Electronic Supplementary Material (ESI) for Dalton Transactions

C–X Bond Formation and Cleavage in the Reactions of the Ditungsten Hydride Complex $[W_2(\eta^5\text{-}C_5H_5)_2(H)(\mu\text{-}PCy_2)(CO)_2]$ with Small Molecules having Multiple C–X bonds (X = C, N, O).

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Electronic Supporting Information

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures,[1] and distilled prior to use. Petroleum ether refers to that fraction distilling in the range 338-343 K. Compound $[W_2Cp_2(H)(\mu\text{-}PCy_2)(CO)_2]$ (**1**) (Cp= η^5-C_5H_5) was prepared as described previously.[2] All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns, kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR C–O bond stretching frequencies were measured in solution, are given in cm^{-1} and are referred to as ν(CO) (solvent). Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.52 (^{31}P{^{1}H}) or 75.48 MHz (^{13}C{^{1}H}) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H and ^{13}C), and external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in Hertz.

Preparative Procedures, Spectroscopic and Microanalytical data for the New Compounds.

Reaction of Compound 1 with $C_2(CO_2Me)_2$. Neat dimethyl acetylenedicarboxylate (20 μL, 0.16 mmol) was added to a solution of compound **1** (0.040 g, 0.053 mmol) in toluene (4 mL) at 273 K, and the mixture was stirred at that temperature for 3 h to give a green solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane and the extract was chromatographed through an alumina column (activity IV) at 253 K. Elution with the same solvent gave two green fractions. Removal of the solvents from the latter fractions under vacuum gave respectively compound *cis*-$[W_2Cp_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(CO_2Me)=CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**3**) (0.025 g, 53%) and compound $[W_2Cp_2\{\mu\text{-}\eta^1,\kappa\text{:}\eta^2\text{-}C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**4**) (0.021 g, 38%), both as green powders. The crystals of **4** used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K.

*Data for compound **3**.* Anal. Calcd for $C_{30}H_{39}O_6PW_2$: C, 40.29; H, 4.40; Found: C, 40.03; H, 4.22. ν(CO) (toluene): 1940 (vs), 1851 (m), 1697 (m), 1677 (w). ^{1}H NMR (C_6D_6, 400.13 MHz): δ 5.22 (s, 1H, CH), 5.16 (s, 5H, Cp), 4.77 (d, J_{HP} = 1, 5H, Cp), 3.60, 3.59 (2s, OMe), 2.33-2.80 (m, 22H, Cy). ^{31}P{^{1}H} NMR (C_6D_6): δ 113.3 (s, J_{PW} = 351, 255). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): δ 244.4, 222.6 (2s, WCO), 184.6, 176.8 (2s, CO_2Me), 154.1 (s, μ-C), 88.2, 87.0 (2s, Cp), 51.8 [d, J_{CP} = 31, C^1(Cy)], 51.4, 50.8 (2s, OMe), 44.1 [d, J_{CP} = 19, C^1(Cy)], 35.0, 34.3, 33.5, 33.3 [4s, C^2(Cy)], 33.5 (s, CH),

28.4 [d, J_{CP} = 12, C^3(Cy)], 28.3 [d, J_{CP} = 9, C^3(Cy)], 28.1, 27.8 [2d, J_{CP} = 13, C^3(Cy)], 26.9, 26.8 [2s, C^4(Cy)].

Data for compound ***4***. Anal. Calcd for $C_{36}H_{45}O_{10}PW_2$: C, 41.72; H, 4.38; Found: C, 41.49; H, 4.25. ν(CO) (toluene): 1880 (vs), 1843 (m), 1708 (m). ^{1}H NMR: δ 5.61, 5.24 (2s, 2 x 5H, Cp), 3.79, 3.65, 3.56, 3.55 (4s, 4 x 3H, OMe), 3.11 (s, J_{HW} = 5, 1H, CH), 2.80-0.50 (m, 22H, Cy). ^{31}P{^{1}H} NMR: δ 157.1 (s, J_{PW} = 224, 120). ^{13}C{^{1}H} NMR: δ 234.2 (d, J_{CP} = 3, WCO), 233.3 (s, WCO), 232.8 (s, W–*C*=C), 186.6, 185.8, 178.5, 176.4 (4s, *C*O_2Me), 163.8 (s, W–C=*C*), 131.6 (s, *C*=CHCO$_2$Me), 98.6, 91.8 (2s, Cp), 55.5 (s, OMe), 55.0 [d, J_{CP} = 23, C^1(Cy)], 51.8, 51.2, 50.5 (3s, OMe), 46.2 [d, J_{CP} = 16, C^1(Cy)], 36.0 [s, C^2(Cy)], 34.0, 33.5 [2d, J_{CP} = 3, C^2(Cy)], 32.3 [d, J_{CP} = 5, C^2(Cy)], 29.5 [d, J_{CP} = 13, C^3(Cy)], 28.8 [d, J_{CP} = 9, C^3(Cy)], 28.6 [d, J_{CP} = 12, C^3(Cy)], 28.4 [d, J_{CP} = 11, C^3(Cy)], 27.0, 26.8 [2s, C^4(Cy)], 23.3 (s, J_{CW} = 28, C=*C*HCO$_2$Me).

Preparation of [W_2Cp_2{μ-κ,η:κ,η-C{CHN(4-MeO-C_6H_4)}N(4-MeO-C_6H_4)}(μ-PCy_2)$(CO)_2$] (5). A solution of compound **1** (0.020 g, 0.027 mmol) in dichloromethane (8 mL) was added dropwise to neat CN(4-MeO-C_6H_4) (0.012 g, 0.09 mmol) for 15 min, and the mixture was further stirred at room temperature for 45 min. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:2) and the extract chromatographed through an alumina column (activity IV) at 285 K. Elution with dichloromethane gave a yellow fraction yielding, after removal of the solvents under vacuum, compound **5** as a yellow-orange solid (0.017 g, 62 %). Anal. Calcd for $C_{40}H_{47}N_2O_4PW_2$: C, 47.17; H, 4.65; N, 2.75. Found: C, 47.01; H, 4.68; N, 2.69. IR (CH_2Cl_2): ν(CO) 1868 (m, sh), 1853 (vs), ν(CN) 1581 (m). ^{1}H NMR (400.13 MHz): δ 7.09 (m, 2H, C_6H_4), 6.79 (m, 4H, C_6H_4), 6.60 (m, 2H, C_6H_4), 5.61 (s, 1H, CHN), 5.26, 4.95 (2s, 2 x 5H, Cp), 3.78, 3.75 (2s, 2 x 3H, OMe), 2.00-1.00 (m, 22H, Cy). ^{31}P{^{1}H} NMR: δ 69.7 (s, J_{PW} = 217, 168). ^{13}C{^{1}H} NMR: δ 237.8, 225.6 (2d, J_{CP} = 5, WCO), 178.8 (s, CH), 157.8, 155.2 [2s, C^4(C_6H_4)], 141.6, 143.2 [2s, C^1(C_6H_4)], 125.2, 123.0 [2s, C^2(C_6H_4)], 113.7, 113.3 [2s, C^3(C_6H_4)], 90.4 (s, Cp), 89.2 (d, J_{CP} = 24, μ-CN), 85.9 (s, Cp), 55.8, 55.7 (2s, OMe), 49.6 [d, J_{CP} = 22, C^1(Cy)], 41.8 [d, J_{CP} = 10, C^1(Cy)], 35.5 [d, J_{CP} = 2, C^2(Cy)], 35.3 [d, J_{CP} = 3, C^2(Cy)], 34.9 [d, J_{CP} = 5, C^2(Cy)], 33.3 [s, C^2(Cy)], 28.9 [d, J_{CP} = 11, C^3(Cy)], 28.6 [d, J_{CP} = 12, C^3(Cy)], 28.5 [d, J_{CP} = 9, C^3(Cy)], 28.3 [d, J_{CP} = 10, C^3(Cy)], 26.9, 26.7 [2s, C^4(Cy)].

Preparation of [W_2Cp_2{μ-CNH(2,6-$Me_2C_6H_3$)}(μ-PCy_2){CN(2,6-$Me_2C_6H_3$)}(CO)] (6). Neat CN(2,6-$Me_2C_6H_3$) (0.008 g, 0.06 mmol) was added to a solution of compound **1** (0.020 g, 0.027 mmol) in dichloromethane, and the mixture was stirred at room temperature for 1 h to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:4) and the extract was chromatographed through an alumina column (activity IV) at 263 K. Elution

with the same solvent mixture gave an orange fraction yielding, after removal of the solvents under vacuum, compound **6** as an orange microcrystalline solid (0.024 g, 90%). The crystals used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated diethyl ether solution of the complex at 278 K. In solution this compound was shown (by NMR) to exist as an equilibrium mixture of two isomers (**A** and **B**) with the **A**:**B** ratio being ca. 3:1 in CD_2Cl_2. Anal. Calcd for $C_{41}H_{51}N_2OPW_2$: C, 49.92; H, 5.21; N, 2.84. Found: C, 49.51; H, 4.98; N, 2.69. IR (CH_2Cl_2): 1975 (w, br), 1913 (w, br), 1829 (vs), 1589 (w).

*Data for isomer **A***. IR (Nujol mull): 1868 (w, h), 1841 (vs), 1589 (w). ^{1}H NMR (400.13 MHz): δ 9.85 (s, 1H, NH), 7.30-7.10 (m, 3H, C_6H_3), 6.80 [d, J_{HH} = 8, 2H, $H^3(C_6H_3)$], 6.69 [t, J_{HH} = 8, 1H, $H^4(C_6H_3)$], 5.24, 4.90 (2s, 2 x 5H, Cp), 2.33, 2.19 (2s, 2 x 3H, Me), 1.85 (s, 6H, Me), 2.60-0.50 (m, 22H, Cy). ^{31}P{^{1}H} NMR: δ 62.3 (s, J_{PW} = 312, 304). ^{13}C{^{1}H} NMR (100.63 MHz): δ 335.4 (s, μ-C), 224.9 (d, J_{CP} = 4, WCO), 215.6 [d, J_{CP} = 4, WCN], 146.1, 137.7 [2s, $C^1(C_6H_3)$], 136.7, 136.4 [2s, $C^{2,6}(C_6H_3)$], 128.9, 128.0, 127.1, 123.3 [4s, $CH(C_6H_3)$], 128.1 [s, $2C^{2,6}(C_6H_3)$], 127.7 [s, $2CH(C_6H_3)$], 88.1, 86.7 (2s, Cp), 48.7 [d, J_{CP} = 22, C^1Cy)], 47.3 [d, J_{CP} = 26, C^1(Cy)], 36.8 [d, J_{CP} = 2, C^2(Cy)], 36.0, 35.8, 33.8 [3s, C^2(Cy)], 28.9 [d, J_{CP} = 12, C^3(Cy)], 28.7 [d, J_{CP} = 10, C^3(Cy)], 28.5 [d, J_{CP} = 11, C^3(Cy)], 28.0 [d, J_{CP} = 12, C^3(Cy)], 27.0, 26.3 [2s, C^4(Cy)], 19.4, 18.9 (2s, Me), 19.1 (s, 2Me).

*Data for isomer **B***. ^{1}H NMR (400.13 MHz): δ 9.76 (s, 1H, NH), 7.30-7.10 (m, 3H, C_6H_3), 6.80 [d, J_{HH} = 8, 2H, $H^3(C_6H_3)$], 6.68 [t, J_{HH} = 8, 1H, $H^4(C_6H_3)$], 5.44, 4.73 (2s, 2 x 5H, Cp), 2.35, 2.13 (2s, 2 x 3H, Me), 1.80 (s, 6H, Me), 2.60-0.50 (m, 22H, Cy). ^{31}P{^{1}H} NMR: δ 58.1 (s, J_{PW} = 316, 299). ^{13}C{^{1}H} NMR (100.63 MHz): δ 337.5 (s, μ-C), 218.2 (s, WCO), 209.9 [d, J_{CP} = 5, WCN], 146.8, 137.3 [2s, $C^1(C_6H_3)$], 136.8, 134.1 [2s, $C^{2,6}(C_6H_3)$], 135.8 [s, $2C^{2,6}(C_6H_3)$], 128.7, 128.1, 127.0, 123.2 [4s, $CH(C_6H_3)$], 127.5 [s, $2CH(C_6H_3)$], 87.3, 86.7 (2s, Cp), 48.8 [d, J_{CP} = 27, C^1(Cy)], 46.7 [d, J_{CP} = 23, C^1(Cy)], 36.5 [d, J_{CP} = 3, C^2(Cy)], 36.0, 35.9, 33.8 [3s, C^2(Cy)], 29.0 [d, J_{CP} = 12, C^3(Cy)], 28.8, 28.6 [2d, J_{CP} = 10, C^3(Cy)], 28.1 [d, J_{CP} = 14, C^3(Cy)], 27.0, 26.4 [2s, C^4(Cy)], 19.3, 18.9 (2s, Me), 19.1 (s, 2Me).

Reaction of Compound 1 with (4-Me-C_6H_4)C(O)H. Neat (4-Me-C_6H_4)C(O)H (20 μL, 0.17 mmol) was added to a solution of compound **1** (0.050 g, 0.067 mmol) in toluene (5 mL) and the mixture was stirred at 388 K for 1 h to give a dark brown solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:1) and the extracts were chromatographed through an alumina column (activity IV) at 263 K. Elution with the same solvent mixture gave an orange fraction yielding, after removal of the solvents under vacuum, compound $[W_2Cp_2\{CH_2(4\text{-Me-}C_6H_4)\}(O)(\mu\text{-}PCy_2)(CO)_2]$ (**7**) as an orange microcrystalline solid

(0.028 g, 48%). The crystals of **7** used in the X-ray diffraction study were grown from a concentrated petroleum ether solution of the complex at 253 K. Elution with dichloromethane gave another orange fraction yielding analogously compound $[W_2Cp_2\{\mu\text{-}\eta\text{:}\eta,\kappa\text{-}C(O)CH_2(4\text{-}Me\text{-}C_6H_4)\}(O)(\mu\text{-}PCy_2)(CO)]$ (**8**) as an orange solid (0.014 g, 25%). The crystals of **8** used in the X-ray diffraction study were grown by the slow diffusion of a layer of petroleum ether into a concentrated dichloromethane solution of the complex at 253 K.

Data for compound 7. Anal. Calcd for $C_{32}H_{41}O_3PW_2$: C, 44.06; H, 4.74; Found: C, 44.39; H, 4.68. ν(CO) (petroleum ether): 1923 (vs), 1838 (s). ^{1}H NMR: δ 7.20-7.05 (m, 4H, C_6H_4), 5.58, 5.36 (2s, 2 x 5H, Cp), 5.03 (dd, J_{HH} = 13, J_{HP} = 6, 1H, WCH_2), 3.04 (dd, J_{HH} = 13, J_{HP} = 3, 1H, WCH_2), 2.40 (s, Me, 3H), 2.90-0.50 (m, 22H, Cy). $^{31}P\{^1H\}$ NMR: δ 170.9 (s, J_{PW} = J_{PW} = 200). $^{13}C\{^1H\}$ NMR: δ 228.5 (s, WCO), 226.3 (d, J_{CP} = 24, WCO), 150.6 [s, $C^1(C_6H_4)$], 133.5 [s, $C^4(C_6H_4)$], 130.1, 129.0 [2s, $C^{2,3}(C_6H_4)$], 103.6, 89.2 (2s, Cp), 43.3 [d, J_{CP} = 27, C^1(Cy)], 38.9 [d, J_{CP} = 16, C^1(Cy)], 33.1, 32.0 [2s, C^2(Cy)], 31.4 [d, J_{CP} = 4, $2C^2$(Cy)], 28.3 [d, J_{CP} = 11, C^3(Cy)], 28.2, 28.1 [2d, J_{CP} = 12, C^3(Cy)], 27.8 [d, J_{CP} = 13, C^3(Cy)], 27.0, 26.7 [2s, C^4(Cy)], 21.0 (s, CH_3), 18.7 (d, J_{CP} = 7, WCH_2).

*Data for compound **8**.* Anal. Calcd for $C_{33}Cl_2H_{43}O_3PW_2$(**8**·CH_2Cl_2): C, 41.40; H, 4.53. Found: C, 41.45; H, 4.60. ν(CO) (petroleum ether): 1863 (vs). ^{1}H NMR: δ 7.50, 7.25 (2d, J_{HP} = 8, 2 x 2H, C_6H_4), 5.26 (d, J_{HP} = 2, 5H, Cp), 5.02 (s, Cp), 4.73, 3.74 (2d, J_{HH} = 12, 2 x 1H, CH_2), 2.40 (s, 3H, Me), 2.50-1.00 (m, 22H, Cy). $^{31}P\{^1H\}$ NMR: δ 145.8 (s, J_{PW} = 299, 289). $^{13}C\{^1H\}$ NMR: δ 235.3 (d, J_{CP} = 4, WCO), 203.0 (s, μ-C), 141.7 [s, $C^1(C_6H_4)$], 136.0 [s, $C^4(C_6H_4)$], 130.2, 129.1 [2s, $C^{2,3}(C_6H_4)$], 100.4, 88.0 (2s, Cp), 66.0 (s, CH_2), 57.0 [d, J_{CP} = 14, C^1(Cy)], 49.0 [d, J_{CP} = 25, C^1(Cy)], 36.9 [d, J_{CP} = 4, C^2(Cy)], 35.6 [s, C^2(Cy)], 34.7 [d, J_{CP} = 5, C^2(Cy)], 33.8 [d, J_{CP} = 2, C^2(Cy)], 28.9 [d, J_{CP} = 11, $2C^3$(Cy)], 28.7 [d, J_{CP} = 10, C^3(Cy)], 28.4 [d, J_{CP} = 11, C^3(Cy)], 26.9, 26.8 [2s, C^4(Cy)], 21.3 (s, Me).

X-ray Structure Determination of Compound 4·CH_2Cl_2. The X-ray data collection was performed at 100 K on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated Mo-Kα radiation at 100 K. The software APEX[3] was used for collecting frames with the ω/ϕ scans measurement method. Twinning was found to occur in the crystal. The experimental data were treated as two domain twinned data, with the second domain being rotated from the first domain by 6.1 degrees about the reciprocal axis 0.174, 0.552, 1.000 and real axis 0.083, 1.000, 0.409. The program Cell Now[4] was used to determine the twin law, the cell dimensions and orientation matrixes, and a multi-scan absorption correction was applied with TWINABS.[5] Using the program suite WinGX,[6] the structure was solved by Patterson interpretation and phase

expansion, and refined with full-matrix least squares on F^2 with SHELXL97.[7] During the solution process, the compound was found to crystallize with one molecule of dichloromethane. During the refinement stages, a fully anisotropic model was attempted but the temperature factors of C(8), C(10), C(13) and C(21) became non-positive definite. Therefore, these atoms were refined anisotropically in combination with the instructions DELU and SIMU and a convenient convergence was obtained. All hydrogen atoms were geometrically placed and refined using a riding model, except for H(12), which was located in the Fourier maps and refined isotropically, riding also on its parent atom.

X-ray Structure Determination of Compound 6 . The X-ray data collection was performed as described for compound **4**. The Bruker software SAINT[8] was used for the data reduction, and a multi-scan absorption correction was applied with SADABS.[9] Twinning was found to occur in the crystal, but it was not possible to find the twin law. Using the program suite WinGX,[6] the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least squares on F^2 with SHELXL97.[7] During the refinement stages a fully anisotropic model was attempted but, due to poor quality of the diffraction data, not all of the positional parameters and the anisotropic temperature factors of all the non-H atoms could be refined anisotropically as usual. So an important number of atoms had to be refined anisotropically in combination with the instructions DELU and SIMU, and yet 7 carbon atoms had to be eventually refined isotropically to prevent their temperature factors from becoming non-positive definite. All hydrogen atoms were geometrically placed and refined using a riding model except for H(1), which was located in the Fourier map and was refined isotropically, also riding on its parent atom. Nevertheless, a restraint of the N–H distance to 0.8 Å was necessary for a convenient convergence.

X-ray Structure Determination of Compound 7. The X-ray data collection, data reduction, absorption correction, structure solution and refinements were performed as described for **6**. During the refinement stages, a fully anisotropic model was attempted but the temperature factors of several carbon atoms (the carbonyl C(2); C(3), C(5) and C(6) in the benzyl substituent and C(11), C(14), C(15), C(17) and C(20) in the Cp rings) became non-positive definite. Therefore, these atoms were refined anisotropically in combination with the instructions DELU and SIMU and a convenient convergence was obtained. All hydrogen atoms were geometrically placed and refined using a riding model.

X-ray Structure Determination of Compound 8·CH_2Cl_2. The X-ray data collection was performed at 120 K on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo-Kα. The software SMART[10] was used for collecting

frames with the ω scans measurement method. Data reduction, absorption corrections and structure solution and refinements were performed as described for **6** and **7**. During the solution process, the compound was found to crystallize with one molecule of dichloromethane. During the solution process, the compound was found to crystallize with one molecule of dichloromethane. During the refinement stages, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, except atom C(16) which was refined anisotropically in combination with the instructions DELU and SIMU, to prevent its temperature factors to become non-positive definite. After applying these soft restraints a convenient convergence was obtained. All hydrogen atoms were geometrically placed and refined using a riding model. Upon convergence the strongest residual peaks (5.94-4.09 e A-3), were located around the tungsten atoms.

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