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**(dppe)Pt{S<sub>2</sub>C<sub>2</sub>(2-pyridyl)(CH<sub>2</sub>CH<sub>2</sub>OH)}, 1.** (dppe)Pt(SH)<sub>2</sub> (250 mg, 0.379 mmol) and 1-(2-pyridyl)-2-bromo-4-acetoxy-butan-1-one (114 mg, 0.417 mmol) were stirred in DMF for 18h. The DMF was removed in vacuo and the solid was chromatographed on a 1 x 20 cm alumina column where the product eluted with CH<sub>2</sub>Cl<sub>2</sub>. The eluent was evaporated to dryness to give (dppe)Pt{S<sub>2</sub>C<sub>2</sub>(2-pyridyl)(CH<sub>2</sub>CH<sub>2</sub>OAc)} in 70% yield (266 mg, 0.265 mmol). To a solution of 0.1 M K<sub>2</sub>CO<sub>3</sub> in MeOH was added (dppe)Pt{S<sub>2</sub>C<sub>2</sub>(2-pyridyl)(CH<sub>2</sub>CH<sub>2</sub>OAc)} (160 mg, 0.172 mmol). The solution was stirred at 25 °C for 1h and the resulting mixture was concentrated in vacuo. The resulting solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O and concentrated in vacuo to yield **1** in 91% yield (138 mg, 0.172 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.34 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 7.82-7.75 (m, 8H, PC<sub>6</sub>H<sub>5</sub> and 1H, C<sub>5</sub>H<sub>4</sub>N), 7.53-7.41 (m, 12H, PC<sub>6</sub>H<sub>5</sub> and 1H, C<sub>5</sub>H<sub>4</sub>N), 7.02 (m, 1H, C<sub>5</sub>H<sub>4</sub>N), 3.94 (t, 2H, CH<sub>2</sub>O, J<sub>H-H</sub> = 5 Hz), 2.90 (br t, 2H, CH<sub>2</sub>, J<sub>H-H</sub> = 5 Hz), 2.68 (broad singlet, 1H, OH), 2.50 (m, 4H, PC<sub>2</sub>H<sub>2</sub>). <sup>31</sup>P NMR (DMSO): δ 45.6 (second order, major line spacing of 13 and 15 Hz with Pt satellites, J<sub>Pt-P</sub> = 2748 Hz). IR (thin film, cm<sup>-1</sup>): 3210 (w), 3053 (w), 2959 (w), 2851 (w), 1587 (s), 1542 (w), 1464 (w), 1435 (s), 1237 (m), 1104 (s). High resolution mass spectrum (FAB) calc. *m/z* = 804.10498 for C<sub>35</sub>H<sub>32</sub>ONP<sub>2</sub>S<sub>2</sub><sup>196</sup>Pt; found 804.10785.

**[(dppe)Pt{S<sub>2</sub>C<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>-N-2-pyridinium))][BPh<sub>4</sub>], 2.** Complex **1** (200 mg, 0.228 mmol) was dissolved in dry pyridine (10 mL) and cooled to -10° C. To this solution was added p-toluenesulfonylchloride (87 mg, 0.456 mmol). The reaction mixture was allowed to warm to room temperature over 1h and the reaction was quenched by the addition of 1 mL of water. The pyridine solution were subsequently removed in vacuo. The resulting solid was dissolved in 5 mL of MeOH to which 1 mL of a NaBPh<sub>4</sub> saturated MeOH solution was added.

Complex **2** was isolated in 56% yield (152 mg, 0.127 mmol) by filtration of the orange solid, which was washed with 3 X 5 mL of MeOH.

Alternatively, complex **2** can be prepared from a range of chlorophosphates as described for diethylchlorophosphate. Complex **1** (200 mg, 0.228 mmol) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (10 mL) at 20°C. To this solution was added (78 mg, 0.456 mmol) of diethylchlorophosphate and triazole (311 mg, 4.5 mmol). The reaction mixture was stirred for an 1h and the reaction was quenched by the addition of 1 mL of water. The  $\text{CH}_2\text{Cl}_2$  was removed and the resulting solid was dissolved in 5 mL of MeOH to which 1 mL of a  $\text{NaBPh}_4$  saturated MeOH solution was added. Complex **2** was isolated in 55% yield (149 mg, 0.125 mmol) by filtration of the orange solid, which was washed with 3 X 5 mL of MeOH.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.49 (m, 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.62-7.58 (m, 8H,  $\text{PC}_6\text{H}_5$ , and 1H  $\text{C}_5\text{H}_4\text{N}$ ), 7.45-7.37 (m, 12H,  $\text{PC}_6\text{H}_5$  and 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 7.13-7.09 (m, 9H,  $\text{B}(\text{C}_6\text{H}_5)_4$ ), 7.00 (m, 1H,  $\text{C}_5\text{H}_4\text{N}$ ), 6.87-6.80 (m, 9H,  $\text{B}(\text{C}_6\text{H}_5)_4$ ), 6.69-6.62 (m, 2H,  $\text{B}(\text{C}_6\text{H}_5)_4$ ), 3.93 (t, 2H,  $\text{CH}_2$ ,  $J_{\text{H-H}} = 7$  Hz), 2.60 (t, 2H,  $\text{CH}_2$ ,  $J_{\text{H-H}} = 7$  Hz), 2.38 (m, 4H,  $\text{PC}_2\text{H}_4$ ).  $^{31}\text{P}$  NMR (DMSO):  $\delta$  47.3 (second order, major line spacing of 13 and 16 Hz with Pt satellites,  $J_{\text{Pt-P}} = 2790$  Hz). IR (thin film,  $\text{cm}^{-1}$ ): 3054 (w), 2960 (w), 1620 (s), 1494 (s), 1435 (s), 1264 (m), 1104 (m). High resolution mass spectrum (FAB) calc.  $m/z = 787.11670$  for  $\text{C}_{35}\text{H}_{32}\text{NP}_2\text{S}_2^{195}\text{Pt}$ ; found 787.10992.

**Preparation of Cellulose Acetate-TEC films containing (dppe)Pt{S<sub>2</sub>C<sub>2</sub>(2-pyridyl)(CH<sub>2</sub>CH<sub>2</sub>OH)}.** To a solution of acetone was added cellulose acetate and triethylcitrate (0-150 wt.% of CA) and **1** (0.3 wt.% of CA). The mixture was cast to yield a 0.5 mm film when the solvent was evaporated. The films were stored at 4 °C in the dark prior to use.

**Preparation of RTV-108 and RTV-118 films containing (dppe)Pt{S<sub>2</sub>C<sub>2</sub>(2-pyridyl)(CH<sub>2</sub>CH<sub>2</sub>OH)}.** Films of the silicones were cast into a 0.5 mm thick film by pressing the elastomer between two wax-coated LEXAN plates which were separated by a 0.5 mm anodized aluminum template. The elastomer was allowed to cure in place for four days. The film was then impregnated by immersing the cured film in a methylene chloride solution for 30 min. The loadings of the lumiphore were between 0.1 and 1% based on the molar extinction coefficients of the metal complexes.

**Relative Rates of Solution-Phase Phosphate Ester Detection.** To a solution of **1** (0.1 mM) and triazole (11 mM) in dry CH<sub>2</sub>Cl<sub>2</sub> was added a phosphate, thiophosphate or phosphinate ester (1 mM) at 25 °C. Room-temperature excitation and emission spectra were acquired with a SLM AB2 fluorescence spectrometer. Emission spectra were corrected for instrumental response using factors supplied by the manufacturer. Oxygen free luminescence measurements were made on solutions that were deoxygenated by three freeze-pump thaw N<sub>2</sub>-backfill cycles in a fluorescence cell equipped with a reservoir and a Teflon valve. The solution was excited at 450 nm and the emissions monitored at 605 and 710 nm.

**Gas Phase Detection of Phosphate Esters.** A cellulose acetate-TEC film (and RTV-118 or RTV-108 film) impregnated with **1** were suspended in an evacuated vessel which was back filled with nitrogen flowing through P(OEt)<sub>2</sub>(O)X, X= Cl, F, or CN. The exposure level of the various phosphates were calculated from the room temperature vapor pressures. After exposure the film was mounted on a glass slide which was placed in a N<sub>2</sub> flushed quartz cuvet at 90° to the incident light of a SLM AB2 fluorescence spectrometer. The sample was excited at 470 nm and the emissions monitored at 570 and 675 nm.