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Fundamental Organometallic Chemistry Under Bimetallic Influence: Driving β -hydride Elimination and Diverting Migratory Insertion at Cu and Ni

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General Considerations

Unless otherwise specified, all reactions and manipulations were performed under purified N₂ in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Reaction solvents (tetrahydrofuran, toluene, pentane, diethyl ether, acetonitrile) were sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC, or purified by repeated freeze-pump-thaw-cycles followed by prolonged storage over activated, 3-Å molecular sieves (benzene, NMR solvents). Literature Methods were used to synthesize (6Pr)CuCl¹, (6Pr)CuOtBu,¹ FeCp(CO)₂Bpin,² RuCp*(CO)₂Bpin,³ RuCp*(CO)₂H,⁴ WCp*(CO)₃H,⁵ Na[Mn(CO)₅],⁶ IPrCuOtBu,⁷ (^{tBu}POCOP)NiH,⁸ (^{iPr}POCOP)NiH,⁸ WCp(CO)₃H.⁹ All products matched previously reported literature values. Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification.

Physical Measurements

NMR spectra were recorded at ambient temperature using Bruker Avance DPX-400 and Bruker Avance DRX-500 spectrometers. ¹H NMR and ¹³C{¹H} NMR chemical shifts were referenced to residual solvent peaks. ¹¹B NMR chemical shifts were referenced to an external standard of BF₃·OEt₂ (δ =0). ³¹P{¹H} NMR chemical shifts were referenced to an external standard of *o*-phosphoric acid in water (δ =0). GC data was obtained using a Shimadzu GC-2010 Gas Chromatograph. Single-crystal X-ray diffraction studies were performed using a Bruker SMART X2S benchtop diffractometer fitted with an Oxford Crystreams desktop cooler.

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Synthesis of Mn(CO)₅**Bpin**. In a nitrogen filled glovebox, pinacol (164.7 mg, 1.39 mmol) was added to a 20-mL scintillation vial and dissolved in pentane (5 mL). The solution was placed in the glovebox freezer freezer (-35 °C). Once cooled, BCl₃ (1.0 M in hexanes, 2.2 mL, 2.2 mmol) was added to a vigorously stirring solution. The reaction was allowed to proceed for 1 hour. The solution was then concentrated *in vacuo* to a volume of approximately 3 mL. The solution was pipette-filtered through Celite (to remove the resultant precipitate) into a stirring suspension of Na[Mn(CO)₅] (299.0 mg, 1.37 mmol) in pentane (5 mL). The reaction changed from a colorless suspension to a yellow solution with a green precipitate. After 16 h, the solution was pipette-filtered through Celite into a tared vial. The resulting yellow solution was dried *in vacuo*, resulting in a yellow powder. Crude yield: 296.0 mg, 0.919 mmol, 67%. The sample was recrystallized by cooling a concentrated pentane solution to -35 °C to obtain a spectroscopically pure material. Recrystallized yield: 160.8 mg, 0.499 mmol, 36%. ¹H NMR (500 MHz, C₆D₆): δ 1.02 (s, 12H, CH₃). ¹¹B NMR (160.47 MHz, C₆D₆): δ 46.62. ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 212.44, 210.99, 84.27, 24.56. IR (solid, cm⁻¹): 2984.45, 2105.76, 2012.06 (v_{co}), 1959.74 (v_{co}), 1265.02, 1104.42, 848.14, 764.05, 645.31. Anal. Calcd for C₁₁H₁₂BMnO₇: C, 41.04; H, 3.76. Found: C, 40.67; H, 3.68.



Figure S1: ¹H NMR spectrum of Mn(CO)₅Bpin



Figure S2: ¹¹B NMR spectrum of Mn(CO)₅Bpin



Figure S3: ¹³C{¹H} NMR spectrum of Mn(CO)₅Bpin



Figure S4: Infrared spectrum of Mn(CO)₅Bpin

Synthesis of 6PrCuFeCp(CO)₂. In a nitrogen filled glovebox, 6PrCuCl (148.0 mg, 0.294 mmol) and K[FeCp(CO)₂] (76.4 mg, 0.354 mmol) were added to a 20-mL scintillation vial and suspended in toluene (10 mL). The reaction mixture was stirred for 16 h and then pipette-filtered through Celite. The red solution was dried *in vacuo* resulting a red and yellow solid. The powder was then suspended in pentane and stirred for 1 h to remove excess [FeCp(CO)₂]₂ from the solid. The suspended solid was then filtered and washed with pentane (2x 3 mL) and dried *in vacuo* resulting in a yellow solid. Yield: 87.5 mg, 0.136 mmol, 46%. An analytically pure sample was prepared by vapor diffusion of pentane into a concentrated solution in toluene at -35 °C for 48 h. ¹H NMR (500 MHz, C₆D₆): δ 7.23 (m, 2H, *p*-CH), 7.14 (d, *J* = 7.6 Hz, 4H, *m*-CH), 4.04 (s, 5H, Cp), 3.11 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 2.78 (t, *J* = 5.8 Hz, 4H, NCH₂), 1.61 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.52 (quin, *J* = 6.3 Hz, 2H, NCH₂CH₂), 1.20 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 220.57, 198.22, 145.72, 142.23, 129.57, 125.10, 77.55, 46.48, 29.05, 25.11, 24.60, 20.26. IR (solid, cm⁻¹): 2961.19, 2927.12, 2867.00 1915.69 (v_{co}), 1848.63 (v_{co}), 1496.98, 1444.15, 1301.05, 1201.86, 579.11. Anal. Calcd for C₃₅H₄₅CuFeN₂O₂: C, 65.16; H, 7.03; N, 4.34. Found: C, 65.49; H, 7.28; N, 4.36.



Figure S5: ¹H NMR spectrum of 6PrCuFeCp(CO)₂



Figure S6: ¹³C{¹H} NMR spectrum of 6PrCuFeCp(CO)₂



Figure S7: Infrared spectrum of 6PrCuFeCp(CO)₂

Synthesis of 1. In a nitrogen filled glovebox, 6PrCuOtBu (329.7 mg, 0.609 mmol) and B₂pin₂ (183.7 mg, 0.723 mmol) were added to a 20-mL scintillation vial and dissolved in pentane (10 mL). The reaction mixture was stirred for 30 minutes at room temperature after which styrene (120 μ L, 1.04 mmol) was syringed in. The reaction mixture was stirred for another 30 minutes resulting in the generation of a tan precipitate. The tan precipitate was filtered off and washed with pentane (2x 5 mL) and dried in vacuo. Crude Yield: 181.3 mg, 0.259 mmol, 43%. An analytically pure sampled was prepared by vapor diffusion of pentane into a concentrated solution of Et₂O at -35 $^{\circ}$ C for 24 h resulting in white crystals. Crystal Yield: 84.5 mg, 0.121 mmol, 20%. ¹H NMR (500 MHz, C₆D₆): δ 7.20 (t, J = 7.7 Hz 2H, p-CH), 7.04 (m, 6H), 6.71 (t, J = 7.1 Hz, 1H, p-CH), 6.60 (d, J = 7.6, 2H, o-CH), 2.90 (m, 4H, CH(CH₃)₂), 2.65 (t, J = 5.8 Hz, 4H, NCH₂), 2.24 (dd, J = 11.4, 5.1 Hz, 1H), 1.43 (quin, J = 6.0 Hz, 2H, NCH₂CH₂), 1.35 (d, J = 6.8 Hz, 6H, CH(CH₃)₂), 1.30 (dd, J = 15.8, 4.2 Hz, 1H, CH(CH₂)), 1.26 (d, J = 6.9 Hz, 6H, CH(CH₃)₂), 1.16 (dd, J = 6.9, 3.1 Hz, 12H, CH(CH₃)₂), 1.07 (dd, J = 15.7, 5.1 Hz, 1H, CH(CH₂)), 0.95 (s, 6H, C(CH₃)₂), 0.90 (s, 6H, C(CH₃)₂). ¹¹B NMR (160.47 MHz, C₆D₆): δ 35.20. ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 204.37, 159.12, 145.55, 145.48, 142.05, 129.17, 127.37, 124.77, 124.67, 116.54, 81.78, 45.67, 30.22, 28.92, 28.89, 25.24, 24.97, 24.86, 24.80, 24.73, 24.67, 20.31, 14.65. IR (solid, cm⁻¹): 2960.76, 2924.08, 2864.40, 1588.13, 1501.12, 1452.43, 1322.35, 1299.53, 1201.18, 1146.68, 968.62, 802.88, 755.47, 692.11. Anal. Calcd for C₄₂H₆₀BCuN₂O₂: C, 72.14; H, 8.65; N, 4.01. Found: C, 73.08; H, 9.20; N, 4.11. While elemental analysis data fall outside the acceptable range of ±0.4%, the enclosed spectral data are presented as evidence of purity.



Figure S8: ¹H NMR spectrum of **1**.



Figure S9: ¹¹B NMR spectrum of **1**.



Figure S10: ${}^{13}C{}^{1}H$ NMR spectrum of **1**.



Figure S11: Infrared spectrum of 1

Synthesis of 4. The synthesis of **4** was modified from a previously published procedure.⁷ In a nitrogen filled glovebox, IPrCuOtBu (100 mg, 0.190 mmol) and 5-decyne (168 μL, 0.952 mmol) were added to a 20-mL scintillation vial and dissolved in toluene (10 mL). While stirring, triethoxysilane (70 μL, 0.381 mmol) was syringed in. The scintillation vial was wrapped in tin foil and the solution was stirred at room temperature for 16 h. The solution was dried *in vacuo* to obtain **4** (106 mg, .181 mmol, 95% yield). ¹H NMR (500 MHz, C₆D₆): δ 7.25 (t, *J* = 7.8 Hz, 2H, *p*-CH), 7.11 (d, *J* = 7.8 Hz, 4H, *m*-CH), 6.27 (s, 2H, NCH), 5.47 (tt, *J* = 6.4, 1.7 Hz, 1H, C_βH), 2.64 (sept, *J* = 6.9 Hz, 4H, CH(CH₃)₂), 2.40 (t, *J* = 7.3 Hz, 2H), 2.34 (q, *J* = 7.0 Hz, 2H), 1.46 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 1.44 – 1.27 (m, 8H), 1.10 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂), 0.94 (dt, *J* = 21.3, 7.2 Hz, 6H). ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 186.43, 169.28, 145.64, 135.27, 133.96, 130.07, 123.82, 121.72, 36.30, 36.13, 33.54, 28.74, 28.39, 24.76, 23.56, 23.25, 22.82, 14.67, 14.34. Anal. Calcd for C₃₇H₅₅CuN₂: C, 75.14; H, 9.37; N, 4.74. Found: C, 74.38; H, 9.37; N, 4.93. While elemental analysis data fall outside the acceptable range of ±0.4%, the enclosed spectral data are presented as evidence of purity.



Figure S12: ¹H NMR spectrum of **4**.



Figure S13: ¹³C{¹H} NMR spectrum of 4

Synthesis of (^{tBu}**POCOP)NiWCp(CO)**₃. In a nitrogen filled glovebox, (^{tBu}POCOP)NiH (250 mg, 0.547 mmol) and WCp(CO)₃H (182.6 mg, 0.547 mmol) were added to a 100-mL round bottom flask and dissolved in toluene (25 mL). The reaction was stirred overnight for 12 h. The solution was dried *in vacuo* resulting in a dark orange powder. The solid was washed with pentanes to remove unreacted starting material and dried *in vacuo* to obtain (^{tBu}POCOP)NiWCp(CO)₃ (389mg, 90% yield). An analytically pure sampled was prepared by vapor diffusion of pentane into a concentrated solution of toluene at -35 °C to give orange crystals. ¹H NMR (500 MHz, C₆D₆): δ 6.74 (t, 1H, *J* = 8.0 Hz, *p*-ArH), 6.36 (d, 2H, *J* = 8.0 Hz, *m*-ArH), 5.2 (s, 5H, Cp), 1.35 (vt, 36H, *J*_{H-P} = 7.4 Hz, *CH*₃). ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 223.31, 170.17, 129.67, 105.83, 86.85, 38.76, 27.50. ³¹P{¹H} NMR (161.92 MHz, C₆D₆): δ 186.31. IR (solid, cm⁻¹): 2962.67, 1910.44 (v_{co}), 1817.19 (v_{co}), 1654.02 (v_{co}), 1259.10, 1086.13, 1017.15, 990.94, 789.58. Anal. Calcd for C₃₀H₄₄O₅P₂NiW: C, 45.66; H, 5.62. Found: C, 44.86; H, 5.63. While elemental analysis data fall outside the acceptable range of ±0.4%, the enclosed spectral data are presented as evidence of purity.



Figure S14: ¹H NMR spectrum of ^{tBu}(POCOP)NiWCp(CO)₃



Figure S15: ¹³C{¹H} NMR spectrum of ^{tBu}(POCOP)NiWCp(CO)₃



Figure S16: ³¹P{¹H} NMR spectrum of ^{tBu}(POCOP)NiWCp(CO)₃



Figure S17: Infrared spectrum of ^{tBu}(POCOP)NiWCp(CO)₃

Synthesis of (^{*i*P}**POCOP**)**NiWCp(CO**)₃. In a nitrogen filled glovebox, (^{*i*pr}POCOP)**NiH** (50.0 mg, 0.125 mmol) and WCp(CO)₃H (41.6 mg, 0.125 mmol) were added to a 20-mL scintillation vial and dissolved in pentane (10 mL). The reaction mixture was stirred overnight for 12 h. The solution was dried *in vacuo* resulting in a dark green powder to obtain 80 mg, 87% yield. An analytically pure sample was prepared by vapor diffusion of pentane into a concentrated solution of toluene at -35 °C to give black crystals. ¹H NMR (400 MHz, C₆D₆): δ 6.96 (t, 1H, *J* = 7.8, *p*-Ar*H*), 6.65 (d, 2H, *J* = 7.8, *m*-Ar*H*), 4.88 (s, 5H, Cp), 2.41 (m, 4H, C*H*(CH₃)₂), 1.45 (vq, 12H, *J*_{H-P} = 7.3 Hz, C*H*₃) 1.26 (vq, 12H, *J*_{H-P} = 6.9 Hz, C*H*₃). ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 224.14, 168.06, 130.26, 104.83, 88.15, 30.38, 17.80, 17.17. ³¹P{¹H} NMR (161.92 MHz, C₆D₆): δ 178.26. IR (solid, cm⁻¹): 3107.66, 2962.17, 2930.37, 2873.58, 1891.33 (v_{co}), 1800.25 (v_{co}), 1774.43 (v_{co}), 1435.44, 995.61, 841.47, 656.37, 479.64. Anal. Calcd for C₂₆H₃₆O₅P₂NiW: C, 42.60; H, 4.95. Found: C, 42.39; H, 4.94.



Figure S18: ¹H NMR spectrum of ^{iPr}(POCOP)NiWCp(CO)₃



Figure S19: ¹³C{¹H} NMR spectrum of ^{*i*Pr}(POCOP)NiWCp(CO)₃



Figure S20: ³¹P{¹H} NMR spectrum of ^{*i*Pr}(POCOP)NiWCp(CO)₃



Figure S21: Infrared spectrum of ^{iPr}(POCOP)NiWCp(CO)₃

Procedure for the thermal decomposition study of 1. In a nitrogen filled glovebox, **1** (6.1 mg, 0.00872 mmol) and C_6Me_6 (1.7 mg, 0.0105) were dissolved in C_6D_6 (1 mL). The reaction mixture was pipette-filtered through Celite into a J-Young NMR tube. The tube was sealed and mixed. It was placed in an oil bath at 70 °C for 48 h. After completion, the ¹H and ¹¹B spectra were recorded.



Figure S22: ¹H NMR spectrum of the thermal decomposition study of 1 at t = 0.



Figure S23: ¹¹B NMR spectrum of the thermal decomposition study of 1 at t = 0.



Figure S24: ¹H NMR spectrum of the thermal decomposition study of **1** at 70 °C after 48 h.



Figure S25: ¹¹B NMR spectrum of the thermal decomposition study of **1** at 70 °C after 48 h.

Procedure for the bimetallic cooperation between 1 and FpBpin. In a nitrogen filled glovebox, **1** (8.3 mg, 0.0119 mmol), FpBpin (3.7 mg, 0.0123 mmol), and C₆Me₆ (4.1 mg, 0.0290 mmol) were dissolved in C₆D₆ (1 mL). The reaction mixture was pipette-filtered through Celite into a J-Young NMR tube. The J-Young NMR tube was sealed and mixed. It was placed in an oil bath at 70 °C for 48 h. After completion, the ¹H and ¹¹B spectra were recorded.



Figure S26: ¹H NMR spectrum of the bimetallic cooperation between **1** and FpBpin at t = 0.



Figure S27: ¹¹B NMR spectrum of the bimetallic cooperation between 1 and FpBpin at t = 0.



Figure S28: ¹H NMR spectrum of the bimetallic cooperation between **1** and FpBpin at 70 °C after 48 h.



Figure S29: ¹¹B NMR spectrum of the bimetallic cooperation between **1** and FpBpin at 70 °C after 48 h.

General Procedure for alkylcopper β -hydride elimination between 1 and [M_{co}]. In a nitrogen filled glovebox, 1 (approx. 5 mg), [M_{co}] (1 equiv.), and decane (1 equiv.) were dissolved in benzene (1 mL). The reaction mixture was pipette-filtered through Celite into a J-Young NMR tube. The J-Young NMR tube was sealed and mixed. It was placed in an oil bath at 70 °C for 48 h. After the reaction time completed, the solution was pipette-filtered through Silica and diluted with THF (10 mL). Gas chromatography analysis was performed.

Procedure for the reaction between 4 and Mn(CO)₅**Bpin.** In a nitrogen filled glovebox, **4** (6.2 mg, 0.0105 mmol) and Mn(CO)₅Bpin (3.4 mg, 0.0106 mmol) were dissolved in C₆D₆ (600 μ L). The solution was added to a J-young tube and heated to 50 °C for 16 h. The ¹H and ¹¹B NMR spectra were recorded.



Figure S30: ¹H NMR spectrum of the reaction between **4** and Mn(CO)₅Bpin



Figure S31: ¹¹B NMR spectrum of the reaction between **4** and Mn(CO)₅Bpin

Procedure for the Reaction of (tBu **POCOP**)**NiWCp(CO**)₃ **with H**₂. In a nitrogen filled glovebox, (tBu POCOP)**NiWCp(CO**)₃ (5 mg, 0.00634 mmol) was dissolved C₆D₆ (600 µL). The mixture was pipette filtered through Celite into a J-young tube. The tube was fitted to a Schlenk line and exposed to three cycles of freeze-pump-thaw, followed by backfilling with H₂ (1 atm). The solution was mixed for five minutes and stored on its side for 24 h.



Figure S32: ¹H NMR spectrum of the reaction between ^{tBu}(POCOP)NiWCp(CO)₃ and H₂



Figure S33: ³¹P{¹H} NMR spectrum of the reaction between ^{tBu}(POCOP)NiWCp(CO)₃ and H₂

Procedure for the Reaction of $({}^{iPr}$ **POCOP)NiWCp(CO**)₃ **with phenylacetylene.** In a nitrogen filled glovebox, $({}^{iPr}$ **POCOP)NiWCp(CO**)₃ (5mg, 0.00682 mmol) was dissolved in C₆D₆ (1 mL). To this solution, phenylacetylene (0.7uL, 0.00682 mmol) was syringed in. The mixture was stirred overnight for 12 h. An aliquot (0.5 mL) was transferred to a J-young tube to be monitored by NMR.



Figure S34: ¹H NMR spectrum of the reaction between ^{*i*Pr}(POCOP)NiWCp(CO)₃ and phenylacetylene



Figure S35: ³¹P{¹H} NMR spectrum of the reaction between ^{*i*Pr}(POCOP)NiWCp(CO)₃ and phenylacetylene

Procedure for the Reaction of (^{iPr}**POCOP)NiH, WCp(CO)**₃**H and phenylacetylene.** In a nitrogen filled glovebox, (^{iPr}POCOP)NiH (12 mg, 0.030 mmol) and WCp(CO)₃H (10 mg, 0.030 mmol) were added to a scintillation vial and dissolved in C₆D₆ (1 mL). Immediately, phenylacetylene (3.2 uL, 0.030 mmol) was syringed in. The reaction mixture was stirred overnight for 12 h. An aliquot (0.5 mL) was transferred to a J-young tube to be monitored by NMR.



Figure S36: ¹H NMR spectrum of the reaction between ^{*i*Pr}(POCOP)NiH, WCp(CO)₃H, and phenylacetylene



Figure S37: ${}^{31}P{}^{1}H$ NMR spectrum of the reaction between ${}^{Pr}(POCOP)NiH$, WCp(CO)₃H, and phenylacetylene

Emprical formula	$C_{30}H_{44}NiO_5P_2W$		
Formula weight	789.15		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P -1		
Unit cell dimensions	a = 8.0617 (8) Å	α = 103.562 (3)	
	b = 11.4269 (11) Å	β = 95.996 (3)	
	c = 18.1147 (15) Å	γ = 94.204 (3)	
Volume	1605.0 (3) Å ³		
Z	2		
Density (calculated)	1.633 Mg/m ³		
Absorption coefficient	4.302 mm ⁻¹		
F (000)	792.0		
Crystal size	0.6 x 0.5 x 0.2 mm ³		
Theta range for data collection	1.17 to 27.10°		
Index ranges	-10<=h<=10, -14<=k<=14, -22<=l<=22		
Reflections collected	35657		
Independent reflections	6986		
Completeness to theta = 27.10°	98.4%		
Absorption correction	multi-scan		
Refinement method	Full-matrix least-squares on F2		
Data / restraints / parameters	6986 / 0 / 364		
Goodness-of-fit on F ²	0.796		
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.0958		
R indices (all data)	R1 = 0.0380, wR2 = 0.1170		
Largest diff. peak and hole	1.537 and -0.810 e.Å-3		

Table S1: Crystal data and structure refinement for ($^{tBu}POCOP$)NiWCp(CO)₃