Multisite Reactivity of the Central Mo_2CP core in the Unsaturated Carbyne-Bridged Complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$.

M. Angeles Alvarez, M. Esther García, Sonia Menéndez and Miguel A. Ruiz*.

Departamento de Química Orgánica e Inorgánica/IUQOEM,

Universidad de Oviedo, 33071 Oviedo, Spain.

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 $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(CO)_2]$ (**1**) (Cp= η^5-C_5H_5)[2] and N_2CPh_2,[3] were prepared as described previously. All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns, refrigerated by tap water. 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 for carbonyl ligands 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 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.

Preparation of $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-}\kappa^1\text{:}\eta^2\text{-PHCy}_2)(CO)_2](BF_4)$ (2). A solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL) was cooled at 243 K, then $HBF_4{\cdot}OEt_2$ (12 μL of a 54% solution in Et_2O, 0.087 mmol) was added, and the mixture was stirred for 1 min to give a purple solution. The solvent was then removed under vacuum, and the residue was washed with petroleum ether (3 x 5 mL) to give a purple powder (0.051 g, 91%). This product was found to be quite air-sensitive, so satisfactory microanalytical data were not obtained. ν(CO) (CH_2Cl_2): 1981 (w), 1958 (vs). ^{1}H NMR (400.13 MHz) δ 7.56 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.33 [t, J_{HH} = 7, 1H, H^4(Ph)], 7.08 [false d, J_{HH} = 7, 2H, H^2(Ph)], 5.71, 5.56 (2s, 2 x 5H, Cp), 2.86-0.62 (m, 22H, Cy), –4.30 (d, J_{PH} = 117, μ-PH). ^{31}P{^{1}H} NMR (161.97 MHz): δ 131.4. ^{13}C{^{1}H} NMR (100.61 MHz, 253 K): δ 415.3 (s, μ-*C*Ph), 219.5 (s, MoCO), 217.7 (d, J_{CP} = 11, MoCO), 161.8 [s, C^1(Ph)], 128.8 [s, C^2(Ph)], 128.7 [s, C^4(Ph)], 121.6 [s, C^3(Ph)], 94.4, 93.6 (2s, Cp), 46.0 [d, J_{CP} = 24, C^1(Cy)], 39.2 [d, J_{CP} = 25, C^1(Cy)], 34.5, 32.9 [2d, J_{CP} = 2, C^2(Cy)], 32.0, 31.6 [2s, C^2(Cy)], 27.4, 27.2 [2d, J_{CP} = 12, C^3(Cy)], 27.1 [d, J_{CP} = 16, C^3(Cy)], 26.9 [d, J_{CP} = 12, C^3(Cy)], 25.7, 25.5 [2s, 2C^4(Cy)].

Formation of $[Mo_2Cp_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-CHPh})(\mu\text{-PCy}_2)(CO)_2](BF_4)$ (3). A solution of $HBF_4{\cdot}OEt_2$ (12 μL of a 54% solution in Et_2O, 0.087 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL) at room temperature, and the mixture was stirred for 5 min to give a purple solution. The solvent was then

removed under vacuum, and the residue was washed with petroleum ether (3 x 5 mL) to give an air-sensitive purple powder shown (by NMR) to contain a mixture of compounds **2** and **3** in a 3:2 ratio. All attempts to isolate compound **3** out of this mixture were unsuccessful. *Spectroscopic data for **3***: ν(CO) (CH_2Cl_2): 1981 (w), 1958 (vs). ^{1}H NMR (400.13 MHz, 213 K) δ 9.18 (s, 1H, μ-CH), 7.75-7.72 [m, 3H, H^{2,4}(Ph)], 7.68 [false t, J_{HH} = 8, 2H, H^3(Ph)], 5.83, 4.12 (2s, 2 x 5H, Cp), 2.86-1.10 (m, 22H, Cy). ^{31}P{^{1}H} NMR (161.97 MHz, 213 K): δ 214.8. ^{13}C{^{1}H} NMR (100.61 MHz, 213 K): δ 253.8 (d, J_{CP} = 10, MoCO), 223.7 (s, MoCO), 180.0 (s, μ-*C*HPh), 134.0, 133.6, 132.6, 131.8, 128.8 [5s, C$^{2-6}$(Ph)], 115.2 [s, C^1(Ph)], 93.5, 93.1 (2s, Cp), 52.1, 43.9 [2s, br, C^1(Cy)], 33.5 [s, C^2(Cy)], 33.1 [d, J_{CP} = 2, C^2(Cy)], 32.8, 31.4 [2s, C^2(Cy)], 28.3 [d, J_{CP} = 12, C^3(Cy)], 27.8, 27.7, 27.2 [3d, J_{CP} = 10, C^3(Cy)], 26.3, 26.1 [2s, C^4(Cy)].

Preparation of [$Mo_2Cp_2\{\mu$-η^2:η^3-CPhCHC(CO_2Me)}(μ-PCy_2)($CO)_2$] (4). Neat methyl propiolate (40 μL, 0.450mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in toluene (5 mL), and the mixture was stirred at 333 K for 2 h to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with dichloromethane-petroleum ether (1:10) and the extract was chromatographed through an alumina column (activity IV) at 285 K. Elution with dichloromethane-petroleum ether (1:4) gave an orange fraction yielding, after removal of the solvents under vacuum, compound **4** as an orange microcrystalline solid (0.041 g, 73 %). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex, at 253 K. Anal. Calcd for $C_{35}H_{41}Mo_2O_4P$: C, 56.16; H, 5.52. Found: C, 56.46; H, 5.71. IR (CH_2Cl_2): ν(CO) 1916 (m), 1886 (vs), ν(C=O) 1676 (w), 1658 (w). ^{1}H NMR (300.09 MHz): δ 7.34-7.25 [m, 4H, H^{2,3}(Ph)], 7.12 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.79 (d, J_{HP} = 2, 1H, CH), 5.11, 4.65 (2s, 2 x 5H, Cp), 3.54 (s, 3H, OMe), 2.3-0.9 (m, 22H, Cy). ^{31}P{^{1}H} NMR (121.48 MHz): δ 140.3. ^{13}C{^{1}H} NMR (75.46 MHz): δ 251.6 (d, J_{CP} = 12, MoCO), 233.3 (d, J_{CP} = 6, MoCO), 177.2 (s, *C*O_2Me), 145.9 [s, C^1(Ph)], 137.7 (s, μ-*C*Ph), 128.3 [s, C^3(Ph)], 127.0 [s, C^2(Ph)], 126.8 [s, C^4(Ph)], 92.1 (d, J_{CP} = 5, MoCH), 91.2, 88.1 (2s, Cp), 78.4 (d, J_{CP} = 28, μ-*C*CO_2Me), 51.3 [d, J_{CP} = 14, C^1(Cy)], 51.4 (s, OMe), 47.0 [d, J_{CP} = 5, C^1(Cy)], 37.8 [s, C^2(Cy)], 36.5 [d, J_{CP} = 6, C^2(Cy)], 35.5 [d, J_{CP} = 3, C^2(Cy)], 35.2 [d, J_{CP} = 6, C^2(Cy)], 29.6, 29.1 [2d, J_{CP} = 12, C^3(Cy)], 28.8 [d, J_{CP} = 8, C^3(Cy)], 28.6 [d, J_{CP} = 12, C^3(Cy)], 27.1, 26.9 [2s, C^4(Cy)].

Preparation of [$Mo_2Cp_2\{\mu$-η^1:η^2-C(Ph)CO}(μ-PCy_2)(CO)(κ^1-N_2CPh_2)] (5). A Et_2O solution of N_2CPh_2 (3 mL of a 0.08 M solution, 0.24 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL). Solvents were then removed under vacuum and the oily residue was kept under vacuum in the Schlenk tube for 3 h at room temperature. The residue was then dissolved in dichloromethane, the tube was cooled at 77 K, evacuated under vacuum, and then

refilled with CO and closed. The mixture was then stirred while allowing it to reach room temperature slowly for 2 h, to give a green solution which was concentrated under vacuum and then chromatographed through an alumina column (activity IV) at 285 K. Elution with dichloromethane-petroleum ether (1:4) gave a green fraction yielding, after removal of the solvents under vacuum, compound **5** as a green microcrystalline solid (0.058 g, 90%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex, at 253 K. Anal. Calcd for $C_{44}H_{47}Mo_2N_2O_2P$: C, 61.54; H, 5.52; N, 3.26. Found: C, 61.78; H, 5.32; N, 3.11. ν(CO) (CH_2Cl_2): 1864 (s). ^{1}H NMR (300.09 MHz): δ 7.49-7.36 (m, 8H, Ph), 7.32-7.22 (m, 4H, Ph), 7.04 [t, J_{HH} =7, 1H, H^4(Ph)], 6.80 [false d, J_{HH} =7, 2H, H^2(Ph)], 5.09, 4.72 (2s, 2 x 5H, Cp), 2.6-1.2 (m, 21H, Cy), 0.82 (m, 1H, Cy). ^{31}P{^{1}H} NMR (121.48 MHz): δ 216.4. ^{13}C{^{1}H} NMR (75.46 MHz): δ 234.4 (d, J_{CP} = 12, MoCO), 226.0 [s, MoC(O)], 166.7 [s, C^1(Ph)], 149.9 [s, 2C^1(Ph)], 136.5 (s, N_2CPh_2), 134.4 (s, μ-*C*Ph), 131.4, 130.2, 130.0, 129.5, 128.9, 128.6, 128.3, 128.3, 124.7 [9s, C$^{2-4}$(Ph)], 99.0, 91.1 (2s, Cp), 56.0 [d, J_{CP} = 11, C^1(Cy)], 51.8 [d, J_{CP} = 17, C^1(Cy)], 37.3 [s, C^2(Cy)], 37.0 [d, J_{CP} = 5, C^2(Cy)], 35.2 [d, J_{CP} = 3, C^2(Cy)], 35.1 [d, J_{CP} = 6, C^2(Cy)], 29.3 [d, J_{CP} = 10, C^3(Cy)], 29.0 [d, J_{CP} = 9, C^3(Cy)], 28.9 [d, J_{CP} = 13, C^3(Cy)], 28.6 [d, J_{CP} = 9, C^3(Cy)], 26.9 [s, 2C^4(Cy)].

Preparation of [$Mo_2Cp_2(\mu$-CPh)(μ-PCy_2)(CO)(κ^1-N_2CPh_2)] (6). A Et_2O solution of N_2CPh_2 (3 mL of a 0.08 M solution, 0.24 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in dichloromethane (5 mL). Solvents were then removed under vacuum and the oily residue was kept under vacuum in the Schlenk tube for 3 h at room temperature. The residue was then dissolved in toluene, and the mixture was stirred at 353 K for 30 min to give a dark brown 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 285 K. Elution with dichloromethane-petroleum ether (1:9) gave a brown fraction yielding, after removal of the solvents under vacuum, compound **6** as a brown powder (0.058 g, 93%). Anal. Calcd for $C_{43}H_{47}Mo_2N_2OP$: C, 62.17; H, 5.70; N, 3.37. Found: C, 61.85; H, 5.57; N, 3.45. ν(CO) (CH_2Cl_2): 1872 (s). ^{1}H NMR (400.13 MHz): δ 7.53 [m, 1H, H^4(Ph)], 7.40 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.35-7.32 (m, 3H, Ph), 7.26-7.24 (m, 6H, Ph), 7.09 [t, J_{HH} = 7, 1H, H^4(Ph)], 6.76 [false d, J_{HH} = 7, 2H, H^2(Ph)], 5.39, 5.05 (2s, 2 x 5H, Cp), 2.74 (d, br, J_{HP} = 12, 1H, Cy), 2.2-1.2 (m, 21H, Cy). ^{31}P{^{1}H} NMR (161.97 MHz): δ 188.7. ^{13}C{^{1}H} NMR (100.61 MHz): δ 373.5 (d, J_{CP} = 6, μ-*C*Ph), 248.5 (d, J_{CP} = 10, MoCO), 165.4, 148.2, 137.9 [3s, C^1(Ph)], 133.9 (s, N_2CPh_2), 129.6, 129.3, 124.2 [3s, C^4(Ph)], 129.5, 128.8, 128.6, 127.7, 127.6, 123.1 [6s, C^{2,3}(Ph)], 98.9, 91.6 (2s, Cp), 50.0 [d, J_{CP} = 18, C^1(Cy)], 48.0 [s, br, C^1(Cy)], 37.4 [s, C^2(Cy)], 34.7 [d, J_{CP} = 2, C^2(Cy)], 34.6, 33.4

[2s, C^2(Cy)], 29.1 [d, J_{CP} = 12, C^3(Cy)], 28.7 [d, J_{CP} = 11, C^3(Cy)], 28.5 [d, J_{CP} = 10, C^3(Cy)], 28.4 [d, J_{CP} = 11, C^3(Cy)], 26.8, 26.7 [2s, C^4(Cy)].

Preparation of [$Mo_2Cp_2\{\mu$-η,κ:η,κ-C(Ph)Se$\}(\mu$-$PCy_2)(CO)_2$] (7). Solid grey selenium (0.010 g, 0.125 mmol) was added to a solution of compound **1** (0.050 g, 0.075 mmol) in tetrahydrofuran (10 mL), and the mixture was stirred at 333 K for 2 h to give an orange 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 285 K. Elution with dichloromethane-petroleum ether (1:9) gave an orange fraction yielding, after removal of the solvents under vacuum, compound **7** as an orange microcrystalline powder (0.053 g, 92%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex, at 253 K. Anal. Calcd for $C_{31}H_{37}Mo_2O_2PSe$: C, 50.08; H, 5.02. Found: C, 49.68; H, 5.20. ν(CO) (THF): 1889 (sh), 1872 (vs). ^{1}H NMR (300.09 MHz): δ 7.07 [m, 4H, $H^{2,3}$(Ph)], 6.95 [m, 1H, H^4(Ph)], 5.22, 5.12 (2d, J_{HP} = 1, 2 x 5H, Cp), 2.10-1.00 (m, 22H, Cy). ^{31}P{^{1}H} NMR (121.48 MHz): δ 124.3. ^{13}C{^{1}H} NMR (75.46 MHz): δ 242.8 (d, J_{CP} = 11, MoCO), 238.5 (d, J_{CP} = 7, MoCO), 155.2 [s, C^1(Ph)], 130.7 [s, C^2(Ph)], 127.5 [s, C^3(Ph)], 124.8 [s, C^4(Ph)], 91.0, 90.4 (2s, Cp), 89.6 (s, μ-CSe), 51.7 [d, J_{CP} = 22, C^1(Cy)], 51.6 [s, C^1(Cy)], 36.8, 36.5 [2d, J_{CP} = 4, C^2(Cy)], 34.8, 33.9 [2d, J_{CP} = 5, C^2(Cy)], 29.3, 29.1, 28.8 [3d, J_{CP} = 11, C^3(Cy)], 28.6 [d, J_{CP} = 10, C^3(Cy)], 26.9, 26.8 [2s, C^4(Cy)].

X-ray Structure Determination of Compounds 4, 5, and 7. The X-ray intensity data were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated MoK_α radiation at 100 K. The software APEX[4] was used for collecting frames with the ω/ϕ scans measurement method. The SAINT software was used for the data reduction,[5] and a multi-scan absorption correction was applied with SADABS.[6] Using the program suite WINGX[7] the structure was solved by Patterson interpretation and phase expansion using SHELXL97,[8] and refined with full-matrix least squares on F^2 using SHELXL97. All the positional parameters and the anisotropic temperature factors of the non-H atoms were refined anisotropically and all hydrogen atoms were generally placed geometrically and refined isotropically using a riding model. In the case of compound **4**, the H10 atom was located and refined. We note that a molecule of dichloromethane was identified in the lattice of these three compounds. In the case of compound **5**, a second solvent molecule was also present, but it was highly disordered and could not be properly identified nor modelled. Therefore, the SQUEEZE procedure,[9] as implemented in PLATON,[10] was used. Upon squeeze application and convergence, the strongest residual peak (0.81 eA^{-3}) was placed between both molybdenum atoms.

References

(1) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals, 5th Edition*; Butterworth-Heinemann: Oxford, U. K., 2003.

(2) Alvarez, M. A.; García, M. E.; García-Vivó, D.; Martínez, M. E.; Ruiz, M. A. *Organometallics* **2011**, *30*, 2189.

(3) Millar, J. B. *J. Org. Chem.* **1959**, *24*, 560.

(4) *APEX 2, version 2.0-1*; Bruker AXS Inc: Madison, WI, 2005.

(5) *SMART & SAINT Software Reference Manuals, version 5.051 (Windows NT version)*; Bruker Analytical X-ray Instruments: Madison, WI, 1998.

(6) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996.

(7) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(8) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112.

(9) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr. Sect. A* **1990**, *46*, 194.

(10) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2010.