Electronic Supporting Information

Bimetallic ethynylanthracenyl functionalised carbynes

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Author Contributions

AFH was responsible for funding acquisition and project administration. BJF and SSW were responsible for conducting the experiments and the entire characterisation of the products. All authors contributed to the preparation of the original manuscripts and subsequent drafts.

Conflicts of interest

The authors declare no conflicts of interest.

Experimental

Unless otherwise stated, experimental work was carried out at room temperature under a dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques with dried and degassed solvents.

NMR spectra were obtained on a Bruker Avance 400 (¹H at 400.1 MHz, ¹³C at 100.6 MHz, ³¹P at 162.0 MHz) or a Bruker Avance 700 (1H at 700.0 MHz, 13C at 176.1 MHz, 31P 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 proteo-impurity (1H), the deuterated solvent itself (13C), or externally referenced (85% H_3PO_4 in H_2O for ${}^{31}P{}^{1}H$). 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 ¹⁸³W satellites. In some 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 ¹H NMR, 1 decimal place for ¹³C NMR) they are reported as having the same chemical shift. The abbreviation 'pz' is used to refer to the pyrazolyl rings on the Tp* ligands. Spectra provided generally correspond to samples obtained directly from chromatography and may contain residual solvent as recrystallised samples often display reduced solubility. Spectra include resonances in the region 4 < $\delta_{\rm H}$ < 5 due to the BH protons. These signals are especially broad due to the quadrupolar nature of $^{10}/^{11}\text{B}$ nuclei, compromising the precision of both the chemical shift and associated integrals. Being remote from the metal, in our experience these are of limited diagnostic value and are not included in the experimental details below.

Infrared spectra were obtained using a Shimadzu FTIR-8400 spectrometer. The strengths of IR absorptions are denoted by the abbreviations vs (very strong), s (strong), m (medium), w (weak), sh (shoulder) and br (broad). UV/Vis data were collected from solutions in 1 cm quartz cells using a PerkinElmer Lambda 465 spectophotometer. High-resolution electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile or methanol as the matrix.

Data for X-ray crystallography were collected with an Agilent SuperNova CCD diffractometer using Cu-K α radiation (λ = 1.54184 Å) and the CrysAlis PRO software.¹ The structures were solved by intrinsic phasing and refined by full-matrix leastsquares on F^2 using the SHELXT and SHELXL programs.² Hydrogen atoms were located geometrically and refined using a riding model. Diagrams were produced using the CCDC visualisation program Mercury.³

Cyclic voltammetry measurements were recorded using an e-corder 401 potentiostat system from eDaq Pty Ltd. Measurements were carried out at room temperature using Pt disc working-, Pt wire auxiliary- and Ag/AgCl or SCE reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.46 V (CH₂Cl₂) relative to saturated calomel electrode (ipc/ipa = 1, DEp 0.09–0.12 V).⁴ Scan rates were typically 100 mV s⁻¹. Electrochemical solutions contained 0.1 M [NBu₄][PF₆] and *ca* 10⁻³ M complex in reagent grade dichloromethane solvent. Solutions were purged and maintained under a nitrogen atmosphere.



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The complexes $[AuCl(PPh_3)]$,⁵ $[Pd_2(dba)_3 \cdot CHCl_3]$ (dba = dibenzylideneacetone),⁶ and $[Pd(PPh_3)_4]^7$ were prepared according to the literature methods. The gold complex $[AuCl(PCy_3)]$ was prepared by equimolar addition of PCy₃ to $[AuCl(SMe_2)]$.⁸ The synthesis of **1** was reported recently,⁹ details of which are reproduced below.

Synthesis of [W{=CC(C₆H₄)₂CBr}(CO)₂(Tp*)] (1). A solution of 9,10-dibromoanthracene (2.00 g, 5.95 mmol) in diethyl ether/tetrahydrofuran 1:1 (50 mL) at -78 °C was treated with nbutyllithium (1.6 M in hexanes, 3.8 mL, 6.1 mmol). The mixture was warmed to 0 °C and maintained at this temperature for 30 min. After this time, [W(CO)₆] (2.11 g, 6.00 mmol) was added, stirring was continued for 1 h at 0 °C, trifluoroacetic anhydride (0.83 mL, 6.0 mmol) was added, stirring continued for 30 min at 0 °C, and finally K[Tp*] (2.02 g, 6.00 mmol) was added and stirring continued for 16 h at RT to give an orange-brown mixture. The volatiles were removed under reduced pressure and the residue was subjected to column chromatography (60 x 5 cm silica gel column), eluting first with petroleum ether (40-60 °C) followed by 50% v/v CH₂Cl₂/petrol. A dark red band was collected and the volatiles were removed under reduced pressure. Recrystallisation from CH₂Cl₂/methanol gave a dark brown microcrystalline solid with a dark green shimmer of pure **1** (3.13 g, 3.89 mmol, 65%).

IR (CH₂Cl₂, cm⁻¹): 1977s, 1888s vCO. UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})$]: 282 (73700), 428 (14000), 453 (26300), 486 (28100). ¹H NMR (700 MHz, CDCl₃, 25 °C): $\delta_{\rm H}$ = 2.26 (s, 6 H, pzCH₃), 2.42 (s, 3 H, pzCH₃), 2.50 (s, 6 H, pzCH₃), 2.58 (s, 3 H, pzCH₃), 5.85 (s, 1 H, pzCH), 5.89 (s, 2 H, pzCH), 7.28-7.80 (br, 4 H, C₁₄H₈), 8.58, 8.60 (s x 2, 2 H, C₁₄H₈), 8.66–9.20 (br, 2 H, $C_{14}H_8$). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_H = 2.24 (s, 6 H, pzCH₃), 2.41 (s, 3 H, pzCH₃), 2.49 (s, 6 H, pzCH₃), 2.58 (s, 3 H, pzCH₃), 5.87 (s, 1 H, pzCH), 5.90 (s, 2 H, pzCH), 7.28, 7.48, 7.65, 7.83, 8.55 (2 d or m), 8.63, 9.27 (m.br, 1 H, $C_{14}H_8$). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): δ_{C} = 12.9, 13.2, 15.6, 16.1 (pzCH₃), 106.3, 106.7 (pzCH), 122.8 (CBr), 126.5, 127.1 (3 C), 127.5 (2 C), 128.2, 128.3, 130.1, 130.1, 131.9, 134.7 (br, C₁₄H₈), 140.7 (²J_{CW} = 40, W≡C**C**), 144.6, 145.3, 152.0, 152.2 (pzCH₃), 227.1 (¹J_{CW} = 166, CO), 278.5 (${}^{1}J_{CW}$ = 192, W=C). MS (ESI, m/z): Found: 804.1194. Calcd for $C_{32}H_{30}^{11}B^{79}BrN_6O_2^{184}W$ [M]⁺: 804.1216. Anal. Found: C, 47.71; H, 3.76; N, 10.02. Calcd for C₃₂H₃₀BBrN₆O₂W: C, 47.73; H, 3.76; N, 10.44%.

A crystal suitable for structure determination was grown by slow evaporation of a dichloromethane/methanol mixture. Crystal data for $C_{32}H_{30}BBrN_6O_2W$ ($M_w = 805.19 \text{ gmol}^{-1}$): triclinic, space group *P*-1 (no. 2), a = 10.4587(2), b = 11.4422(2), c = 13.8472(3) Å, $\alpha = 77.296(2)$, $\beta = 83.660(2)$, $\gamma = 72.785(2)^\circ$, V = 1542.29(6) Å³, Z = 2, T = 150.0(1) K, $\mu(CuK\alpha) = 8.777$ mm⁻¹, $D_{calc} = 1.734$ Mgm⁻³, 17784 reflections measured (8.252° $\leq 2\Theta \leq 147.754^\circ$), 6200 unique ($R_{int} = 0.0318$, $R_{sigma} = 0.0325$) which were used in all calculations. The final R_1 was 0.0259 ($I > 2\sigma(I)$) and wR_2 was 0.0702 (all data) for 398 refined parameters without restraints. CCDC 2077118.

Synthesis of $[W(\equiv CC_{14}H_8C\equiv CSiMe_3)(CO)_2(Tp^*)]$ (2). A solution of 1a (1.00 g, 1.24 mmol), ethynyltrimethylsilane (2.0

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mL, 14 mmol), $[Pd(PPh_3)_4]$ (150 mg, 0.130 mmol) and Cul (25 mg, 0.13 mmol) in toluene (50 mL) and triethylamine (50 mL) was heated under reflux for 16 h, during which time the solution turned dark red-brown. After cooling to RT, the volatiles were removed under reduced pressure and the residue was subjected to column chromatography (50 x 3 cm silica gel column), eluting initially with petroleum ether (40–60 °C) followed by 50% v/v CH₂Cl₂/petrol. A dark green band was collected and the volatiles were removed under reduced pressure. Recrystallisation of the residue from CH₂Cl₂/methanol gave a green-brown microcrystalline solid of pure **2** (0.81 g, 0.98 mmol, 79%).

IR (CH₂Cl₂, cm⁻¹): 1975s, 1887s v_{CO}. UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})]: =$ 285(76000), 442(16200), 470(34100), 504 (43300). ¹H NMR (700 MHz, CDCl₃, 25 °C): 0.41 (s, 9 H, SiCH₃), 2.22 (s, 6 H, pzCH₃), 2.40 (s, 3 H, pzCH₃), 2.48 (s, 6 H, pzCH₃), 2.55 (s, 3 H, pzCH₃), 5.83 (s, 1 H, pzCH), 5.86 (s, 2 H, pzCH), 7.30-7.65 (br, 4 H, C14H8), 8.55-8.61 (m, 2 H, C14H8), 8.60-9.14 (br, 2 H, C14H8). ¹H NMR (700 MHz, CDCl3, -40 °C): 0.40 (s, 9 H, SiCH₃), 2.19 (s, 6 H, pzCH₃), 2.39 (s, 3 H, pzCH₃), 2.47 (s, 6 H, pzCH₃), 2.55 (s, 3 H, pzCH₃), 5.84 (s, 1 H, pzCH), 5.87 (s, 2 H, pzCH), 7.24, 7.44, 7.61, 7.79, 8.42, 8.54, 8.62, 9.16 (br m, 1 H, C₁₄H₈). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): 0.25 (SiCH₃), 12.9, 13.2, 15.6, 16.1 (pzCH₃), 102.5 (C≡C), 106.3, 106.7 (pzCH), 108.1 (C≡C), 117.0 (CC≡C), 126.6 (2 C), 126.9, 127.1 (3 C), 127.3, 127.4, 130.8, 132.3, 132.5, 133.6 (br, C₁₄H₈), 141.3 (²J_{CW} = 40, W≡CC), 144.6, 145.3, 152.0, 152.3 (pzCCH₃), 227.3 (¹J_{CW} = 167, CO), 279.5 (W≡C). MS (ESI, m/z): Found: 822.2509. Calcd for C37H3911BrN6O2Si184W [M]+: 822.2506. Anal. Found: C, 53.94; H, 4.95; N, 9.72. Calcd for C₃₇H₃₉BN₆O₂SiW: C, 54.03; H, 4.78; N, 10.22%.

A crystal suitable for structure determination was grown by slow evaporation of a chloroform/ethanol mixture and proved to be a chloroform solvate. *Crystal data for* $C_{38}H_{40}BCl_3N_6O_2SiW$ ($M = 941.86 \text{ gmol}^{-1}$): monoclinic, space group $P2_1/c$ (no. 14), a = 14.5631(4), b = 10.4599(3), c = 26.8791(9) Å, $6 = 100.277(3)^\circ$, V = 4028.8(2) Å³, Z = 4, T = 150.0(1) K, μ (Mo K α) = 3.137 mm⁻¹, $D_{calc} = 1.553$ Mgm⁻³, 40625 reflections measured (6.838° $\leq 20 \leq 60.034^\circ$), 10171 unique ($R_{int} = 0.0342$, $R_{sigma} = 0.0392$) which were used in all calculations. The final R_1 was 0.0403 ($I > 2\sigma(I)$) and wR_2 was 0.0881 (all data) for 495 refined parameters with 15 restraints. CCDC 2079031.



Figure S1. Molecular structure of 2 in a crystal of $2 \cdot \text{CHCl}_3$ showing 50% displacement ellipsoids. Pyrazolyl rings are simplified and solvent is omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.831(4), C1–C4 1.431(5), C11–C18 1.437(6), C18–

C19 1.184(6), C19–Si1 1.845(5), W1–C1–C4 177.5(3), C11–C18–C19 177.6(5), C18–C19–Si1 177.3(5).

Synthesis of $[W(\equiv CC_{14}H_8C\equiv CH)(CO)_2(Tp^*)]$ (3). A mixture of 2 (1.00 g, 1.22 mmol) and K₂CO₃ (1.00 g, 7.24 mmol) in CH₂Cl₂ (25 mL), methanol (25 mL) and deionised water (0.5 mL) was stirred at RT for 3 h. After this time, the solution was filtered, additional methanol (75 mL) was added to the filtrate and the dichloromethane removed under reduced pressure. The resulting precipitate was collected by filtration, washed with methanol (3 x 5 mL) and *n*-pentane (3 x 5 mL) and dried *in vacuo* to give a shiny green microcrystalline solid of pure **3** (810 mg, 1.08 mmol, 88%).

IR (CH₂Cl₂, cm⁻¹): 1976s, 1888s v_{CO}. UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})]$: 273(42100), 284(56700), = 435(11100), 463(23000), 496 (28600). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.22 (s, 6 H, pzCH₃), 2.40 (s, 3 H, pzCH₃), 2.48 (s, 6 H, pzCH₃), 2.55 (s, 3 H, pzCH₃), 4.17 (s, 1 H, C≡CH), 5.83 (s, 1 H, pzCH), 5.86 (s, 2 H, pzCH), 7.32–7.75 (br, 4 H, C₁₄H₈), 8.36–9.30 (br, 2 H, C₁₄H₈), 8.60, 8.61 (d, ³J_{HH} = 8.6, 2 H, C₁₄H₈). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_{H} = 2.20 (s, 6 H, pzCH₃), 2.39 (s, 3 H, pzCH₃), 2.47 (s, 6 H, pzCH₃), 2.55 (s, 3 H, pzCH₃), 4.20 (s, 1 H, C≡CH), 5.84 (s, 1 H, pzCH), 5.87 (s, 2 H, pzCH), 7.26 (obs), 7.44, 7.61, 7.80, 8.44, 8.56, 8.64, 9.18 (br m, 8 H, C₁₄H₈). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): δ_{C} =12.9, 13.2, 15.6, 16.2 (pzCH₃), 81.5, 89.9 (C=C), 106.3, 106.7 (pzCH), 124.7 (CC=C), 126.6, 126.7, 127.1, 127.1 (4 C), 127.5, 130.8, 132.6, 132.8, 133.5 (br, C₁₄H₈), 141.5 (²*J*_{CW} = 40, W≡CC), 144.6, 145.3, 152.0, 152.3 (pzCCH₃), 227.2 $({}^{1}J_{CW} = 166, CO), 279.1 (W \equiv C)$. MS (ESI, m/z): Found: 750.2116. Calcd for $C_{34}H_{31}^{11}BN_6O_2^{184}W$ [M]+: 750.2111. Anal. Found: C, 54.42; H, 4.17; N, 10.97%. Calcd for C₃₄H₃₁BN₆O₂W: C, 54.43; H, 4.16; N, 11.20%.

A crystal suitable for structure determination was grown by slow evaporation of a dichloromethane/methanol mixture. *Crystal data for* $C_{34}H_{31}BN_6O_2W$ ($M_w = 750.31$ gmol⁻¹): monoclinic, space group $P2_1/c$ (no. 14), a = 18.9069(11) Å, b =9.5403(5), c = 18.2277(8), $\delta = 111.209(6)^\circ$, V = 3065.2(3) Å³, Z =4, T = 150.0(1) K, μ (Mo K α) = 3.810 mm⁻¹, $D_{calc} = 1.626$ Mgm⁻³, 12748 reflections measured ($6.824^\circ \le 2\Theta \le 58.748^\circ$), 6997 unique ($R_{int} = 0.0233$, $R_{sigma} = 0.0434$) which were used in all calculations. The final R_1 was 0.0317 ($I > 2\sigma(I)$) and wR_2 was 0.0690 (all data) for 458 refined parameters without restraints. CCDC 2079036.



Figure S2. Molecular structure of **3** in a crystal showing 50% displacement ellipsoids. Pyrazolyl rings are simplified and solvent is omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.825(4), C1–C4 1.444(5), C11–C18 1.420(5), C18–C19 1.191(6), W1–C1–C4 178.2(3), C11–C18–C19 177.1(5).

Synthesis of $[W(\equiv CC_{14}H_8C\equiv CAuPPh_3)(CO)_2(Tp^*)]$ (4a). A solution of 2 (200 mg, 0.243 mmol), [AuCl(PPh_3)] (120 mg, 0.242 mmol) and NaOH (50 mg, 1.3 mmol) in CH₂Cl₂ (10 mL) and methanol (10 mL) was stirred at RT in the dark for 3 h. After this time, additional methanol (40 mL) was added and the CH₂Cl₂ was removed under reduced pressure. The resulting bright red suspension was collected by filtration, washed with methanol (3 x 10 mL) and *n*-pentane (3 x 5 mL) and dried *in vacuo* to give a bright red solid of pure **4a** (267 mg, 0.221 mmol, 91%).

IR (CH₂Cl₂, cm⁻¹): 1972s, 1883s v_{CO}. UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})]$: = 287(138000), 454(37600), 482(78400), 517 (94300). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ_H = 2.24 (s, 6 H, pzCH₃), 2.39 (s, 3 H, pzCH₃), 2.46 (s, 6 H, pzCH₃), 2.54 (s, 3 H, pzCH₃), 5.81 (s, 1 H, pzCH), 5.84 (s, 2 H, pzCH), 7.36–7.73 (m, 19 H, C₁₄H₈ & C₆H₅), 8.30–9.40 (br, 2 H, C₁₄H₈), 8.90 (m, 2 H, C14H8). ¹H NMR (700 MHz, CDCl3, -40 °C): δ_{H} = 2.20 (s, 6 H, pzCH₃), 2.38 (s, 3 H, pzCH₃), 2.45 (s, 6 H, pzCH₃), 2.54 (s, 3 H, pzCH₃), 5.83 (s, 1 H, pzCH), 5.85 (s, 2 H, pzCH), 7.20, 7.37 (br, 1 H, C14H8), 7.44-7.65 (m, 16 H, C6H5 & C14H8), 8.41, 8.86, 8.93, 9.16 (br, 1 H, C₁₄H₈). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): δ_C = 12.9, 13.2, 15.6, 16.2 (pzCH₃), 101.3 (d, ³J_{CP} = 26, C=CAu), 106.2, 106.6 (pzCH), 120.3, 125.8, 126.2 (2 C), 126.9 (2 C), 127.2, 128.4, 128.5 (br, $C_{14}H_8$), 129.2 [d, ${}^{2}J_{CP}$ = 11, $C^{2,6}(C_6H_5)$], 129.5 [d, ${}^{1}J_{CP}$ = 56, C¹(C₆H₅)], 131.1 (br, C₁₄H₈), 131.7 [C⁴(C₆H₅)], 132.5, 132.6, 133.9 (br, $C_{14}H_8$), 134.4 [d, ${}^{2}J_{CP}$ = 14, $C^{3,5}(C_6H_5)$], 139.5 (${}^{2}J_{CW}$ = 40, W=CC), 144.4, 145.2 (pzCCH₃), 148.1 (d, ${}^{2}J_{CP}$ = 142, C=CAu), 152.1, 152.2 (pzCCH₃), 227.3 (${}^{1}J_{CW}$ = 167, CO), 281.2 (W=C). ³¹P{¹H} NMR (283 MHz, CDCl₃, -40 °C): δ_P = 42.0 (s). MS (ESI, *m/z*): Found: 1208.2634. Calcd for C₅₂H₄₅¹¹BN₆O₂P¹⁸⁴W¹⁹⁷Au [M]⁺: 1208.2610. Anal. Found: C, 51.75; H, 3.76; N, 6.85. Calcd for C₅₂H₄₅AuBN₆O₂PW: C, 51.68; H, 3.75; N, 6.95%.

Synthesis of $[W(\equiv CC_{14}H_8C\equiv CAuPCy_3)(CO)_2(Tp^*)]$ (4b). A solution of 2 (200 mg, 0.243 mmol), [AuCl(PCy_3)] (124 mg, 0.242 mmol) and NaOH (50 mg, 1.3 mmol) in CH₂Cl₂ (10 mL) and methanol (10 mL) was stirred at RT in the dark for 3 h. After this time, additional methanol (40 mL) was added and the CH₂Cl₂ was removed under reduced pressure. The resulting orange-brown suspension was collected by filtration, washed with methanol (3 x 10 mL) and *n*-pentane (3 x 5 mL) and dried in vacuo to give a dark orange-brown solid of pure **4b** (260 mg, 0.210 mmol, 86%).

IR (CH₂Cl₂, cm⁻¹): 1971s, 1883s v_{CO} UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})$]: = 287(85300), 454sh(21800), 484(43900), 516 (51600). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_{H} = 1.22–1.39 (m, 9 H, C₆H₁₁), 1.49–1.62 (m, 6 H, C₆H₁₁), 1.71–1.81 (m, 3 H, C₆H₁₁), 1.82–1.94 (m, 6 H, C₆H₁₁), 2.00–2.16 (m, 9 H, C₆H₁₁), 2.23 (s, 6 H, pzCH₃), 2.39 (s, 3 H, pzCH₃), 2.46 (s, 6 H, pzCH₃), 2.54 (s, 3 H, pzCH₃), 5.81 (s, 1 H, pzCH), 5.84 (s, 2 H, pzCH), 7.23–7.72 (br, 4 H, C₁₄H₈), 8.50–9.20 (br, 2 H, C₁₄H₈), 8.89 (m, 2 H, C₁₄H₈). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_{H} = 1.22–1.35 (m, 9 H, C₆H₁₁), 1.46–1.59 (m, 6 H, C₆H₁₁), 1.68–1.76 (m, 3 H, C₆H₁₁), 1.82–1.91 (m, 6 H, C₆H₁₁), 1.98–2.10 (m, 9 H, C₆H₁₁), 2.21 (s, 6 H, pzCH₃), 2.38 (s, 3 H, pzCH₃), 2.45 (s, 6 H, pzCH₃), 2.53 (s, 3 H, pzCH₃), 5.83 (s, 1 H, pzCH), 5.84 (s, 2 H, pzCH), 7.18, 7.36,

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7.54, 7.73, 8.39, 8.83, 8.91, 9.14 (br, 1 H, $C_{14}H_8$). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): δ_C = 12.9, 13.2, 15.6, 16.2 (pzCH₃), 25.9 (s, C₆H₁₁), 27.1 (d, ²J_{CP} = 12, C₆H₁₁), 30.6 (C₆H₁₁), 32.8 (d, ¹J_{CP} = 28, PCH), 100.7 (d, ³J_{CP} = 21, C≡CAu), 106.2, 106.6 (pzCH), 120.9 (CC≡C), 124.7, 125.6, 126.0, 126.1, 126.8 (2 C), 127.1, 128.6, 131.1, 132.4 (2 C), 134.0 (br, C₁₄H₈), 139.2 (W≡CC), 144.4, 145.2, 152.2, 152.2 (pzCCH₃), 227.4 (CO), 281.6 (W≡C). C≡CAu not unequivocally identified; anthracenyl carbons assigned tentatively due to low signal-to-noise. ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ_P = 56.1 (s). MS (ESI, *m*/z): Found: 1226.4052. Calcd for C₅₂H₆₃¹¹BN₆O₂P¹⁸⁴W¹⁹⁷Au [M]⁺: 1226.4018. Anal. Found: C, 51.03; H, 5.19; N, 6.88. Calcd for C₅₂H₆₃AuBN₆O₂PW: C, 50.91; H, 5.18; N, 6.85%.

A crystal suitable for structure determination was grown by slow evaporation of a CH₂Cl₂/cyclohexane solution. This was found to contain one cyclohexane and two dichloromethane molecules of solvation. Both solvents were found to be disordered, the cyclohexane specifically across two positions and requiring liberal use of restraints. The CH₂Cl₂ was found to be very highly disordered and necessitated the use of a solvent mask; the data which follow are presented excluding CH₂Cl₂. Crystal data for $C_{58}H_{75}AuBN_6O_2PW$ ($M_w = 1310.83$ gmol⁻¹): monoclinic, space group $P2_1/c$ (no. 14), a = 20.7071(9), b =114.172(5)°, V = 16.1172(4), *c* = 21.1538(9) Å*,* β = 6440.9(5) Å³, Z = 4, T = 150.0(1) K, μ (MoKα) = 4.124 mm⁻ ¹, D_{calc} = 1.352 Mgm⁻³, 24624 reflections measured (6.646° \leq 2 Θ \leq 56.516°), 13018 unique (R_{int} = 0.0377, R_{sigma} = 0.0732) which were used in all calculations. The final R_1 was 0.0510 ($l > 2\sigma(l)$) and wR₂ was 0.1110 (all data) for 790 refined parameters with 272 restraints. CCDC 2079037.



Figure S3. Molecular structure of **4b** in a crystal of **4b**. $(CH_2Cl_2)_2$. (C_6H_{12}) . showing 50% displacement ellipsoids. Pyrazolyl rings are simplified and solvent is omitted for clarity. Selected distances [Å] and angles [°]: W1–C1 1.832(8), C1–C4 1.433(10), C11–C18 1.438(10), C18–C19 1.196(10), C19–Au1 2.010(7), Au1–P1 2.294(2), W1–C1–C4 178.0(6), C11–C18–C19 176.5(8), C18–C19–Au1 176.5(7), C19–Au1–P1 176.2(2).

Synthesisof $[W_2[\mu = CC(C_6H_4)_2CC=CC(C_6H_4)_2CC=)(CO)_4(Tp^*)_2]$ (5). A solution of 3(500 mg, 0.666 mmol) and Cul (13 mg, 0.068 mmol) intetrahydrofuran (20 mL) and triethylamine (20 mL) were stirredat RT overnight without protection from the atmosphere. Afterthis time, the volatiles were removed under reduced pressureand the residue was subjected to column chromatography (60 x5 cm silica gel column), eluting first with petroleum ether (40–60 °C) followed by 50% v/v CH_2Cl_2/petrol. An imperial purpleband was collected and the volatiles were removed underreduced pressure. Recrystallisation from CH_2Cl_2/methanol gave

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a black/purple microcrystalline solid of pure **7** (322 mg, 0.215 mmol, 65%).

IR (CH₂Cl₂, cm⁻¹): 1976s, 1889s v_{CO}. UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})$] = 285(86800), 539br(58900), 600br (48600). ^1H NMR (700 MHz, CDCl₃, 25 °C): δ_{H} = 2.26 (s, 12 H, pzCH₃), 2.42 (s, 6 H, pzCH₃), 2.50 (s, 12 H, pzCH₃), 2.57 (s, 6 H, pzCH₃), 5.84 (s, 2 H, pzCH), 5.89 (s, 4 H, pzCH), 7.37–7.87 (br, 8 H, C₁₄H₈), 8.50–9.30 (br, 4 H, C₁₄H₈), 8.73 (d, ³J_{HH} = 8.8, 4 H, C14H8). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_{H} = 2.24 (s, 12 H, pzCH₃), 2.41 (s, 6 H, pzCH₃), 2.49 (s, 12 H, pzCH₃), 2.57 (s, 6 H, pzCH₃), 5.86 (s, 2 H, pzCH), 5.90 (s, 4 H, pzCH), 7.30, 7.53, 7.72, 7.86, 8.49, 8.70, 8.78, 9.23 (br m, C14H8). 13C{1H} NMR (176 MHz, CDCl₃, -40 °C): δ_{C} = 12.9, 13.2, 15.6, 16.2 (pzCH₃), 84.5, 87.4 (C≡C), 106.3, 106.8 (pzCH), 115.8 (CC≡C), 126.8, 127.1, 127.2, 127.3 (3 C), 127.4, 127.8, 130.9, 133.4, 133.7 (2 C), 141.9 (²J_{CW} = 40, W=CC), 144.7, 145.4, 152.0, 152.3 (pzCCH₃), 227.4 (¹J_{CW} = 166, CO), 279.0 (W=C). MS (ESI, m/z): Found: 1498.4082. Calcd for $C_{68}H_{60}^{11}B_2N_{12}O_4^{184}W_2$ [M]⁺: 1498.4065. Anal. Found: C, 54.53; H, 4.29; N, 10.43. Calcd for C₆₈H₆₀B₂N₁₂O₄W₂: C, 54.50; H, 4.04; N, 11.22%.

A crystal suitable for structure determination was grown by slow evaporation of a chloroform/ethanol mixture and proved be а chloroform disolvate. Crystal data for to C₇₀H₆₂B₂Cl₆N₁₂O₄W₂ (*M_w* = 1737.33 gmol⁻¹): monoclinic, space group P21/n (no. 14), a = 10.5318(2), b = 10.2942(2), c = 32.4695(12) Å, $\beta = 95.664(3)^\circ$, $V = 3503.04(16) Å^3$, Z = 2, T = 1000150.0(1) K, μ (Mo K α) = 3.568 mm⁻¹, D_{calc} = 1.647 Mgm⁻³, 23685 reflections measured (6.928° \leq 20 \leq 56.516°), 7560 unique $(R_{int} = 0.0531, R_{sigma} = 0.0673)$ which were used in all calculations. The final R_1 was 0.0656 ($I > 2\sigma(I)$) and wR_2 was 0.1199 (all data) for 443 refined parameters without restraints. CCDC 2079038.



Figure S4. Molecular structure of **5** in a crystal of **5** ·(CHCl₃)₂ showing 50% displacement ellipsoids. Only one-half of the molecule is crystallographically unique. Pyrazolyl rings are simplified for clarity. Selected distances [Å] and angles [°]: W1–C1 1.844(7), C1–C4 1.433(9), C11–C18 1.428(9), C18–C19 1.205(9), C19–C19' 1.369(14), W1–C1–C4 171.4(6), C11–C18–C19 176.6(8), C18–C19–C19' 179.6(12). Inset: orthogonal view and space-filling diagram.

Synthesisof $[W_2{\mu=\Xi CC(C_6H_4)_2CC \Xi CC_6H_4C \Xi C-C(C_6H_4)_2CC \Xi)(CO)_4(Tp^*)_2]$ C(C_6H_4)_2CC \Xi)(CO)_4(Tp^*)_2](5). A solution of 6 (200 mg, 0.267 mmol), p-diiodobenzene (44 mg, 0.133 mmol), $[Pd(PPh_3)_4]$ mg, 0.027 mmol) and Cul (5 mg, 0.03 mmol) in degassed tetrahydrofuran (20 mL) and triethylamine (20 mL) were stirred at RT for 6 h. After this time, the volatiles were removed under

reduced pressure and the residue was subjected to column chromatography (60 x 5 cm silica gel column), eluting first with petroleum ether (40–60 °C) followed by 50% v/v CH₂Cl₂/petrol. A 'neon pink' band was collected and the volatiles were removed under reduced pressure. Recrystallisation from CH₂Cl₂/methanol gave bright pink crystals (or a green-brown amorphous solid if the CH₂Cl₂ is removed rapidly under reduced pressure) of pure **6** (140 mg, 0.0889 mmol, 67%).

IR (CH₂Cl₂, cm⁻¹): 1975s, 1888s v_{CO} . UV-Vis [CH₂Cl₂: $\lambda_{max}/nm(\epsilon/cm^{-1}Lmol^{-1})] = 288(107300), 335(40500), ca$ 526sh(79300), 554(1800). ¹H NMR (700 MHz, CDCl₃, 25 °C): δ_H = 2.25 (s, 12 H, pzCH₃), 2.41 (s, 6 H, pzCH₃), 2.49 (s, 12 H, pzCH₃), 2.56 (s, 6 H, pzCH₃), 5.84 (s, 2 H, pzCH), 5.88 (s, 4 H, pzCH), 7.35-7.75 (br, 8 H, C₁₄H₈), 7.84 (s, 4 H, C₆H₄), 8.40-9.30 (br, 4 H, C₁₄H₈), 8.71 (d, ³J_{HH} = 8.7, 4 H, C₁₄H₈). ¹H NMR (700 MHz, CDCl₃, -40 °C): δ_H = 2.26 (s, 12 H, pzCH₃), 2.40 (s, 6 H, pzCH₃), 2.48 (s, 12 H, pzCH₃), 2.56 (s, 6 H, pzCH₃), 5.85 (s, 2 H, pzCH), 5.89 (s, 4 H, pzCH), 7.29, 7.50, 7.68 (br m, $C_{14}H_8$), 7.84 (s, 6 H, C_6H_4 and obs C₁₄H₈), 8.47, 8.68, 8.76, 9.21 (br m, C₁₄H₈). ¹³C{¹H} NMR (176 MHz, CDCl₃, -40 °C): δ_{C} = 12.9, 13.2, 15.6, 16.2 (pzCH₃), 90.1 (*C*≡CC₆H₄), 102.4 (C≡*C*C₆H₄), 106.3, 106.8 (pz*C*H), 117.0 (*C*C≡*C*), 123.5 (*i*-C₆H₄), 126.6 (2 C), 127.1, 127.2 (4 C), 127.6, 131.0 (br, $C_{14}H_8),\ 131.7$ (o- $C_6H_4),\ 132.1,\ 132.3,\ 133.8$ (br, $C_{14}H_8),\ 141.3$ $(^2J_{\rm CW}$ = 40, W=CC), 144.6, 145.3, 152.0, 152.3 (pzCCH_3), 227.3 (CO), 279.4 (W≡C). MS (ESI, m/z): Found: 1574.4398. Calcd for C₃₄H₁₈ [M]⁺: C₇₄H₆₄¹¹B₂N₁₂O₄¹⁸⁴W₂ 1574.4378. Anal. Found: C, 56.50; H, 4.33; N, 10.26. Calcd for C₇₄H₆₄B₂N₁₂O₄W₂: C, 56.44; H, 4.10; N, 10.67%.

A crystal suitable for structure determination was grown from a CH₂Cl₂/CH₃CN/*n*-hexane and was found to contain regions of highly disordered solvent which could not be adequately modelled. A solvent mask was applied and the data which follows is presented sans solvent. *Crystal data for* $C_{74}H_{64}B_2N_{12}O_4W_2$ (M_w =1574.69 gmol⁻¹): monoclinic, space group P_{21}/c (no. 14), a = 22.7180(16), b = 9.4131(4), c =18.4744(16) Å, $b = 112.982(10)^\circ$, V = 3637.1(5) Å³, Z = 2, T =150.0(1) K, μ (MoK α) = 3.215 mm⁻¹, $D_{calc} = 1.438$ Mgm⁻³, 14153 reflections measured (6.504° $\leq 20 \leq 56.594^\circ$), 7366 unique ($R_{int} = 0.0341$, $R_{sigma} = 0.0590$) which were used in all calculations. The final R_1 was 0.0454 ($I > 2\sigma(I)$) and wR_2 was 0.1037 (all data) for 434 refined parameters without restraints. CCDC 2079039.

	Table S1. Selected cyclic voltammetry data. See Figs S38-S43				
	E _{ox} ^a	Ered ^a	E½ ª		
2	0.56	0.49	0.53		
3	0.56	0.49	0.53		
4a	0.77	0.49	0.63		
	0.66	0.39	0.53		
40	0.69-0.77	0.47	ca 0.63,		
5	0.76	0.67	0.72		
6	0.76	0.65	0.71		

 a Estimated values measured in CH_2Cl_2/[NBu4][PF_6] 0.1 M at 25 *C at 100 mV s^-1, relative to the ferrocene/ferrocenium redox couple at 0.46 V (CH_2Cl_2).

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Figure S16. ¹H NMR (700 MHz, CDCl₃, -40 °C, δ) of [W(≡CC₁₄H₈C≡CAuPCy₃)(CO)₂(Tp*)] (**4b**).

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Figure S18. ${}^{31}P{}^{1}H$ NMR (162 MHz, CDCl₃, 25 °C, δ) of [W(=CC₁₄H₈C=CAuPCy₃)(CO)₂(Tp*)] (4b).

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Figure S23. ¹H NMR (700 MHz, CDCl₃, -40 °C, δ) of [W₂(µ-=CC₁₄H₈C=CC₆H₄-4-C=CC₁₄H₈C=)(CO)₄(Tp*)₂] (6).

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Figure S25. Infrared spectrum (CH₂Cl₂, cm⁻¹) of [W(\equiv CC₁₄H₈C \equiv CSiMe₃)(CO)₂(Tp^{*})] (2).

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Figure S26. Infrared spectrum (CH₂Cl₂, cm⁻¹) of [W(\equiv CC₁₄H₈C \equiv CH)(CO)₂(Tp*)] (3).

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Figure S27. Infrared spectrum (CH₂Cl₂, cm⁻¹) of [W(\equiv CC₁₄H₈C \equiv CAuPPh₃)(CO)₂(Tp*)] (4a).

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Figure S28. Infrared spectrum (CH₂Cl₂, cm⁻¹) of [W(\equiv CC₁₄H₈C \equiv CAuPCy₃)(CO)₂(Tp^{*})] (4b).

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Figure S29. Infrared spectrum (CH₂Cl₂, cm⁻¹) of $[W_2(\mu = CC_{14}H_8C = CC_{14}H_8C =)(CO)_4(Tp^*)_2]$ (5).

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Figure S31. Electronic spectrum (CH₂Cl₂) of [W(\equiv CC₁₄H₈C \equiv CSiMe₃)(CO)₂(Tp*)] (2).



Figure S32. Electronic spectrum (CH₂Cl₂) of [W(\equiv CC₁₄H₈C \equiv CH)(CO)₂(Tp*)] (3).

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Figure S33. Electronic spectrum (CH₂Cl₂) of [W(\equiv CC₁₄H₈C \equiv CAuPPh₃)(CO)₂(Tp*)] (4a).



Figure S34. Electronic spectrum (CH₂Cl₂) of [W(\equiv CC₁₄H₈C \equiv CAuPCy₃)(CO)₂(Tp*)] (4b).

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Figure S35. Electronic spectrum (CH₂Cl₂) of $[W_2(\mu=\exists CC_{14}H_8C \exists CC_{14}H_8C \exists)(CO)_4(Tp^*)_2]$ (5).

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Figure S36. Electronic spectrum (CH₂Cl₂) of $[W_2(\mu = \Xi CC_{14}H_8C \equiv CC_6H_4 - 4 - C \equiv CC_{14}H_8C \equiv)(CO)_4(Tp^*)_2]$ (6).

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 $\label{eq:Figure S37.} Stacked Electronic Spectra (CH_2Cl_2, nm) for compounds 2–6, adjusted relative to mol of tungsten/anthracenyl groups and the statement of the statement$

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Figure S40. Cyclic Voltammogram (CH₂Cl₂/[NBu₄][PF₆] 0.1 M) at 25 °C at 100 mV s⁻¹ of [W{ \equiv CC(C₆H₄)₂CCAuPPh₃)(CO)₂(Tp*)] (4a)

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Figure S41. Cyclic Voltammogram (CH₂Cl₂/[NBu₄][PF₆] 0.1 M) at 25 °C at 100 mV s⁻¹ of [W{ \equiv CC(C₆H₄)₂CCAuPCy₃)(CO)₂(Tp*)] (4b)

Potential (V)

Figure S42. Cyclic Voltammogram (CH₂Cl₂/[NBu₄][PF₆] 0.1 M) at 25 °C at 100 mV s⁻¹ of [W₂{µ-=CC(C₆H₄)₂C=C=C(C6H₄)₂CC=)(CO)₄(Tp*)₂] (5)

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Figure S43. Cyclic Voltammogram (CH₂Cl₂/[NBu₄][PF₆] 0.1 M) at 25 °C at 100 mV s⁻¹ of [W₂{ μ =CC(C₆H₄)₂C=CC₆H₄C=C(C₆H₄)₂CC=)(CO)₄(Tp*)₂] (**6**).

Figure S44. Mass spectrum of $[W{\equiv CC(C_6H_4)_2CBr}(CO)_2(Tp^*)]$ (1).

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Figure S45. Observed and simulated isotopic distribution for $[W{\equiv CC(C_6H_4)_2CBr}(CO)_2(Tp^*)]$ (1).

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Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 23.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 386 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-50 H: 0-38 11B: 1-1 N: 0-6 O: 0-2 79Br: 0-1 81Br: 0-1 184W: 0-1

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Figure S47. Mass spectrum of $[W(\equiv CC(C_6H_4)_2CC\equiv CSiMe_3)(CO)_2(Tp^*)]$ (2).

Single Mas	s Analysis
------------	------------

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 25.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 526 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-50 H: 0-50 11B: 0-1 N: 0-8 O: 0-2 Si: 0-1 184W: 0-1 BF122A3/AJ 04-Dec-2020 66171 1165 48 (0.113) Cm (36:110) SYNAPTG2-Si#NotSet 1: TOF MS ES+

Figure S48. Elemental Composition Report for [W{≡CC(C₆H₄)₂CCCSiMe₃}(CO)₂(Tp*)] (2).

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10:35:46

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Figure S49. Observed and simulated isotopic distribution for [W(=CC(C₆H₄)₂CC=CSiMe₃)(CO)₂(Tp*)] (2).

Figure S50. Mass spectrum of $[W \{ \equiv CC(C_6H_4)_2CCCH \}(CO)_2(Tp^*)]$ (3).

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Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 25.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 120 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-40 H: 0-40 11B: 0-1 N: 0-6 O: 0-2 184W: 0-1 BF123A/AJ 01-Dec-2020 66163 SYNAPTG2-Si#NotSet 1: TOF MS ES+

Figure S51. Elemental Composition Report for $[W{\equiv}CC(C_6H_4)_2CCCH}(CO)_2(Tp^*)]$ (3).

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1152 80 (0.174) Cm (80:91)

Figure S52. Observed and simulated isotopic distribution for $[W(\equiv CC(C_6H_4)_2CC\equiv CH)(CO)_2(Tp^*)]$ (3).

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Figure S53. Mass spectrum of $[W{\equiv}CC(C_6H_4)_2CC\equiv}CAuPPh_3](CO)_2(Tp^*)]$ (4a).

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1: TOF MS ES+

100-

%

Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 37.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

444 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-60 H: 0-50 11B: 0-1 N: 0-6 O: 0-2 P: 0-1 184W: 0-1 197Au: 0-1

10:54:21 1168 48 (0.113) Cm (48:69)

5.40e+004

1208.2634 1207.2621 1210.2672 1206.2585 1211.2709

1213.2817 1215.3082 1212.2728 1216.3229 1205.2688 1202.2281 1200.2334 0----- m/z 1200.0 1202.0 1204.0 1206.0 1208.0 1210.0 1212.0 1214.0 1216.0 -1.5 Minimum: Maximum: 5.0 3.0 37.0 PPM DBE i-FIT Conf(%) Formula Mass Calc. Mass mDa Norm 1208.2634 1208.2610 2.4 2.0 36.5 1847.5 C52 H45 11B N6 O2 P 184W 197Au n/a n/a

 $\label{eq:Figure S54. Elemental Composition Report for \left[W\left\{ {\equiv} CC(C_6H_4)_2CC{\equiv}CAuPPh_3\right\}(CO)_2(Tp^*)\right] (4a).$

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Figure S55. Observed and simulated isotopic distribution for [W(=CC(C₆H₄)₂CC=CAuPPh₃)(CO)₂(Tp*)] (4a).

Figure S56. Mass spectrum of $[W{\equiv CC(C_6H_4)_2CC\equiv CAuPCy_3}(CO)_2(Tp^*)]$ (4b).

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Chemical Communications

Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 30.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 1489 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-70 H: 0-65 11B: 0-1 N: 0-6 O: 0-2 P: 0-3 184W: 0-1 197Au: 0-1

BF123C/AJ 08-Dec-2020 11:46:09 1183 51 (0.119) Cm (48:51) 66198 SYNAPTG2-Si#NotSet 1: TOF MS ES+ 7.87e+004 1226.4052 100-1225.4038 ,1227,4083 1229.4110 1224.4005 %-1230.4166 1223.4061 1215.5846 1237,4404 1241.4138 .1231.4183 1217.4294 1239.4429 m/z 1217.5 1220.0 1222.5 1225.0 1227.5 1230.0 1232.5 1212.5 1215.0 1235.0 1237.5 1240.0 1242.5 Minimum: -1.55.0 3.0 Maximum: 30.0 Calc. Mass mDa PPM DBE i-FIT Conf(%) Formula Mass Norm 1226.4052 1226.4018 3.4 2.8 27.5 533.0 n/a C52 H63 11B N6 O2 P 184W 197Au n/a

 $\label{eq:Figure S57. Elemental Composition Report for \ [W \{ \equiv CC(C_6H_4)_2CC \equiv CAuPCy_3\}(CO)_2(Tp^*)] \ (\textbf{4b}).$

Figure S58. Observed and simulated isotopic distribution for $[W(\equiv CC(C_6H_4)_2CC\equiv CAuPCy_3)(CO)_2(Tp^*)]$ (4b).

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Figure S59. Mass spectrum of $[W_2{\mu=\Xi CC(C_6H_4)_2C\Xi CC\Xi C(C6H_4)_2CC\Xi)(CO)_4(Tp^*)_2]$ (5)

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Figure S60. Elemental Composition Report for $[W_2{\mu=CC(C_6H_4)_2C=C(C6H_4)_2CC=)(CO)_4(Tp^*)_2]$ (5)

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Figure S61. Observed and simulated isotopic distribution for $[W_2\{\mu=\Xi CC(C_6H_4)_2C\Xi CC=C(C6H_4)_2CC\Xi)(CO)_4(Tp^*)_2]$ (5)

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Chemical Communications

Elemental Composition Report

Single Mass Analysis

Tolerance = 3.0 PPM / DBE: min = -1.5, max = 55.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions 505 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-76 H: 0-80 11B: 0-2 N: 0-12 O: 0-4 184W: 0-2 BF125D2/AJ 08-Dec-2020 2020 RSC Small molecule sample list 1185 65 (0.145) Cm (41:116) SYNAPTG2-SillNotSet 1: TOF MS ES+

Figure S63. Elemental Composition Report for $[W_2\{\mu=\Xi CC(C_6H_4)_2 C \Xi C(C_6H_4)_2 C C(C_6H_4)_2 C C(C_6H_4)_2 C C(C_6H_4)_2 C(C_6H_4)_2 C(C_6H_4)_2 C(C_6H_4)_2 C(C_6H_4)_2 C(C_6H_4)_2 C$

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Figure S64. Observed and simulated isotopic distribution for $[W_2{\mu=\exists CC(C_6H_4)_2C \exists CC_6H_4}C \exists C(C_6H_4)_2CC \exists)(CO)_4(Tp^*)_2]$ (6).

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