Supplementary Material for Chemical Communications

Supporting Information

For

Mixed Metal Bis(μ-oxo) Complexes with $[CuM(\mu\text{-}O)_2]^{n+}$ (M = Ni(III) or Pd(II)) Cores

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Experimental Details

General Considerations. All reagents were obtained from commercial sources and used as received unless stated otherwise. The solvents tetrahydrofuran (THF), diethyl ether (Et_2O), pentane, and toluene were distilled from Na/benzophenone or passed through solvent purification columns (Glass Contour, Laguna, CA). Dichloromethane (CH_2Cl_2) was distilled from calcium hydride or purified by passing through a solvent purification column. Labeled dioxygen was purchased from Cambridge Isotopes, Inc. or Icon Isotopes, Inc. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glove box under a dry nitrogen atmosphere or were manipulated using standard Schlenk techniques. The compounds, $[H(Me_2L^{iPr2})Cu(MeCN)]$,[1] $[H(Me_2L^{Me2})Cu(MeCN)]$ (**4**),[2] $(PPh_3)_2PdO_2$ (**5**),[3] and $PhTt^{tBu}Ni(CO)$[4] (**2**) were prepared as reported previously.

Physical Methods. NMR spectra were recorded on a Varian VI-300 or VXR-300 spectrometer. Chemical shifts (δ) for ^1H or ^{13}C NMR spectra were referenced to residual protium in the deuterated solvent, and for ^{31}P NMR spectra were referenced to external 85% H_3PO_4 in H_2O. UV-vis spectra were recorded on a HP8453 (190-1100 nm) diode array spectrophotometer. Low-temperature spectra were acquired using a custom manufactured vacuum dewar equipped with quartz windows, with low temperatures achieved with the use of a low-temperature MeOH bath circulator. X-band EPR spectra were recorded on a Bruker E-500 spectrometer, with an Oxford Instruments EPR-10 liquid helium cryostat (2-65K, 9.61 GHz). Quantitation of EPR signal intensity was achieved by comparing the double integration of the derivative spectrum to that of $[H(Me_2L^{iPr2})CuCl]$[5] in 1:1 CH_2Cl_2/toluene. Resonance Raman spectra were collected on an Acton 506 spectrometer using a Princeton Intstruments LN/CCD-1100-PB/UVAR detector and ST-1385 controller interfaced with Winspec software. A Spectra-Physics 2030-15 argon laser was used to excite at 457.9 nm. The power was between 60-200 mW. The spectra were obtained at –196 °C (77K) using a backscattering geometry; samples were frozen in a teflon cup or a copper cup attached to a liquid-nitrogen cooled cold-finger. Raman shifts were externally referenced to liquid indene.

$(PPh_3)_2Pd^{18}O_2$. A method adapted from the reported procedure for $(PPh_3)_2Pd^{16}O_2$ was used.[3] In an inert atmosphere, a 50 mL Schlenk flask was charged with a suspension of $Pd(PPh_3)_4$ (100 mg, 8.65 x 10^{-5} mol) in Et_2O (20 mL). The suspension was frozen at –196 °C, the headspace evacuated, and $^{18}O_2$ transferred into the flask. Warming to ambient temperature and stirring for 15 min resulted in deposition of a green solid, which was collected, washed with Et_2O (20 mL), and dried *in vacuo* (42 mg, 72%). FTIR: $\nu(^{18}O\text{-}^{18}O) = 828$ cm^{-1} ($\Delta^{16}O_2\text{-}^{18}O_2 = 48$ cm^{-1}).

UV-vis Experiments. $[H(Me_2L^{iPr2})Cu(O_2)]$ (1) + $PhTt^{tBu}Ni(CO)$ (2). In a typical experiment, $[H(Me_2L^{iPr2})Cu(O_2)]$ (**1**) was prepared in situ by oxygenating a THF solution of $[H(Me_2L^{iPr2})Cu(MeCN)]$ at –80 °C in a UV cell. After complete formation of

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[1] Spencer, D. J. E., Aboelella, N. W.; Reynolds, A. M.; Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 2108.

[2] Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002,** 41, 6307.

[3] Nyman, C. J.; Wymore, C. E.; Wilkinson, G. *J. Chem. Soc. (A)* **1968**, 561.

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[5] Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 7270.

[H(Me_2L^{iPr2})Cu(O_2)] (monitored by UV-vis spectroscopy), excess O_2 was removed by evacuating and purging the UV-vis cell several times with N_2 and then bubbling argon through the solution for approximately 20 min while maintaining a temperature of –80 °C. The UV-vis spectrum was then recorded in order to confirm that no degradation of the spectral features had occurred. One equivalent of PhTt^{tBu}Ni(CO) was then injected via syringe, and product formation was monitored at –80 °C over ~1 d. Final mixed concentrations (assuming dimer formation) were between 0.6-1.0 mM. Exctinction coefficients are reported per complex (assuming dimer formation). λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 440 (br, 8500), 498 (8300).

(PPh_3)$_2$$PdO_2$ (5) + [H(Me_2L^{Me2})Cu($NCCH_3$)] (4). In an inert atmosphere glovebox, a 4 mL sample of a stock solution of (PPh_3)$_2$$PdO_2$ (**5**) in THF (0.2 mM) was placed in a UV cuvette, which was removed from the box and cooled to –80 °C. An initial spectrum was recorded to verify the starting material (shoulder at 335 nm).[6] A sample from a stock solution (0.2 mM) of [H(Me_2L^{Me2})Cu($NCCH_3$)] (**4**) in THF (1 equiv) was injected, resulting in an immediate color change to dark yellow-brown and the appearance of new absorption bands: λ_{max}, nm (ε, $M^{-1}cm^{-1}$): 448 (5900), 600 (sh, 450). A spectrophotometric titration was performed according to a similar protocol, using 0.25-2.0 equiv of Cu(I) reagent and monitoring at 448 nm (Figure S1).

Resonance Raman, EPR, and NMR Experiments. Similar protocols to those used in the UV-vis experiments were followed, except final concentrations were 1.0 mM (EPR, NMR) or ~10 mM (Raman) and solutions were prepared in the appropriate sample containers (teflon cup or coldfinger/Cu cup for Raman, quartz tubes for EPR and NMR).

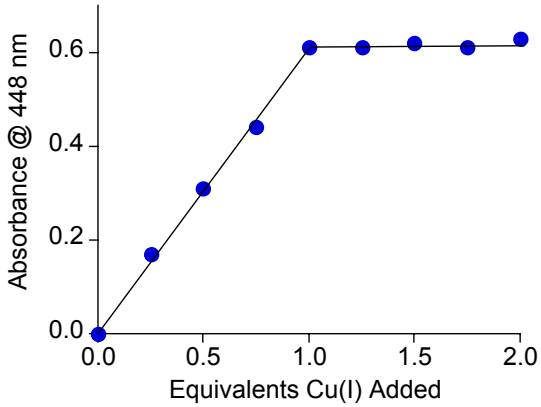

Figure S1. Plot showing results of spectrophotometric titration of (PPh_3)$_2$$PdO_2$ (**5**) with [H(Me_2L^{Me2})Cu($NCCH_3$)] (**4**) in THF at –80 °C.

[6] Deal, D.; Zink, J.I. *Inorg. Chem.* **1981**, *20*, 3995.

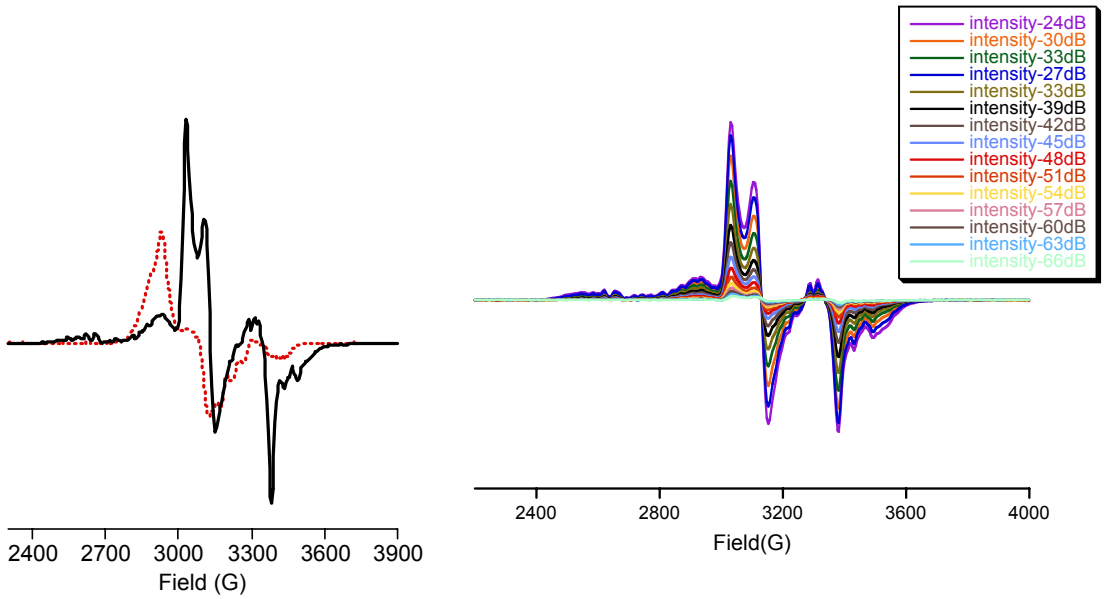

Figure S2. EPR spectra of the solution obtained upon mixing [H(Me_2L^{iPr2})Cu(O_2)] (**1**) and $PhTt^{tBu}$Ni(CO) (**2**) at –80 °C. Left: Solid black line is same as shown in Figure 1b, and dashed red line is of the solution resulting after warming to room temperature. Right: Overlay of spectra obtained at various microwave powers. All spectra obtained at 2K, 9.6 GHz.

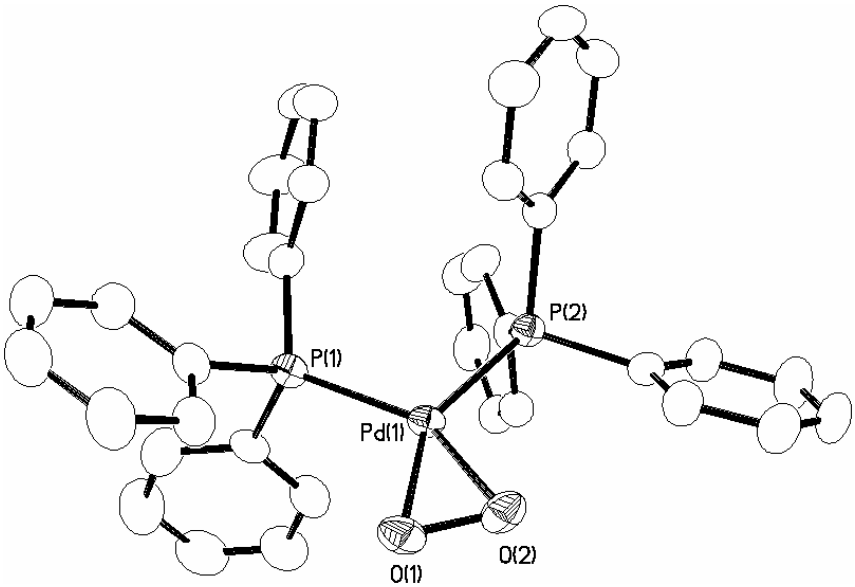

Figure S3. X-ray crystal structure of $(PPh_3)_2PdO_2$ (**5**), with all nonhydrogen atoms shown as 50% thermal ellipsoids.

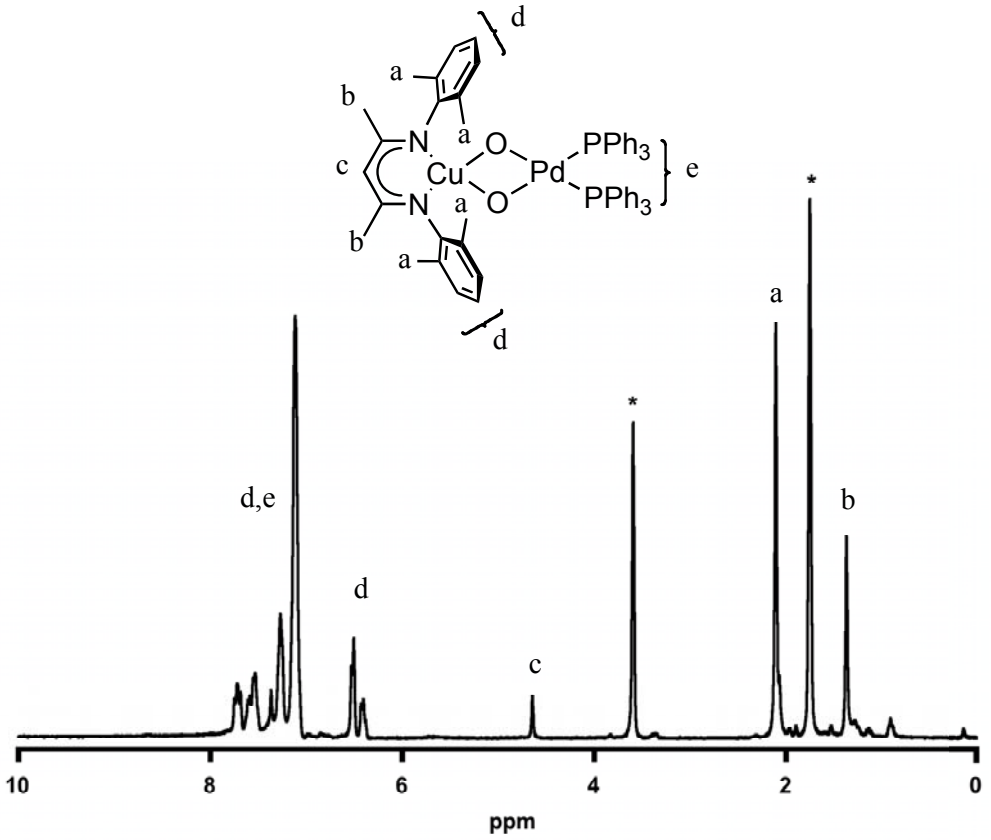

Figure S4. ^{1}H NMR spectrum of $(PPh_3)_2Pd(\mu\text{-}O)_2Cu[H(Me_2L^{Me2})]$ (**6**) (THF-d^8, -80 °C). The peaks labeled with * are from the solvent.

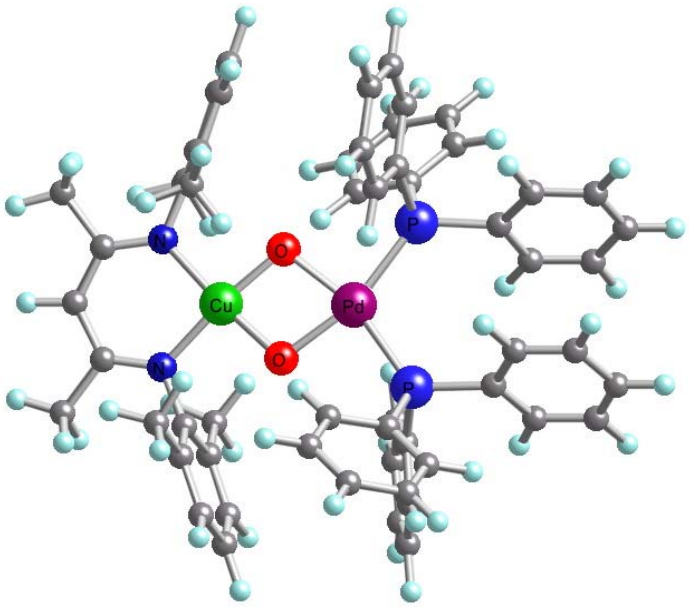

Figure S5. Calculated structure of $(PPh_3)_2Pd(\mu\text{-}O)_2Cu[H(Me_2L^{Me2})]$ (**6**).

Calculations Details

The molecular geometry of **6** was fully optimized at the density functional level of theory (DFT) using the exchange and correlation functionals of Perdew and co-workers[7,8] as modified by Adamo and Barone (*m*PWPW91).[9] Atomic orbital basis functions were taken for Cu and Pd from the Stuttgart/Dresden relativistic effective core potential basis SDD,[10] for N, O, and P from the 6-311G* basis, for C from the 6-31G basis, and for H from the minimal STO-3G basis.[11] Calculations employed the Gaussian 03 electron structure program suite.[12]

Optimized cartesian coordinates (Å)

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