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Figure S6. ¹H NMR Spectrum of [MoPt(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2a) in CDCl₃, 25 °C

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Figure S8. ¹⁹⁵Pt{¹H} NMR Spectrum of [MoPt(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2a)) in CDCl₃, 25 °C

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Figure S9. ¹³C{¹H} NMR Spectrum of [MoPt(μ -C)(CO)₂(PPh₃)₂(Tp^{*})] (2a)) in CDCl₃, 25 °C

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Figure S10. ¹³C{¹H} NMR Spectrum of [MoPt(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2a) in CDCl₃, 25 °C – Phenyl region

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Figure S10. RSC/RSB Joint Mass Spectrometry Facility Analysis Report: [MoPt(µ-C)(CO)₂(PPh₃)₂(Tp*)] (2a)

Instrument: Orbitrap QE, +ve mode ESI at 280k resolution Analysis Date: 2019-08-15

Theoretical m/z (most abundant isotopologue): [M+H]+ ion: 1262.16823 Observed m/z (most abundant isotopologue): [M+H]+ ion: 1262.16794 Mass error: 0.111 ppm

Observed versus simulated spectrum for detected target formulas [M+H]+ ion



Full Spectrum (*m*/*z* = 1181.24429 = [M-Br]⁺):



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Figure S11. Infrared Spectrum of $[MoPt(\mu-C)(CO)_2(PPh_3)_2(Tp^*)]$ (2a) $(CH_2Cl_2, 25 \degree C)$.

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Figure S12. ¹H NMR Spectrum of [WPt(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2b) (400 MHz, CDCl₃, 25 °C)

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Figure S13. ¹³C{¹H} NMR Spectrum of [WPt(µ-C)(CO)₂(PPh₃)₂(Tp*)] (2b) (151 MHz, CDCl₃, 25 °C)

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Figure S14. ${}^{31}P{}^{1}H{}$ NMR Spectrum of [WPt(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2b) (162 MHz, CDCl₃, 25 °C)

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Figure S16. Infrared Spectrum of $[WPt(\mu-C)(CO)_2(PPh_3)_2(Tp^*)]$ (2b) (CH₂Cl₂, 25 °C).

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Figure S17. RSC/RSB Joint Mass Spectrometry Facility Analysis Report

Analyst: Anitha Jeyasingham Instrument: Orbitrap QE, +ve mode ESI at 280k resolution Analysis Date: 2019-08-15 Sample code: LB-2-83

Theoretical m/z (most abundant isotopologue): [M]+ ion: 1347.20534 Observed m/z (most abundant isotopologue): [M]+ ion: 1347.20589 Mass error: 0.290 ppm

Observed versus simulated spectrum for detected target formulas [M]⁺ ion



Full Spectrum



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Figure S18. ¹H NMR Spectrum of [MoPd(μ-C)(CO)₂(PPh₃)₂(Tp*)] (2c)– Observed *in situ* yet unable to be isolated (400 MHz, d₆-benzene, 25 °C, δ):

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Figure S19. ¹³C NMR Spectrum of [MoPd(μ -C)(CO)₂(PPh₃)₂(Tp*)] (2c) – Observed *in situ* yet unable to be isolated (176 MHz, d₆-benzene , 25 °C, δ):

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Figure S20. ³¹P NMR Spectrum of [MoPd(μ -C)(CO)₂(PPh₃)₂(Tp^{*})] (2c) – Observed *in situ* yet unable to be isolated (162 MHz, d₆-benzene, 25 °C, δ):

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Figure S21. Infrared Spectrum of [MoPd(µ-C)(CO)₂(PPh₃)₂(Tp*)] (2c) – Observed *in situ* yet unable to be isolated (CaF₂, CH₂Cl₂, 25 °C, v):

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Figure S22. Infrared Spectrum of [MoPd(µ-C)(CO)₂(PPh₃)₂(Tp*)] (2c) – Observed *in situ* yet unable to be isolated (CaF₂, THF, 25 °C, v):

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Figure S23. Infrared Spectrum of [MoPd(μ-C)(CO)₂(PPh₃)₂(Tp*)] (2c) – Observed *in situ* yet unable to be isolated (CaF₂, CHCl₃, 25 °C, ν):

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Figure S24. Observation of $[WPd(\mu-C)Br(CO)_2(PPh_3)_2(Tp^*)]$ (2d) $-{}^{13}C{}^{1}H$ NMR spectrum (151 MHz, C₆D₆, 25 °C)

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Figure S25. Observation of [WPd(μ -C)Br(CO)₂(PPh₃)₂(Tp^{*})] (2d) – ³¹P{¹H} NMR spectrum (162 MHz, C₆D₆, 25 °C)

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Figure S26. Observation of [WPd(μ -C)Br(CO)₂(PPh₃)₂(Tp^{*})] (2d) –¹H NMR spectrum (400 MHz, C₆D₆, 25 °C)

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Figure S27. Infrared Spectrum of [WPd(μ-C)(CO)₂(PPh₃)₂(Tp*)] (2d) – Observed *in situ* yet unable to be isolated (CaF₂, CH₂Cl₂, 25 °C) Peaks at 1987 and 1895 cm⁻¹ correspond to unreacted 1b.

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Figure S28. Infrared Spectrum of [WPd(μ-C)(CO)₂(PPh₃)₂(Tp*)] (2d) – Observed *in situ* yet unable to be isolated (CaF₂, CHCl₃, 25 °C) Peaks at 1989 and 1896 cm⁻¹ correspond to unreacted 1b.

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Figure S29. Infrared Spectrum of [WPd(μ-C)(CO)₂(PPh₃)₂(Tp*)] (2d) – Observed *in situ* yet unable to be isolated (CaF₂, benzene, 25 °C) Peaks at 1987 and 1897 cm⁻¹ correspond to unreacted 1b.

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Figure S30. ¹H NMR Spectrum of $[Mo_2Pd_2(\mu-C)_2Br_2(CO)_4(PPh_3)_2(Tp^*)_2]$ (5a) (400 MHz, CDCl₃, 25 °C)

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Figure S31. ${}^{13}C{}^{1}H$ NMR Spectrum of [Mo₂Pd₂(μ -C)₂Br₂(CO)₄(PPh₃)₂(Tp*)₂] (5a) (151 MHz, C₆D₆, 25 °C)

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Figure S32. ³¹P{¹H} NMR Spectrum of $[Mo_2Pd_2(\mu-C)_2Br_2(CO)_4(PPh_3)_2(Tp^*)_2]$ (5a) (162 MHz, CDCl₃, 25 °C) δ_P = 25.0 (OPPh₃)

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Figure S33. Infrared Spectrum of $[Mo_2Pd_2(\mu-C)_2Br_2(CO)_4(PPh_3)_2(Tp^*)_2]$ (5a) (THF, 25 °C)

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Figure S34. Mass Spectrum of $[(Tp^*)Mo(CO_2) = (\mu - C) - Pd(PPh_3)]_2(\mu - Br)_2(5a)$ (ESI): $[M+Na]^+$

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Figure S35. ¹H NMR Spectrum of [MoPd(μ –C)Br(CO)₂(dppe)(Tp*)] (6) (400 MHz, CD₂Cl₂, 25 °C)

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Figure S36. ³¹P{¹H} NMR Spectrum of [MoPd(μ–C)Br(CO)₂(dppe)(Tp*)] (6) (162 MHz, CD₂Cl₂, 25 °C)

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Figure S37. ¹³C{¹H} NMR Spectrum of [MoPd(µ–C)Br(CO)₂(dppe)(Tp*)] (6) (176 MHz, CD₂Cl₂, 25 °C)

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Figure S38. IR Spectrum of [MoPd(µ–C)Br(CO)₂(dppe)(Tp*)] (6) (CH₂Cl₂, 25 °C)

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Figure S39. RSC/RSB Joint Mass Spectrometry Facility Analysis Report: IR Spectrum of [MoPd(µ–C)Br(CO)₂(dppe)(Tp*)] (6)

Instrument: Orbitrap QE, +ve mode ESI at 280k resolution Analysis Date: 2019-08-15

Theoretical m/z (most abundant isotopologue): [M]+ ion: 1135.11396 Observed m/z (most abundant isotopologue): [M]+ ion: 1135.11401 Mass error: 0.869 ppm



Full Spectrum:



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Figure S40. ¹H NMR Spectrum of [WPd(μ –CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (7) (400 MHz, CDCl₃, 25 °C)

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Figure S41. ³¹P{¹H} NMR Spectrum of [WPd(μ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (7) (162 MHz, CDCl₃, 25 °C)

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Figure S42. ³¹P{¹H} NMR Spectrum of [WPd(μ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (7) with excess PPh₃ (162 MHz, CDCl₃, 25 °C)

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Figure S43. ¹³C{¹H} NMR Spectrum of [WPd(μ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (7) (176 MHz, CDCl₃, 50 °C, sparingly soluble)

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Figure S44. Infrared Spectrum of [WPd(µ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (7) (THF, 25 °C)

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Figure S45. Mass Spectrum of [WPd(µ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (7) (ESI)

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Figure S46. ¹H NMR Spectrum of [WPd(μ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (8) (400 MHz, CDCl₃, 25 °C)

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Figure S47. ${}^{31}P{}^{1}H$ NMR Spectrum of [WPd(µ–CPPh₃)Br(CO)₂(Tp^{*})] (8) (176 MHz, C₆D₆, 25 °C)

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Figure S48. ¹³C{¹H} NMR Spectrum of [WPd(µ–CPPh₃)Br(CO)₂(PPh₃)(Tp*)] (8) (141 MHz, CDCl₃, 25 °C)

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Figure S49. Infrared Spectrum of [WPd(µ–CPPh₃)Br(CO)₂(Tp*)] (8) (CH₂Cl₂, 25 °C)

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Figure S50. Infrared Spectrum of [WPd(µ–CPPh₃)Br(CO)₂(Tp*)] (8) (ATR)

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Selected Spectra for Propargylidynes – see also Reference 13

Figure S51. ¹H NMR Spectrum of $[(Tp^*)(CO)_2Mo(=C-C=C-Ph)]$ (600 MHz, CDCl₃, 25 °C, δ):

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Figure S52. ¹³C NMR Spectrum of [(Tp*)(CO)₂Mo(=C–C=C–Ph)] (151 MHz, CDCl₃, 25 °C, δ):

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Figure S53. Infrared Spectrum of [(Tp*)(CO)₂Mo(=C-C=C-Ph)] (NaCl, CH₂Cl₂, 25 °C)

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Figure S54. ¹H NMR Spectrum of $[(Tp^*)(CO)_2W(=C-C=C-Ph)]$ (400 MHz, CDCl₃, 25 °C, δ):

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Figure S55. ¹³C NMR Spectrum of [(Tp*)(CO)₂W(=C-C=C-Ph)] (101 MHz, CDCl₃, 25 °C, δ):

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Figure S56. Infrared Spectrum of [(Tp*)(CO)₂W(=C–C=C–Ph)] (NaCl, CH₂Cl₂, 25 °C)

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Figure S57. ¹H NMR Spectrum of [(Tp*)(CO)₂W(=C-C=C-SiMe₃)] (400 MHz, CDCl₃, 25 °C, δ):

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Figure S58. ¹³C NMR Spectrum of [(Tp*)(CO)₂W(=C–C=C–SiMe₃)] (101 MHz, CDCl₃, 25 °C, δ):

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Figure S59. Infrared Spectrum of [(Tp*)(CO)₂W(=C-C=C-SiMe₃)] (CH₂Cl₂, 25 °C)

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Figure S60. ¹H NMR Spectrum of [(Tp*)(CO)₂Mo(=C-C=C-SiMe₃)] (600 MHz, CDCl₃, 25 °C, δ):

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Figure S61. ¹³C NMR Spectrum of [(Tp*)(CO)₂Mo(=C–C=C–SiMe₃)] (151 MHz, CDCl₃, 25 °C, δ):

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Figure S62. Infrared Spectrum of [(Tp*)(CO)₂Mo(=C–C=C–SiMe₃)] (NaCl, CH₂Cl₂, 25 °C)

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Figure S63. ³¹P{¹H} NMR Spectrum of [W(=CPPh₃)(CO)₂(Tp^{*})]Br ([9]Br) (162 MHz, CDCl₃, 25 °C). The salt [W(=CPPh₃)(CO)₂(Tp^{*})]PF₆ has been described previously however δ_P was not reported.

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Figure S64. ¹H NMR Spectrum of $[W(=CPPh_3)(CO)_2(Tp^*)]Br$ ([9]Br] (400 MHz, CDCl3, 25 °C). The salt $[W(=CPPh_3)(CO)_2(Tp^*)]PF_6$ has been described previously with δ_H (CD₂Cl₂) = 7.79 (m, 15 H, C₆H₅), 6.00, 5.86 (pzH), 2.43, 2.34, 2.33, 2.02 (pzCH₃).

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Figure S65. ¹³C NMR Spectrum of [(Tp*)W(CO₂)≡(μ−C)−PPh₃][Br] (100 MHz, CDCl₃, 25 °C, δ):

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Figure S66. ³¹P NMR Spectrum of [(Tp*)W(CO₂)=(μ–C)–PPh₃][Br] (162 MHz, CDCl₃, 25 °C, δ):

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Figure S67. Infrared Spectrum of $[(Tp^*)W(CO_2)=(\mu-C)-PtBr(PPh_3)_2]$ (CaF₂, CH₂Cl₂, 25 °C, v):

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