Interplay of Metal-Allyl and Metal-Metal Bonding in Dimolybdenum Allyl Complexes

Supplementary Information

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Experimental Procedures

General Considerations. All manipulations were performed under an inert atmosphere or vacuum using standard glovebox, vacuum-line, and Schlenk techniques. Solvents were dried by elution from columns of activated alumina according to the procedure by Grubbs *et al*[1] and subsequently degassed by standard techniques and stored over activated 4 Å molecular sieves. All reactions were carried out at atmospheric pressure (600 mTorr at Los Alamos, elevation 7200 ft). Tetraallyldimolybdenum was prepared from tetrakis(acetato)dimolybdenum[2] using a standard literature procedure.[3] All other chemicals were purchased from Aldrich and dried prior to use. All NMR spectra were recorded on a Varian Unity 300 MHz or Bruker Advance 300 or 400 MHz spectrometers. All ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the chemical shifts of the solvent as a secondary standard. ^{31}P NMR shifts are reported relative to an external 85% H_3PO_4 standard.

X-Ray Crystallography. Single-crystal X-ray diffraction experiments for **2** and **3** were performed on a Brüker P4/CCD/PC diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Diffraction data were refined using SHELXTL PC.[4] Single crystals of **2** were grown from a concentrated toluene and hexane solution at -30 °C inside the glovebox freezer. Similarly, crystals of **3** were obtained by cooling a concentrated pentane solution of this complex to -30 °C. The crystals were coated in mineral oil and mounted on a glass fiber at -70 °C. A hemisphere of data was collected using a combination of ϕ and ω scans, with 30 second frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement was performed using SMART[5] software. Frame integration and final cell parameter calculation were carried out using SAINT[6] software. The data were corrected for absorption using the SADABS[7] program. Decay of reflection intensity was not observed. The structures were solved using difference Fourier techniques. The initial solutions revealed the metal center and the majority of all other non-hydrogen positions. The remaining atomic positions were determined from subsequent Fourier syntheses. All hydrogen atoms were placed in ideal positions, with C-H distances held at 0.96 (methine), 0.97 (methylene), and 0.98 Å (methyl). The hydrogen atoms were refined using a riding model, with their isotropic temperature factors set to 1.2 (methine, methylene) or 1.5 (methyl) times the isotropic U of the attached carbon atom.

DFT Calculations. The hybrid B3LYP DFT approximation (as implemented in the GDV package[8]) was used to determine the geometries and associated frequencies of the local minima and transition states connecting them. The metal centers were described by the "small core" LANL2 relativistic core potential[9] and the associated LANL2TZ(f) basis set.[10] The 6-31G* basis set was used on the ligand atoms. All stationary points were verified to be minima or saddles by explicit computation of the second derivatives of the energy with respect to nuclear displacement.

Preparation of $Mo_2(allyl)_4(PMe_3)_2$ (2): A cooled solution (-30 °C) of PMe_3 (21.3 mg, 0.28 mmol) in toluene (2 mL) was added to a cold solution (-78 °C) of $Mo_2(allyl)_4$ (50 mg, 0.14 mmol) in toluene (10 mL). The mixture was placed in a freezer (-30 °C) for two days whereupon the mother liquor was decanted yielding dark green crystals. These crystals were then washed with 2 mL of cold pentane (-80 °C) then dried *in vacuo* below -30 °C. Yield: 48 mg, 67% yield. ^1H NMR (299.9 MHz, toluene-d_8, -20 °C): δ = 6.50 (m, 2H, $CH_2C\mathit{H}CH_2$-**A**), 4.01 (m, 2H, $CH_2C\mathit{H}CH_2$-**B**), 3.80 (ddt, 2H, $^3J_{HH}$ = 8.7 Hz, syn-$C\mathit{H}_2CHC\mathit{H}_2$-**B**), 3.10 (m, 2H, $^3J_{HH}$ = 8.1 Hz, syn-$C\mathit{H}_2CHC\mathit{H}_2$-**B**), 1.30 (obscured m, 2H, anti-$C\mathit{H}_2CHC\mathit{H}_2$-**A**), 1.26 (d, 18H, $^2J_{HP}$ = 6.3 Hz, $P(C\mathit{H}_3)_3$), 1.08 (m, 2H, $^3J_{HH}$ = 12.3 Hz, anti-$C\mathit{H}_2CHC\mathit{H}_2$-**A**), 0.60 (dd, H, $^3J_{HH}$ = 10.5 Hz, syn-

CH_2CHCH_2-**A**), 0.47 (d, 2H, $^3J_{HH}$ = 14.7 Hz, anti-CH_2CHCH_2-**B**), -0.46 (m, 2H, $^3J_{HH}$ = 13.8 Hz, anti-CH_2CHCH_2-**B**), -0.79 (dd, 2H, $^3J_{HH}$ = 9.3 Hz, syn-CH_2CHCH_2-**A**). $^{13}C\{^1H\}$ NMR (75.4 MHz, toluene-d_8, -20 °C) δ = 113.32 (s, CH_2CHCH_2), 104.63 (s, CH_2CHCH_2), 60.07 (s, CH_2CHCH_2), 51.70 (s, CH_2CHCH_2), 51.01 (s, CH_2CHCH_2), 43.58 (s, CH_2CHCH_2), 18.24 (br m, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, -20 °C): δ = 13.8 (s).

Crystallographic data for **2**: $C_{18}H_{38}Mo_2P_2$, M = 508.30, monoclinic, space group $P21/n$, a = 10.7554(7), b = 8.8269(6), c = 11.9843(8) Å, b = 108.515(1) °, V = 1078.9(1) Å^3, Z = 2, μ = 1.307 mm^{-1}, T = 203 K, $R1$ [$I > 2s(I)$] = 0.0572, $wR2$ [$I > 2s(I)$] = 0.1323, GooF = 1.097.

Preparation of $Mo_2(allyl)_2(PMe_3)_2$ (ONp)$_2$ (3): A cooled solution (-35 °C) of PMe_3 (21 mg, 0.28 mmol) in toluene (2 mL) was added to a cooled solution (-35 °C) of **1** (50 mg, 0.14 mmol) in toluene (5 mL). The resulting green solution was kept at -35 °C for 24 hours before adding a cooled solution of 22 mg of neopentyl alcohol (0.25 mmol) in approximately 2 mL of toluene. After 24 hours at -35 °C, the resulting green solution was allowed to warm to ambient temperature and stir for an additional 24 hours. The solvent was removed *in vacuo* to yield 69 mg of a greenish-blue microcrystalline solid of which **3** was spectroscopically identified as the major product (~70%). Recystallization of this solid from a concentrated pentane solution (-35 °C) afforded 13 mg (15% isolated yield) of spectroscopically pure **3** as a crystalline solid. This complex was prepared in a similar fashion from the addition of 2 equivalents of neopentyl alcohol to isolated **2**. ^1H NMR (400.1 MHz, toluene-d_8, 23 °C): δ = 4.33 (quintet, 2H, $^3J_{HH}$ = 8.0 Hz, CH_2CHCH_2**)**, 3.70 (d, 2H, $^3J_{HH}$ = 8.0 Hz, CH_2CHCH_2), 3.54 (d, 2H, $^3J_{HH}$ = 8.0 Hz, CH_2CHCH_2**)**, 2.65 (br m, 2H, OCH_2), 1.00 (d, 18H, $^2J_{HP}$ = 5.5 Hz, $P(CH_3)_3$), 0.96 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, toluene-d_8, 23 °C) δ = 101.97 (s, CH_2CHCH_2), 81.95 (m, OCH_2), 54.38 (s, CH_2CHCH_2), 34.62 (s, $C(CH_3)_3$), 27.28 (s, C(CH_3)$_3$), 12.62 (m, P(CH_3)$_3$). $^{31}P\{^1H\}$ NMR (162.0 MHz, toluene-d_8, 23 °C): δ = -18.03 (s).

Crystallographic data for **3**: $C_{22}H_{50}Mo_2O_2P_2$, M = 600.48, monoclinic, space group $P2/n$, a = 11.935(3), b = 8.710(2), c = 14.177(4) Å, b = 97.592(5) °, V = 1460.8(7) Å^3, Z = 4, μ = 0.982 mm^{-1}, T = 203 K, $R1$ [$I > 2s(I)$] = 0.0698, $wR2$ [$I > 2s(I)$] = 0.1318, GooF = 1.194. Refinement of this data set revealed a disordered Mo_2 unit, orthogonal to the principal Mo-Mo axis. This disorder was modelled by refining both dimolybdenum units with a shared free variable that assigned site occupation on the basis of observed electron density. The site-occupancy factors of Mo1 were allowed to vary against Mo1’ and were constrained so that the total Mo_2 occupancy was unity. This resulted in site occupancy factors of 0.881 and 0.119 for the two orientations. Analysis of the difference map failed to reveal candidates for disordered ligand sites associated with the minor-occupancy Mo_2 unit. Examination of reciprocal space plots including several hundred reflections show no evidence of twinning. The refinement is consistent with a whole molecule disorder for which there are many precedents. The space group, P2/n, is unambiguously determined from systematic absences. All 8 reflections corresponding to the 2sub1 screw axis are strongly observed, thus ruling out space group p2sub1/n. Finally, we feel the 88% refinement of the ligand set would not improve the structure (less than one electron per site), and that a full occupancy refinement is justified.

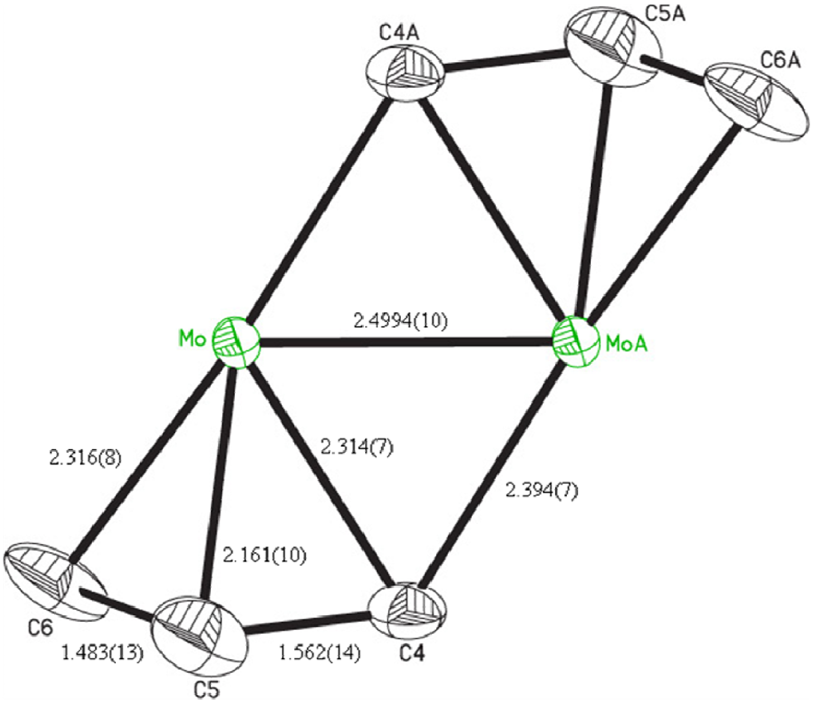

Figure S1. Solid state representation of the molybdenum core and bridging allyl ligands in **2** at 30% probability ellipsoids.

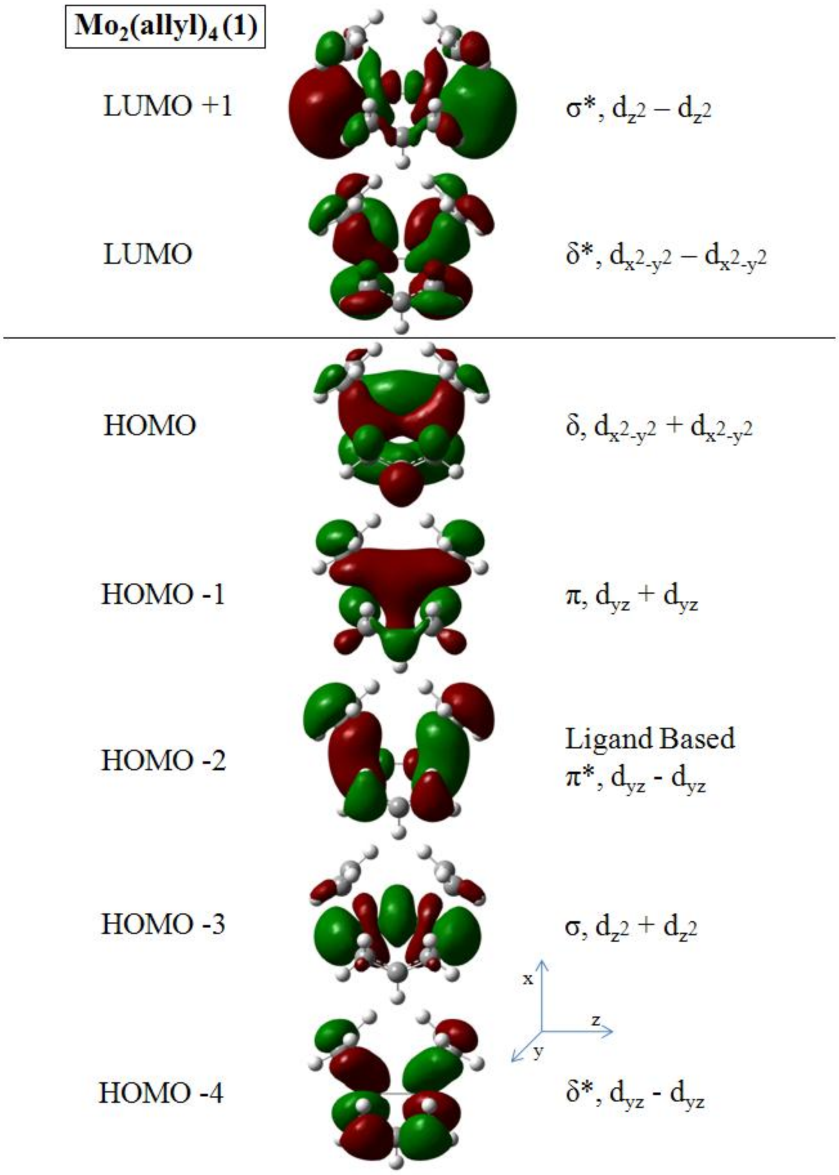

Figure S2. Frontier molecular orbital diagram calculated for **1** at the B3LYP/LANL2TZ(f)/6-31G* level of DFT.

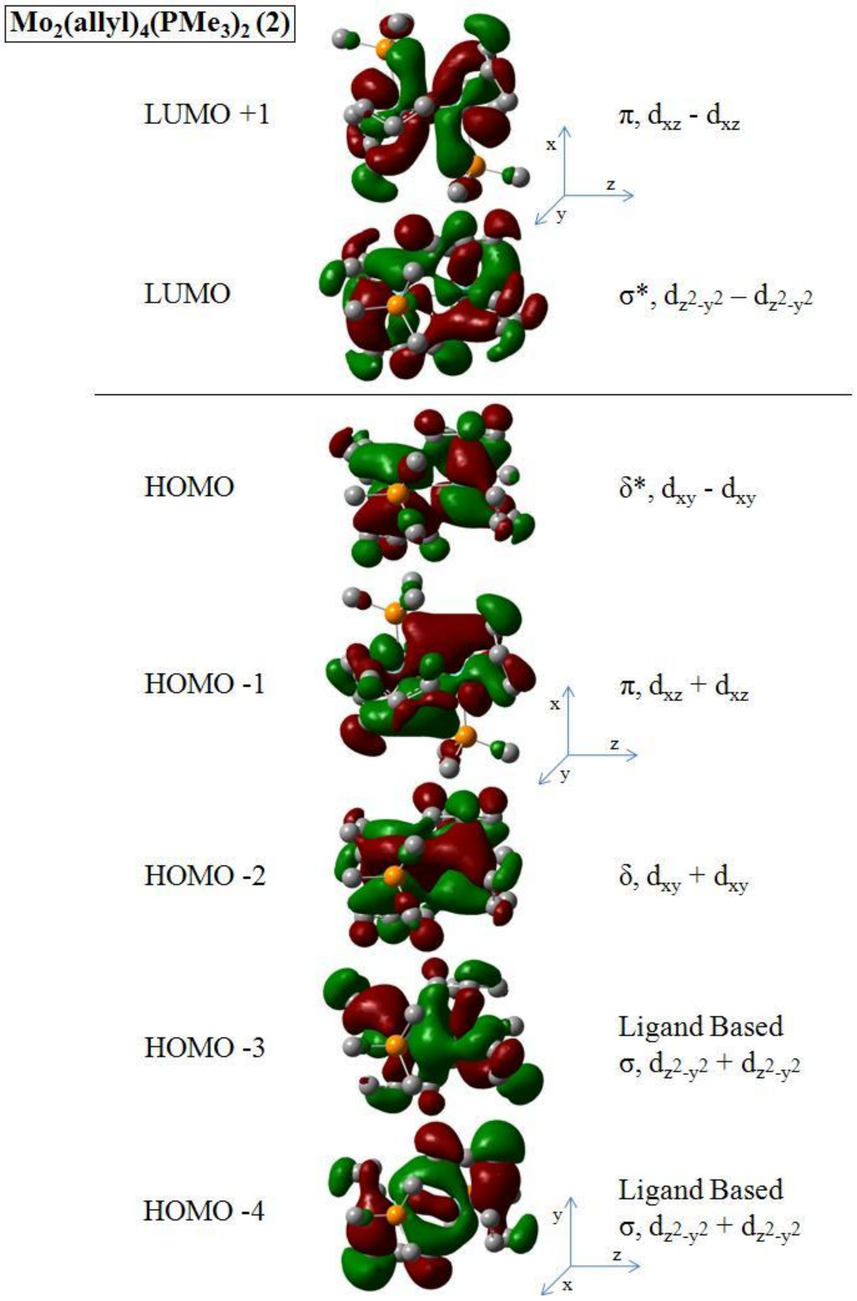

Figure S3. Frontier molecular orbital diagram calculated for **2** at the B3LYP/LANL2TZ(f)/6-31G* level of DFT.

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