Electronic Supplementary Information (ESI)

Experimental

Experimental Section

General. When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded in Bruker Avance, 200, 300 or 400 MHz, NMR spectrometers. The NMR assignments were performed, in some cases, with the help of APT, HMQC and HMBC experiments. Chart 1 shows the atom numbering used in the NMR assignments. [$ClCH_2$pyH-2]Cl (Lancaster), $ClCH_2SMe$, C_5H_4NMe-4 (pic), $PTol_3$, xylylisocyanide (XyNC), AgTfO, HTfO (Fluka), 4,4'-di-tertbutyl-2,2'-bipyridine (tbbpy), K^{t}BuO, $AgClO_4$, AgAcO (Aldrich), NaAcO (Sigma), MeCN (Carlo Erba), dimethylacetylenedicarboxylate (DMAD (Alfa Aesar) were obtained from commercial sources. The oxime $C_6H_5C(NH_2)$=NOH (**A**) was prepared as described in the literature.[5] The complex [Pd{*C,N*-C_6H_4{$C(NH_2)$=NOH}-2}(μ-Cl)]$_2$ (**1**) was previously reported but we include here its IR and NMR spectral data which were poorly described. The solvents were distilled before use.

Synthesis of [Pd{*C,N*-C_6H_4{$C(NH_2)$=NOH}-2}(μ-Cl)]$_2$ (1). A suspension containing $PdCl_2$ (360 mg, 2.03 mmol) and LiCl (175 mg, 4.12 mmol) in MeOH (6 mL) was refluxed for 40 min and then allowed to cool at room temperature. To the resulting red solution was added another containing benzamidoxime (276 mg, 2.03 mmol) and NaAcO (167 mg, 2.03 mmol) in MeOH (5 mL), the reaction mixture was refluxed for 5 h, allowed to cool and filtered through a short pad of Celite. The solution was concentrated to 2 mL and H_2O (20 mL) was added. The suspension was filtered and the cream colored solid collected was extracted with a Et_2O/CH_2Cl_2 mixture (20/5 mL, 3 x 25 mL). The combined extracts were filterd through Celite, the solution was concentrated to 5 mL and n-pentane (20 mL) was added. The

suspension was filtered and the solid collected was washed with n-pentane (2 x 5 mL) and dried, first by suction and then in an oven at 70 ºC for 45 min ti give **1** as a yellowish-cream solid (278 mg, 1.00 mmol, 49%). Mp: 209 ºC (decomp). ^{1}H NMR (d_6-acetone, 400 MHz, 25 ºC) δ 6.89 (br, 2 H, NH_2), 6.98 (td, 1 H, H^5, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 2 Hz), 7.06 (td, 1 H, H^4, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 1 Hz), 7.30 (d, broad, 1 H, H^6, $^{3}J_{HH}$ = 8 Hz), 7.38 (dd, 1 H, H^3, $^{3}J_{HH}$ = 8 Hz, $^{4}J_{HH}$ = 2 Hz), 8.31 (br, 1 H, OH). ^{13}C{^{1}H} NMR (d_6-acetone, 100 MHz, 25 ºC) δ 124.2 (CH^3), 125.2 (C^4), 129.2 (C^5), 133.7 (C^6), 137.4 (C^2), 148.6 (C^1), 164.2 (C^7). IR (cm^{-1}): ν(NH) + ν(OH), 3469 br, 3382 br; ν(C=N), 1668. Various bands in the 250-350 cm^{-1} region impeded the unequivocal assignment of the ν(PdCl) bands. Anal. Found: C, 30.40; H, 2.67; N, 10.40 Calcd for $C_{14}H_{14}Cl_2N_4O_2Pd_2$: C, 30.35; H, 2.55; N, 10.11.

Synthesis of *SP-4-4*-[Pd{*C,N*-C_6H_4{$C(NH_2)$=NOH}-2}Cl(L)] (L = $PTol_3$, Tol = C_6H_4Me-4 (2a); CNXy, Xy = $C_6H_3Me_2$-2,6 (2b), pic = C_5H_4NMe-4 (2c)). To a suspension of **1** (for **2a**, 62 mg, 0.22 mmol; for **2b**, 103 mg, 0.37 mmol; for **2c**, 65 mg, 0.24 mmol) in CH_2Cl_2 (5 mL) was added the equimolar amount of the appropriate ligand [for **2a**, solid $PTol_3$, 68 mg, 0.22 mmol; for **2b**, a solution of CNXy, 49 mg, 0.37 mmol, in CH_2Cl_2(5 mL), added dropwise; for **2c**, pic, 23 μL, 0.24 mmol). The resulting solution was stirred for 30 min, filtered through a short pad of Celite, and concentrated almost to dryness. The residue was stirred with Et_2O (for **2a**, 20; for **2b**, 10 mL) or an Et_2O/n-pentane mixture (**2c**, 1:10, 11 mL) until a white or greenish (**2c**) suspension formed which was filtered. The solid collected was washed with Et_2O (2 mL) and dried by suction to give the title compound as a white solid (for **2a**, 109 mg, 0.19 mmol, 84%; for **2b**, 129 mg, 0.32 mmol, 92%). **2c** was recrystallized from CH_2Cl_2 and n-pentane and dried in an oven at 70 ºC for 1 h to give a greenish-white powder (68 mg, 0.18 mmol, 78%). Crystals of **2a** suitable for an X-ray diffraction study grew from $CDCl_3$ and Et_2O by the liquid diffusion method.

2a: Mp: 238 ºC (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ºC) δ 2.36 (s, 9 H, Me,

Tol), 5.17 (s, br, 2 H, NH_2), 6.42 (ddd, 1 H, H^6, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 5.6 Hz, $^5J_{HH}$ ó $^4J_{HP}$ = 1 Hz), 6.55 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 6.93 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 6.96 (td, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.16 ("dd", *meta*-H, Tol, $^3J_{HH}$ = 8 Hz, $^4J_{HP}$ = 2 Hz), 7.58 ("dd", *ortho*-H, Tol, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 8 Hz), 9.31 (d, 1 H, OH, $^4J_{HP}$ = 3 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 ºC) δ 21.5 (Me, Tol), 122.1 (C^3), 123.8 (C^4), 127.6 (d, *ipso*-C, Tol, $^1J_{CP}$ = 53 Hz), 128.8 (C^5), 128.9 (d, *meta*-C, Tol, $^3J_{CP}$ = 11 Hz), 135.1 (d, *ortho*-C, Tol, $^2J_{CP}$ = 13 Hz), 138.1 (d, C^6, $^3J_{CP}$ = 11 Hz), 138.3 (d, C^2, $^3J_{CP}$ = 1 Hz), 141.0 (d, *para*-C, Tol, $^4J_{CP}$ = 2 Hz), 150.5 (C^1), 157.7 (C^7). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 ºC) δ 40.2. IR (cm^{-1}): ν(NH) + ν(OH), 3479, 3315, 3260; ν(C=N), 1675; ν(PdCl), 298. Anal. Found: C, 57.65; H, 5.19; N, 5.16 Calcd for $C_{28}H_{28}ClN_2OPPd$: C, 57.85; H, 4.85; N, 4.82.

2b: Mp: 105 ºC. ^1H NMR ($CDCl_3$, 400 MHz, 25 ºC) δ 2.53 (s, 6 H, Me, Xy), 5.30 (s, br, 2 H, NH_2), 7.07 (t, 1 H, H^5, $^3J_{HH}$ = 7 Hz), 7.08 (d, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.13 (d, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 7.17 (d, 2 H, *meta*-Xy, $^3J_{HH}$ = 8 Hz), 7.29 (t, 1 H, *para*-Xy, $^3J_{HH}$ = 8 Hz), 7.34 (d, 1 H, H^6, $^3J_{HH}$ = 8 Hz), 8.66 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 ºC) δ 18.9 (Me, Xy), 123.0 (C^3), 124.8 (C^4), 126.1 (br, *ipso*-Xy), 12.2 (*meta*-Xy), 130.0 (*para*-Xy), 130.3 (C^5), 135.8 (*ortho*-Xy), 137.0 (C^6), 150.2 (C^1), 158.7 (C^7), C^2 not observed. IR (cm^{-1}): ν(NH) + ν(OH), 3468, 3352; ν(C≡N), 2188; ν(C=N), 1676; ν(PdCl), 286. Anal. Found: C, 47.00; H, 3.95; N, 10.05. Calcd for $C_{16}H_{16}ClN_3OPd$: C, 47.08; H, 3.95; N, 10.29.

2c: Mp: 134 ºC. ^1H NMR ($CDCl_3$, 400 MHz, 25 ºC) δ 2.46 (s, 3 H, Me, pic), 5.20 (s, br, 2 H, NH_2), 6.29 (d, 1 H, H^6, $^3J_{HH}$ = 8 Hz), 6.94 (t, 1 H, H^5, $^3J_{HH}$ = 8 Hz), 7.00 (d, 1 H, H^3, $^3J_{HH}$ = 7 Hz), 7.04 (t, 1 H, H^4, $^3J_{HH}$ = 7 Hz), 7.25 (d, 2 H, *meta*-H, pic, $^3J_{HH}$ = 6 Hz), 8.59 (s, 1 H, OH), 8.69 (d, 2 H, *ortho*-H, pic, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 ºC) δ 21.3 (Me, pic), 122.2 (C^3), 124.3 (C^4), 126.4 (*meta*-pic, 129.2(C^5), 131.4 (C^6), 137.4 (C^2), 149.9 (*para*-pic), 150.4 (C^1), 152.4 (*ortho*-pic), 157.7 (C^7). IR (cm^{-1}): ν(NH) + ν(OH), 3462, 3304; ν(C=N), 1660; ν(PdCl), 297. Anal. Found: C, 41.84; H, 3.72; N, 11.01 Calcd for

$C_{13}H_{14}ClN_3OPd$: C, 42.19; H, 3.81; N, 11.35.

Synthesis of [Pd{*C*,*N*-C_6H_4{$C(NH_2)$=NOH}-2}(L_2)]ClO_4 (L = NC_5H_4Me-4, pic (3a); L_2 = 4,4'-di-*tert*-buthyl-bipyridine, tbbpy (3b)). To a suspension of **1** (for **3a**, 106 mg, 0.38 mmol; for **3b**, 137 mg, 0.49 mmol) in CH_2Cl_2 (15 mL) was added the appropriate ligand (for **3a**, pic, 80 μL, 0.76 mmol; for **3b**, tbbpy, 133 mg, 0.49 mmol) and excess $NaClO_4 \cdot H_2O$ (100 mg, 0.71 mmol). The reaction mixture was stirred for 30 min, concentrated under vacuum to dryness, the residue was stirred with CH_2Cl_2 (20 mL) and the suspension was filtered. The filtrate was concentrated under vacuum to 1 mL and Et_2O (20 mL) was added. The suspension was filtered, the solid collected was washed with Et_2O (2 x 3 mL) and dried by suction to give **3b** as a yellow solid (270 mg, 0.44 mmol, 90%) or an off white solid which was recrystallized from CH_2Cl_2 and Et_2O and dried in an oven at 75 ºC for 30 min to give **3a** as greenish-white solid (144 mg, 0.27 mmol, 72%).

3a: Mp: 173 ºC (decomp). ^{1}H NMR (d_6-acetone, 400 MHz, 25 ºC) δ 2.39 (s, 3 H, Me, pic), 2.47 (s, 2H, Me, pic), 6.12 (d, 1 H, H ^{6}), 6.95 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.11 (td, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.21 (s, br, 2 H, NH_2), 7.39 (d, 2 H, *meta*-pic, $^3J_{HH}$ = 6 Hz), 7.53 (d, 2 H, *meta*-pic, $^3J_{HH}$ = 6 Hz), 7.58 (dd, 1 H, H^3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 8.53 (s, 1 H, OH), 8.65 (d, 2 H, *ortho*-pic, $^3J_{HH}$ = 6 Hz), 8.88 (d, 2 H, *ortho*-pic, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (d_6-acetone, 100 MHz, 25 ºC) δ 21.0 (Me, pic), 21.1 (Me, pic), 124.5 (C^3), 125.6 (C^4), 127.1 (*meta*-pic), 128.3 (*meta*-pic), 130.3 (C^5), 133.4 (C^6), 138.0 (C^2), 151.1 (*ortho*-pic), 151.9 (br, *para*-pic), 152.0 (C^1), 152.6 (*ortho*-pic), 152.8 (*para*-pic), 170.0 (C^7). Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 138 (5.08 x 10^{-4} M in acetone). IR (cm^{-1}): ν(NH) + ν(OH), 3481, 3361; ν(C=N), 1647, ν(ClO) 1094, δ (OClO) 624. Anal. Found: C, 43.14; H, 3.92; N, 10.29. Calcd for $C_{19}H_{21}ClN_4O_5Pd$: C, 43.28; H, 4.01; N, 10.63.

3b: Mp: 259 ºC (decomp). H NMR (d_6-acetone, 300 MHz, 25 ºC) δ 1.42 (s, 9 H, Me, tbbpy), 1.46 (s, 9 H, tbbpy), 2.90 (s, br, 2 H, NH_2), 7.09-7.14 (m, 2 H, Ar), 7.22 (s, br, 1 H),

7.35 (s, br, 1H), 7.48 (s, br, 1 H), 7.81 (m, 2 H, H^5, tbbpy) 8.53 (s, 1H, H^3, tbbpy), 8.54 (s, 1H, H^3, tbbpy), 8.83 (d, 1 H, H^6, tbbpy, $^3J_{HH}$ = 5 Hz), 9.28 (d, 1 H, H^6, tbbpy, $^3J_{HH}$ = 4 Hz). $^{13}C\{^1H\}$ NMR (d_6-acetone, 75 MHz, 25 ºC) δ 30.4 (Me, tbbpy), 36.3 (*C*Me_3), 36.4 (*C*Me_3), 120.8 (CH, tbbpy), 121.8 (CH), 124.4 (CH, tbbpy), 125.0 (CH), 150.9 (CH) 152.5 (CH, tbbpy), 154.8(C^4, tbbpy), 157.3 (C^{ft}), 165.5 (C^2, tbbpy), 165.7 (C^7), C^1 and C^2 not observed. Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 131 (4. 99 x 10^{-4}M in acetone). IR (cm^{-1}): ν(NH) + ν(OH), 3483, 3352; ν(C=N), 1642, ν(ClO) 1098, δ (OClO) 624. Anal. Found: C, 49.11; H, 4.83; N, 9.14. Calcd for $C_{25}H_{31}ClN_4O_5Pd$: C, 49.27; H, 5.13; N, 9.19.

Synthesis of PPN[Pd{*C*,*N*-C_6H_4{$C(NH_2)$=NOH}-2}Cl_2] (PPN = Ph_3P=N=PPh_3 (4)). To a suspension of **1** (55 mg, 0.20 mmol) in CH_2Cl_2 (15 mL) was added the equimolar amount of [PPN]Cl (113 mg). An almost clear solution formed which was stirred for 2.5 h and filtered through a short pad of Celite. The filtrate was concentrated under vacuum to 1 mL and Et_2O (20 mL) was added. A suspension formed which was filtered, the solid was washed with Et_2O (2 x 3 mL) and dried, first by suction, and then in an oven at 75 ºC for 2 h to give to give **4** as a pale tan solid (132 mg, 0.16 mmol, 78%). Mp: 240 ºC (decomp). ^1H NMR (d_6-acetone, 400 MHz, 25 ºC) δ 6.02 (s, br, 2 H, NH_2), 6.83 (ddd, 1 H, H^5, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 6.86 (ddd, 1H, H^4, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.14 (dd, 1 H, H^3, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.54-7.59 (m, 6 H, *para*-CH, PPN), 7.66-7.75 (m, 24 H, *ortho* + *meta*-CH, PPN), 7.80 (dd, 1 H, H^6, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 9.81 (s, 1 H, OH). (CD_2Cl_2, 400 MHz, 25 ºC) δ 4.97 (s, br, 2 H, NH_2), 6.85 (m, 1 H, Ar), 6.93-6.99 (m, 2H, Ar), 7.46-7.51 (m, 24 H, *ortho*- + *meta*-PPN), 7.65-7.69 (m, 6 H, *para*-PPN), 7.69-7.71 (m, 1 H, Ar), 9.44 (s, br, 1 H, OH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 ºC) δ 121.4 (C^3), 123.3 (C^4), 127.4 (d, *ipso*-C, PPN, J_{CP} = 108 Hz), 128.4 (C^5), 129.8 (m, *ortho*- or *meta*-C, PPN), 132.5 (m, *ortho*- or *meta*-C, PPN), 134.1 (*para*-C, PPN), 135.0 (C^6), 137.6 (C^2), 148.9 (C^1), 156.8 (C^7), C^2). $^{31}P\{^1H\}$ NMR (121 MHz, d_6-acetone, 25 ºC) δ 21.3. Λ_M ($\Omega^{-1}cm^2mol^{-1}$) = 108 (3.85 x 10^{-4}M in

acetone). IR (cm^{-1}): ν(NH) + ν(OH), 3461, 3315; ν(C=N), 1672; ν(PdCl), 268, 220. Anal. Found: C, 60.66; H, 4.40; N, 4.79. Calcd for $C_{43}H_{37}Cl_2N_3OP_2Pd$: C, 60.69; H, 4.38; N, 4.94.

Synthesis of [Pd{μ-*C,N,O*-C_6H_4{$C(NH_2)$=NO}-2}($PTol_3$)]$_2$ (5). To a solution of complex **2a** (72 mg, 0.12 mmol) in degassed CH_2Cl_2 (10 mL), kept under nitrogen atmosphere, was added K^{t}BuO (16 mg, 0.14 mol). The resulting suspension was stirred for 4 h and then filtered in the air through a short pad of Celite. The solution was concentrated to 1 mL and n-hexane (20 q mL) was added and the solid washed with CH_2Cl_2 (4 x 20 mL). The combined filtrates were concentrated under vacuum to 1 mL and n-hexane (20 mL) was added. The suspension was filtered, the solid collected was recrystallized from CH_2Cl_2 (2 mL) and a 1:2 mixture of Et_2O and n-hexane (15 mL) and dried, first by suction and then in an oven at 70 ºC for1 h to give **5** (61 mg, 0.11 mmol, 93%) as a yellow solid. Mp:206 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ºC) δ 2.34 (s, 9 H, Me, Tol), 3.95 (s, br, 2 H, NH_2), 6.32 (td, 1 H, H^5, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 6.41 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 6.71 (dd, 1 H, H^4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.77 (t, 1 H, H^3, $^3J_{HH}$ = 8 Hz), 7.16 (d, *meta*-H, Tol, $^3J_{HH}$ = 7 Hz), 7.58 ("dd", *ortho*-H, Tol, $^3J_{HP}$ = 11 Hz, $^3J_{HH}$ = 8 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC) δ 21.4 (Me, Tol), 120.6 (C^3), 122.8 (C^4), 125.4 (C^5), 128.2 (d, *ipso*-C, Tol, $^1J_{CP}$ = 47 Hz), 129.1 (d, *meta*-C, Tol, $^3J_{CP}$ = 10 Hz), 135.0 (d, *ortho*-C, Tol, $^2J_{CP}$ = 13 Hz), 138.1 (d, C^6, $^3J_{CP}$ = 11 Hz), 140.3 (C^2), 141.4 (*para*-C, Tol), 153.2 (d, C^1, $^2J_{CP}$ = 5 Hz), 160.5 (C^7). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC) δ 36.7. IR (cm^{-1}): ν(NH) 3480, 3348, ν(C=N), 1603. Anal. Found: C, 61.73; H, 5.04; N, 4.96 Calcd for $C_{28}H_{27}N_2OPPd$: C, 61.72; H, 4.99; N, 5.14.

Synthesis of [Pd{*C,N,N'*-C_6H_4{$C(NH_2)$=NOCH_2(C_5H_4N-2)}-2}($PTol_3$)]ClO_4 (6). To a mixture containing K^{t}BuO (21.2 mg, 0.19 mmol) and [$ClCH_2$pyH-2]Cl (15.5 mg, 0.09 mmol) in degassed CH_2Cl_2 (10 mL) was added, under N_2 atmosphere, another solution containing complex **2a** (54 mg, 0.09 mmol) in the same solvent (5 mL) and the mixture was stirred for 1 h. The solvent was removed under vacuum and acetone (10 mL) and

$NaClO_4 \cdot H_2O$ (25 mg, 0.18 mmol) were successively added to the residue in the open air. The reaction mixture was stirred for 1 additional hour, and the solvent removed again under vacuum. The residue was stirred with CH_2Cl_2 (15 mL), the resulting suspension was filtered, the solution was concentrated to 1 mL and Et_2O (10 mL) was added. The suspension was stirred in an ice/water bath for a few min, and filtered. The solid collected was washed with Et_2O (2 mL) and dried, first by suction and then in an oven at 70 ºC for 1 h to give **7** as a pale yellow solid (58 mg, 0.08 mmol, 88%). Crystals of **6** suitable for an X-ray diffraction study grew from CH_2Cl_2 and Et_2O by the liquid diffusion method. Mp: 295 ºC (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ºC) δ 2.35 (s, 9 H, Me, Tol), 5.19 (s, 2 H, CH_2), 6.45 (dd, 1 H, H^6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 5 Hz), 6.52 (s, br, 2 H, NH_2), 6.62 (t, 1 H, H^5, $^3J_{HH}$ = 8 Hz), 6.87 (t, 1 H, H^{12}, $^3J_{HH}$ = 7 Hz), 7.04 (t, 1 H, H^4, $^3J_{HH}$ = 8 Hz), 7.16 (d, *meta*-H, Tol, $^3J_{HH}$ = 7 Hz), 7.45 (d, 1 H, H^3, $^3J_{HH}$ = 8 HZ), 7.49 (dd, *ortho*-H, Tol, $^3J_{HP}$ = 12 Hz, $^3J_{HH}$ = 7 Hz), 7.52 (d, 1 H, H^{10}, $^3J_{HH}$ = 7 Hz), 7.68 (d, 1 H, H^{13}, $^3J_{HH}$ = 7 Hz), 7.78 (td, 1 H, H^{11}, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC) δ 21.4 (Me, Tol), 124.8 (C^{12}), 125.1 (C^3), 125.6 (C^4), 125.9 (d, *ipso*-C, Tol, $^1J_{CP}$ = 52 Hz), 126.7 (C^{10}), 129.8 (d, *meta*-C, Tol, $^3J_{CP}$ = 11 Hz), 129.9 (C^5), 134.8 (d, *ortho*-C, Tol, $^2J_{CP}$ = 13 Hz), 137.0 (d, C^2, $^3J_{CP}$ = 1 Hz), 137.9 (d, C^6, $^3J_{CP}$ = 12 Hz), 139.7 (C^{11}), 142.3 (d, *para*-C, Tol, $^4J_{CP}$ = 2 Hz), 148.7 (d, C^1, $^2J_{CP}$ = 3 Hz), 152.5 (d, C^{13}, $^3J_{CP}$ = 3 Hz), 153.2 (C^9) 163.8 (C^7). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC) δ 39.9. IR (cm^{-1}): ν(NH), 3486, 3368; ν(C=N), 1654; ν(ClO) 1080, δ (OClO) 621. Anal. Found: C, 55.46; H, 4.48; N, 5.64 Calcd for $C_{34}H_{33}ClN_3O_5PPd$: C, 55.45; H, 4.52; N, 5.71.

Synthesis of [Pd{*C,N,*-C(N=Xy)C_6H_4{$C(NH_2)$=NOH}-2}Cl(CNXy)] (7). To a solution of **2b** (85 mg, 0.21 mmol) in CH_2Cl_2 (15 mL) was dropwise added another solution of XyNC (27.3 mg, 0.21 mmol) in the same solvent (5 mL). After three days of stirring the solution was concentrated under vacuum to 10 mL and Et_2O (10 mL) was added. The suspension was filtered to remove a small amount of an yellow-orange solid the ^{1}H NMR of

which coincides with that of the Pd(I) complex $[PdCl(CNXy)_2]_2$,[12] the solution was concentrated (1 mL) and Et_2O (15 mL) was added. The suspension was filtered and the solid collected was washed with Et_2O (2 x 2 mL) and dried by suction to give **7** as a cream colored solid (25 mg, 0.04 mmol, 20%). When the mother liquor was further concentrated (5 mL) and Et_2O (15 mL) was added, a suspension formed which was filtered, dried (75 mg), and shown by ^1H NMR to contain a 1.3:1 mixture of **2b** and **7** which we could not separate. Mp: 196-198 ºC (decomp). ^1H NMR (200 MHz, $CDCl_3$, 25ºC): δ 2.12 (s, 6 H, Me, Xy^{Pd}), 2.28 (s, 6 H, Me, Xy^{im}), 5.65 (s, br, 2 H, NH_2), 6.81-6.89 (m, 3 H, *meta*-CH, Xy^{im} + *para*-CH, Xy^{im}), 7.02 (d, 2 H, *meta*-CH, Xy^{Pd}, $^3J_{HH}$ = 8 Hz), 7.19 (dd, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$= 7 Hz), 7.46-7.69 (m, 4 H, Ar + Xy), 9.54 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 ºC) δ 18.6 (Me) 19.1(Me), 123.6 (*para*-CH, Xy^{im}), 125.5, (CH^6), 126.5 (CH^3), 127.1 (*ortho*-C, Xy^{im}), 127.3 (*ipso*-C, Xy^{Pd}), 127.7 (*meta*-CH, Xy^{Pd}), 127.9 (*meta*-CH, Xy^{im}), 129.1 (CH^4), 129.6 (*para*-CH, Xy^{Pd}), 132.2 (CH^5), 135.2 (*ortho*-C, Xy^{Pd}), 135.6 (C^1), 137.4 (C^2), 149.7 (*ipso*-C, Xy^{im}), 150.9 (C^7), 175.6 (*C*=NXy). IR (cm^{-1}): ν(NH) + (OH), 3456, 3273, 3242; ν(C≡N) 2190, 2158 (sh); ν(C=N), ν(C=N), 1661, 1615. Anal. Found: C, 55.57; H, 4.81; N, 9.91. Calcd for $C_{25}H_{25}ClN_4OPd$: C, 55.67; H, 4.67; N, 10.39. Crystals of **7** suitable for an X-ray diffraction study grew by the liquid diffusion method, from a mixture **2b**:**7** dissolved in CH_2Cl_2 and layered with n-pentane.

Synthesis of [{Pd(tbbpy)}$_2${*C,N,N',O*-C$_6$H$_4${C(NH)=NO}-2}]ClO$_4$ (tbbpy = 4,4'-di-tert-buthylbipyridine (8). To a solution of **3b** (50 mg, 0.08 mmol) in acetone (5mL) were successively added tbbpy (22 mg, 0.08 mmol) and $Pd(OAc)_2$ (18 mg, 0.08 mmol). The solution turned redish within a few minutes and, after being stirred overnight, it was of purple-red color. It was filtered through a short pad of Celite, concentrated under vacuum to 1 mL and Et_2O (15 mL) was added. The suspension was filtered and the deep purple solid collected was washed with Et_2O (2 x 5 mL) and dried, first by suction and then in an oven at

80 ºC overnight. Yield: 77 mg, 0.078 mmol, 96%, Mp: 257 ºC. ^{1}H NMR (300 MHz, d_6-acetone, 25ºC): δ 1.36 (s, 9 H, Me, ^{t}Bu), 1.43 (s, 9 H, Me, ^{t}Bu), 1.45 (s, 9 H, Me, ^{t}Bu), 1.49 (s, 9 H, Me, ^{t}Bu), 2.80 (s, 1 H), 2.84 (H_2O), 6.96 (m, 2 H), 7.25 (m, 2 H), 7.55 (a, br, 1 H), 7.82 (d, 1 H, $^{3}J_{HH}$ = 5 Hz), 7.89 (s, 1 H), 7.97 (s, 1 H), 8.49 (s, 2 H, tbbpy), 8.59 (s, 2 H, ,tbbpy), 8.80 (s, vbr, 1 H), 8.90 (s, br, 1 H), 8.99 (d, 1 H, $^{3}J_{HH}$ = 5 Hz), 10.09 (s, vbr, 1 H). ^{13}C{^{1}H} NMR (75 MHz, d_6-acetone, 25 ºC) δ 30.4 (Me, ^{t}Bu), 30.5 (Me, ^{t}Bu, double intensity), 30.6 (Me, ^{t}Bu), 36.3 (*C*Me$_3$, double intensity), 36.4 (*C*Me$_3$), 36.5 (*C*Me$_3$), 120.3 (CH), 120.9 (CH), 121.2 (CH), 121.4 (CH), 122.2 (CH), 122.3 (CH), 124.3 (CH), 124.7 (CH), 124.8 (CH), 125.1 (CH), 125.2 (CH), 127.0 (CH), 130.9 (CH), 136.9 (CH), 149.3 (CH), 149.4 (CH), 149.64 (C), 149.67 (C), 149.70 (C), 152.0 (CH), 152.1 (CH), 152.4 (CH), 154.9 (C, tbbpy), 155.3 (C, tbbpy), 156.2 (C, tbbpy), 157.2 (C, tbbpy), 164.8 (C, tbbpy), 165.01 (C, tbbpy), 165.06 (C, tbbpy), 165.13 (C, tbbpy). IR (cm^{-1}): ν(NH), 3379; ν(C=N) 1616, ν(ClO) 1095, δ (OClO) 623. Anal. Found: C, 52.37; H, 5.47; N, 8.48. Calcd for $C_{43}H_{53}ClN_6O_5Pd_2$: C, 52.58; H, 5.44; N, 8.56. Λ_M ($\Omega^{-1}\cdot cm^2\cdot mol^{-1}$): 107 (3.06 x 0^{-4} M in acetone). Crystals of **8·solvents** grew by the liquid diffusion method using CH_2Cl_2 and Et_2O.

X-ray Crystallography. Compounds **2a**, **6** and **7** were measured on a Bruker Smart APEX machine and compound **8** on a Bruker D8Quest machine. Data were collected using monochromated Mo-Kα radiation in w scan for compounds **2a**, **6** and **7** and monochromated Cu-Kα radiation in w and φ scan forr **8** The structures were solved by direct methods. All were refined anisotropically on F^2. The methyl hydrogens were refined using a rigid groups and the other hydrogens were refined using a riding mode. The NH_2 and OH hydrogens were refined as free and with DFIX in compound **7** and **8** and SADI in compounds **2a** and **6**.

Special features: Compound **8** has one *tert*-butyl group disordered over two positions, ca 71:29% and a poorly-resolved region of residual electron density that could not be adequately modelled and so was "removed" using the program SQUEEZE, which is part of the PLATON

system. The void volume per cell was 1761.9 Å^3, with a void electron count per cell of 421. This additional solvent was not taken into account when calculating derived parameters such as the formula weight, because the nature of the solvent was uncertain.

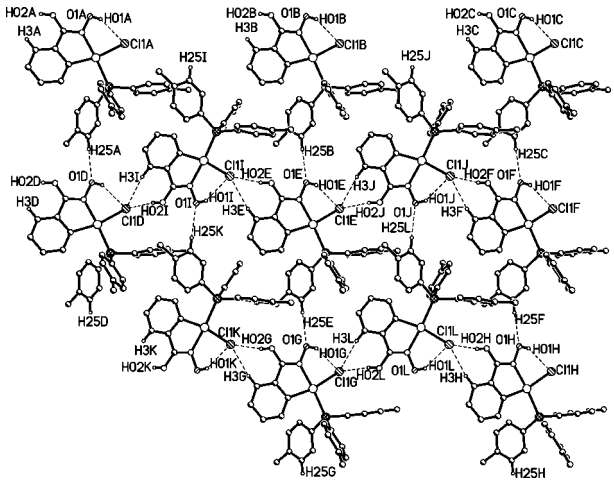

Figure 1. Layers parallel to the *ab* plane in **2a** formed through O-H···Cl, N-H···Cl, C-H···Cl and C-H···O hydrogen bonds.

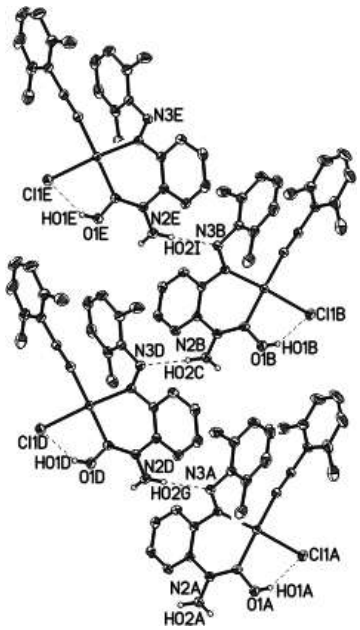

Figure 2. Chains along the *b* axis in **7** formed through N-H···N hydrogen bonds

Table 1. Crystal data and structure refinement of complexes **2a**, **6**, **7** and **8**.

Complex	**2a**	**6**	**7**	**8**
Formula	$C_{28}H_{28}ClN_2OPPd$	$C_{44}H_{33}ClN_3O_5PPd$	$C_{25}H_{25}ClN_4OPd$	$C_{43}H_{53}ClN_6O_5Pd_2$
Fw	581.34	736.45	539.34	982.16
Temperature (K)	100(2) K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P 2(1)/n	P -1	P 2(1)/c	C 2/c
a (Å)	11.8915(8)	9.4517(9)	14.058(7)	25.9442(11)
b (Å)	15.4151(11)	11.4744(11)	11.058(5)	21.3161(9)
c (Å)	14.5332(11)	14.6828(14)	14.952(7)	20.3264(8)
α (deg)	90	101.775(2)	90	90
β (deg)	93.245(2)	93.311(2)	94.647(8)	121.104(2)
γ (deg)	90	94.011(2)	90	90
Volume ($Å^3$)	2659.8(3)	1550.8(3)	2316.7(19)	9625.0(7)
Z	4	2	4	8
ρ_{calcd} ($Mg\ m^{-3}$)	1.452	1.577	1.546	1.356
μ (mm^{-1})	0.881	0.784	0.941	6.907
F(000)	1184	752	1096	4016
crystal size (mm)	0.19x0.18x0.14	0.20x0.08x0.05	0.22 x 0.12 x 0.10	0.27 x 0.17 x 0.15
θ range (deg)	1.93 to 28.72	1.82 to 28.73	2.29 to 28.70	2.87 to 66.87
no. rflns coll	32031	19050	27358	84208
no. indep rflns / R_{int}	6463 / 0.0251	7303 / 0.0260	5603 / 0.0319	8527 / 0.0441
Transmission	0.8866 / 0.8137	0.9618 / 0.7404	0.9117 / 0.6295	0.2058 / 0.0733
restraints/parameters	1 / 322	1 / 417	3 / 305	505 / 525
Goodness of fit on F^2	1.066	1.039	1.047	1.179
*R*1 ($I>2\sigma(I)$)	0.0240	0.0274	0.0304	0.0703
*wR*2 (all reflns)	0.0636	0.0688	0.0776	0.1837
Larg. diff. peak/hole ($e.Å^{-3}$)	0.493 / -0.253	0.520 / -0.473	0.992 / -0.748	2.882 / -0.552