

**Supporting Information for**

**Palladium-Gold Oxo Complexes<sup>‡</sup>**

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**Experimental**

$\text{Pd}(\text{Bu}^t_2\text{bpy})\text{Cl}_2$  ( $\text{Bu}^t_2\text{bpy}$  = 4,4'-di-tert-butyl-2,2'-bipyridine)<sup>1</sup> and  $[(\text{LAu})_3(\mu^3\text{-O})]\text{BF}_4$  ( $\text{L} = \text{PPh}_3$ )<sup>2</sup> were prepared by literature procedures. Although the complexes did not appear to be air-sensitive experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox or on a Schlenk line with dried and degassed solvents stored under dinitrogen over 4 Å molecular sieves or sodium metal. NMR spectra were recorded on a Bruker AMX-250, -300, or -500 spectrometers at ambient probe temperatures. Shifts are given in *ppm* with positive values downfield of TMS (<sup>1</sup>H and <sup>13</sup>C) or external  $\text{H}_3\text{PO}_4$  (<sup>31</sup>P). <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded in proton decoupled mode. Desert Analytics performed the microanalyses (inert atmosphere). The presence of solvents of crystallization in the analyzed samples was confirmed by NMR spectroscopy. The Chemistry Mass Spectrometry Facility at the Ohio State University collected the mass spectral data for the organic products.

**$[(\text{Bu}^t_2\text{bpy})\text{Pd}(\mu^3\text{-O})(\text{AuL})_2](\text{BF}_4)_2$  (1) (L=PPh<sub>3</sub>).** A solution of  $\text{Pd}(\text{Bu}^t_2\text{bpy})\text{Cl}_2$  (89.0 mg, 0.200 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) was added to a stirred solution of  $[(\text{LAu})_3(\mu^3\text{-O})]\text{BF}_4$  (296 mg, 0.200 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL). The mixture changed from yellow to orange within 5 min. The reaction was further stirred for 25 min and then concentrated in vacuo to ca 3 mL. Toluene (6 ml) was added and the mixture was cooled at -30 °C for 24 h. The resulting fine microcrystalline orange product was isolated by filtration. Yield: 137 mg (73 %). Crystals for the X-ray analysis were obtained by recrystallization from  $\text{CD}_2\text{Cl}_2/\text{Ether}$ . Anal. Calcd (found) for  $\text{C}_{72}\text{H}_{78}\text{N}_4\text{Au}_2\text{B}_2\text{F}_8\text{O}_2\text{P}_2\text{Pd}_2$ : C, 46.15 (45.83); H, 4.16 (4.24); N, 2.99 (2.83). <sup>1</sup>H NMR (250 MHz,

<sup>1</sup> Z. Qin, M. C. Jennings, and R. J. Puddephatt, *Inorg. Chem.*, 2002, **41**, 3967

<sup>2</sup> (a) Yang, Y.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 1946-1951. (b) Nesmeyanov, A. N.; Perevalova, E. G.; Struchkov, Y. T.; Antipin, M. Y.; Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* **1980**, *201*, 343-349.

CD<sub>2</sub>Cl<sub>2</sub>): 8.64 (d, 4H, J<sub>HH</sub> = 5.9 Hz, 6,6'-H-bpy), 8.08 (d, 4H, J<sub>HH</sub> = 1.9 Hz, 3,3'-H-bpy), 7.54 (dd, 4H, J<sub>HH</sub> = 5.9 & 1.9 Hz, 5,5'-H-bpy), 7.44-7.26 (m, 30H, Ph), 1.43 (s, 36H, Bu<sup>t</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (101.2 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 26.6 (s).

**[(Bu<sup>t</sup><sub>2</sub>bpyPd)<sub>4</sub>(μ<sup>3</sup>-O)<sub>3</sub>(AuL)](BF<sub>4</sub>)<sub>3</sub> (2) (L=PPh<sub>3</sub>). *Method A.* A solution of Pd(Bu<sup>t</sup><sub>2</sub>bpy)Cl<sub>2</sub> (100.0 mg, 0.224 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added with stirring to [(LAu)<sub>3</sub>(μ<sup>3</sup>-O)]BF<sub>4</sub> (250 mg 0.168 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The homogeneous mixture was further stirred for 40 min and then concentrated in vacuo to ca 4 ml. To this solution, xylene (6 ml) was added drop-wise at room temperature. After 4 days the fine microcrystalline orange product was isolated by filtration. Yield: 95 mg (75 %).**

*Method B.* A CH<sub>2</sub>Cl<sub>2</sub> solution (4 mL) of [(Bu<sup>t</sup><sub>2</sub>bpyPd)(μ<sup>3</sup>-O)(AuL)]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> (75.0 mg, 0.040 mmol) was added to a stirred solution/suspension of Pd(Bu<sup>t</sup><sub>2</sub>bpy)Cl<sub>2</sub> (36.0 mg, 0.080 mmol) (250 mg 0.168 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL). Within 10 min and the color of the homogeneous mixture changed from yellow to orange. Solution was further stirred for 45 min and then concentrated in vacuo (4 ml). To this solution, toluene (8 ml) was added drop-wise. After a couple of days the fine orange microcrystalline product was isolated by filtration. Yield: 42 mg (46 %).

Crystals for the X-ray analysis were initially obtained by recrystallization from 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>/toluene but these gave very poor results and contained badly disordered toluene. Recrystallization from 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>/xylene gave better crystals for the X-ray analysis as reported here.

Anal. Calcd (found) for C<sub>90</sub>H<sub>111</sub>N<sub>8</sub>AuB<sub>3</sub>F<sub>12</sub>O<sub>3</sub>PPd<sub>4</sub>0.5p-xylene: C, 48.64 (48.77); H, 4.87 (5.00); N, 4.82 (4.72). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 9.34 (d, 2H, J<sub>HH</sub> = 6.2 Hz, 6,6'-H-bpy), 9.17 (d, 2H, J<sub>HH</sub> = 6.0 Hz, 6,6'-H-bpy), 8.59 (d, 2H, J<sub>HH</sub> = 5.9 Hz, 6,6'-H-bpy), 8.38 (d, 2H, J<sub>HH</sub> = 6.0 Hz, 6,6'-H-bpy), 8.26 (dd, 2H, J<sub>HH</sub> = 5.1 Hz, J<sub>HH</sub> = 1.9 Hz, 5,5'-H-bpy), 8.20 (dd, 2H, J<sub>HH</sub> = 6.1 Hz, J<sub>HH</sub> = 1.9 Hz, 5,5'-H-bpy), 8.04 (d, 2H, J<sub>HH</sub> = 1.9 Hz, 3,3'-H-bpy), 7.98 (d, 2H, J<sub>HH</sub> = 1.9 Hz, 3,3'-H-bpy), 7.80 (d, 2H, J<sub>HH</sub> = 1.9 Hz, 3,3'-H-bpy), 7.76 (dd, 2H, J<sub>HH</sub> = 6.0 Hz, J<sub>HH</sub> = 1.9 Hz, 5,5'-H-bpy), 7.32 (d, 2H, J<sub>HH</sub> = 1.9 Hz, 3,3'-H-bpy), 7.28 (dd, 2H, J<sub>HH</sub> = 5.9 Hz, J<sub>HH</sub> = 2.0 Hz, 5,5'-H-bpy), 7.16-7.04 (m, 15H, Ph), 1.53 (s, 18H, Bu<sup>t</sup>), 1.42 (s, 18H, Bu<sup>t</sup>), 1.32 (s, 18H, Bu<sup>t</sup>), 1.29 (s, 18H, Bu<sup>t</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 25.7 (s).