Electronic Supplementary Information (ESI)

Experimental

General

Synthesis of complex 1

Synthesis of complexes 2

Synthesis of complexes 3

Synthesis of complex 4

Synthesis of complexes 5 and 6

Synthesis of complex 7

Synthesis of complex 8

X-ray crystal structure determination
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$_2$SMe, C$_5$H$_4$NMe-4 (pic), PTol$_3$, xylylisocyanide (XyNC), AgTfO, HTfO (Fluka), 4,4'-di-tertbutyl-2,2'-bipyridine (tbbpy), K'BuO, AgClO$_4$, AgAcO (Aldrich), NaAcO (Sigma), MeCN (Carlo Erba), dimethylacetylenedicarboxylate (DMAD (Alfa Aesar) were obtained from commercial sources. The oxime C$_6$H$_5$C(NH$_2$)=NOH (A) was prepared as described in the literature. The complex [Pd{C,N-C$_6$H$_4$[C(NH$_2$)=NOH]-2}(\mu-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$_6$H$_4$[C(NH$_2$)=NOH]-2}(\mu-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$_2$O (20 mL) was added. The suspension was filtered and the cream colored solid collected was extracted with a Et$_2$O/CH$_2$Cl$_2$ mixture (20/5 mL, 3 x 25 mL). The combined extracts were filtered 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 °C for 45 min to give 1 as a yellowish-cream
solid (278 mg, 1.00 mmol, 49%). Mp: 209 °C (decomp). $^1$H NMR (d$_6$-acetone, 400 MHz, 25
°C) δ 6.89 (br, 2 H, NH$_2$), 6.98 (td, 1 H, H$^5$, $^3$J$\text{HH}$ = 8 Hz, $^4$J$\text{HH}$ = 2 Hz), 7.06 (td, 1 H, H$^4$, $^3$J$\text{HH}$
= 8 Hz, $^4$J$\text{HH}$ = 1 Hz), 7.30 (d, broad, 1 H, H$^6$, $^3$J$\text{HH}$ = 8 Hz), 7.38 (dd, 1 H, H$^3$, $^3$J$\text{HH}$ = 8 Hz,
$^4$J$\text{HH}$ = 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$^{-1}$):
v(NH) + v(OH), 3469 br, 3382 br; v(C=N), 1668. Various bands in the 250-350 cm$^{-1}$ region
impeded the unequivocal assignment of the v(PdCl) bands.

Anal. Found: C, 30.40; H, 2.67; N, 10.40 Calcd for C$_{14}$H$_{14}$Cl$_2$N$_4$O$_2$Pd$_2$: C, 30.35; H, 2.55; N, 10.11.

**Synthesis of SP-4-4-[Pd(C,N-C$_6$H$_4$(C(NH$_2$)=NOH)-2]Cl(L)] (L = PTol$_3$, Tol =
C$_6$H$_4$Me-4 (2a); CNXY, XY = C$_6$H$_3$Me$_2$-2,6 (2b), pic = C$_5$H$_4$NMe$_4$-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$_2$Cl$_2$ (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$_2$Cl$_2$(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$_2$O (for 2a, 20; for 2b, 10 mL) or an Et$_2$O/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$_2$O (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$_2$Cl$_2$ and n-pentane and dried in an oven at 70 °C 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$_2$O by the liquid diffusion method.

**2a:** Mp: 238 °C (decomp). $^1$H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 2.36 (s, 9 H, Me,
2b: Mp: 105 °C. $^1$H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 2.53 (s, 6 H, Me, Xy), 5.30 (s, br, 2 H, NH$_2$), 7.07 (t, 1 H, H$^5$, 3$^J_{HH}$ = 7 Hz), 7.08 (d, 1 H, H$^3$, 3$^J_{HH}$ = 7 Hz), 7.13 (d, 1 H, H$^4$, 3$^J_{HH}$ = 7 Hz), 7.17 (d, 2 H, meta-Xy, 3$^J_{HH}$ = 8 Hz), 7.29 (t, 1 H, para-Xy, 3$^J_{HH}$ = 8 Hz), 7.34 (d, 1 H, H$^6$, 3$^J_{HH}$ = 8 Hz), 8.66 (s, 1 H, OH). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, 25 °C) 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$_{16}$Cl$_2$OPd: C, 47.08; H, 3.95; N, 10.29.

2c: Mp: 134 °C. $^1$H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 2.46 (s, 3 H, Me, pic), 5.20 (s, br, 2 H, NH$_2$), 6.29 (d, 1 H, H$^6$, 3$^J_{HH}$ = 8 Hz), 6.94 (t, 1 H, H$^5$, 3$^J_{HH}$ = 8 Hz), 7.00 (d, 1 H, H$^3$, 3$^J_{HH}$ = 7 Hz), 7.04 (t, 1 H, H$^4$, 3$^J_{HH}$ = 7 Hz), 7.25 (d, 2 H, meta-H, pic, 3$^J_{HH}$ = 6 Hz), 8.59 (s, 1 H, OH), 8.69 (d, 2 H, ortho-H, pic, 3$^J_{HH}$ = 6 Hz). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, 25 °C) 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
C₁₃H₁₄ClN₃OPd: C, 42.19; H, 3.81; N, 11.35.

Synthesis of \([\text{Pd}\{\text{C,N-C₆H₄(C(NH)₂)=NOH}\}-2\}(\text{L}_2)\text{ClO}_4\) (L = NC₅H₄Me-4, pic (3a); L₂ = 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 CH₂Cl₂ (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 NaClO₄·H₂O (100 mg, 0.71 mmol). The reaction mixture was stirred for 30 min, concentrated under vacuum to dryness, the residue was stirred with CH₂Cl₂ (20 mL) and the suspension was filtered. The filtrate was concentrated under vacuum to 1 mL and Et₂O (20 mL) was added. The suspension was filtered, the solid collected was washed with Et₂O (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 CH₂Cl₂ and Et₂O 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). ¹H NMR (d₆-acetone, 400 MHz, 25 ºC) δ 2.39 (s, 3 H, Me, pic), 2.47 (s, 2H, Me, pic), 6.12 (d, 1 H, H₆), 6.95 (td, 1 H, H⁵, 3J_HH = 8 Hz, 4J_HH = 1 Hz), 7.11 (td, 1 H, H⁴, 3J_HH = 8 Hz, 4J_HH = 1 Hz), 7.21 (s, br, 2 H, NH₂), 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, H³, 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). ¹³C{¹H} NMR (d₆-acetone, 100 MHz, 25 ºC) δ 21.0 (Me, pic), 21.1 (Me, pic), 124.5 (C³), 125.6 (C⁴), 127.1 (meta-pic), 128.3 (meta-pic), 130.3 (C⁵), 133.4 (C⁶), 138.0 (C²), 151.1 (ortho-pic), 151.9 (br, para-pic), 152.0 (C¹), 152.6 (ortho-pic), 152.8 (para-pic), 170.0 (C⁷).

λ_M (Ω⁻¹cm²mol⁻¹) = 138 (5.08 x 10⁻⁴ M in acetone). IR (cm⁻¹): v(NH) + v(OH), 3481, 3361; v(C=N), 1647, v(ClO) 1094, δ (OCIO) 624. Anal. Found: C, 43.14; H, 3.92; N, 10.29. Calcd for C₁₉H₂₁ClN₄O₅Pd: C, 43.28; H, 4.01; N, 10.63.

3b: Mp: 259 ºC (decomp). H NMR (d₆-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, NH₂), 7.09-7.14 (m, 2 H, Ar), 7.22 (s, br, 1 H),
7.35 (s, br, 1H), 7.48 (s, br, 1H), 7.81 (m, 2 H, tbbpy) 8.53 (s, 1H, H^3, tbbpy), 8.54 (s, 1H, H^3, tbbpy), 8.83 (d, 1 H, H^6, tbbpy, J_HH = 5 Hz), 9.28 (d, 1 H, H^6, tbbpy, J_HH = 4 Hz).

^{13}C\{^1H\} NMR (d_6-acetone, 75 MHz, 25 °C) δ 30.4 (Me, tbbpy), 36.3 (CMe3), 36.4 (CMe3), 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.

A_M (Ω^1cm^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 (OCIO) 624.


**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 °C for 2 h to give 4 as a pale tan solid (132 mg, 0.16 mmol, 78%). Mp: 240 °C (decomp).

^1H NMR (d_6-acetone, 400 MHz, 25 °C) δ 6.02 (s, br, 2 H, NH_2), 6.83 (ddd, 1 H, H^5, J_HH = 7 Hz, J_HH = 2 Hz), 6.86 (ddd, 1H, H^6, J_HH = 7 Hz, J_HH = 2 Hz), 7.14 (dd, 1 H, H^3, J_HH = 7 Hz, J_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, J_HH = 7 Hz, J_HH = 2 Hz), 9.81 (s, 1 H, OH). (CD_2Cl_2, 400 MHz, 25 °C) 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). ^13C\{^1H\} NMR (100 MHz, CD_2Cl_2, 25 °C) 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^4), 156.8 (C^7), C^2. ^31P\{^1H\} NMR (121 MHz, d_6-acetone, 25 °C) δ 21.3. A_M (Ω^1cm^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 C₄₃H₇7Cl₂N₃OP₂Pd: C, 60.69; H, 4.38; N, 4.94.

Synthesis of [Pd{μ-С,N,O-С₆H₄(C(NH₂)=NO)-2}(PTo1₃)]₂ (5). To a solution of complex 2a (72 mg, 0.12 mmol) in degassed CH₂Cl₂ (10 mL), kept under nitrogen atmosphere, was added K'tBuO (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 was filtered with CH₂Cl₂ (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 CH₂Cl₂ (2 mL) and a 1:2 mixture of Et₂O and n-hexane (15 mL) and dried, first by suction and then in an oven at 70 ºC for 1 h to give 5 (61 mg, 0.11 mmol, 93%) as a yellow solid. Mp:206 ºC.

1H NMR (CDCl₃, 400 MHz, 25 ºC) δ 2.34 (s, 9 H, Me, Tol), 3.95 (s, br, 2 H, NH₂), 6.32 (td, 1 H, H₅, 3J₆H₅ = 8 Hz, 4J₅H₅ = 2 Hz), 6.41 (dd, 1 H, H⁶, 3J₆H₆ = 8 Hz, 4J₅H₆ = 2 Hz), 6.71 (dd, 1 H, H⁴, 3J₃H₄ = 8 Hz, 4J₂H₄ = 1 Hz), 6.77 (t, 1 H, H₃, 3J₃H₃ = 8 Hz), 7.16 (d, meta-H, Tol, 3J₃H₃ = 7 Hz), 7.58 ("dd", ortho-H, Tol, 3J₃H₅ = 11 Hz, 3J₃H₃ = 8 Hz). 13C{¹H} NMR (100 MHz, CDCl₃, 25 ºC) δ 21.4 (Me, Tol), 120.6 (C³), 122.8 (C⁴), 125.4 (C⁵), 128.2 (d, ipso-C, Tol, 1JCP = 47 Hz), 129.1 (d, meta-C, Tol, 3JCP = 10 Hz), 135.0 (d, ortho-C, Tol, 2JCP = 13 Hz), 138.1 (d, C⁶, 3JCP = 11 Hz), 140.3 (C²), 141.4 (para-C, Tol), 153.2 (d, C¹, 2JCP = 5 Hz), 160.5 (C⁷). 31P{¹H} NMR (121 MHz, CDCl₃, 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 C₂₈H₂₇N₂OPPd: C, 61.72; H, 4.99; N, 5.14.

Synthesis of [Pd{C,N,N'-C₆H₄(C(NH₂)=NOCH₂(C₅H₄N-2))-2}(PTo1₃)]ClO₄ (6). To a mixture containing K'tBuO (21.2 mg, 0.19 mmol) and [ClCH₂pyH-2]Cl (15.5 mg, 0.09 mmol) in degassed CH₂Cl₂ (10 mL) was added, under N₂ 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
NaClO₄·H₂O (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 CH₂Cl₂ (15 mL), the resulting suspension was filtered, the solution was concentrated to 1 mL and Et₂O (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 Et₂O (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 CH₂Cl₂ and Et₂O by the liquid diffusion method. Mp: 295 ºC (decomp).

1H NMR (CDCl₃, 400 MHz, 25 ºC) δ 2.35 (s, 9 H, Me, Tol), 5.19 (s, 2 H, CH₂), 6.45 (dd, 1 H, H⁶, ³JHH = 8 Hz, ⁴JHH = 5 Hz), 6.52 (s, br, 2 H, NH₂), 6.62 (t, 1 H, H⁵, ³JHH = 8 Hz), 7.04 (t, 1 H, H⁴, ³JHH = 8 Hz), 7.16 (d, meta-H, Tol, ³JHH = 7 Hz), 7.45 (d, ipso-C, Tol, ¹JCp = 52 Hz), 124.8 (C₁₂), 125.1 (C₃), 125.6 (C₄), 125.9 (d, ortho-C, Tol, ²JCp = 13 Hz), 137.0 (d, C², ³JCp = 1 Hz), 137.9 (d, C⁵, ³JCp = 12 Hz), 139.7 (C¹¹), 142.3 (d, para-C, Tol, ⁴JCp = 2 Hz), 148.7 (d, C¹, ²JCp = 3 Hz), 152.5 (d, C¹³, ³JCp = 3 Hz), 153.2 (C⁹) 163.8 (C⁷). ³¹P{¹H} NMR (121 MHz, CDCl₃, 25 ºC) δ 39.9. IR (cm⁻¹): v(NH), 3486, 3368; v(C=N), 1654; v(ClO) 1080, δ (OCIO) 621. Anal. Found: C, 55.46; H, 4.48; N, 5.64 Calcd for C₃₄H₃₃ClN₃O₅Pd: C, 55.45; H, 4.52; N, 5.71.

**Synthesis of [Pd{C₅Nₓ−C(N=XY)C₆H₄(C(NH₂)=NOH)−2}Cl(CNXy)] (7).** To a solution of 2b (85 mg, 0.21 mmol) in CH₂Cl₂ (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 Et₂O (10 mL) was added. The suspension was filtered to remove a small amount of an yellow-orange solid the ¹H NMR of
which coincides with that of the Pd(I) complex \([\text{PdCl(CNXY)}_2]\), the solution was concentrated (1 mL) and \(\text{Et}_2\text{O}\) (15 mL) was added. The suspension was filtered and the solid collected was washed with \(\text{Et}_2\text{O}\) (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 \(\text{Et}_2\text{O}\) (15 mL) was added, a suspension formed which was filtered, dried (75 mg), and shown by \(^1\text{H} \text{NMR}\) to contain a 1.3:1 mixture of 2b and 7 which we could not separate. Mp: 196-198 °C (decomp). \(^1\text{H} \text{NMR}\) (200 MHz, CDCl\(_3\), 25°C): \(\delta\) 2.12 (s, 6 H, Me, Xy\(^{\text{Pd}}\)), 2.28 (s, 6 H, Me, Xy\(^{\text{im}}\)), 5.65 (s, br, 2 H, NH\(_2\)), 6.81-6.89 (m, 3 H, meta-CH, Xy\(^{\text{im}}\) + para-CH, Xy\(^{\text{im}}\)), 7.02 (d, 2 H, meta-CH, Xy\(^{\text{Pd}}\), \(^3J_{\text{HH}} = 8\) Hz), 7.19 (dd, 1 H, Ar, \(^3J_{\text{HH}} = 8\) Hz, \(^3J_{\text{HH}} = 7\) Hz), 7.46-7.69 (m, 4 H, Ar + Xy), 9.54 (s, 1 H, OH). \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (75 MHz, CDCl\(_3\), 25 ºC) \(\delta\) 18.6 (Me), 19.1(Me), 123.6 (para-CH, Xy\(^{\text{im}}\)), 125.5, (CH\(^6\)), 126.5 (CH\(^3\)), 127.1 (ortho-C, Xy\(^{\text{im}}\)), 127.3 (ipso-C, Xy\(^{\text{Pd}}\)), 127.7 (meta-CH, Xy\(^{\text{Pd}}\)), 127.9 (meta-CH, Xy\(^{\text{im}}\)), 129.1 (CH\(^4\)), 129.6 (para-CH, Xy\(^{\text{Pd}}\)), 132.2 (CH\(^5\)), 135.2 (ortho-C, Xy\(^{\text{Pd}}\)), 135.6 (C\(^1\)), 137.4 (C\(^2\)), 149.7 (ipso-C, Xy\(^{\text{im}}\)), 150.9 (C\(^7\)), 175.6 (C=NXY). IR (cm\(^{-1}\)): \(\nu\)(NH) + (OH), 3456, 3273, 3242; \(\nu\)(C=\(\text{N}\)) 2190, 2158 (sh); \(\nu\)(C=\(\text{N}\)), v(C=N), 1661, 1615. Anal. Found: C, 55.57; H, 4.81; N, 9.91. Calcd for C\(_{25}\)H\(_{25}\)ClN\(_4\)OPd: 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\(_2\)Cl\(_2\) and layered with n-pentane.

**Synthesis of \([\{\text{Pd(tbbpy)}\}_2\{C,N,N',O-C_6\text{H}_4\{C(\text{NH})=\text{NO}\}-2\}]\text{ClO}_4\) (tbbpy = 4,4'-diter-butylbipyridine (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 \(\text{Et}_2\text{O}\) (15 mL) was added. The suspension was filtered and the deep purple solid collected was washed with \(\text{Et}_2\text{O}\) (2 x 5 mL) and dried, first by suction and then in an oven at
80 °C overnight. Yield: 77 mg, 0.078 mmol, 96%, Mp: 257 °C. $^1$H NMR (300 MHz, d$_6$-acetone, 25ºC): δ 1.36 (s, 9 H, Me, tBu), 1.43 (s, 9 H, Me, tBu), 1.45 (s, 9 H, Me, tBu), 1.49 (s, 9 H, Me, tBu), 2.80 (s, 1 H), 2.84 (H$_2$O), 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), 8.99 (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, tBu), 30.5 (Me, tBu, double intensity), 30.6 (Me, tBu), 36.3 (CMe$_3$, double intensity), 36.4 (CMe$_3$), 36.5 (CMe$_3$), 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$^{-1}$): v(NH), 3379; v(C=N) 1616, v(ClO) 1095, δ (OCIO) 623. Anal. Found: C, 52.37; H, 5.47; N, 8.48. Calcd for C$_{43}$H$_{53}$ClN$_6$O$_5$Pd$_2$: C, 52.58; H, 5.44; N, 8.56. $\Lambda_M$ (Ω$^{-1}$·cm$^2$·mol$^{-1}$): 107 (3.06 x 10$^{-4}$ M in acetone). Crystals of 8·solvents grew by the liquid diffusion method using CH$_2$Cl$_2$ and Et$_2$O.

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 $\phi$ scan for 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 Å³, 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.

<table>
<thead>
<tr>
<th>Complex</th>
<th>2a</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C₂₈H₂₈Cl₂OPd</td>
<td>C₄₄H₃₃Cl₃O₅Pd</td>
<td>C₂₅H₂₅Cl₄OPd</td>
<td>C₄₃H₅₃Cl₆O₅Pd₂</td>
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<tr>
<td>Fw</td>
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<td>736.45</td>
<td>539.34</td>
<td>982.16</td>
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<tr>
<td>Temperature (K)</td>
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<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<td>Triclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
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<tr>
<td>Space group</td>
<td>P 2(1)/n</td>
<td>P -1</td>
<td>P 2(1)/c</td>
<td>C 2/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.8915(8)</td>
<td>9.4517(9)</td>
<td>14.058(7)</td>
<td>25.9442(11)</td>
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<tr>
<td>b (Å)</td>
<td>15.4151(11)</td>
<td>11.4744(11)</td>
<td>11.058(5)</td>
<td>21.3161(9)</td>
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<tr>
<td>c (Å)</td>
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<td>14.6828(14)</td>
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<td>α (deg)</td>
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<tr>
<td>β (deg)</td>
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<td>93.311(2)</td>
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<td>γ (deg)</td>
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<td>2316.7(19)</td>
<td>9625.0(7)</td>
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<td>Z</td>
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<td>8</td>
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<td>ρcalcd (Mg m⁻³)</td>
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<td>μ (mm⁻¹)</td>
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<td>F(000)</td>
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<td>crystal size (mm)</td>
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<td>θ range (deg)</td>
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<td>1.82 to 28.73</td>
<td>2.29 to 28.70</td>
<td>2.87 to 66.87</td>
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<td>no. indep rflns / Rint</td>
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<td>5603 / 0.0319</td>
<td>8527 / 0.0441</td>
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<td>3 / 305</td>
<td>505 / 525</td>
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<td>1.039</td>
<td>1.047</td>
<td>1.179</td>
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<td>R1 (I&gt;2σ(I))</td>
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<td>Larg. diff. peak/hole (e.Å⁻³)</td>
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<td>2.882 / -0.552</td>
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