Electronic Supplementary Information for

Cycloaddition of phosphanylidene-$\square^4$-phosphoranes ArP=PMe_3 and quinones to yield 1,3,2-dioxophospholanes

Xufang Chen, Rhett C. Smith, and John D. Protasiewicz*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106-7078

General All manipulations were carried out in a MBraun Labmaster 130 dry box under an atmosphere of N_2. Acetonitrile was distilled from CaH_2 under nitrogen; all other solvents were distilled from sodium benzophenone ketyl prior to use. Compounds **1** and **2** were prepared as previously reported (S. Shah and J. D. Protasiewicz *J. Chem. Soc. Chem. Commun.* 1998, 1585). NMR spectra were recorded on Varian Gemini instruments. Proton and phosphorus spectra are referenced to residual solvent signals and 85% phosphoric acid, respectively.

3,5-di-*tert*-buytlbenzo-2-(2,6-dimesityl-phenyl)-1,3,2-dioxaphospholane (4a). To 0.361 g (0.858 mmol) of DmpP=PMe_3 in 7 mL of toluene was added 0.189 g (0.858 mmol) 3,5-di-*tert*-butyl-*o*-benzo-quinone in 7 mL of toluene dropwise with stirring. The yellow solution became lighter during the reaction. The solvent was evaporated after stirring 1.0 h further. The residue was extracted with *n*-hexane and filtered. White crystalline solid was obtained after solvent was removed under reduced pressure. Crystals suitable for X-ray analysis were grown from Et_2O/CH_3CN at –35°C. Yield: 0.456 g (94.1 %). m. p. = 154-156°C. ^1H NMR (300 MHz, $CDCl_3$): □ = 1.23 (s, 9H); 1.25 (s, 9H); 1.76 (s, 6H); 2.14 (s, 6H); 2.36 (s, 6H); 5.87 (d, 1H, J = 2.0 Hz); 6.73 (d, 1H, J = 2.1 Hz); 6.78 (s, 2H); 6.94 (dd, 2H, $^3J_{HH}$ = 7.6Hz, $^4J_{PH}$ = 1.8 Hz); 6.99(s, 2H,); 7.47 (t, 1H, J = 7.6 Hz). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): □ = 20.81 (d, J = 5.3 Hz); 21.33 (s); 21.67 (s); 29.89 (s); 31.63 (s); 34.36 (s), 34.45 (s); 108.07 (d, J = 1.6 Hz); 116.34 (s); 127.86 (s); 128.28 (s); 130.07 (s); 131.56 (s); 134.01 (s); 135.94 (d, J = 2.0 Hz); 136.64 (s); 136.86 (d, J = 1.7 Hz); 137.32 (d, J = 4.6 Hz); 143.69 (s); 144.30 (s); 144.69 (s); 146.94 (s); 147.06 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): □ = 194.3. Anal. Calcd for $C_{38}H_{45}PO_2$ (564.75): C, 80.81; H, 8.04. Found: C, 80.20; H, 8.17. HRMS (FAB) calcd for $C_{38}H_{46}O_2P$ (MH^+) 565.3235, found 565.3236.

3,5-di-*tert*-butylbenzo-2-(2,4,6-tri-*tert*-butylphenyl)-1,3,2-dioxaphospholane (4b). To 0.401 g (1.14 mmol) Mes*P=PMe_3 in 8 mL of toluene was added a solution of 0.251 g (1.14 mmol) 3,5-di-*tert*-butyl-*o*-benzoquinone in 8 mL of toluene dropwise with stirring. The yellow solution became lighter and after 45 min, the solvent was evaporated. The residue was extracted with 10 mL of *n*-heptane. Solvent was removed under reduced pressure until crystalline solid appeared. Yield: 0.555 g (98.0 %), m.p. 100-101°C. ^1H NMR (300 MHz, $CDCl_3$): □ = 1.12 (s, 9H); 1.20 (s, 9H); 1.24 (s, 9H); 1.52 (s, 18H); 6.65 (d, 1H, J = 1.9 Hz); 6.75 (d, 1H, J = 2.2 Hz); 7.01 (d, 2H, J = 1.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): □ = 30.23 (s); 31.02 (s); 31.57 (s); 34.14 (d, J = 9.2 Hz); 34.36 (s); 34.44 (s); 34.54 (s); 39.49 (d, J = 2.7 Hz); 108.03 (s); 115.70 (s); 121.21 (s); 134.22 (s); 141.28 (s); 142.41 (s); 144.00 (s); 146.94 (d, J = 7.4 Hz); 149.54 (s); 156.62 (d, J = 6.8 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): □ = 195.9. Anal. Calcd for $C_{32}H_{49}PO_2$ (496.71): C, 77.38; H, 9.94. Found: C, 77.47; H, 10.16. HRMS (FAB) calcd for $C_{32}H_{50}O_2P$ (MH^+) 497.3549, found 497.3548.

3,4,5,6-tetrachlorobenzo-2-(2,6-dimesityl-phenyl)-1,3,2-dioxaphospholane (3a). To 0.230 g (0.547 mmol) of DmpP=PMe_3 in 5 mL of toluene was added 0.135 g (0.547 mmol) of tetrachloro-*o*-benzoquinone in 5 mL of toluene slowly with stirring at –35°C. The yellow color changed to greenish brown during the reaction. The solvent was removed under reduced pressure after 0.5 h. The solid was extracted with *n*-hexane and filtered. White crystals were obtained from *n*-hexane at –35°C overnight. Yield: 0.146 g (45.1 %). m. p. 234-235°C. ^1H NMR (300 MHz, $CDCl_3$): □ = 2.03 (s, 12H); 2.26 (s, 6H); 6.81 (s, 4H); 7.12 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.0 Hz); 7.66 (t, 1H, J = 7.6 Hz). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): □ = 21.04 (s); 21.16 (s); 127.96 (s); 130.05 (d, J = 1.8 Hz); 134.14 (s); 135.46 (d, J = 8.0); 136.15 (d, J = 2.2 Hz); 137.59 (s); 137.80 (s); 138.59 (s); 144.52 (s); 147.29 (s); 147.81 (s). $^{31}P\{^1H\}$ (121.5 Mhz, $CDCl_3$): □ = 230.1. Anal. Calcd for $C_{30}H_{25}PO_2Cl_4$ (590.31): C, 61.04; H, 4.27. Found: C, 61.26; H, 4.40. HRMS (FAB) calcd for $C_{30}H_{26}O_2PCl_4$ (MH^+) 589.0425, found 589.0424.

3,4,5,6-tetrachlorobenzo-2-(2,4,6-tri-*tert*-butyl-phenyl)-1,3,2-dioxaphospholane (3b). To 0.375 g (1.06 mmol) Mes*P=PMe_3 in 6 mL of toluene was added 0.262 g (1.06 mmol) tetrachloro-*o*-benzoquinone in 6 mL of toluene dropwise with stirring. The yellow color changed to greenish brown upon mixing. The reaction was complete after 0.5 h (as judged by ^{31}P NMR spectroscopy). The solvent was removed under reduced pressure. The solid was extracted by *n*-hexane. A white crystalline solid was obtained after recrystallization twice from *n*-hexane at –35°C. Yield: 0.222 g (40.0 %). ^1H NMR (300 Mhz, $CDCl_3$): □ = 1.21(s, 9H); 1.54 (d, 18H, J = 1.1 Hz); 7.13 (d, 2H, J = 1.1 Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): □ = 217.5.