 Mgm^{-3}, μ(Mo $K\alpha$) = 3.003 mm^{-1}, T = 100(0) K, yellow needle 0.46 x 0.10 x 0.08mm, 19277 independent measured reflections (θ_{max} = 60.0°), R_1 = 0.0334, wR_2 = 0.0518 for 15430 reflections [$I > 2\sigma(I)$], 763 parameters, 12 restraints. CDCC 1988587.

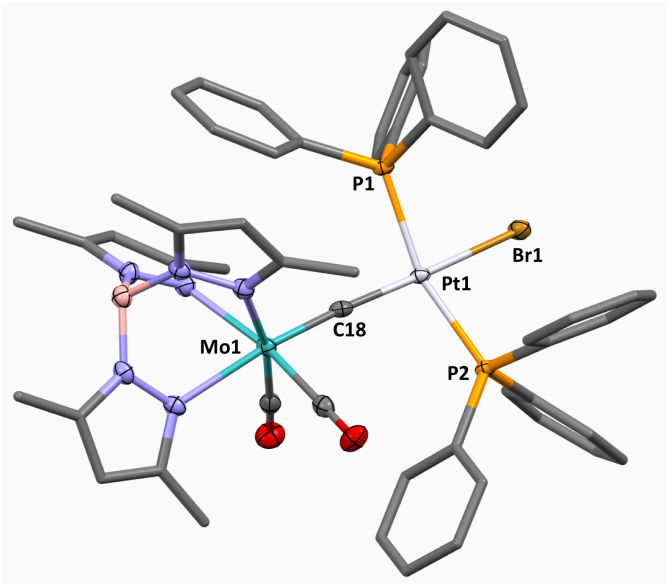

Figure S1. Molecular structure of [MoPt(μ-C)(μ-Br)$(CO)_2(PPh_3)_2$(Tp*)] (**2a**) in a crystal of **2a**.$(OEt_2)_3$ (50% displacement ellipsoids, hydrogen atoms and solvent omitted, pyrazolyl and phenyl groups simplified). Selected bond lengths (Å) and angles (°): Pt1–C18 1.951(3), Pt1–P2 2.3262(6), Pt1–P1 2.3267(6), Pt1 Br1 2.5448(3), Mo1–C18 1.828(3), C18–Pt1–P2 97.89(7), C18–Pt1–P1 94.16(7), P2–Pt1–P1 162.40(2), C18–Pt1–Br1 177.09(7), P2–Pt1–Br1 84.223(18), P1–Pt1–Br1 84.230(18), Mo1–C18–Pt1 173.97(15).

Synthesis of [WPt(μ-C)Br$(CO)_2(PPh_3)_2$] (2b) - Note: This compound exists as a single compound or a pair of inseparable rotational isomers depending on solvent used in its synthesis.

Single Compound - A yellow solution containing [W(≡CBr)$(CO)_2$(Tp*)] (**1b**: 0.793 g, 1.27 mmol) and $[Pt(PPh_3)_4]$ (1.54 g, 1.23 mmol) was stirred in toluene (36 mL) for 16 hours at 60 °C. The resulting orange solution was freed of volatiles *in vacuo* to give a crude residue. Flash column chromatography (silica gel, N_2, neat petroleum ether followed by neat CH_2Cl_2) was performed eluting a major orange compound before removing solvent under reduced pressure. A recrystallization of the residue from a mixture of CH_2Cl_2 into EtOH gave an orange solid which was collected via vacuum filtration. The solid was washed with EtOH (2 x 10 mL) and n-hexane (10 mL) before drying *in vacuo* for 3 hours to afford compound **2b** as a fine orange powder (1.18 g, 0.88 mmol, 77% yield). Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation of Et_2O at 0 °C. IR (CH_2Cl_2, cm^{-1}): 1945 vs ν_{CO}, 1854 vs ν_{CO}. IR (ATR, cm^{-1}): 1935 vs ν_{CO}, 1838 vs ν_{CO}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H = 7.94 (m, 6 H, C_6H_5), 7.48 – 7.37 (m, 15 H, C_6H_5), 7.13 (m, 3 H, C_6H_5), 6.96 (m, 6 H, C_6H_5), 5.56 (s, 2 H, pz*CH*), 5.50 (s, 1 H, pz*CH*), 2.58 (s, 6 H, pz*CH*$_3$), 2.31 (s, 6 H, pz*CH*$_3$), 2.17 (s, 3 H, pz*CH*$_3$), 1.98 (s, 3 H, pz*CH*$_3$) ppm. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C) δ_C = 317.2 (t, $^2J_{CP}$ = 8, W≡C–Pt), 230.7 ($^1J_{CW}$ = 179, CO), 151.7(1C), 151.2(2C), 143.5 (1C), 143.3 [2C, $C^{3,5}$(pz)], 135.3 [d, $^2J_{CP}$ =11, $C^{2,6}(C_6H_5)$], 135.2 [d, $^2J_{CP}$ =11, $C^{2,6}(C_6H_5)$], 132.4 [dd, $^1J_{CP}$ = 53, $^3J_{CP}$ = 5 $C^1(C_6H_5)$], 131.3 [dd, $^1J_{CP}$ = 53, $^3J_{CP}$ = 5 $C^1(C_6H_5)$], 130.0 129.8 [$C^4(C_6H_5)$], 128.0 [d, $^3J_{CP}$ = 11, $C^{3,5}(C_6H_5)$], 127.2 [d, $^3J_{CP}$ = 11 Hz, $C^{2,6}(C_6H_5)$], 106.7 106.0 [C^4(pz)], 17.4 14.8 12.9 12.4 (pz*C*H$_3$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ_P = 26.25 (d, $^2J_{PP}$ = 443, $^1J_{PPt}$ = 3178), 22.19 (d, $^2J_{PP}$ = 443, $^1J_{PPt}$ = 3200 Hz) ppm. $^{195}Pt\{^1H\}$ NMR (85.7 MHz, $CDCl_3$, 25 °C) δ_{Pt} = –3821 (t, $^1J_{PtP}$ = 3200 Hz). MS (ESI, *m/z*): Found: 1347.20589. Calcd for $C_{54}H_{52}BBrN_6O_2P_2PtW$ $[M]^+$: 1347.20534. Anal. Found: C, 48.91; H, 3.80; N, 6.26%.Calcd for $C_{54}H_{52}BBrN_6O_2P_2PtW$: C, 48.09; H, 3.89; N, 6.23%.

Rotomeric mixture - A yellow solution containing [W(≡CBr)-$(CO)_2$(Tp*)] (**1b**: 0.783 g, 1.24 mmol) and $[Pt(PPh_3)_4]$ (1.48 g, 1.19 mmol) was stirred in benzene (36 mL) for 16 hours at 60 °C. The resulting orange solution was freed of volatiles under reduced pressure to give a crude residual solid. Subsequent recrystallization from a mixture of CH_2Cl_2 into EtOH gave an orange solid which was be collected via vacuum filtration. The solid was washed with EtOH (2 x 10 mL) and n-hexane (10 mL) before drying *in vacuo* for 4 hours to afford compound **2b** as a fine orange powder (1.23 g, 0.92 mmol, 77% yield). IR (CH_2Cl_2, cm^{-1}): 1988 m ν_{CO}, 1948 vs ν_{CO}, 1894 m ν_{CO}, 1854 vs ν_{CO},. ^1H NMR (600 MHz, $CDCl_3$, 25 °C) δ_H = 7.98 – 7.91 (m, 12 H, C_6H_5), 7.43 – 7.39 (m, 27 H, C_6H_5), 7.16 – 7.11 (m, 6 H, C_6H_5), 7.00 – 6.95 (m, 11 H, C_6H_5), 5.56 (s, 2 H, pz*CH*), 5.55 (s, 2 H, pz*CH*), 5.51 (s, 1 H, pz*CH*), 5.50 (s, 1 H, pz*CH*), 2.58 (s, 6 H, pz*CH*$_3$), 2.57 (s, 6 H, pz*CH*$_3$), 2.33 (s, 6 H, pz*CH*$_3$), 2.32 (s, 6 H, pz*CH*$_3$), 2.19 (s, 3 H, pz*CH*$_3$), 2.18 (s, 3 H, pz*CH*$_3$), 2.00 (s, 3 H, pz*CH*$_3$), 1.99 (s, 3 H, pz*CH*$_3$) NB: Stated integrals are relative to each rotamer and are not scaled to take account of different populations. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C) δ_C = 318.7 (W≡*C*–Pt), 230.7 ($^1J_{CW}$ = 178, CO), 151.5, 151.0, 143.4, 143.0 [$C^{3,5}$(pz)], 135.2 – 134.8, m, C_6H_5), 131.8 [dd, $^1J_{CP}$ = 52, $^3J_{CP}$ = 5, $C^1(C_6H_5)$], 130.7 [dd, $^1J_{CP}$ = 53, $^3J_{CP}$ = 5, $C^1(C_6H_5)$], 130.0 129.8 [$C^4(C_6H_5)$], 128.0 [t, $^2J_{CP}$ = 11, $C^{3,5}(C_6H_5)$], 127.3 [t, $^3J_{CP}$ = 11, $C^{2,6}(C_6H_5)$], phenyl resonances corresponding to the previously mentioned isomer are omitted for clarity, 106.5 105.8 [C^4(pz)], 17.2, 17.0, 14.7, 12.7, 12.2 (pz*C*H$_3$) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C) δ_P = 28.27 (d, $^2J_{PP}$ = 443), 26.21 (d, $^2J_{PP}$ = 443), 23.91 (d, $^2J_{PP}$ = 443), 22.11 (d, $^2J_{PP}$ = 443 Hz, $^1J_{PtP}$ not determined due to insufficient signal/noise). ^{195}Pt NMR (85.7 MHz, $CDCl_3$, 25 °C) δ_{Pt} = –3718 (t, $^1J_{PtP}$ = 3214), –3821 (t,

$^{1}J_{PtP}$ = 3202 Hz) ppm MS (ESI, *m/z*): Found: 1268.2884. Calcd for $C_{54}H_{52}BN_6O_2P_2PtW$ $[M–Br]^+$: 1268.2890. Anal. Found: C, 48.10; H, 4.04; N, 6.10%. Calcd for $C_{54}H_{52}BBrN_6O_2P_2PtW$: C, 48.09; H, 3.89; N, 6.23%.

Crystal data for $C_{54}H_{52}BBrN_6O_2P_2PtW$, M_W = 1648.61, monoclinic, $P2_1/n$, a = 9.5923 (1) Å, b = 22.6404 (4) Å, c = 23.4154 (3) Å, β = 98.636 (1)°, V = 5027.55(12) Å^3, Z = 4, ρ_{calc} = 1.782 Mgm^{-3}, μ(Cu $K\alpha$) = 11.21 mm^{-1}, T = 150(0) K, plate {clear light orange}, 9886 independent measured reflections (θ = 73.8), R_1 = 0.037, wR_2 = 0.098 for 8545 reflections [$I > 2\sigma(I)$], 619 parameters, no restraints. CDCC 1988588.

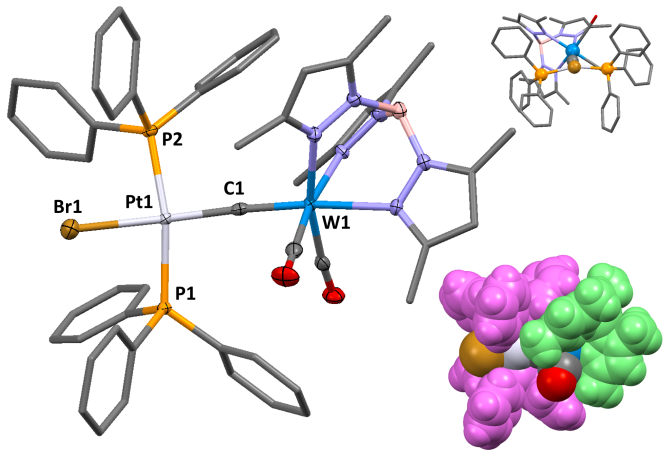

Figure S2. Molecular structure of **2b** in a crystal (50% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Pt1–Br1 2.5274(7), Pt1–P1 2.3265(12), Pt1–P2 2.3256(12), Pt1–C1 1.934(6), W1–C1 1.856(6), W1–C1–Pt1 169.2(3), C1–Pt1–Br1 169.19(15), P2–Pt1–P1 160.28(5). Insets = view along Br1…Pt1 vector and space filling representation indicating steric clash between Tp* (green) and phosphine (cerise) ligands.

Observation of [MoPd(μ-C)Br(CO)$_2$(PPh$_3$)$_2$(Tp*)] (2c) - An NMR sample of [Mo(≡CBr)(CO)$_2$(Tp*)] (**1a**: 35 mg, 65 μmol) and [Pd(PPh$_3$)$_4$] (80 mg, 69 μmol) in d$_6$-benzene (0.5 mL) was prepared under argon. Upon combination, the solution colour rapid changed from yellow to a bright red. The sample was subjected to NMR spectroscopic analysis after 1 hour at which time the title compound predominated in solution. Solutions in a variety of solvents were similarly prepared for investigation by infra-red spectroscopy but with a shorter mixing time such that in general **1a** predominated. IR (THF, cm^{-1}): 1971 m ν_{CO}, 1888 m, ν_{CO}. IR (CH_2Cl_2, cm^{-1}): 1974 m ν_{CO}, 1886 m, ν_{CO}. IR ($CHCl_3$, cm^{-1}): 1974 br ν_{CO}, 1889 br ν_{CO}. IR (CaF_2, cm^{-1}): 1973 br ν_{CO}, 1891 br ν_{CO}. ^{1}H NMR (400 MHz, benzene-d$_6$, 25 °C) δ_H = 8.33 (t, $^1J_{HH}$ = 9 Hz, 3 H, C_6H_5), 7.82 (m, 4 H, C_6H_5), 7.53 (m, 16 H, C_6H_5), 7.02 (m, 3 H, C_6H_5), 6.92 (m, 4 H, PPh), 5.64 (s, 1 H, pzC*H*), 5.48 (s, 2 H, pzC*H*), 2.65 (s, 3 H, pzCH_3), 2.29 (s, 3 H, pzCH_3), 2.28 (s, 6 H, pzCH_3), 2.22 (s, 3 H, pzCH_3), 2.16 (s, 3 H, pzCH_3) ppm. ^{13}C{^{1}H} NMR (176 MHz, benzene-d$_6$, 25 °C, δ_C = 353.8 (m, Mo≡C–Pd), 224.7 (C≡O), 151.7, 151.5 [C^5(pz)], 145.0, 144.3 [C^3(pz)], 132.4 [d, $^3J_{CP}$ = 9, $C^{2,6}$(C_6H_5)], 129.9 [d, $^2J_{CP}$ = 37 Hz, $C^{3,5}$(pz)], 107.0 106.6 [C^4(pz)], 15.7, 14.8, 12.6, 12.5 (pzCH_3); some aryl resonance assignments equivocal due to excess PPh$_3$ and C_6D_6. ^{31}P{^{1}H} NMR (162 MHz, benzene-d$_6$, 25 °C) δ_P = 25.90 (d, $^2J_{PP}$ = 423), 20.72 (d, $^2J_{PP}$ = 421 Hz). No crystal suitable for single crystal X-ray diffraction could be produced due to ensuing further reaction upon protracted work up or crysallisation.

Observation of [WPd(μ-C)Br(CO)$_2$(PPh$_3$)$_2$(Tp*)] (2d) - An NMR sample of [W(≡CBr)(CO)$_2$(Tp*)] (**1b**: 27 mg, 43 μmol) and [Pd(PPh$_3$)$_4$] (50 mg, 43 μmol) in d$_6$-benzene (0.5 mL) was prepared under argon. Upon combination, the solution colour rapidly changed from yellow to a bright red. The sample was investigated by NMR spectroscopic analysis after 1 hour to observe the title compound **2d** in solution. IR (THF, cm^{-1}): 1962 sh ν_{CO}, 1956 vs ν_{CO}, 1872 sh ν_{CO}, 1865 vs ν_{CO}. IR (CH_2Cl_2, cm^{-1}): 1957 br ν_{CO}, 1865 br, ν_{CO}. IR ($CHCl_3$, cm^{-1}): 1960 br, ν_{CO}, 1866 br ν_{CO}. IR (C_6H_6): 1957 s ν_{CO}, 1872, 1864 ν_{CO}. ^{1}H NMR (400 MHz, benzene-d$_6$, 25 °C) δ_H = 8.36 (t, $^1J_{HH}$ = 9, 6 H, C_6H_5), 7.79 (t, $^1J_{HH}$ = 9, 8 H, C_6H_5), 7.34 (t, $^1J_{HH}$ = 8 Hz, 6 H, C_6H_5), 7.04 – 6.97 (m, 4 H, C_6H_5), 6.94 – 6.87 (m, 6 H, C_6H_5), 5.54 (s, 2 H, pzCH), 5.40 (s, 1 H, pzCH), 2.35 (s, 3 H, pzCH_3), 2.23 (s, 6 H, pzCH_3), 2.17 (s, 6 H, pzCH_3), 2.11 (s, 3 H, pzCH_3), NB: Time-course experiments allowed the identification of resonances due to free PPh$_3$ and these are omitted from the listing. ^{13}C{^{1}H} NMR (151 MHz, benzene-d$_6$, 25 °C) δ_C = 333.3 (m, W≡C–Pd), 231.1 ($^2J_{CW}$ = 179, C≡O), 151.9, 151.4, 143.6, 143.3 [$C^{3,5}$(pz)], 132.9 [dd, $^1J_{CP}$ = 42 Hz, $^2J_{CP}$ = 4, C^1(C_6H_5)], 129.8 [d, $^2J_{CP}$ = 29 Hz, $C^{3,5}$(C_6H_5)], 107.3, 107.1 [C^4(pz)], 18.1, 15.1, 12.7, 12.3 (pzCH_3); some aryl resonance assignments equivocal due to excess PPh$_3$ and C_6D_6. ^{31}P{^{1}H} NMR (162 MHz, benzene-d$_6$, 25 °C) δ_P = 28.81 (d, $^1J_{PP}$ = 428), 23.23 (d, $^1J_{PP}$ = 428 Hz). Resonances at δ_C = 222.2 and 198.2 correspond to the CO and CBr ligands of unreacted **1b**. Crystals suitable for elemental microanalysis or X-ray crystallography were not acquired due to subsequent conversions in solution to other products within the time-frame for slow crystal growth.

Synthesis of [Mo$_2$Pd$_2$(μ-C)$_2$(μ-Br)$_2$(CO)$_4$(PPh$_3$)$_2$(Tp*)$_2$] (5a) – A mixture **of** [Mo(≡CBr)CO)$_2$(Tp*) (**1a**: 480 mg, 0.881 mmol) and [Pd(PPh$_3$)$_4$] (1.001 g, 0.866 mmol) in benzene (20 mL) was stirred at room temperature for 3 hours darkening to red. Complete conversion of starting material was confirmed via infra-red spectroscopic analysis upon which the solvent was removed under reduced pressure to afford a red residue. This was subjected to an ultrasonic bath in *n*-hexane (10 mL) for several minutes until an orange powder formed. The powder was recrystallised from a mixture of THF and *n*-hexane before collection by vacuum filtration. Further washed with *n*-hexane (3 x 10 mL) and *n*-pentane (10 mL) before drying *in vacuo* for 5 hrs provided the title compound **5a** (768 mg, 0.422 mmol, 97% yield). Crystals suitable for X-ray diffraction were obtained by the vapour diffusion of *n*-hexane into a solution of **5a** in benzene at 5 °C. IR (THF, cm^{-1}): 1977 vs ν_{CO}, 1911 vs ν_{CO}, 1897 vs ν_{CO}; IR spectroscopic analysis was performed in THF

as this compound is sensitive to halogenated and protic solvents. ^{1}H NMR (400 MHz, Benzene-d_6, 25 °C) δ_H = 7.91 (m, 1 H, C_6H_5), 7.77 – 7.73 (m, 2 H, C_6H_5), 7.71 – 7.60 (m, 8 H, C_6H_5), 7.08 – 6.97 (m, 5 H, C_6H_5), 6.95 – 6.88 (m, 4 H, C_6H_5), 6.87 – 6.83 (m, 2 H, C_6H_5), 6.78 – 6.63 (m, 8 H, C_6H_5), 5.34 (s, 2 H, pzCH), 5.30 (s, 1 H, pzCH), 2.54 (s, 6 H, $pzCH_3$), 2.29 (s, 3 H, $pzCH_3$), 2.16 (s, 6 H, $pzCH_3$), 2.04 (s, 3 H, $pzCH_3$). ^{13}C{^{1}H} NMR (151 MHz, Benzene-d_6, 25 °C) δ_C = 330.8 (br.s, Mo≡C–Pd), 229.0 (CO), 150.9 [C^5(pz)], 143.7, 143.0 [C^3(pz)], 135.7, 134.5 (C_6H_5), 132.5 [d, $^{2}J_{CP}$ = 10, $C^{2,6}$(C_5H_6)], 131.6, 130.6, 130.4 (C_6H_5), 128.5 [d, $^{1}J_{CP}$ = 12 Hz, $C^{3,5}$(C_6H_5)], 106.5, 106.1 [C^4(pz)], 16.7, 14.8, 12.7, 12.5 ($pzCH_3$); equivocal assignment of C_6H_5 resonances due to C_6D_6 resonance. NMR data acquisition compromised by low solubility in non-halogenated solvents. ^{31}P{^{1}H} NMR (162 MHz, Benzene-d_6, 25 °C) δ_P = 26.3 (br., hhw = 15 Hz). MS (ESI, *m/z*): Found: 1739.1014. Calcd for $C_{72}H_{74}B_2Br_2Mo_2N_{12}O_4P_2Pd_2Na_1$ $[M+Na]^+$: 1843.00915. Found: 1843.00201.

Crystal data for $C_{72}H_{74}B_2Br_2Mo_2N_{12}O_4P_2Pd_2$, M_w = 2005.73, monoclinic, $P2_1/n$, a = 27.0575 (4) Å, b = 11.7128 (2) Å, c = 29.6534 (3) Å, β = 104.965 (1)°, V = 9079.0 (2) Å^3, Z = 4, ρ_{calc} = 1.437 Mg m^{-3}, μ(Cu $K\alpha$) = 7.17 mm^{-1}, T = 150(0) K, block (clear light orange), 17953 independent measured reflections (θ_{max} = 73.8 °), R_1 = 0.057, wR_2 = 0.137 for 14248 reflections [$I > 2\sigma(I)$], 895 parameters without restraints. CDCC 1988590.

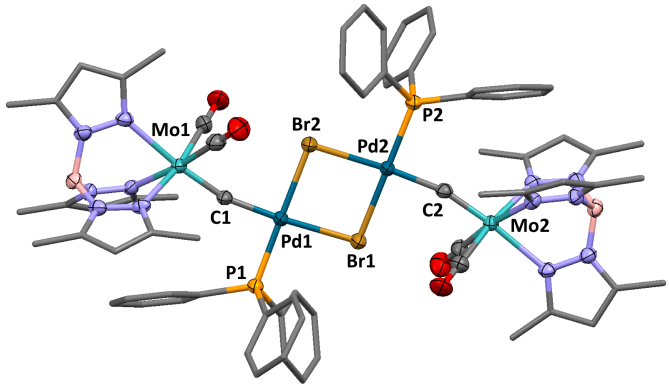

Figure S3. Molecular structure of **5a** in a crystal (50% displacement ellipsoids, pyrazolyl and phenyl groups simplified, hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Pd1–Br1 2.5653(8), Pd1–Br2 2.5046(8), Pd1–P1 2.2675(15), Pd1–C1 1.922(6), Pd2–Br1 2.5100(8), Pd2–Br2 2.5668(8), Pd2–P2 2.2676(15), Pd2–C2 1.923(6), Mo1–C1 1.808(6), Mo2–C2 1.805(6), Mo1–C1–Pd1 166.1(3), Mo2–C2–Pd2 166.5(3).

A dichloromethane solvate was also structurally characterised: *Crystal data for* $C_{72}H_{74}B_2Br_2Mo_2N_{12}O_4P_2Pd_2.(CH_2Cl_2)_4$, M_w = 2159.20, monoclinic, $P2_1/n$, a = 11.39770(10) Å, b = 30.1539(4) Å, c = 13.29850(10) Å, β = 109.4280(10)°, V = 4310.25(8) Å^3, Z = 2, ρ_{calc} = 1.664 Mg m^{-3}, μ(Mo $K\alpha$) = 1.961 mm^{-1}, T = 100(0) K, red prism 0.28 x 0.26 x 0.14 mm, 10386 independent measured reflections (θ_{max} = 56.0 °), R_1 = 0.0435, wR_2 = 0.1083 for 9460 reflections [$I > 2\sigma(I)$], 506 parameters with 0 restraints. CDCC 1988589.

Crystal Structure of $[Mo_2Pt_2(\mu\text{-}C)_2(\mu\text{-}Br)_2(CO)_4(PPh_3)_2(Tp^*)_2].(Et_2O)_{2.5}$ (5c) - *Crystal data for* $C_{82}H_{99}B_2Br_2Mo_2N_{12}O_{6.5}P_2Pt_2$, M_w = 2182.17, monoclinic, $P2_1/n$, a = 26.9732(5) Å, b = 11.6694(2) Å, c = 29.6570 (3) Å, β = 105.134(1)°, V = 9011.1(3) Å^3, Z = 4, ρ_{calc} = 1.608 Mg m^{-3}, μ(Mo $K\alpha$) = 4.345 mm^{-1}, T = 100(0) K, orange needle, 0.35 x 0.11 x 0.08 mm, 20512 independent measured reflections (θ_{max} = 54.9 °), R_1 = 0.0458, wR_2 = 0.1031 for 16495 reflections [$I > 2\sigma(I)$], 1007 parameters with 53 restraints. CDCC 1988591.

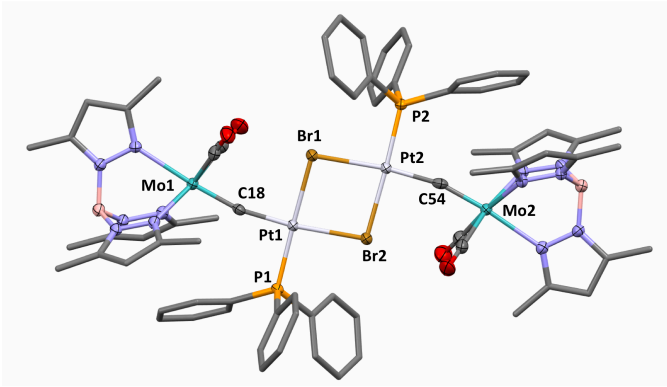

Figure S4. Molecular structure of $[Mo_2Pt_2(\mu\text{-}C)_2(\mu\text{-}Br)_2(CO)_4(PPh_3)_2(Tp^*)_2]$ (**5c**) in a crystal of **5c**.$(OEt_2)_{2.5}$ (50% displacement ellipsoids, hydrogen atoms and solvent omitted, pyrazolyl and phenyl groups simplified). Selected bond lengths (Å) and angles (°): Pt1 C18 1.934(6), Pt1–P1 2.2402(14), Pt1–Br1 2.5095(6), Pt1–Br2 2.5708(6), Pt2–C54 1.926(6), Pt2–P2 2.2356(14), Pt2–Br2 2.5031(6), Pt2–Br1 2.5687(6), Mo1–C18 1.810(6), Mo2–C54 1.817(6), C18–Pt1–P1 92.27(16), C18–Pt1–Br1 89.27(16), P1–Pt1–Br1 177.34(4), C18–Pt1–Br2 173.03(16), P1–Pt1–Br2 94.36(4), Br1–Pt1–Br2 84.025(19), C54–Pt2–P2 92.79(17), C54–Pt2–Br2 89.49(17), P2–Pt2–Br2 177.69(4), C54–Pt2–Br1 172.85(17), P2–Pt2–Br1 93.51(4), Br2–Pt2–Br1 84.197(19), Pt1–Br1–Pt2 95.47(2), Pt2–Br2–Pt1 95.57(2), Mo1–C18–Pt1 167.3(3), Mo2–C54–Pt2 166.7(3).

Synthesis of $[MoPd(\mu\text{-}C)Br(CO)_2(dppe)(Tp^*)]$ (6) - A solution containing $[Mo_2Pd_2(\mu\text{-}C)_2(\mu\text{-}Br)_2(CO)_4(PPh_3)_2(Tp^*)_2]$ (**5a**: 101 mg, 0.056 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe: 84 mg, 0.211 mmol) in THF (10 mL) was stirred for 16 hours. The resulting orange solution was freed of volatiles under reduced pressure affording an orange solid. The resulting residue was immediately recrystallised from concentration of CH_2Cl_2 into *n*-hexane to give an orange powder. This was collected via vacuum filtration and thoroughly washed with EtOH (3 x 10 mL) and Et_2O (3 x 10 mL) before drying *in vacuo* to give the title compound as a pale orange powder (65 mg, 0.062 mmol, 55% isolated yield). Crystals suitable for X-ray diffraction were obtained by the slow evaporation of $CHCl_3$ at ambient temperature. IR (CH_2Cl_2, cm^{-1}): 1971 vs ν_{CO}, 1884 vs ν_{CO}. ^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ_H = 7.80 (m, 4 H, C_6H_5), 7.59 (m, 4 H, C_6H_5), 7.49 (m, 6 H, C_6H_5), 7.30 (m, 2 H, C_6H_5), 7.07 (br, 4 H, C_6H_5), 5.61 (s, 3 H, pzC*H*), 2.36 (s, 12 H, $pzCH_3$), 2.23 (s, 6 H, $pzCH_3$), 2.02, 1.96 (dt x 2, 2 H x 2, $^{1}J_{PH} \approx {}^{3}J_{HH}$ = 8 Hz, PCH_2) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 25 °C) δ_C = 375.9 (br. dd, $^{2}J_{CP}$ = 70, 8 Hz, Mo≡*C*–Pd), 231.1 (CO), 151.4, 151.0 [C^5(pz)], 145.0, 144.2 [C^3(pz)], 134.0, 133.9 [d x 2, $^{2}J_{CP}$ = 11, $C^{2,6}$(C_6H_5)], 131.8, 131.4 [s x 2, C^4(C_6H_5)], 130.7 [1C, d, $^{1}J_{CP}$ = 36, C^1(C_6H_5)], 129.2 [d, $^{2}J_{CP}$ = 10, $C^{3,5}$(C_6H_5)], 129.1 [1C, d, $^{1}J_{CP}$ = 36, C^1(C_6H_5)], 128.7 [d, $^{2}J_{CP}$ = 11, $C^{3,5}$(C_6H_5)], 106.2 105.9 [C^4(pz)], 23.5, 23.3 (d x 2, $^{1}J_{CP}$ = 12 Hz, PCH_2), 16.6, 14.4, 12.9, 12.6 ($pzCH_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): Two rotamers are apparent on this ^{31}P NMR timescale in a ratio of 1:7. Minor rotamer: δ_P = 46.48, 34.36 (d x 2, $^{2}J_{PP}$ = 33). Major rotamer: δ_P = 45.96 (d.br),

35.50 (d) ($^2J_{PP}$ = 31 Hz). MS (ESI, *m/z*): Found: 966.1305. Calcd for $C_{44}H_{46}BMoN_6O_2P_2Pd$ $[M–Br]^+$: 966.1365.

Crystal Structure of [MoPd(μ-C)Br(CO)$_2$(dppe)(Tp*)] (6) - A single crystal diffraction study confirmed the connectivity however the data set was of poor quality and although the refinement returned reasonable geometric parameters, these should be considered with appropriate caution. *Crystal data for* $C_{44}H_{46}BBrMoN_6O_2P_2Pd$, M_w = 1045.87, monoclinic, *C2/c*, *a* = 42.971(3) Å, *b* = 10.4460(5) Å, *c* = 20.5602(10) Å, β = 94.607(6)°, *V* = 9199.1(9) Å^3, *Z* = 8, ρ_{calc} = 1.510 Mg m^{-3}, μ(Cu *K*α) = 7.395 mm^{-1}, *T* = 150(0) K, clear light orange plate, 0.083 x 0.041 x 0.029 mm, 9109 independent measured reflections (θ_{max} = 74.3 °), R_1 = 0.096, wR_2 = 0.2556 for 4590 reflections [$I > 2\sigma(I)$], 529 parameters without restraints. CCDC 1588592.

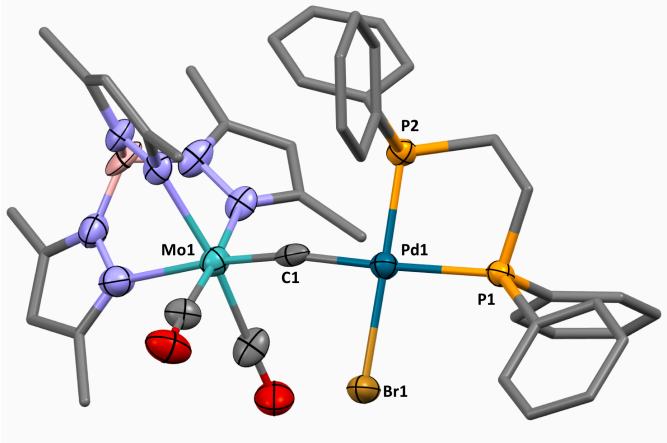

Figure S5. Molecular structure of [MoPd(μ-C)Br(CO)$_2$(dppe)(Tp*)] (**6**) in a crystal (50% displacement ellipsoids, hydrogen atoms and solvent omitted, pyrazolyl and phenyl groups simplified). Selected bond lengths (Å) and angles (°): Pd1–Br1 2.4778(17), Pd1–P1 2.376(3), Pd1–P2 2.264(3), Pd1–C1 2.008(14), Mo1–C1 1.787(14), P1–Pd1–Br1 94.95(9), P2–Pd1–Br1 177.35(10), P2–Pd1–P1 85.26(11), C1–Pd1–Br1 88.1(3), C1–Pd1–P1 170.5(3), C1–Pd1–P2 92.1(3), Mo1–C1–Pd1 167.9(7).

Synthesis of [WPd(μ–CPPh$_3$)Br(CO)$_2$(PPh$_3$)(Tp*)] (7) – A mixture of [W(≡CBr)(CO)$_2$(Tp*)] (**1b**: 152 mg, 0.242 mmol) and [Pd(PPh$_3$)$_4$] (294 mg, 0.254 μmol) in benzene (10 mL) was stirred for 20 hours at ambient temperature evolving from a yellow to a bright red colour. The solvent was removed under reduced pressure before recrystallisation by the addition of *n*-hexane into a benzene solution at 60 °C prior to cooling to ambient temperature, and then storage at 5 °C. This was performed twice, discarding the pale orange supernatant both times. The ensuing red solid was collected via vacuum filtration in an argon charged glove-box and washed with *n*-pentane (2 x 10 mL). This afforded the title compound as a red solid (193 mg, 0.153 mmol, 63% isolated yield). Crystals suitable for X-ray diffraction were grown from the vapour diffusion of *n*-hexane into a solution of **7** in benzene under an argon atmosphere at ambient temperature. IR (THF, cm^{-1}): 1940 vs ν_{CO}, 1910 br. ν_{CO}, 1809 sh ν_{CO}, 1797 br ν_{CO}. ^{1}H NMR (700 MHz, benzene-d$_6$, 50 °C) δ_H = 8.00 (m, 5 H, C_6H_5), 7.75 (m, 5 H, C_6H_5), 7.18 (m, overlapping solvent, 7 H, C_6H_5), 7.12 (t, $^1J_{HH}$ = 7, 3 H, C_6H_5), 7.01 (t, $^1J_{HH}$ = 7 Hz, 4 H, C_6H_5), 6.93 (m, 6 H, C_6H_5), 5.33 (s, 1 H, pzC*H*), 5.11 (s, 2 H, pzC*H*), 2.42 (s, 3 H, pzCH_3), 2.17 (s, 6 H, pzCH_3), 2.01 (s, 9 H, pzCH_3) ppm. ^{13}C{^{1}H} NMR (176 MHz, benzene-d$_6$, 50 °C, very poorly soluble, only limited data acquired) δ_C 153.0, 152.5, 144.5, 143.9 [$C^{3,5}$(pz)], 135.5 (m, C_6H_5), 135.4 (t, $^2J_{CP}$ = 6, PPh), 134.9 (m, C_6H_5), 133.9 (d, $^1J_{CP}$ = 19, C_6H_5), 132.6 (t, $^1J_{CP}$ = 23 Hz, C_6H_5), 131.8 (m, C_6H_5), 129.9 (C_6H_5), 128.9 (C_6H_5), 128.9 (C_6H_5), 128.6 (C_6H_5), 128.4 (C_6H_5), 107.3 (pz*C*H), 107.0 (pz*C*H), 17.8 (pzCH_3), 16.9 (pzCH_3), 15.9 (pzCH_3), 15.9 (pzCH_3), 15.2 (pzCH_3), 12.5 (pzCH_3), 12.5 (pzCH_3) ppm. ^{31}P NMR (162 MHz, benzene-d$_6$, 50 °C) δ_P = 10.73 (br, *C*PPh$_3$). ^{31}P NMR (162 MHz, benzene-d$_6$ + PPh$_3$, 25 °C) δ_P = 13.35 ($^2J_{CP}$ = 112 Hz, *C*PPh), –5.28 (s.br., PPh$_3$) ppm. MS (ESI, *m/z*): Found: 1179.2261. Calcd for $C_{54}H_{52}BN_6O_2P_2PdW$ $[M-Br]^+$: 1179.2256. Despite multiple attempts, a suitable sample could not be obtained for elemental analysis. While retaining it colour in air, this compound rapidly decomposes in the absence of excess PPh$_3$ (to *inter alia* **8**) in the following solvents: $CHCl_3$, CH_2Cl_2, MeOH, EtOH, Et_2O, MeCN and deuterated variants

Crystal data for $C_{54}H_{52}B$ $BrN_6O_2P_2PdW$, *M* = 1259.92, monoclinic, $P2_1/n$, *a* = 21.7995 (4) Å, *b* = 12.8236 (1) Å, *c* = 22.8740 (4) Å, β = 111.409 (2)º, *V* = 5953.16 (19) Å^3, *Z* = 4, ρ_{calc} = 1.406 Mg m^{-3}, μ(Cu *K*α) = 7.57 mm^{-1}, *T* = 150(0) K, plate {clear light red}, 10888 independent measured reflections (θ = 68.3 º), R_1 = 0.056, wR_2 = 0.166 for 10888 reflections [$I > 2\sigma(I)$], 619 parameters. CDCC 1988593.

[WPd(μ–CPPh$_3$)Br(CO)$_2$(Tp*)] (8) – To a flask charged with [W(≡CPPh$_3$)(CO)$_2$(Tp*)]Br ([**9**]Br: 101 mg, 0.125 mmol) and [Pd$_2$(dba)$_3$] (63 mg, 0.069 mmol) was added THF (5 mL) to give a purple solution that quickly evolved to an orange brown mixture. This was stirred vigorously for 90 minutes before volatiles were removed under reduced pressure to afford a brown residue. The residue was purified via flash chromatography (silica gel, 1–10 % THF/CH_2Cl_2 gradient elution) to elute a brown compound at 5% eluent strength. This was the major component and was freed of solvent before recrystallization from a mixture of CH_2Cl_2 and *n*-hexane to provide an orange powder that was collected via vacuum filtration, washed with *n*-hexane (3 x 10 mL) and *n*-pentane (5 mL) and dried in vacuo for 2 hours to give **8** (36 mg, 0.036 mmol, 29% isolated yield). IR (CH_2Cl_2, cm^{-1}): 1947 s ν_{CO}, 1791 s ν_{CO}. IR (ATR, cm^{-1}): 1930 s ν_{CO}, 1774 s ν_{CO}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ_H 7.62 – 7.51 (m, 9 H, C_6H_5), 7.39 – 7.31 (m, 6 H, C_6H_5), 5.73 (s, 1 H, pzC*H*), 5.49 (s, 2 H, pzC*H*), 2.45 (overlapping singlets, 6 H and 3 H, pzCH_3), 2.27 (s, 3 H, pzCH_3), 1.71 (s, 6 H, pzCH_3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C) δ_C = 238.7 ($^1J_{CW}$ = 147, CO), 232.1 ($^1J_{CW}$ = 178, *C*PPh$_3$), 153.0, 152.7, 145.4, 144.5 [$C^{3,5}$(pz)], 134.1 [d, $^2J_{CP}$ = 10, $C^{2,6}$(C_6H_5)], 133.0 [s, C^4(C_6H_5)], 129.1 [d, $^2J_{CP}$ = 12 Hz, $C^{3,5}$(C_6H_5)], 123.1 [d, $^1J_{CP}$ = 88 Hz, C^1[C_6H_5)], 107.4, 107.3 [C^4(pz)], 17.5, 15.3, 12.8 (pzCH_3). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C) δ_P = 7.18 ($^2J_{PW}$ =

119 Hz). MS (ESI, *m/z*): Found: 916.1357. Calcd for $C_{36}H_{37}BN_6O_2PPdW$ $[M+H]^+$: 916.1369.

Crystal data for $C_{36}H_{37}BBrN_6O_2PPdW\cdot(CHCl_3)_3$, M_w = 1355.76, triclinic, *P*-1 (No. 2), a = 11.4100 (4) Å, b = 13.4275 (5) Å, c = 17.2454 (5) Å, α = 85.274 (3)° , β = 87.055 (2)°, γ = 70.722 (3)°, V = 2485.43 (15) Å^3, Z = 2, ρ_{calc} = 1.812 Mgm^{-3}, μ(Cu $K\alpha$) = 4.03 mm^{-1}, T = 150(0) K, clear dark red block, 0.24 x 0.11 x 0.04 mm, 10177 independent measured reflections (θ_{max} = 26.4 °), R_1 = 0.040, wR_2 = 0.089 for 8724 reflections [$I > 2\sigma(I)$], 556 parameters without restraints. CDCC 1988594.

Synthesis of [W(≡C–PPh$_3$)(CO)$_2$(Tp*)[Br] ([9]Br) – A solution of [W(≡CBr)(CO)$_2$(Tp*)] (**1b**: 1.021 g, 1.620 mmol) and triphenylphosphine (1.773 g, 6.76 mmol) in acetonitrile (40 mL) was stirred at 40 °C for 20 hours. The resulting purple solution was evaporated under reduced pressure affording a purple oil. The resulting residue was purified via flash column chromatography (silica gel) initially eluting with neat CH_2Cl_2 before eluting with 5% THF/CH_2Cl_2. A purple band was collected, and the solvent was removed under reduced pressure to provide a purple oil. As recrystallization attempts resulted in more oils, ultra-sonication in *n*-hexane (10 mL) with mechanical crushing eventually resulted in a purple powder. This could be collected via vacuum filtration washing with *n*-hexane and *n*-pentane before being dried *in vacuo* to provide the title compound (784 mg, 0.88 mmol, 55% isolated yield). IR (CH_2Cl_2, cm^{-1}): 2025 s ν_{CO}, 1940 s ν_{CO}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H = 7.84 (m, 3 H, C_6H_5), 7.70 (m, 6 H, C_6H_5), 7.63 – 7.56 (m, 6 H, C_6H_5), 5.97 (s, 2 H, pzCH), 5.81 (s, 1 H, pzCH), 2.41 (s, 6 H, pzCH_3), 2.31 (s, 3 H, pzCH_3), 2.30 (s, 3 H, pzCH_3), 1.99 (s, 6 H, pzCH_3) ppm. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C) δ_H = 241.6 ($^1J_{CP}$ not resolved), 224.0 (WCO, $^1J_{CW}$ = 158), 153.1 151.5 147.1 146.4 [C^{3,5}(pz)], 135.2 [d, $^4J_{CP}$ = 3, C^4(C_6H_5)], 133.3 [d, $^3J_{CP}$ = 11, C^{3,5}(C_6H_5)], 130.6 [d, $^2J_{CP}$ = 13, C^{2,6}(C_6H_5)], 120.5 [d, $^1J_{CP}$ = 90 Hz, C^1(C_6H_5)], 108.2 107.7 [C^4(pz)], 16.7 15.4, 12.89, 12.85 (pz*C*H$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C) δ_P = 10.2 ($^1J_{PW}$ = 162 Hz) ppm. Data associated with the cation [**9**]$^+$ correspond to those reported by Templeton for the salt [**9**]PF_6.

Notes and references

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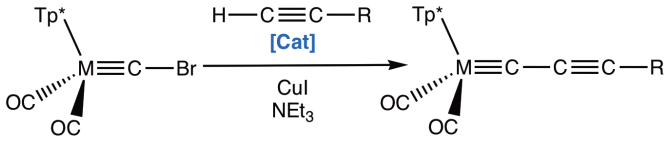
Table S1. C–C Cross coupling reactions employing isolated μ-carbido and phosphoniocarbyne complexes



Entry	M	R	[cat]	[cat] mol%	Yield (%)[a]
1	W	Ph	$[Pd(PPh_3)_4]$	10	78
2	W	$SiMe_3$	$[Pd(PPh_3)_4]$	10	91
3	W	Ph	**2b**	10	trace
4	W	$SiMe_3$	**2b**	10	trace
5	W	Ph	**2b**	100	43
6	W	$SiMe_3$	**2b**	100	34
7	Mo	Ph	**5a**	5	66
8	Mo	$SiMe_3$	**5a**	5	73
9	W	$SiMe_3$	**6**	10	trace
10	W	Ph	**7**	10	11
11	W	$SiMe_3$	**7**	10	72
12	W	Ph	**8**	10	trace
13	W	$SiMe_3$	**8**	10	trace
14	W	$SiMe_3$	$[Pd_2(dba)_3]$	10	trace

[a]Isolated yields from chromatography and recrystallization. Trace defines product was observed *via* UV irradiation on silica TLC plate, however was not generated in sufficient amounts to be isolated via column chromatography.