Electronic Supplementary Information for Dalton Transactions

Orthopalladation of Iminophosphoranes: Synthesis, Structure and Study of Stability

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ELECTRONIC SUPPLEMENTARY INFORMATION

Complete Experimental Section

Safety note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See Wolsey, W. C. *J. Chem. Ed.* **1973**, *50*, A335-A337. The organic azides are *highly hazardous* materials which can explode, and whose preparation and manipulation must be carried out with maximum caution. They must be stored at low temperature (T ≈ 0 °C) and dissolved in an inert solvent.[1]

General Methods. Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyser. Infrared spectra (4000-200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from nujol mulls between polyethylene sheets. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 or dmso-d_6 solutions at 25 ºC (other temperatures were specified) on Bruker ARX-300, AvanceII-300, Avance-400 and Avance-500 spectrometers (δ, ppm; J, Hz); ^{1}H and $^{13}C\{^{1}H\}$ were referenced using the solvent signal as internal standard while $^{31}P\{^{1}H\}$ was externally referenced to H_3PO_4 (85%). The ^{1}H SELNO-1D and SELRO-1D NMR experiments were performed with optimized mixing times (D8/P15), depending of the irradiated signal. ESI/APCI mass spectra were recorded using an Esquire 3000 ion – trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Helium served as a cooling gas for the ion trap and collision gas for MS^n experiments. Other mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. The starting azides $N_3CH_2CO_2Me$, $N_3CH_2CONMe_2$, $N_3CH_2CH_2SMe$ and N_3CH_2-2-NC_5H_4 were prepared according to published procedures.[1]

Synthesis of [$Ph_3P=NCH_2COOMe$] (1a). To a solution of $N_3CH_2CO_2Me$ (0.795 g, 6.90 mmol) in freshly distilled CH_2Cl_2 (10 mL) under Ar atmosphere, a solution of PPh_3 (1.80 g, 6.90 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise. The addition was completed in 20 min, and during this time the evolution of N_2 was evident. The resulting solution was stirred at room temperature for 12 h, until the evolution of N_2 ceased. Then, the solvent was evaporated to dryness, giving **1a** as a slightly pink oil. The compound can be used in subsequent reactions without further purification. Yield: 1.952 g (81.0%). Anal. Calc. for $C_{21}H_{20}NO_2P$ (349.36): C, 72.20; H, 5.77; N, 4.01. Found: C, 71.70; H, 5.69; N, 3.85. IR (ν, cm^{-1}): 1746 (ν_{CO}), 1295 (ν_{PN}). MS (MALDI) [m/z, (%)]: 350 (100) $[M+H]^+$. ^1H NMR ($CDCl_3$): δ = 3.48 (s, 3H, OMe), 3.82 (d, 2H, $^3J_{PH}$ = 21.8, CH_2), 7-33-7.35 (m, 6H, H_m, PPh_3), 7.36-7.42 (m, 3H, H_p, PPh_3), 7.56-7.61 (m, 6H, H_o, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 48.21 (d, $^2J_{PC}$ = 3.4, CH_2), 51.43 (OMe), 128.41 (d, $^3J_{PC}$ = 11.6, C_m, PPh_3), 130.83 (d, $^1J_{PC}$ = 97.1, C_i, PPh_3), 131.44 (d, $^4J_{PC}$ = 2.7, C_p, PPh_3), 132.62 (d, $^2J_{PC}$ = 9.1, C_o, PPh_3), 175.44 (d, $^3J_{PC}$ = 17.5, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 15.58.

Synthesis of [$Ph_3P=NCH_2CONMe_2$] (1b). Compound **1b** was obtained following the same experimental procedure than that described for **1a**. Thus, $N_3CH_2C(O)NMe_2$ (0.208 g, 1.50 mmol) was reacted with PPh_3 (0.393 g, 1.50 mmol) in dry CH_2Cl_2 (30 mL) to give **1b** as a white solid. Yield: 0.570 g (83.3%). Anal. Calc. for $C_{22}H_{23}N_2OP$ (362.4): C, 72.91; H, 6.40; N, 7.73. Found: C, 71.98; H, 6.69; N, 7.75. IR (ν, cm^{-1}): 1639 (ν_{CO}), 1304 (ν_{PN}). MS (MALDI) [m/z, (%)]: 363.1 (100) $[M+H]^+$. ^1H NMR ($CDCl_3$): δ = 2.77 (s, 3H, NMe), 3.17 (s, 3H, NMe), 3.94 (d, 2H, $^3J_{PH}$ = 16.5, CH_2), 7.42-7.48 (m, 6H, H_m, PPh_3), 7.50-7.56 (m, 3H, H_p, PPh_3), 7.66-7.72 (m, 6H, H_o, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 16.37.

Synthesis of [$Ph_3P=NCH_2CH_2SMe$] (1c). Compound **1c** was obtained following the same preparaative method than that described for **1a**. Thus, $N_3CH_2CH_2SMe$ (1.21 g, 10.3 mmol) was reacted with PPh_3 (2.71 g, 10.3 mmol) in dry CH_2Cl_2 (50 mL) to give **1c** as a white solid.

Yield: 3.31 g (91.6%). Anal. Calc. for $C_{21}H_{22}NPS$ (351.4): C, 71.77; H, 6.31; N, 3.99. Found: C, 71.42; H, 5.99; N, 3.47. IR (ν, cm^{-1}): 1246 (ν_{PN}). MS (MALDI) [m/z, (%)]: 352 (55) $[M+H]^+$. ^1H NMR ($CDCl_3$): δ = 1.93 (s, 3H, SMe), 2.59 (m, 2H, CH_2S), 3.23 (m, 2H, NCH_2), 7.38-7.41 (m, 6H, H_m, PPh_3) 7.45-7.48 (m, 3H, H_p, PPh_3), 7.57-7.63 (m, 6H, H_o, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.65 (SMe), 39.04 (d, $^3J_{PC}$ = 17.3, CH_2S), 45.76 (d, $^2J_{PC}$ = 4.89, NCH_2), 128.50 (d, $^3J_{PC}$ = 12.1, C_m, PPh_3), 131.94 (d, $^4J_{PC}$ = 2.7, C_p, PPh_3), 132.07 (d, $^2J_{PC}$ = 9.8, C_o, PPh_3), 132.68 (d, $^1J_{PC}$ = 77.6, C_i, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 12.20.

Synthesis of [Ph_3P=NCH_2-2-NC_5H_4] (1d). Compound **1d** was obtained following the same preparative method than that described for **1a**. Thus, N_3CH_2-2-NC_5H_4 (1.35 g, 10.1 mmol) was reacted with PPh_3 (2.63 g, 10.1 mmol) in dry CH_2Cl_2 (40 mL) to give **1d** as a yellow oil. Yield: 3.75 g (100%). Anal. Calc. for $C_{24}H_{21}N_2P$ (368.4): C, 78.24; H, 5.75; N, 7.60. Found: C, 78.13; H, 6.03; N, 7.16. IR (ν, cm^{-1}): 1306 (ν_{PN}). MS (MALDI) [m/z, (%)]: 369 (100) $[M+H]^+$. ^1H NMR ($CDCl_3$): δ = 4.43 (d, 2H, $^3J_{PH}$ =17.2, CH_2), 6.94-6.97 (m, 1H, H_5, py), 7.21-7.24 (m, 1H, H_3, py), 7.34-7.39 (m, 6H, H_m, PPh_3), 7.40-7.45 (m, 3H, H_p, PPh_3), 7.59-7.64 (m, 6H, H_o, PPh_3), 7.86 (d, 1H, $^3J_{HH}$ = 7.8, H_4, py), 8.32 (d, 1H, $^3J_{HH}$ = 4.4, H_6, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 46.86 (CH_2), 120.20 (C_5, py), 120.80 (C_3, py), 127.48 (d, $^3J_{PC}$ =12.1, C_m, PPh_3), 130.91 (d, $^4J_{PC}$ = 2.7, C_p, PPh_3), 131.07 (d, $^2J_{PC}$ = 9.8, C_o, PPh_3), 131.34 (d, $^1J_{PC}$ = 140.1, C_i, PPh_3), 135.55 (C_4, py), 148.29 (C_6, py), 160.97 (C_2, py). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 13.70.

Synthesis of [Pd(μ-Cl){C_6H_4(PPh_2=NCH_2COOMe-κ-C,N)-2}]$_2$ (2a). To a solution of **1a** (1.950 g, 5.58 mmol) in CH_2Cl_2 (20 mL), $Pd(OAc)_2$ (1.250 g, 5.58 mmol) was added, and the resulting mixture was refluxed for 1 h. After the reaction time, decomposition is evident. The cooled black suspension was treated with charcoal for 15 min, and then filtered over Celite giving a deep orange solution. This solution, which contains the acetate bridge intermediate, was evaporated to dryness. The oily brown residue was redissolved in MeOH and treated with

an excess of anhydrous LiCl (0.946 g, 22.3 mmol). After few seconds an orange solid precipitated, but the stirring was maintained for additional 3 h at 25 °C. The resulting suspension was filtered, and the orange solid was washed with MeOH (20 mL) and Et_2O (50 mL), dried by suction and identified as the equilibrium mixture **2a**. Yield: 1.340 g (49%). Compound **2a** crystallized as **2a·2CHCl$_3$** from slow vapour diffusion of Et_2O into a $CHCl_3$ solution of the crude compound. These crystals were used for spectroscopic and analytic measurements. Anal. Calc. for $[C_{42}H_{38}Cl_2N_2O_4P_2Pd_2]\cdot 2CHCl_3$ (1219.12): C, 43.35; H, 3.31; N, 2.30. Found: C, 43.32; H, 3.52; N, 2.29. IR (ν, cm^{-1}): 1725 (ν_{CO}), 1254 (ν_{PN}). MS (FAB+) [m/z, (%)]: 943 (100) $[M_2 - Cl]^+$. ^{1}H NMR ($CDCl_3$): δ = 3.44-3.67 (very broad, 5H, CH_2 + OMe), 6.72-6.76 (m, 1H, H_3, C_6H_4), 6.87 (dd, 1H, $^4J_{HH}$ = 5.4, $^3J_{HH}$ = 9.3, H_4, C_6H_4), 7.00 (t, 1H, $^3J_{HH}$ = 5.4, H_5, C_6H_4), 7.42-7.46 (m, 4H, H_m, PPh_2), 7.53-7.56 (m, 3H, 2 H_p (PPh_2) + H_6 (C_6H_4)), 7.67-7.71 (m, 4H, H_o, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 48.69 (CH_2), 51.76 (OMe), 124.13 (d, $^3J_{PC}$ = 14.4, C_4, C_6H_4), 128.24 (d, $^2J_{PC}$ = 12.3, C_3, C_6H_4), 129.05 (d, $^3J_{PC}$ =11.3, C_m, PPh_2), 131.91 (C_p, PPh_2), 132.10 (d, $^4J_{PC}$ = 9.2, C_5, C_6H_4), 132.98 (d, $^2J_{PC}$ = 9.3, C_o, PPh_2), 134.89 (d, $^3J_{PC}$ =10.3, C_6, C_6H_4), 174.75 (CO). Signals to be assigned to the carbon atoms C_i (PPh_2) and C_1, C_2 (C_6H_4) were not observed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 57.50. ^{1}H NMR ($CDCl_3$, 253 K): δ = 3.53 (OMe), 3.55 (OMe), 3.61 (d, $^3J_{PH}$ = 18.6, CH_2), 3.72 (d, $^3J_{PH}$ = 18.9, CH_2), 3.82 (OMe), 3.88 (d, $^3J_{PH}$ = 7.6, CH_2), 6.84-6.88 (m, H_3, C_6H_4), 6.98-7.01 (m, H_4, C_6H_4), 7.07-7.15 (m, H_5, C_6H_4), 7.52-7.55 (m, H_m, PPh_3), 7.63-7.66 (m, H_p (PPh_3) + H_6 (C_6H_4)), 7.75-7.79 (m, H_o, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 253K): δ = 50.55 (mononuclear), 58.12, 58.17 (cis + trans dinuclear). Dinuclear/mononuclear molar ratio = 5/1.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CONMe_2-κ-C,N,O)-2}(Cl)] (2b). Complex **2b** was prepared following the same preparative method than that described for **2a**. Thus, **1b** (0.570 g, 1.53 mmol) was reacted with $Pd(OAc)_2$ (0.343 g, 1.53 mmol) in refluxing CH_2Cl_2 (20 mL), and with excess LiCl (0.946 g, 22.3 mmol) in MeOH (20 mL) to give **2b** as a yellow solid.

Yield: 0.215 g (27.4%). Anal. Calc. for $C_{22}H_{22}ClN_2OPPd$ (503.3): C, 52.45; H, 4.40; N, 5.56. Found: C, 51.90; H, 4.85; N, 5.46. IR (ν, cm^{-1}): 1607 (ν_{CO}), 1258 (ν_{PN}). MS (FAB+) [m/z, (%)]: 467 (100) $[M-Cl]^+$. ^1H NMR (DMSO-d_6): δ = 2.81 (s, 3H, NMe), 2.85 (s, 3H, NMe), 3.96 (d, 2H, $^3J_{PH}$ = 6.8, CH_2), 6.84-6.89 (m, 1H, C_6H_4), 6.96-7.00 (m, 1H, C_6H_4), 7.05-7.08 (m, 1H, C_6H_4), 7.65-7.78 (m, 11H, 1H (C_6H_4) + 10H (PPh_2)). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 48.13.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CH_2SMe-κ-C,N,S)-2}(Cl)] (2c). Complex **2c** was prepared following the same preparative method than that described for **2a**, except that the reaction time was 5 h. Thus, **1c** (0.675 g, 1.72 mmol) was reacted with $Pd(OAc)_2$ (0.386 g, 1.72 mmol) in CH_2Cl_2 (20 mL), and with excess LiCl (0.291 g, 6.80 mmol) in MeOH (20 mL) to give **2c** as a deep yellow solid. Yield: 0.426 g (57.2%). Anal. Calc. for $C_{21}H_{21}ClNPPdS$ (492.0): C, 51.22; H, 4.29; N, 2.84. Found: C, 51.11; H, 4.24; N, 2.92. IR (ν, cm^{-1}): 1228 (ν_{PN}). MS (FAB+) [m/z, (%)]: 492 (27) $[M]^+$. ^1H NMR (CD_2Cl_2): δ = 2.32 (s, 3H, SMe), 2.79 (s, br, 2H, SCH_2), 2.91 (dd, 2H, $^3J_{HH}$ = 5.8, $^2J_{PH}$ = 12.6, NCH_2), 6.82 (ddd, 1H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5, $^3J_{PH}$ = 9.1, H_3, C_6H_4), 6.98 (tdd, 1H, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.1, $^4J_{PH}$ = 5.0, H_4, C_6H_4), 7.17 (tt, 1H, $^4J_{HH}$ = 1.6, $^3J_{PH}$ = 7.7, H_5, C_6H_4), 7.50-7.54 (m, 4H, H_m, PPh_2), 7.61-7.68 (m, 6H, $4H_o$ + $2H_p$, PPh_2), 7.92 (ddd, 1H, $^4J_{HH}$ = 1.0, $^3J_{HH}$ = 9.4, $^4J_{PH}$ = 1.9, H_6, C_6H_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 17.77 (SMe), 42.41 (d, $^3J_{PC}$ =18.4, SCH_2), 45.40 (NCH_2), 124.40 (d, $^3J_{PC}$ =14.6, C_4, C_6H_4), 127.01 (d, $^1J_{PC}$ = 83.6, C_i, PPh_2), 128.51 (d, $^2J_{PC}$ = 12.1, C_3, C_6H_4), 129.15 (d, $^3J_{PC}$ = 11.5, C_m, PPh_2), 131.07 (d, $^4J_{PC}$ = 3.2, C_5, C_6H_4), 132.57 (d, $^3J_{PC}$ = 9.7, C_o, PPh_2), 133.02 (d, $^4J_{PC}$ = 2.5, C_p, PPh_2), 136.43 (d, $^3J_{PC}$ = 14.8, C_6, C_6H_4), 140.67 (d, $^2J_{PC}$ = 141, C_2, C_6H_4), 157.21 (d, $^2J_{PC}$ = 20.2, C_1, C_6H_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 50.37.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2-C_5H_4N-2'-κ-C,N,N)-2}(Cl)] (2d). Complex **2d** was prepared following the same preparative method than that described for **2a**, except that the reaction solvent was toluene. Thus, **1d** (0.300 g, 0.81 mmol) was reacted with $Pd(OAc)_2$ (0.18

g, 0.81 mmol) in refluxing toluene (20 mL), and with excess LiCl (0.210 g, 5.00 mmol) in MeOH (20 mL) to give **2d** as a deep orange solid. Yield: 0.315 g (76%). Anal. Calc. for $C_{24}H_{20}ClN_2PPd$ (509.2): C, 56.55; H, 3.95; N, 5.50. Found: C, 56.10; H, 3.47; N, 5.16. IR (ν, cm^{-1}): 1287 (ν_{PN}). MS (FAB+) [m/z, (%)]: 507 (20) $[M-2H]^+$. ^1H NMR ($CDCl_3$): δ = 4.41 (d, 2H, $^3J_{PH}$ = 7.0, CH_2), 6.80 (ddd, 1H, $^4J_{HH}$ = 1.4, $^3J_{HH}$ = 7.6, J_{PH} = 11.2, C_6H_4), 6.95 (m, 1H, C_6H_4), 7.10 (d, 1H, J_{HH} = 7.8, C_6H_4), 7.15-7.19 (m, 2H, H_4, H_5, py), 7.52-7.57 (m, 4H, H_m, PPh_2), 7.61-7.66 (m, 3H, $2H_p$ (PPh_2) + 1H (C_6H_4)), 7.74-7.79 (m, 4H, H_o, PPh_2), 8.12 (ddd, 1H, $^5J_{HH}$ = 0.7, $^4J_{HH}$ = 2.3, $^3J_{HH}$ = 7.8, H_3, py), 8.98 (dd, 1H, $^5J_{HH}$ = 0.7, $^3J_{HH}$ = 5.3, H_6, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 51.43 (CH_2), 119.51 (C_6H_4), 121.33 (py), 123.00 (d, J_{PC} =15.1, C_6H_4), 126.05 (d, $^1J_{PC}$ = 83.7, C_i, PPh_2), 127.99 (d, J_{PC} = 22.0, C_6H_4), 128.25 (d, $^3J_{PC}$ = 11.5, C_m, PPh_2), 130.0 (d, J_{PC} = 3.2, py), 131.76 (d, $^2J_{PC}$ = 9.8, C_o, PPh_2), 132.09 (d, $^4J_{PC}$ = 2.7, C_p, PPh_2), 136.18 (C_6H_4), 137.58 (d, $^4J_{PC}$ = 14.7, C_3, py), 141.05 (d, $^1J_{PC}$ = 142.4, C_2, C_6H_4), 148.22 (C_6, py), 153.97 (d, $^2J_{PC}$ = 19.0, C_1, C_6H_4), 165.40 (d, $^3J_{PC}$ = 17.5, C_2, py). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 48.53.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2COOMe-κ-C,N)-2}$(NCMe)_2$](ClO_4) (3a). A suspension of **2a** (0.200 g, 2.03 mmol) in dry NCMe (15 mL) was treated with $AgClO_4$ (0.084 g, 4.07 mmol), and the resulting suspension was stirred at 25 °C for 1h with exclusion of light. After the reaction time, the insoluble AgCl was filtered, and the resulting solution was evaporated to small volume (≈ 2 mL). By Et_2O (20 mL) addition and further stirring, **3a** was obtained as a white solid. Yield: 0.187 g (72.5%). Anal. Calc. for $C_{25}H_{25}ClN_3O_6PPd$ (636.3): C, 47.19; H, 3.96; N, 6.60. Found: C, 47.31; H, 3.64; N, 6.82. IR (ν, cm^{-1}): 2291 (ν_{CN}), 1741 (ν_{CO}), 1216 (ν_{PN}). MS (FAB+) [m/z, (%)]: 455 (100) $[M-2NCMe-ClO_4]^+$. ^1H NMR ($CDCl_3$): δ = 2.00 (s, 3H, NCMe), 2.51 (s, 3H, NCMe), 3.83 (s, 3H, OMe), 3.88 (d, 2H, $^3J_{PH}$ = 8.1, CH_2), 6.90 (ddd, 1H, J_{HH} = 0.6, J_{HH} = 2.8, J_{HH} = 7.2, C_6H_4), 7.11-7.18 (m, 1H, C_6H_4), 7.21-7.29 (m, 2H, C_6H_4), 7.60-7.77 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 2.16 (NC*Me*), 3.79 (NC*Me*), 49.12

(CH_2), 54.87 (OMe), 124.25 (d, $^1J_{PC}$ = 50.1, C_i, PPh_2), 125.97 (d, J_{PC} = 14.5, C_6H_4), 129.86 (d, $^3J_{PC}$ =11.9, C_m, PPh_2), 130.16 (C_6H_4), 131.90 (C_6H_4), 132.16 (d, $^2J_{PC}$ =10.2, C_o, PPh_2), 134.22 (d, $^4J_{PC}$ =1.0, C_p, PPh_2), 136.20 (d, J_{PC} = 13.3, C_6H_4), 178.4 (d, $^3J_{PC}$ =2.2, CO). Signals to assign to C^1, C^2 (C_6H_4) and CN carbon atoms were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 57.64.

Synthesis of [PdCl{C_6H_4(PPh_2=NCH_2COOMe-κ-C,N)-2}(PPh_3)] (4a). To a suspension of **2a** (0.150 g, 1.52 mmol) in 15 mL of CH_2Cl_2, PPh_3 (0.080 g, 3.05 mmol) was added. The initial suspension gradually dissolved and, after the reaction time (1 h), a clear yellow solution was obtained. Any insoluble impurity was filtered at this point and discarded. The resulting clear solution was evaporated to dryness and Et_2O (20 mL) was added to the oily residue. Further stirring allowed the isolation of **4a** as a yellow solid. Yield: 0.176 g (77.2%). Anal. Calc. for $C_{39}H_{34}ClNO_2P_2Pd$ (751.9): C, 62.00; H, 4.50; N, 1.80. Found: C, 61.97; H, 3.92; N, 1.63. IR (ν, cm^{-1}): 1762 (ν_{CO}), 1262 (ν_{PN}). MS (FAB+) [m/z, (%)]: 717 (100) $[M\text{-}Cl]^+$. ^1H NMR ($CDCl_3$): δ = 3.43 (s, 3H, OMe), 4.12 (dd, 2H, $^4J_{PH}$ = 19.7, $^3J_{PH}$ = 5.3, CH_2), 6.39 (t, 1H, $^3J_{HH}$ = 7.5, H_5, C_6H_4), 6.54 (dt, 1H, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.5, H_6, C_6H_4), 6.65 (dd, 1H, $^3J_{HH}$ = 7.3, $^4J_{PH}$ = 12.1, H_4, C_6H_4), 6.82 (ddd, 1H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5, $^3J_{PH}$ = 9.0, H_3, C_6H_4), 7.16-7.20 (m, 6H, H_m, PPh_3), 7.25-7.30 (m, 3H, H_p, PPh_3), 7.44-7.49 (td, 4H, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 2.5, H_m, PPh_2), 7.54-7-58 (m, 8H, 6H_o (PPh_3) + 2H_p (PPh_2)) 7.80 (dd, 4H, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 11.3, H_o, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 47.83 (d, $^3J_{PC}$ = 2.3, CH_2), 51.46 (s, OMe), 122.87 (d, J_{PC} = 14.1, C_6H_4), 127.78 (d, $^3J_{PC}$ = 10.7, C_m, PPh_3), 128.09 (d, J_{PC} = 10.9, C_6H_4), 128.76 (d, $^3J_{PC}$ =11.4, C_m, PPh_2), 129.19 (C_6H_4), 130.08 (d, $^4J_{PC}$ =1.9, C_p, PPh_3), 130.39 (d, $^1J_{PC}$ = 65.8, C_i, PPh_2), 131.94 (d, $^1J_{PC}$ = 48.8, C_i, PPh_3), 132.50 (d, $^4J_{PC}$ = 2.1, C_p, PPh_2), 133.37 (d, $^2J_{PC}$ = 9.7, C_o, PPh_2), 135.25 (d, $^2J_{PC}$ = 11.7, C_o, PPh_3), 139.75 (dd, J_{PC} = 13.2, J_{PC}=14.8, C_6H_4), 141.16 (d, $^1J_{PC}$ = 136.6, C_2, C_6H_4), 159.34 (d, $^2J_{PC}$ = 18.8, C_1, C_6H_4), 173.98 (d, $^3J_{PC}$ = 10.8, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 38.82 (d, $^3J_{PP}$ = 2.5, PPh_3), 46.76 (d, $^3J_{PP}$ = 2.9, $C_6H_4PPh_2$).

Synthesis of [PdCl{C_6H_4(PPh_2=NCH_2COOMe-κ-C,N)-2}(py)] (5a). Complex **5a** was prepared following a synthetic method similar to that reported for **4a**. Thus, **2a** (0.150 g, 1.52 mmol) was reacted with py (72 µl, 7.02 mmol) for 12 h to give **5a** as a yellow solid. Yield: 0.129 g (74.5%). Anal. Calc. for $C_{26}H_{24}ClN_2O_2PPd$ (568.9): C, 54.84; H, 4.20; N, 4.90. Found: C, 54.64; H, 4.68; N, 5.00. IR (ν, cm^{-1}): 1751 (ν_{CO}), 1292 (ν_{PN}). MS (FAB+) [m/z, (%)]: 534 (40) $[M-Cl]^+$, 454 (100) $[M-Cl-Py]^+$. ^1H NMR ($CDCl_3$): δ = 3.47 (s, 3H, OMe), 3.87 (d, 2H, $^3J_{PH}$ = 19.7, CH_2), 6.13 (d, 1H, $^3J_{HH}$ = 7.0, H_6, C_6H_4), 6.85-6.94 (m, 3H, H_3, H_4, H_5, C_6H_4), 7.26 (dt, 2H, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 6.5, H_m, py), 7.46 (dt, 4H, $^4J_{PH}$ = 3.0, $^3J_{HH}$ = 7.3, H_m, PPh_2), 7.56 (m, 2H, H_p, PPh_2), 7.71 (tt, 1H, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.5, H_p, py), 7.76 (ddd, 4H, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.2, $^3J_{PH}$ = 8.3, H_o, PPh_2), 8.84 (dd, 2 H, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 6.3 Hz, H_o, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 48.46 (CH_2), 51.53 (OMe), 123.89 (d, J_{PC} = 14.0, C_6H_4), 125.05 (C_m, py), 127.25 (d, $^1J_{PC}$ = 99.1, C_i, PPh_2), 128.20 (d, J_{PC} = 21.0, C_6H_4), 128.98 (d, $^3J_{PC}$ =11.6, C_m, PPh_2), 130.51 (d, J_{PC} = 2.8, C_6H_4), 132.79 (d, $^4J_{PC}$ = 2.4, C_p, PPh_2), 133.08 (d, $^2J_{PC}$ = 12.5, C_o, PPh_2), 134.56 (d, $^3J_{PC}$ = 15.3, C_6, C_6H_4), 137.36 (C_p, py), 139.77 (d, $^1J_{PC}$ = 139.8, C_2, C_6H_4), 153.69 (C_o, py), 155.50 (d, $^2J_{PC}$ = 22.7, C_1, C_6H_4), 173.45 (d, $^3J_{PC}$ = 8.9, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 56.10.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2COOMe-κ-C,N,O)-2}(PPh_3)](ClO_4) (6a). *Method A.* A solution of **4a** (0.130 g, 1.77 mmol) in dry THF (20 mL) was treated with $AgClO_4$ (0.036 g, 1.77 mmol), and the resulting suspension was stirred with exclusion of light for 1 h. After the reaction time the insoluble AgCl was filtered over Celite, and the resulting yellow solution was evaporated to dryness. By Et_2O addition (25 mL) and further stirring, complex **6a** was obtained as a yellow solid. Yield: 0.112 g (77.5%). *Method B.* To a solution of **2a** (0.150 g, 0.15 mmol) in THF (20 mL), $AgClO_4$ (0.063 g, 0.30 mmol) was added, and the resulting solution was stirred for 30 min at room temperature with exclusion of light. The thus obtained

suspension was filtered, and the resulting solution was treated with PPh_3 (0.08 g, 0.3 mmol) and stirring at 25 °C for 5 h. At the end of the reaction time, the solution was evaporated to dryness and the residue treated with Et_2O (15 mL). Further stirring gives **6a** as a yellow solid. Yield: 0.188 g (77%). Anal. Calc. for $C_{39}H_{34}ClNO_6P_2Pd$ (816.5): C, 57.36; H, 4.19; N, 1.71. Found: C, 57.33; H, 4.12; N, 1.69. IR (ν, cm^{-1}): 1644 (ν_{CO}), 1272 (ν_{PN}). MS (FAB+) [m/z, (%)]: 716 (100) $[M\text{-}ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ = 3.76 (s, 3H, OMe), 4.14 (dd, 2H, $^4J_{PH}$ = 7.2, $^3J_{PH}$ = 2.4, CH_2), 6.67 (m, 1H, H_6, C_6H_4), 6.78 (m, 1H, H_5, C_6H_4), 6.92-7.03 (m, 2H, H_4, H_3, C_6H_4), 7.44-7.61 (m, 10H, PPh_2), 7.64-7.82 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 49.27 (CH_2), 55.09 (s, OMe), 125.31 (d, $^3J_{PC}$ = 14.7, C_4, C_6H_4), 125.85 (d, $^1J_{PC}$ = 86.9, C_i, PPh_2), 127.67 (d, $^1J_{PC}$ = 87.4, C_i, PPh_3), 128.87 (d, $^2J_{PC}$ = 11.0, C_m, PPh_3), 129.87 (d, $^2J_{PC}$ = 11.9, C_m, PPh_2), 131.23 (d, $^2J_{PC}$ = 20.4, C_3, C_6H_4), 131.68 (d, $^4J_{PC}$ = 2.1, C_p, PPh_3), 131.97 (dd, $^4J_{PC}$ =3.1, $^4J_{PC}$ =5.3, C_5, C_6H_4), 132.57 (d, $^3J_{PC}$ = 10.2, C_o, PPh_2), 134.08 (d, $^4J_{PC}$ = 2.4, C_p, PPh_2), 134.80 (d, $^3J_{PC}$ = 12.3, C_o, PPh_3), 140.39 (t, $^3J_{PC}$ = 13.6, C_6, C_6H_4), 141.93 (dd, $^1J_{PC}$ = 139.6, $^4J_{PC}$ = 1.6, C_2, C_6H_4), 147.32 (dd, $^2J_{PC}$ = 15.1, $^2J_{PC}$ = 3.2, C_1, C_6H_4), 186.12 (dd, $^3J_{PC}$ = 23.1, $^3J_{PC}$ = 5.5, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 39.29 (PPh_3), 47.55 ($C_6H_4PPh_2$).

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2COOMe-κ-C,N,O)-2}(py)](ClO_4) (7a). Complex **7a** was prepared following the same synthetic method than that reported for **6a**, method A. Thus, **5a** (0.086 g, 1.52 mmol) was reacted with $AgClO_4$ (0.031 g, 1.52 mmol) in THF (20 mL) to give **7a** as a yellow solid. Yield: 0.044 g (29.3%). Anal. Calc. for $C_{26}H_{24}ClN_2O_6PPd$ (633.3): C, 49.30; H, 3.81; N, 4.42. Found: C, 49.48; H, 3.61; N, 4.39. IR (ν, cm^{-1}): 1652 (ν_{CO}), 1264 (ν_{PN}). MS (FAB+) [m/z, (%)]: 533 (90) $[M\text{-}ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ = 3.85 (s, 3H, OMe), 4.00 (d, 2H, $^3J_{PH}$ = 6.9, CH_2), 6.38 (td, 1H, $^3J_{HH}$ = 4.1, $^4J_{HH}$ = 1.2, H_6, C_6H_4), 6.89-6.99 (m, 1H, H_5, C_6H_4), 7.08-7.15 (m, 2H, H_3, H_4, C_6H_4), 7.60-7.80 (m, 12H, 10H (PPh_2) + $2H_m$ (py)), 8.07 (tt, 1H, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 7.7, H_p, py), 8.90 (td, 1H, $^4J_{HH}$ = 1.5, $^3J_{HH}$ = 4.8, H_o, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 49.12 (CH_2), 55.11 (OMe), 125.57 (d, $^1J_{PC}$ = 86.8, C_i, PPh_2),

125.44 (d, J_{PC} = 14.7, C_6H_4), 126.48 (C_m, py), 129.80 (d, $^3J_{PC}$ = 11.9, C_m, PPh_2), 130.27 (d, $^2J_{PC}$ = 20.9, C_5, C_6H_4), 132.11 (d, $^4J_{PC}$ = 2.8, C_6H_4), 132.60 (d, $^2J_{PC}$ =10.3, C_o, PPh_2), 134.00 (d, $^4J_{PC}$ = 2.5, C_p, PPh_2), 134.53 (d, $^3J_{PC}$ =13.4, C_6, C_6H_4), 139.31 (C_p, py), 139.96 (d, $^1J_{PC}$ = 140.6, C_2, C_6H_4), 146.77 (d, $^2J_{PC}$ = 16.1, C_1, C_6H_4), 152.72 (C_o, py), 184.59 (d, $^3J_{PC}$ = 5.8, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 53.13.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CONMe_2-κ-C,N,O)-2}(NCMe)](ClO_4) (3b). Complex **3b** was prepared following a synthetic method similar to that reported for **3a**. Thus, **2b** (0.100 g, 0.97 mmol) was reacted with $AgClO_4$ (0.040 g, 1.94 mmol) in NCMe (10 mL) to give **3b** as a white solid. Yield: 0.102 g (79.4%). Anal. Calc. for $C_{24}H_{25}ClN_3O_5PPd$ (608.1): C, 47.36; H, 4.14; N, 6.91. Found: C, 47.27; H, 4.50; N, 6.53. IR (ν, cm^{-1}): 2326, 2293 (ν_{CN}), 1609 ($\nu_{C=O}$), 1259 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 467 (100) $[M - NCMe - ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ = 2.51 (s, 3H, NCMe), 2.93 (s, 3H, NMe), 3.00 (s, 3H, NMe), 3.95 (d, 2H, $^3J_{PH}$ = 6.8, CH_2), 6.92 (ddd, 1H, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.2, $^4J_{PH}$ = 11.2, H_6, C_6H_4), 7.13-7.18 (m, 1H, H_5, C_6H_4), 7.24-7.31 (m, 2H, H_3, H_4, C_6H_4), 7.66-7.71 (m, 4H, H_m, PPh_2), 7.74-7.80 (m, 6H, $4H_o$+$2H_p$, PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 3.59 (NC*Me*), 36.04 (NMe), 38.22 (NMe), 49.55 (NCH_2), 119.25 (NC), 125.18 (d, $^1J_{PC}$ = 89.6, C_i, PPh_2), 125.49 (d, $^4J_{PC}$ = 5.1, C_5, C_6H_4), 129.76 (d, $^3J_{PC}$ = 12.3, C_m, PPh_2), 130.31 (d, $^3J_{PC}$ = 20.6, C_6, C_6H_4), 132.05 (d, $^3J_{PC}$ = 2.1, C_4, C_6H_4), 132.63 (d, $^2J_{PC}$ = 10.3, C_o, PPh_2), 134.05 (d, $^3J_{PC}$ = 2.1, C_p, PPh_2), 135.67 (d, $^2J_{PC}$ = 13.3, C_3, C_6H_4), 141.12 (d, $^1J_{PC}$ = 144.2, C_2, C_6H_4), 147.24 (d, $^2J_{PC}$ = 16.4, C_1, C_6H_4), 180.51 (d, $^3J_{PC}$ = 18.5, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 55.23.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CONMe_2-κ-C,N,O)-2}(PPh_3)](ClO_4) (6b). To a solution of **3b** (0.040 g, 0.061 mmol) in CH_2Cl_2 (15 mL), PPh_3 (0.020 g, 0.061 mmol) was added. The resulting solution was stirred for 40 min at 25 °C, then evaporated to dryness. By Et_2O (25 mL) addition to the oily residue and further stirring, **6b** was obtained as yellow solid. The yield was quantitative (0.044 g). Anal. Calc. for $C_{40}H_{37}ClN_2O_5P_2Pd$ (829.5): C,

57.92; H, 4.50; N, 3.38. Found: C, 57.81; H, 4.78; N, 3.70. IR (ν, cm^{-1}): 1602 ($\nu_{C=O}$), 1257 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 729 (100) $[M - ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ = 2.36 (s, 3H, NMe), 2.75 (s, 3H, NMe), 4.04 (dd, 2H, $^4J_{PH}$ = 1.3, $^3J_{PH}$ = 7.4, CH_2), 6.56 (m, 1H, H_6, C_6H_4), 6.66 (m, 1H, C_6H_4), 6.81-6.88 (m, 2H, C_6H_4), 7.37 (m, 6H, H_m, PPh_3), 7.45 (m, 3H, H_p, PPh_3), 7.60 (m, 6H, H_o, PPh_3), 7.64-7.72 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 36.38 (NMe), 38.45 (NMe), 49.67 (d, $^2J_{PC}$ = 1.4, NCH_2), 124.69 (d, J_{PC} =14.7, C_6H_4), 126.32 (d, $^1J_{PC}$ = 86.2, C_i, PPh_2), 128.70 (d, $^3J_{PC}$ = 10.8, C_m, PPh_3), 129.41 (d, $^1J_{PC}$ = 49.1, C_i, PPh_3), 129.80 (d, $^2J_{PC}$ =11.8, C_o, PPh_3), 130.94 (d, J_{PC} = 20.8, C_6H_4), 131.37 (d, $^4J_{PC}$ = 2.3, C_p, PPh_3), 131.48 (d, J_{PC} = 5.1, C_6H_4), 132.78 (d, $^3J_{PC}$ = 10.1, C_m, PPh_2), 133.81 (d, $^4J_{PC}$ = 2.7, C_p, PPh_2), 134.93 (d, $^2J_{PC}$ = 12.2, C_o, PPh_2), 140.54 (t, J_{PC} = 26.7, C_6H_4), 143.25 (dd, $^3J_{PC}$ = 10.4, $^1J_{PC}$ = 131.0, C_2, C_6H_4), 150.26 (dd, $^2J_{PC}$ = 5.0, $^2J_{PC}$ = 16.3, C_1, C_6H_4), 181.85 (dd, $^3J_{PC}$ = 5.5, $^3J_{PC}$ = 19.8, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 38.91 (d, $^3J_{PP}$ = 5.2, PPh_3), 46.31 (d, PPh_2N).

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CONMe_2-κ-C,N,O)-2}(py)](ClO_4) (7b). Complex **7b** was prepared through a synthetic procedure similar to that described for **6b**. Thus, **3b** (0.040 g, 0.061 mmol) was reacted with py (5.19 μl, 0.061 mmol) in CH_2Cl_2 (10 mL) to give **7b** as a yellow solid. Yield: 0.031 g (90.6%). Anal. Calc. for $C_{27}H_{27}ClN_3O_5PPd$ (646.10): C, 50.15; H, 4.21; N, 6.50. Found: C, 49.80; H, 4.26; N, 6.13. IR (ν, cm^{-1}): 1607 ($\nu_{C=O}$), 1259 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 546 (75) $[M\text{-}ClO_4]^+$, 467 (100) $[M\text{-py-}ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ = 2.82 (s, 3H, NMe), 2.83 (s, 3H, NMe), 3.91 (d, 2H, $^3J_{PH}$ = 6.8, CH_2), 6.39 (m, 1H, H_6, C_6H_4), 6.84 (m, 1H, H_5, C_6H_4), 6.97-7.05 (m, 2H, H_3, H_4, C_6H_4), 7.50 (m, 2H, H_m, py), 7.58 (m, 4H, H_m, PPh_2), 7.67-7.72 (m, 6H, $4H_o$+$2H_p$, PPh_2), 7.94 (tt, 1H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.5, H_p, py), 8.79 (dd, 2 H, $^3J_{HH}$ = 6.3, $^4J_{HH}$ = 1.3, H_o, py). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 35.84 (NMe), 37.99 (NMe), 49.39 (NCH_2), 124.88 (d, $^2J_{PC}$ = 14.8, C_3, C_6H_4), 125.62 (d, $^1J_{PC}$ = 86.1, C_i, PPh_2), 126.00 (C_m, py), 129.54 (d, $^3J_{PC}$ =11.8, C_m, PPh_2), 130.16 (d, $^4J_{PC}$ = 21.2, C_5, C_6H_4), 131.68 (d, $^3J_{PC}$ = 3.1, C_4, C_6H_4), 132.51 (d, $^2J_{PC}$ = 10.2, C_o, PPh_2), 133.72 (d, $^4J_{PC}$ = 2.8, C_p,

PPh_2), 134.30 (d, $^3J_{PC}$ =13.7, C_6, C_6H_4), 138.85 (C_p, py), 141.84 (d, $^1J_{PC}$ = 139.5, C_2, C_6H_4), 149.77 (d, $^2J_{PC}$ = 17.0, C_1, C_6H_4), 152.42 (C_o, py), 180.54 (d, $^3J_{PC}$ = 18.1, CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 51.41.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CH_2SMe-κ-C,N,S)-2}(NCMe)](ClO_4) (3c). Complex **3c** was prepared following a synthetic method similar to that reported for **3a**. Thus, **2c** (0.200 g, 2.30 mmol) was reacted with $AgClO_4$ (0.046 g, 2.30 mmol) in NCMe (10 mL) to give **3c** as a yellow solid. Yield: 0.166 g (67.1%). Anal. Calc. for $C_{23}H_{24}ClO_4N_2PPdS$ (597.4): C, 46.20; H, 4.04; N, 4.68; S, 5.30. Found: C, 46.00; H, 3.91; N, 4.61; S, 6.00. IR (ν, cm^{-1}): 2324, 2293 (ν_{CN}), 1230 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 497 (100) $[M - ClO_4]^+$. ^1H NMR (DMSO-d_6): δ = 2.07 (s, 3H, NCMe), 2.46 (s, 3H, SMe), 3.04 (t, 2H, $^3J_{HH}$ = 5.2, SCH_2), 3.26 (m, 2H, NCH_2), 7.17-7.28 (m, 2H, H_3, H_4, C_6H_4), 7.42 (t, 1H, $^3J_{HH}$ = 8.0, H_5, C_6H_4), 7.67-7.82 (m, 10H, PPh_2), 7.94 (dd, 1H, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.6, H_6, C_6H_4). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ = 0.02 (NC*Me*), 14.38 (SMe), 39.56 (d, $^2J_{PC}$ = 15.2, CH_2S), 44.08 (CH_2N), 116.99 (NC), 124.84 (d, $^1J_{PC}$ = 86.0, C_i, PPh_2), 125.29 (d, J_{PC} = 13.5, C_6H_4), 128.60 (d, $^3J_{PC}$ = 11.7, C_m, PPh_2), 129.58 (d, J_{PC} = 21.0, C_6H_4), 131.34 (d, $^2J_{PC}$ = 10.2, C_o, PPh_2), 132.71 (d, $^4J_{PC}$ = 1.7, C_p, PPh_2), 133.51 (d, J_{PC} = 14.7, C_6H_4), 140.81 (d, $^1J_{PC}$= 135.6, C_2, C_6H_4), 156.04 (d, $^2J_{PC}$= 20.8, C_1, C_6H_4). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = 54.27.

Synthesis of [Pd{C_6H_4(PPh_2=NCH_2CH_2SMe-κ-C,N,S)-2}(py)](ClO_4) (7c). Complex **7c** was prepared through a synthetic procedure similar to that described for **6b**. Thus, **3c** (0.075 g, 0.14 mmol) was reacted with a large excess of py (68 μl, 1.68 mmol) in CH_2Cl_2 (10 mL) to give **7c** as a yellow solid. Yield: 0.066 g (99.3%). Anal. Calc. for $C_{26}H_{26}ClO_4N_2PPdS$ (635.1): C, 49.13; H, 4.12; N, 4.41. Found: C, 48.70; H, 3.47; N, 4.86. IR (ν, cm^{-1}): 1604 ($\nu_{C=O}$), 1221 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]: 534 (75) $[M - ClO_4]^+$, 456 (100) $[M\text{-}ClO_4 - py]^+$. ^1H NMR (CD_2Cl_2): δ = 2.48 (s, 3H, SMe), 3.19 (m, 2H, SCH_2), 3.33 (m, 2H, NCH_2), 6.45 (m, 1H, H_6, C_6H_4), 7.21 (m, 1H, C_6H_4), 7.30-7.34 (m, 2H, C_6H_4), 7.72 (m, 4H, H_m, PPh_2), 7.84 (m, 2H,

H_p, PPh_2), 7.91-7.97 (m, 6H, $4H_o$ (PPh_2) + $2H_m$ (py)), 8.25 (tt, 1H, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.5, H_p, py), 9.06 (dd, 2H, $^3J_{HH}$ = 6.3, $^4J_{HH}$ = 1.5, H_o, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 17.41 (SMe), 42.34 (d, $^2J_{PC}$ = 16.9, CH_2S), 46.12 (CH_2N), 126.40 (d, $^3J_{PC}$ = 14.7, C_6, C_6H_4), 127.19 (s, C_i, PPh_2), 128.38 (d, $^3J_{PC}$ = 10.9, C_m, PPh_2), 130.63 (d, J_{PC} = 21.2, C_6H_4), 132.86 (d, J_{PC} = 3.1, C_6H_4), 133.28 (d, $^2J_{PC}$ = 10.0, C_o, PPh_2), 134.34 (d, $^3J_{PC}$ = 16.9, C_6, C_6H_4), 134.47 (d, $^4J_{PC}$ = 2.6, C_p, PPh_2), 141.93 (d, $^1J_{PC}$ = 138.3, C_2, C_6H_4), 153.30 (C_o, py), 157.52 (d, $^2J_{PC}$ = 20.6, C_1, C_6H_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 53.96.

Synthesis of [Pd(Ph_3P=NCH_2CH_2SMe-κ-N,S)$(Cl)_2$] (8). To a solution of **1c** (0.538 g, 1.53 mmol) in CH_2Cl_2 (15 mL), $Pd(OAc)_2$ (0.307 g, 1.53 mmol) was added, and the resulting mixture was refluxed for 1 h. After the reaction time, the red solution was evaporated to dryness, and the deep red residue was dissolved in MeOH (10 mL). The treatment of this solution with an excess of anhydrous LiCl (0.232 g, 5.48 mmol) and gentle stirring for 12 h at 25 °C, gives **8** as a yellow solid, which was filtered, washed with MeOH (5 mL) and Et_2O (50 ml) and dried by suction. Yield: 0.612 g (75.7%). Anal. Calc. for $C_{21}H_{22}Cl_2NPPdS$ (528.3): C, 47.70; H, 4.19; N, 2.65. Found: C, 47.83; H, 4.39; N, 2.77. IR (ν, cm^{-1}): 1232 ($\nu_{P=N}$). MS (FAB+) [m/z, (%)]:492 (27) $[M - Cl]^+$. ^1H NMR (CD_2Cl_2): δ = 1.79 (s, 3H, SMe), 2.09 (m, 1H, SCH_2), 2.40 (m, 1H, SCH_2), 2.66 (m, 1H, NCH_2), 3.16 (m, 1H, NCH_2), 7.36-7.39 (m, 6H, H_m, PPh_3), 7.43-7.46 (m, 3H, H_p, PPh_3), 7.62-7.67 (m, 6H, H_o, PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 21.97 (SMe), 41.14 (d, $^3J_{PC}$ =11.4, SCH_2), 53.13 (NCH_2), 127.21 (d, $^1J_{PC}$ =102.4, C_i, PPh_3), 129.02 (s, $^3J_{PC}$ =12.5, C_m, PPh_3), 133.24 (d, $^4J_{PC}$ = 2.8, C_p, PPh_3), 134.16 (d, $^2J_{PC}$ = 9.6, C_o, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 37.54.

Crystal Structure Determination and Data Collection of Complexes 2a·2$CHCl_3$, 3b, 7b and 8. Crystals of adequate quality for X-ray measurements were grown by vapour diffusion of Et_2O into CH_2Cl_2 (**3b**, **7b**) or $CHCl_3$ solutions (**2a**, **8**) of the corresponding crude products at room temperature. A single crystal of each compound (dimensions specified in Table 1)

was mounted at the end of a quartz fiber in a random orientation, covered with magic oil and placed under the cold stream of nitrogen. Data collection was performed at 100 K or 123 K (see Table 1) on Bruker Smart CCD or Oxford Diffraction Xcalibur2 diffractometers using graphite-monocromated Mo-K_α radiation (λ = 0.71073 Å). In all cases an hemisphere of data was collected based on three ω-scan or ϕ-scan runs. The diffraction frames were integrated using the programs SAINT[2] or CrysAlis RED[3] and the integrated intensities were corrected for absorption with SADABS.[4]

Structure Solution and Refinement. The structures were solved and developed by direct or Patterson methods.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[6]

(1) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem. Int. Ed.* **2005**, *44*, 5188.

(2) SAINT Version 5.0: Bruker Analytical X-ray Systems, Madison, WI.

(3) CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.27p8, 2005.

(4) Sheldrick, G. M. SADABS: Empirical absorption correction program, Göttingen University, **1996**.

(5) Sheldrick, G.M. SHELXS-86, *Acta Crystallogr.* **1990**, *A46*, 467.

(6) Sheldrick, G.M. SHELXL-97: FORTRAN program for the refinement of crystal structures from diffraction data. Göttingen University, **1997**. Molecular graphics were done using the commercial package SHELXTL-PLUS, Release 5.05/V: © **1996**, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin.

Table S1. Crystal data and structure refinement for **2a.2CHCl$_3$**.

Empirical formula	C44 H40 Cl8 N2 O4 P2 Pd2	
Formula weight	1219.12	
Temperature	123(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.9958(2) Å	α= 90°.
	b = 13.5663(3) Å	β= 99.8661(14)°.
	c = 14.8552(2) Å	γ = 90°.
Volume	2381.76(7) Å^3	
Z	2	
Density (calculated)	1.700 Mg/m^3	
Absorption coefficient	1.315 mm^{-1}	
F(000)	1216	
Crystal size	0.24 x 0.23 x 0.11 mm^3	
Theta range for data collection	4.10 to 27.49°.	
Index ranges	-15<=h<=15, -15<=k<=17, -19<=l<=19	
Reflections collected	29116	
Independent reflections	5463 [R(int) = 0.0337]	
Completeness to theta = 27.49°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8653 and 0.7042	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5463 / 42 / 309	
Goodness-of-fit on F^2	1.139	
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.0912	
R indices (all data)	R1 = 0.0576, wR2 = 0.0950	
Largest diff. peak and hole	1.296 and -0.876 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **2a.2CHCl$_3$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	4204(1)	221(1)	859(1)	31(1)
Cl(1)	5981(1)	-467(1)	791(1)	55(1)
C(1)	4303(3)	-33(3)	2180(3)	23(1)
C(2)	5284(3)	-246(3)	2791(3)	27(1)
C(3)	5236(4)	-507(3)	3682(3)	30(1)
C(4)	4213(4)	-566(3)	3992(3)	31(1)
C(5)	3227(3)	-333(3)	3408(3)	26(1)
C(6)	3278(3)	-56(3)	2516(3)	22(1)
P(1)	2081(1)	205(1)	1670(1)	22(1)
C(7)	1430(3)	-964(3)	1339(3)	27(1)
C(8)	1461(4)	-1340(4)	478(3)	39(1)
C(9)	1041(5)	-2274(4)	258(4)	60(2)
C(10)	615(5)	-2833(4)	890(5)	62(2)
C(11)	579(4)	-2466(4)	1745(5)	52(1)
C(12)	991(4)	-1538(4)	1973(4)	39(1)
C(13)	1049(3)	939(3)	2097(3)	25(1)
C(14)	-99(4)	744(4)	1878(3)	34(1)
C(15)	-864(4)	1382(4)	2179(4)	44(1)
C(16)	-486(4)	2192(4)	2690(4)	44(1)
C(17)	646(5)	2382(4)	2920(4)	49(1)
C(18)	1420(4)	1765(3)	2613(3)	38(1)
N(1)	2642(3)	761(3)	918(2)	28(1)
C(19)	2028(3)	1376(3)	208(3)	30(1)
C(20)	2623(3)	2347(3)	146(3)	30(1)
O(1)	3310(3)	2713(2)	725(2)	38(1)
O(2)	2239(3)	2766(3)	-663(2)	40(1)
C(21)	2711(5)	3717(4)	-804(4)	49(1)
C(22)	5910(5)	3276(4)	1070(3)	70(2)
Cl(2)	6163(2)	2030(2)	927(2)	81(1)
Cl(3)	6260(3)	3890(2)	51(2)	96(1)
Cl(4)	6739(2)	3778(3)	2010(2)	87(1)
Cl(2A)	5298(5)	4409(4)	999(5)	80(2)
Cl(3A)	6678(7)	2889(8)	328(5)	123(4)
Cl(4A)	6598(5)	3078(8)	2238(4)	85(3)

Table S3. Bond lengths [Å] and angles [°] for **2a.2CHCl$_3$**.

Pd(1)-C(1)	1.976(4)
Pd(1)-N(1)	2.028(3)
Pd(1)-Cl(1)	2.3439(11)
Pd(1)-Cl(1)#1	2.4464(11)
Cl(1)-Pd(1)#1	2.4464(11)
C(1)-C(2)	1.388(5)
C(1)-C(6)	1.404(5)
C(2)-C(3)	1.381(6)
C(2)-H(2)	0.9300
C(3)-C(4)	1.385(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.378(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.389(5)
C(5)-H(5)	0.9300
C(6)-P(1)	1.775(4)
P(1)-N(1)	1.590(3)
P(1)-C(13)	1.788(4)
P(1)-C(7)	1.798(4)
C(7)-C(8)	1.384(6)
C(7)-C(12)	1.394(6)
C(8)-C(9)	1.382(8)
C(8)-H(8)	0.9300
C(9)-C(10)	1.371(9)
C(9)-H(9)	0.9300
C(10)-C(11)	1.371(9)
C(10)-H(10)	0.9300
C(11)-C(12)	1.374(7)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(14)	1.386(6)
C(13)-C(18)	1.386(6)
C(14)-C(15)	1.390(6)
C(14)-H(14)	0.9300
C(15)-C(16)	1.368(7)
C(15)-H(15)	0.9300
C(16)-C(17)	1.368(8)
C(16)-H(16)	0.9300
C(17)-C(18)	1.384(7)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
N(1)-C(19)	1.443(5)
C(19)-C(20)	1.509(6)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-O(1)	1.193(5)
C(20)-O(2)	1.338(5)
O(2)-C(21)	1.438(6)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-Cl(3A)	1.639(6)
C(22)-Cl(2A)	1.699(6)
C(22)-Cl(4)	1.711(5)
C(22)-Cl(2)	1.737(5)
C(22)-Cl(4A)	1.809(6)
C(22)-Cl(3)	1.837(5)
C(22)-H(22)	0.9800

C(22)-H(22A)	0.9908
Cl(2)-H(22A)	1.5403
Cl(2A)-H(22)	1.4272

C(1)-Pd(1)-N(1)	85.36(14)
C(1)-Pd(1)-Cl(1)	94.23(11)
N(1)-Pd(1)-Cl(1)	177.75(11)
C(1)-Pd(1)-Cl(1)#1	177.20(12)
N(1)-Pd(1)-Cl(1)#1	93.87(9)
Cl(1)-Pd(1)-Cl(1)#1	86.44(4)
Pd(1)-Cl(1)-Pd(1)#1	93.56(4)
C(2)-C(1)-C(6)	117.4(3)
C(2)-C(1)-Pd(1)	125.8(3)
C(6)-C(1)-Pd(1)	116.7(3)
C(3)-C(2)-C(1)	120.6(4)
C(3)-C(2)-H(2)	119.7
C(1)-C(2)-H(2)	119.7
C(2)-C(3)-C(4)	121.2(4)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(5)-C(4)-C(3)	119.5(4)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	119.2(4)
C(4)-C(5)-H(5)	120.4
C(6)-C(5)-H(5)	120.4
C(5)-C(6)-C(1)	122.0(4)
C(5)-C(6)-P(1)	124.6(3)
C(1)-C(6)-P(1)	113.3(3)
N(1)-P(1)-C(6)	101.79(17)
N(1)-P(1)-C(13)	112.75(19)
C(6)-P(1)-C(13)	112.64(18)
N(1)-P(1)-C(7)	116.3(2)
C(6)-P(1)-C(7)	106.17(18)
C(13)-P(1)-C(7)	107.07(19)
C(8)-C(7)-C(12)	119.4(4)
C(8)-C(7)-P(1)	119.9(4)
C(12)-C(7)-P(1)	120.3(3)
C(9)-C(8)-C(7)	119.3(5)
C(9)-C(8)-H(8)	120.3
C(7)-C(8)-H(8)	120.3
C(10)-C(9)-C(8)	120.6(6)
C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7
C(11)-C(10)-C(9)	120.5(5)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(10)-C(11)-C(12)	119.6(6)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
C(11)-C(12)-C(7)	120.5(5)
C(11)-C(12)-H(12)	119.8
C(7)-C(12)-H(12)	119.8
C(14)-C(13)-C(18)	119.7(4)
C(14)-C(13)-P(1)	122.1(3)
C(18)-C(13)-P(1)	118.1(3)
C(13)-C(14)-C(15)	119.4(4)
C(13)-C(14)-H(14)	120.3
C(15)-C(14)-H(14)	120.3
C(16)-C(15)-C(14)	120.3(5)

C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	120.7(5)
C(15)-C(16)-H(16)	119.6
C(17)-C(16)-H(16)	119.6
C(16)-C(17)-C(18)	119.8(5)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1
C(17)-C(18)-C(13)	120.1(4)
C(17)-C(18)-H(18)	120.0
C(13)-C(18)-H(18)	120.0
C(19)-N(1)-P(1)	124.3(3)
C(19)-N(1)-Pd(1)	122.5(2)
P(1)-N(1)-Pd(1)	111.33(18)
N(1)-C(19)-C(20)	111.2(3)
N(1)-C(19)-H(19A)	109.4
C(20)-C(19)-H(19A)	109.4
N(1)-C(19)-H(19B)	109.4
C(20)-C(19)-H(19B)	109.4
H(19A)-C(19)-H(19B)	108.0
O(1)-C(20)-O(2)	124.1(4)
O(1)-C(20)-C(19)	126.5(4)
O(2)-C(20)-C(19)	109.4(4)
C(20)-O(2)-C(21)	115.3(4)
O(2)-C(21)-H(21A)	109.5
O(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
Cl(3A)-C(22)-Cl(2A)	122.4(5)
Cl(3A)-C(22)-Cl(4)	111.2(5)
Cl(2A)-C(22)-Cl(4)	82.8(3)
Cl(3A)-C(22)-Cl(2)	58.4(4)
Cl(2A)-C(22)-Cl(2)	162.9(4)
Cl(4)-C(22)-Cl(2)	113.5(3)
Cl(3A)-C(22)-Cl(4A)	112.4(4)
Cl(2A)-C(22)-Cl(4A)	108.3(4)
Cl(2)-C(22)-Cl(4A)	85.0(4)
Cl(3A)-C(22)-Cl(3)	50.0(4)
Cl(2A)-C(22)-Cl(3)	72.4(3)
Cl(4)-C(22)-Cl(3)	108.0(3)
Cl(2)-C(22)-Cl(3)	105.7(3)
Cl(4A)-C(22)-Cl(3)	136.6(5)
Cl(3A)-C(22)-H(22)	138.4
Cl(2A)-C(22)-H(22)	57.1
Cl(4)-C(22)-H(22)	109.8
Cl(2)-C(22)-H(22)	109.8
Cl(4A)-C(22)-H(22)	105.2
Cl(3)-C(22)-H(22)	109.9
Cl(3A)-C(22)-H(22A)	104.3
Cl(2A)-C(22)-H(22A)	103.6
Cl(4)-C(22)-H(22A)	132.9
Cl(2)-C(22)-H(22A)	61.8
Cl(4A)-C(22)-H(22A)	103.8
Cl(3)-C(22)-H(22A)	118.5
H(22)-C(22)-H(22A)	48.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2a.2CHCl$_3$**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	22(1)	49(1)	24(1)	15(1)	7(1)	6(1)
Cl(1)	33(1)	106(1)	29(1)	27(1)	13(1)	29(1)
C(1)	26(2)	19(2)	25(2)	2(1)	4(1)	0(1)
C(2)	23(2)	30(2)	28(2)	1(2)	2(2)	-2(2)
C(3)	32(2)	30(2)	25(2)	-1(2)	-4(2)	4(2)
C(4)	39(2)	38(2)	17(2)	1(2)	3(2)	4(2)
C(5)	30(2)	26(2)	23(2)	2(2)	7(2)	1(2)
C(6)	24(2)	18(2)	23(2)	1(1)	2(1)	-1(1)
P(1)	20(1)	25(1)	21(1)	3(1)	4(1)	-1(1)
C(7)	21(2)	27(2)	31(2)	-2(2)	-1(2)	0(2)
C(8)	37(2)	41(3)	36(2)	-8(2)	-4(2)	10(2)
C(9)	68(4)	40(3)	61(4)	-23(3)	-24(3)	16(3)
C(10)	45(3)	23(3)	101(5)	-12(3)	-37(3)	5(2)
C(11)	36(3)	30(3)	85(4)	5(3)	-2(3)	-8(2)
C(12)	35(2)	32(3)	50(3)	-2(2)	10(2)	-8(2)
C(13)	27(2)	24(2)	25(2)	7(2)	7(2)	2(2)
C(14)	29(2)	36(3)	36(2)	-1(2)	7(2)	1(2)
C(15)	30(2)	51(3)	52(3)	4(2)	14(2)	9(2)
C(16)	52(3)	36(3)	49(3)	8(2)	20(2)	19(2)
C(17)	56(3)	29(3)	60(3)	-8(2)	7(3)	9(2)
C(18)	33(2)	31(3)	49(3)	-2(2)	1(2)	1(2)
N(1)	21(2)	38(2)	25(2)	13(2)	6(1)	1(2)
C(19)	22(2)	40(3)	29(2)	13(2)	5(2)	3(2)
C(20)	24(2)	39(3)	29(2)	9(2)	10(2)	12(2)
O(1)	42(2)	37(2)	37(2)	0(1)	7(2)	1(2)
O(2)	32(2)	49(2)	38(2)	22(2)	8(1)	5(1)
C(21)	54(3)	42(3)	58(3)	23(3)	31(3)	12(2)
C(22)	44(3)	67(4)	97(5)	-18(4)	13(3)	-1(3)
Cl(2)	50(1)	55(1)	140(2)	-17(1)	22(1)	-1(1)
Cl(3)	101(2)	81(2)	113(2)	-7(2)	35(2)	-14(2)
Cl(4)	54(1)	100(2)	112(2)	-44(2)	33(1)	-25(2)
Cl(2A)	67(4)	67(4)	102(5)	23(4)	1(3)	-21(3)
Cl(3A)	111(7)	190(12)	75(5)	-47(6)	35(5)	-7(7)
Cl(4A)	32(3)	160(9)	62(4)	5(5)	2(3)	29(4)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2a.2CHCl$_3$**.

	x	y	z	U(eq)
H(2)	5981	-211	2598	33
H(3)	5903	-647	4081	36
H(4)	4192	-761	4589	38
H(5)	2535	-361	3610	32
H(8)	1761	-968	51	47
H(9)	1048	-2526	-323	72
H(10)	348	-3465	737	75
H(11)	277	-2844	2167	62
H(12)	976	-1291	2555	47
H(14)	-356	191	1534	41
H(15)	-1637	1258	2032	52
H(16)	-1005	2617	2883	53
H(17)	896	2925	3281	58
H(18)	2189	1904	2752	46
H(19A)	1273	1496	335	36
H(19B)	1956	1036	-373	36
H(21A)	2526	4172	-356	74
H(21B)	2402	3952	-1404	74
H(21C)	3518	3663	-744	74
H(22)	5110	3380	1103	83
H(22A)	5257	2819	993	104

Table S6. Crystal data and structure refinement for **2d**.

Empirical formula	C24 H20 Cl N2 P Pd	
Formula weight	509.24	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.2481(3) Å	α= 90°.
	b = 15.4741(4) Å	β= 104.696(3)°.
	c = 12.6043(4) Å	γ = 90°.
Volume	2122.06(10) $Å^3$	
Z	4	
Density (calculated)	1.594 Mg/m^3	
Absorption coefficient	1.089 mm^{-1}	
F(000)	1024	
Crystal size	0.60 x 0.33 x 0.22 mm^3	
Theta range for data collection	2.81 to 32.35°.	
Index ranges	-16<=h<=16, -22<=k<=22, -18<=l<=17	
Reflections collected	21998	
Independent reflections	6652 [R(int) = 0.0268]	
Completeness to theta = 32.35°	87.8 %	
Max. and min. transmission	0.7957 and 0.5612	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6652 / 0 / 262	
Goodness-of-fit on F^2	0.963	
Final R indices [I>2sigma(I)]	R1 = 0.0303, wR2 = 0.0781	
R indices (all data)	R1 = 0.0499, wR2 = 0.0817	
Largest diff. peak and hole	1.907 and -0.527 $e.Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6793(1)	1073(1)	2796(1)	18(1)
P(1)	4643(1)	2168(1)	3127(1)	18(1)
Cl(1)	7711(1)	-108(1)	2211(1)	38(1)
N(1)	6101(2)	2136(1)	3305(2)	21(1)
N(2)	8439(2)	1702(1)	3627(2)	21(1)
C(1)	5084(2)	711(1)	2110(2)	20(1)
C(2)	4690(2)	21(1)	1385(2)	27(1)
C(3)	3456(3)	-120(2)	889(2)	33(1)
C(4)	2547(2)	406(2)	1103(2)	34(1)
C(5)	2887(2)	1088(2)	1820(2)	27(1)
C(6)	4129(2)	1245(1)	2303(2)	21(1)
C(7)	3963(2)	3118(1)	2391(2)	20(1)
C(8)	2752(2)	3362(2)	2299(2)	29(1)
C(9)	2250(3)	4044(2)	1616(2)	40(1)
C(10)	2963(3)	4474(2)	1035(2)	40(1)
C(11)	4161(3)	4247(2)	1142(2)	34(1)
C(12)	4672(2)	3564(1)	1816(2)	24(1)
C(13)	4167(2)	2122(1)	4383(2)	21(1)
C(14)	4102(2)	1322(2)	4860(2)	25(1)
C(15)	3819(3)	1262(2)	5871(2)	34(1)
C(16)	3621(3)	2007(2)	6402(2)	35(1)
C(17)	3704(3)	2805(2)	5951(2)	34(1)
C(18)	3977(2)	2870(2)	4932(2)	28(1)
C(19)	6954(2)	2670(1)	4108(2)	22(1)
C(20)	8254(2)	2433(1)	4149(2)	19(1)
C(21)	9220(2)	2942(2)	4708(2)	25(1)
C(22)	10415(2)	2682(2)	4751(2)	32(1)
C(23)	10599(2)	1936(2)	4225(2)	34(1)
C(24)	9603(2)	1467(2)	3665(2)	28(1)

Table S8. Bond lengths [Å] and angles [°] for **2d**.

Pd(1)-C(1)	1.978(2)
Pd(1)-N(1)	1.9942(17)
Pd(1)-N(2)	2.1180(19)
Pd(1)-Cl(1)	2.3108(6)
P(1)-N(1)	1.5985(18)
P(1)-C(6)	1.774(2)
P(1)-C(13)	1.797(2)
P(1)-C(7)	1.802(2)
N(1)-C(19)	1.461(3)
N(2)-C(24)	1.348(3)
N(2)-C(20)	1.351(3)
C(1)-C(2)	1.403(3)
C(1)-C(6)	1.424(3)
C(2)-C(3)	1.387(4)
C(3)-C(4)	1.387(3)
C(4)-C(5)	1.378(3)
C(5)-C(6)	1.396(3)
C(7)-C(12)	1.389(3)
C(7)-C(8)	1.391(3)
C(8)-C(9)	1.389(4)
C(9)-C(10)	1.387(4)
C(10)-C(11)	1.366(4)
C(11)-C(12)	1.385(4)
C(13)-C(14)	1.386(3)
C(13)-C(18)	1.392(3)
C(14)-C(15)	1.392(3)
C(15)-C(16)	1.379(4)
C(16)-C(17)	1.373(4)
C(17)-C(18)	1.397(3)
C(19)-C(20)	1.495(3)
C(20)-C(21)	1.381(3)
C(21)-C(22)	1.391(3)
C(22)-C(23)	1.372(4)
C(23)-C(24)	1.371(4)
C(1)-Pd(1)-N(1)	87.64(8)
C(1)-Pd(1)-N(2)	167.59(8)
N(1)-Pd(1)-N(2)	79.96(7)
C(1)-Pd(1)-Cl(1)	95.75(6)
N(1)-Pd(1)-Cl(1)	176.26(5)
N(2)-Pd(1)-Cl(1)	96.64(5)
N(1)-P(1)-C(6)	103.18(10)
N(1)-P(1)-C(13)	113.52(11)
C(6)-P(1)-C(13)	111.00(10)
N(1)-P(1)-C(7)	112.57(10)
C(6)-P(1)-C(7)	108.84(11)
C(13)-P(1)-C(7)	107.65(10)
C(19)-N(1)-P(1)	123.41(14)
C(19)-N(1)-Pd(1)	116.60(14)
P(1)-N(1)-Pd(1)	116.76(10)
C(24)-N(2)-C(20)	118.4(2)
C(24)-N(2)-Pd(1)	127.83(16)
C(20)-N(2)-Pd(1)	113.73(14)
C(2)-C(1)-C(6)	115.2(2)
C(2)-C(1)-Pd(1)	127.70(16)
C(6)-C(1)-Pd(1)	116.92(16)
C(3)-C(2)-C(1)	121.9(2)
C(2)-C(3)-C(4)	121.5(2)

C(5)-C(4)-C(3)	118.8(2)
C(4)-C(5)-C(6)	120.0(2)
C(5)-C(6)-C(1)	122.6(2)
C(5)-C(6)-P(1)	122.48(16)
C(1)-C(6)-P(1)	114.76(18)
C(12)-C(7)-C(8)	120.1(2)
C(12)-C(7)-P(1)	116.71(17)
C(8)-C(7)-P(1)	122.92(17)
C(9)-C(8)-C(7)	119.6(2)
C(10)-C(9)-C(8)	119.6(3)
C(11)-C(10)-C(9)	120.8(3)
C(10)-C(11)-C(12)	120.2(2)
C(11)-C(12)-C(7)	119.7(2)
C(14)-C(13)-C(18)	119.7(2)
C(14)-C(13)-P(1)	118.52(16)
C(18)-C(13)-P(1)	121.49(17)
C(13)-C(14)-C(15)	120.4(2)
C(16)-C(15)-C(14)	119.4(2)
C(17)-C(16)-C(15)	120.9(2)
C(16)-C(17)-C(18)	120.0(2)
C(13)-C(18)-C(17)	119.6(2)
N(1)-C(19)-C(20)	110.50(17)
N(2)-C(20)-C(21)	121.8(2)
N(2)-C(20)-C(19)	117.26(19)
C(21)-C(20)-C(19)	120.9(2)
C(20)-C(21)-C(22)	118.9(2)
C(23)-C(22)-C(21)	119.1(2)
C(24)-C(23)-C(22)	119.4(2)
N(2)-C(24)-C(23)	122.4(2)

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	21(1)	16(1)	17(1)	0(1)	6(1)	3(1)
P(1)	18(1)	18(1)	18(1)	-3(1)	6(1)	0(1)
Cl(1)	34(1)	29(1)	48(1)	-13(1)	9(1)	10(1)
N(1)	18(1)	19(1)	26(1)	-6(1)	6(1)	-2(1)
N(2)	21(1)	22(1)	19(1)	4(1)	6(1)	3(1)
C(1)	27(1)	18(1)	14(1)	1(1)	5(1)	0(1)
C(2)	37(1)	18(1)	25(1)	-3(1)	7(1)	2(1)
C(3)	40(2)	24(1)	32(1)	-10(1)	5(1)	-9(1)
C(4)	31(1)	31(1)	34(1)	-4(1)	0(1)	-9(1)
C(5)	25(1)	27(1)	28(1)	-1(1)	5(1)	-1(1)
C(6)	24(1)	21(1)	19(1)	-1(1)	8(1)	-2(1)
C(7)	24(1)	18(1)	18(1)	-3(1)	3(1)	3(1)
C(8)	24(1)	30(1)	31(1)	-2(1)	5(1)	2(1)
C(9)	34(1)	41(2)	39(2)	-3(1)	-1(1)	14(1)
C(10)	55(2)	28(1)	31(2)	6(1)	0(1)	14(1)
C(11)	53(2)	22(1)	26(1)	-1(1)	9(1)	-2(1)
C(12)	31(1)	21(1)	20(1)	-3(1)	6(1)	-1(1)
C(13)	18(1)	25(1)	18(1)	-3(1)	5(1)	0(1)
C(14)	24(1)	30(1)	21(1)	-1(1)	5(1)	-1(1)
C(15)	37(1)	41(2)	23(1)	4(1)	8(1)	-4(1)
C(16)	36(1)	52(2)	19(1)	-6(1)	10(1)	0(1)
C(17)	40(2)	41(1)	24(1)	-9(1)	12(1)	4(1)
C(18)	33(1)	28(1)	23(1)	-4(1)	8(1)	0(1)
C(19)	21(1)	22(1)	22(1)	-5(1)	5(1)	0(1)
C(20)	22(1)	21(1)	14(1)	5(1)	5(1)	0(1)
C(21)	26(1)	26(1)	21(1)	3(1)	4(1)	-4(1)
C(22)	24(1)	37(1)	31(1)	5(1)	0(1)	-8(1)
C(23)	20(1)	40(1)	40(2)	11(1)	8(1)	4(1)
C(24)	26(1)	28(1)	30(1)	7(1)	11(1)	6(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for **2d**.

	x	y	z	U(eq)
H(2A)	5285	-362	1231	32
H(3A)	3229	-588	390	39
H(4A)	1705	299	762	40
H(5A)	2277	1451	1985	32
H(8A)	2270	3064	2702	34
H(9A)	1422	4215	1548	48
H(10A)	2615	4933	556	48
H(11A)	4646	4557	754	40
H(12A)	5502	3402	1884	29
H(14A)	4252	812	4496	30
H(15A)	3762	713	6191	40
H(16A)	3424	1967	7091	42
H(17A)	3577	3313	6331	41
H(18A)	4032	3421	4615	33
H(19A)	6803	2587	4841	26
H(19B)	6815	3287	3907	26
H(21A)	9071	3460	5057	30
H(22A)	11095	3017	5138	38
H(23A)	11409	1747	4249	40
H(24A)	9738	958	3290	33

Table S11. Crystal data and structure refinement for **3b**·CH_2Cl_2.

Empirical formula	C25 H27 Cl3 N3 O5 P Pd	
Formula weight	693.22	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 8.0096(12) Å	α= 90°.
	b = 22.592(3) Å	β= 92.464(3)°.
	c = 15.594(2) Å	γ = 90°.
Volume	2819.2(7) $Å^3$	
Z	4	
Density (calculated)	1.633 Mg/m^3	
Absorption coefficient	1.040 mm^{-1}	
F(000)	1400	
Crystal size	0.18 x 0.08 x 0.07 mm^3	
Theta range for data collection	1.59 to 25.00°.	
Index ranges	-9<=h<=9, -26<=k<=26, -18<=l<=18	
Reflections collected	20461	
Independent reflections	4972 [R(int) = 0.1116]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.743	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4972 / 31 / 383	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R1 = 0.0586, wR2 = 0.1245	
R indices (all data)	R1 = 0.0942, wR2 = 0.1408	
Largest diff. peak and hole	0.639 and -1.136 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3b**·CH_2Cl_2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8656(1)	539(1)	8981(1)	24(1)
C(1)	9881(8)	1245(3)	8663(4)	26(2)
C(2)	10686(8)	1355(3)	7899(4)	31(2)
C(3)	11534(8)	1871(3)	7761(4)	36(2)
C(4)	11609(8)	2313(3)	8369(4)	32(2)
C(5)	10842(8)	2235(3)	9135(4)	29(2)
C(6)	9986(8)	1706(3)	9275(4)	25(2)
P(1)	8960(2)	1569(1)	10241(1)	24(1)
C(7)	7192(8)	2047(3)	10287(4)	25(2)
C(8)	6233(9)	2076(3)	11022(4)	32(2)
C(9)	4861(8)	2441(3)	11018(5)	38(2)
C(10)	4407(9)	2779(3)	10326(5)	38(2)
C(11)	5308(9)	2745(3)	9596(5)	38(2)
C(12)	6692(8)	2384(3)	9581(4)	30(2)
C(13)	10271(8)	1709(3)	11179(4)	25(2)
C(14)	11365(8)	1281(3)	11446(4)	31(2)
C(15)	12416(8)	1359(3)	12166(4)	31(2)
C(16)	12352(9)	1872(3)	12621(4)	33(2)
C(17)	11249(8)	2317(3)	12355(4)	31(2)
C(18)	10210(8)	2242(3)	11631(4)	29(2)
N(1)	8546(7)	879(2)	10141(3)	25(1)
C(19)	7649(8)	533(3)	10775(4)	28(2)
C(20)	7109(8)	-45(3)	10377(4)	26(2)
O(1)	7313(5)	-142(2)	9588(3)	26(1)
N(2)	6424(6)	-438(2)	10864(3)	27(1)
C(21)	6015(9)	-320(3)	11755(4)	33(2)
C(22)	5877(8)	-1012(3)	10529(4)	32(2)
N(3)	8717(7)	183(2)	7805(4)	30(1)
C(23)	8651(8)	-2(3)	7135(5)	35(2)
C(24)	8555(10)	-230(4)	6258(4)	48(2)
C(25)	4662(10)	820(4)	5787(5)	49(2)
Cl(1)	2826(3)	1223(1)	5632(2)	82(1)
Cl(2)	6096(3)	1175(1)	6498(1)	53(1)
Cl(3)	6775(2)	860(1)	3578(1)	43(1)
O(2A)	7597(13)	533(6)	4271(7)	75(5)
O(3A)	7825(19)	998(6)	2921(9)	78(6)
O(4A)	5349(14)	542(6)	3308(8)	56(4)
O(5A)	6240(20)	1386(4)	3995(8)	99(7)
O(2B)	7689(15)	292(4)	3567(12)	63(6)
O(3B)	7060(20)	1134(7)	2759(7)	67(7)
O(4B)	5108(11)	727(7)	3643(12)	79(8)
O(5B)	7500(20)	1179(7)	4232(7)	64(6)

Table S13. Bond lengths [Å] and angles [°] for **3b**·CH_2Cl_2.

Pd(1)-C(1)	1.948(6)
Pd(1)-N(1)	1.972(5)
Pd(1)-N(3)	2.004(6)
Pd(1)-O(1)	2.122(4)
C(1)-C(2)	1.401(9)
C(1)-C(6)	1.414(9)
C(2)-C(3)	1.370(9)
C(2)-H(2)	0.9300
C(3)-C(4)	1.377(10)
C(3)-H(3)	0.9300
C(4)-C(5)	1.378(9)
C(4)-H(4)	0.9300
C(5)-C(6)	1.400(9)
C(5)-H(5)	0.9300
C(6)-P(1)	1.775(6)
P(1)-N(1)	1.598(5)
P(1)-C(7)	1.786(7)
P(1)-C(13)	1.791(6)
C(7)-C(12)	1.385(9)
C(7)-C(8)	1.408(9)
C(8)-C(9)	1.373(9)
C(8)-H(8)	0.9300
C(9)-C(10)	1.359(10)
C(9)-H(9)	0.9300
C(10)-C(11)	1.376(10)
C(10)-H(10)	0.9300
C(11)-C(12)	1.377(9)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(14)	1.358(9)
C(13)-C(18)	1.398(9)
C(14)-C(15)	1.386(9)
C(14)-H(14)	0.9300
C(15)-C(16)	1.360(9)
C(15)-H(15)	0.9300
C(16)-C(17)	1.391(9)
C(16)-H(16)	0.9300
C(17)-C(18)	1.384(8)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
N(1)-C(19)	1.471(8)
C(19)-C(20)	1.502(9)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-O(1)	1.268(7)
C(20)-N(2)	1.302(8)
N(2)-C(22)	1.459(8)
N(2)-C(21)	1.467(8)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
N(3)-C(23)	1.124(8)
C(23)-C(24)	1.461(10)
C(24)-H(24A)	0.9600

C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-Cl(1)	1.737(8)
C(25)-Cl(2)	1.755(8)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
Cl(3)-O(5B)	1.360(8)
Cl(3)-O(4B)	1.377(8)
Cl(3)-O(3A)	1.389(7)
Cl(3)-O(4A)	1.398(7)
Cl(3)-O(5A)	1.430(7)
Cl(3)-O(2A)	1.445(7)
Cl(3)-O(3B)	1.446(9)
Cl(3)-O(2B)	1.478(9)

C(1)-Pd(1)-N(1)	87.6(2)
C(1)-Pd(1)-N(3)	93.6(2)
N(1)-Pd(1)-N(3)	178.7(2)
C(1)-Pd(1)-O(1)	167.8(2)
N(1)-Pd(1)-O(1)	80.20(19)
N(3)-Pd(1)-O(1)	98.6(2)
C(2)-C(1)-C(6)	115.2(6)
C(2)-C(1)-Pd(1)	128.2(5)
C(6)-C(1)-Pd(1)	116.6(5)
C(3)-C(2)-C(1)	122.3(7)
C(3)-C(2)-H(2)	118.8
C(1)-C(2)-H(2)	118.8
C(2)-C(3)-C(4)	121.1(7)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(3)-C(4)-C(5)	119.7(7)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	118.9(6)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(5)-C(6)-C(1)	122.7(6)
C(5)-C(6)-P(1)	122.0(5)
C(1)-C(6)-P(1)	115.3(5)
N(1)-P(1)-C(6)	100.9(3)
N(1)-P(1)-C(7)	115.6(3)
C(6)-P(1)-C(7)	109.0(3)
N(1)-P(1)-C(13)	111.3(3)
C(6)-P(1)-C(13)	112.7(3)
C(7)-P(1)-C(13)	107.3(3)
C(12)-C(7)-C(8)	118.2(6)
C(12)-C(7)-P(1)	120.3(5)
C(8)-C(7)-P(1)	121.5(5)
C(9)-C(8)-C(7)	119.3(7)
C(9)-C(8)-H(8)	120.4
C(7)-C(8)-H(8)	120.4
C(10)-C(9)-C(8)	121.8(7)
C(10)-C(9)-H(9)	119.1
C(8)-C(9)-H(9)	119.1
C(9)-C(10)-C(11)	119.6(7)
C(9)-C(10)-H(10)	120.2
C(11)-C(10)-H(10)	120.2
C(10)-C(11)-C(12)	119.9(7)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0

C(11)-C(12)-C(7)	121.1(6)
C(11)-C(12)-H(12)	119.4
C(7)-C(12)-H(12)	119.4
C(14)-C(13)-C(18)	119.6(6)
C(14)-C(13)-P(1)	118.2(5)
C(18)-C(13)-P(1)	122.2(5)
C(13)-C(14)-C(15)	121.3(7)
C(13)-C(14)-H(14)	119.4
C(15)-C(14)-H(14)	119.4
C(16)-C(15)-C(14)	119.7(7)
C(16)-C(15)-H(15)	120.2
C(14)-C(15)-H(15)	120.2
C(15)-C(16)-C(17)	119.9(7)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(18)-C(17)-C(16)	120.4(6)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(17)-C(18)-C(13)	119.0(6)
C(17)-C(18)-H(18)	120.5
C(13)-C(18)-H(18)	120.5
C(19)-N(1)-P(1)	123.9(4)
C(19)-N(1)-Pd(1)	116.8(4)
P(1)-N(1)-Pd(1)	116.9(3)
N(1)-C(19)-C(20)	109.0(5)
N(1)-C(19)-H(19A)	109.9
C(20)-C(19)-H(19A)	109.9
N(1)-C(19)-H(19B)	109.9
C(20)-C(19)-H(19B)	109.9
H(19A)-C(19)-H(19B)	108.3
O(1)-C(20)-N(2)	121.6(6)
O(1)-C(20)-C(19)	120.2(6)
N(2)-C(20)-C(19)	118.3(6)
C(20)-O(1)-Pd(1)	113.4(4)
C(20)-N(2)-C(22)	121.6(6)
C(20)-N(2)-C(21)	123.0(6)
C(22)-N(2)-C(21)	115.1(5)
N(2)-C(21)-H(21A)	109.5
N(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(2)-C(22)-H(22A)	109.5
N(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
N(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(23)-N(3)-Pd(1)	175.5(6)
N(3)-C(23)-C(24)	178.9(8)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Cl(1)-C(25)-Cl(2)	112.1(4)
Cl(1)-C(25)-H(25A)	109.2
Cl(2)-C(25)-H(25A)	109.2

Cl(1)-C(25)-H(25B)	109.2
Cl(2)-C(25)-H(25B)	109.2
H(25A)-C(25)-H(25B)	107.9
O(5B)-Cl(3)-O(4B)	116.4(9)
O(5B)-Cl(3)-O(3A)	100.5(10)
O(4B)-Cl(3)-O(3A)	136.4(11)
O(5B)-Cl(3)-O(4A)	144.6(9)
O(4B)-Cl(3)-O(4A)	29.3(7)
O(3A)-Cl(3)-O(4A)	113.9(7)
O(5B)-Cl(3)-O(5A)	49.2(6)
O(4B)-Cl(3)-O(5A)	80.5(10)
O(3A)-Cl(3)-O(5A)	110.7(6)
O(4A)-Cl(3)-O(5A)	107.7(8)
O(5B)-Cl(3)-O(2A)	62.8(8)
O(4B)-Cl(3)-O(2A)	104.2(9)
O(3A)-Cl(3)-O(2A)	113.3(7)
O(4A)-Cl(3)-O(2A)	107.6(6)
O(5A)-Cl(3)-O(2A)	102.8(7)
O(5B)-Cl(3)-O(3B)	111.0(7)
O(4B)-Cl(3)-O(3B)	110.4(8)
O(3A)-Cl(3)-O(3B)	29.4(7)
O(4A)-Cl(3)-O(3B)	96.4(9)
O(5A)-Cl(3)-O(3B)	96.2(8)
O(2A)-Cl(3)-O(3B)	142.8(9)
O(5B)-Cl(3)-O(2B)	105.8(8)
O(4B)-Cl(3)-O(2B)	107.1(7)
O(3A)-Cl(3)-O(2B)	82.5(8)
O(4A)-Cl(3)-O(2B)	87.1(8)
O(5A)-Cl(3)-O(2B)	152.4(8)
O(2A)-Cl(3)-O(2B)	49.8(6)
O(3B)-Cl(3)-O(2B)	105.4(8)

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3b**·CH_2Cl_2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	26(1)	25(1)	21(1)	-2(1)	2(1)	1(1)
C(1)	20(3)	30(4)	26(4)	4(3)	-1(3)	-2(3)
C(2)	35(4)	35(4)	25(4)	0(3)	3(3)	3(3)
C(3)	29(4)	52(5)	27(4)	4(4)	5(3)	-3(4)
C(4)	25(4)	37(4)	33(4)	6(3)	-3(3)	-4(3)
C(5)	26(4)	30(4)	30(4)	0(3)	-5(3)	-4(3)
C(6)	25(4)	31(4)	19(3)	5(3)	1(3)	1(3)
P(1)	28(1)	24(1)	21(1)	0(1)	1(1)	-1(1)
C(7)	24(4)	24(4)	28(4)	-3(3)	-1(3)	-6(3)
C(8)	38(4)	32(4)	25(4)	0(3)	2(3)	-6(3)
C(9)	25(4)	50(5)	38(4)	-9(4)	7(3)	-2(4)
C(10)	35(4)	33(4)	46(5)	-12(4)	5(4)	-1(3)
C(11)	39(4)	42(5)	33(4)	-3(4)	-8(3)	2(4)
C(12)	28(4)	34(4)	27(4)	-2(3)	1(3)	2(3)
C(13)	27(4)	29(4)	19(3)	-2(3)	6(3)	-4(3)
C(14)	39(4)	27(4)	26(4)	3(3)	4(3)	-3(3)
C(15)	32(4)	30(4)	33(4)	3(3)	-3(3)	0(3)
C(16)	35(4)	37(4)	27(4)	3(3)	0(3)	-3(3)
C(17)	44(4)	22(4)	27(4)	-7(3)	1(3)	-3(3)
C(18)	32(4)	27(4)	29(4)	-3(3)	5(3)	-1(3)
N(1)	32(3)	23(3)	21(3)	-3(2)	2(2)	-3(2)
C(19)	26(3)	26(4)	30(4)	3(3)	1(3)	0(3)
C(20)	20(3)	25(4)	33(4)	-1(3)	0(3)	5(3)
O(1)	36(3)	22(2)	21(2)	-5(2)	4(2)	4(2)
N(2)	29(3)	22(3)	30(3)	-1(2)	8(2)	0(2)
C(21)	36(4)	35(4)	29(4)	0(3)	8(3)	-3(3)
C(22)	32(4)	24(4)	39(4)	-2(3)	2(3)	0(3)
N(3)	32(3)	26(3)	33(3)	-9(3)	2(3)	0(3)
C(23)	31(4)	28(4)	45(5)	-7(4)	2(3)	-6(3)
C(24)	49(5)	68(6)	25(4)	-16(4)	7(4)	0(4)
C(25)	62(5)	35(5)	49(5)	-7(4)	8(4)	6(4)
Cl(1)	95(2)	74(2)	74(2)	-28(1)	-25(2)	43(2)
Cl(2)	67(1)	43(1)	51(1)	4(1)	7(1)	-1(1)
Cl(3)	44(1)	39(1)	45(1)	4(1)	-4(1)	-4(1)
O(2A)	59(7)	111(13)	55(8)	22(9)	-5(6)	9(8)
O(3A)	66(10)	92(13)	82(10)	20(8)	53(8)	-2(8)
O(4A)	52(7)	64(8)	51(9)	9(7)	-12(6)	-12(6)
O(5A)	230(20)	26(6)	39(7)	0(5)	16(10)	14(9)
O(2B)	55(9)	27(8)	106(16)	7(8)	-13(9)	10(6)
O(3B)	109(17)	22(8)	74(13)	5(7)	49(11)	12(10)
O(4B)	38(9)	160(20)	40(12)	-6(11)	2(7)	-22(11)
O(5B)	95(13)	49(12)	46(9)	-9(8)	-28(8)	-22(9)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for **3b**·CH_2Cl_2.

	x	y	z	U(eq)
H(2)	10644	1069	7471	38
H(3)	12068	1923	7249	43
H(4)	12175	2663	8263	38
H(5)	10892	2529	9552	34
H(8)	6527	1852	11505	38
H(9)	4224	2456	11502	45
H(10)	3492	3031	10346	46
H(11)	4983	2966	9114	46
H(12)	7301	2367	9087	36
H(14)	11409	929	11139	37
H(15)	13163	1062	12338	38
H(16)	13044	1924	13109	40
H(17)	11210	2668	12665	37
H(18)	9482	2542	11449	35
H(19A)	6679	752	10951	33
H(19B)	8373	462	11278	33
H(21A)	6816	-49	12009	49
H(21B)	6044	-684	12074	49
H(21C)	4917	-150	11767	49
H(22A)	6177	-1048	9941	48
H(22B)	4686	-1045	10561	48
H(22C)	6408	-1321	10863	48
H(24A)	8922	69	5872	71
H(24B)	7422	-338	6105	71
H(24C)	9259	-573	6222	71
H(25A)	5168	764	5239	58
H(25B)	4400	432	6013	58

Table S16. Crystal data and structure refinement for **7b**.

Empirical formula	C27 H27 Cl N3 O5 P Pd	
Formula weight	646.34	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.1099(11) Å	α= 90°.
	b = 13.2935(11) Å	β= 106.6200(10)°.
	c = 16.0085(13) Å	γ = 90°.
Volume	2673.3(4) Å^3	
Z	4	
Density (calculated)	1.606 Mg/m^3	
Absorption coefficient	0.897 mm^{-1}	
F(000)	1312	
Crystal size	0.13 x 0.10 x 0.09 mm^3	
Theta range for data collection	2.23 to 27.56°.	
Index ranges	-16<=h<=17, -16<=k<=17, -20<=l<=20	
Reflections collected	17019	
Independent reflections	6119 [R(int) = 0.0497]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9224 and 0.7984	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6119 / 0 / 345	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.0888	
R indices (all data)	R1 = 0.0625, wR2 = 0.0971	
Largest diff. peak and hole	0.758 and -0.429 e.Å^{-3}	

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	3177(1)	1060(1)	6021(1)	14(1)
C(1)	4307(3)	1483(3)	5505(2)	18(1)
C(2)	5379(3)	1249(3)	5785(2)	26(1)
C(3)	6089(3)	1626(3)	5368(3)	32(1)
C(4)	5759(3)	2252(3)	4654(2)	28(1)
C(5)	4700(3)	2485(3)	4349(2)	23(1)
C(6)	3974(3)	2108(3)	4758(2)	16(1)
P(1)	2589(1)	2381(1)	4381(1)	14(1)
C(7)	2027(3)	1858(2)	3316(2)	15(1)
C(8)	2537(3)	1081(3)	3013(2)	19(1)
C(9)	2017(3)	595(3)	2233(2)	22(1)
C(10)	999(3)	893(3)	1768(2)	23(1)
C(11)	506(3)	1663(3)	2062(2)	21(1)
C(12)	1010(3)	2158(3)	2835(2)	17(1)
C(13)	2351(3)	3710(2)	4276(2)	14(1)
C(14)	2378(3)	4240(3)	3531(2)	20(1)
C(15)	2249(3)	5268(3)	3496(3)	26(1)
C(16)	2095(3)	5781(3)	4206(3)	27(1)
C(17)	2040(3)	5271(3)	4928(3)	28(1)
C(18)	2178(3)	4233(3)	4973(2)	21(1)
N(1)	2156(2)	1882(2)	5122(2)	18(1)
C(19)	1040(3)	1807(3)	5094(2)	18(1)
C(20)	942(3)	1134(3)	5842(2)	15(1)
O(1)	1757(2)	756(2)	6357(2)	18(1)
N(2)	-9(2)	945(2)	5925(2)	17(1)
C(21)	-112(3)	310(3)	6643(2)	23(1)
C(22)	-1003(3)	1371(3)	5368(2)	25(1)
N(3)	4127(2)	230(2)	7011(2)	19(1)
C(23)	3873(3)	-738(3)	7093(2)	23(1)
C(24)	4386(3)	-1324(3)	7803(3)	29(1)
C(25)	5187(3)	-893(3)	8449(3)	32(1)
C(26)	5463(3)	95(3)	8373(3)	29(1)
C(27)	4918(3)	628(3)	7647(2)	23(1)
Cl(1)	8287(1)	2822(1)	3098(1)	20(1)
O(2)	8241(2)	2994(2)	2208(2)	37(1)
O(3)	7297(2)	3115(2)	3243(2)	33(1)
O(4)	9140(2)	3396(2)	3661(2)	31(1)
O(5)	8477(2)	1772(2)	3292(2)	32(1)

Table S18. Bond lengths [Å] and angles [°] for **7b**.

Pd(1)-C(1)	1.974(3)
Pd(1)-N(1)	1.988(3)
Pd(1)-N(3)	2.037(3)
Pd(1)-O(1)	2.118(2)
C(1)-C(2)	1.383(5)
C(1)-C(6)	1.419(5)
C(2)-C(3)	1.384(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.380(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.370(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.392(5)
C(5)-H(5)	0.9300
C(6)-P(1)	1.780(3)
P(1)-N(1)	1.599(3)
P(1)-C(7)	1.794(3)
P(1)-C(13)	1.794(3)
C(7)-C(8)	1.391(5)
C(7)-C(12)	1.393(5)
C(8)-C(9)	1.398(5)
C(8)-H(8)	0.9300
C(9)-C(10)	1.387(5)
C(9)-H(9)	0.9300
C(10)-C(11)	1.365(5)
C(10)-H(10)	0.9300
C(11)-C(12)	1.390(5)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(18)	1.388(5)
C(13)-C(14)	1.394(5)
C(14)-C(15)	1.376(5)
C(14)-H(14)	0.9300
C(15)-C(16)	1.388(6)
C(15)-H(15)	0.9300
C(16)-C(17)	1.360(6)
C(16)-H(16)	0.9300
C(17)-C(18)	1.391(5)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
N(1)-C(19)	1.454(4)
C(19)-C(20)	1.530(5)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-O(1)	1.253(4)
C(20)-N(2)	1.316(4)
N(2)-C(21)	1.462(4)
N(2)-C(22)	1.467(4)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
N(3)-C(27)	1.337(5)
N(3)-C(23)	1.345(5)
C(23)-C(24)	1.384(5)

C(23)-H(23)	0.9300
C(24)-C(25)	1.371(6)
C(24)-H(24)	0.9300
C(25)-C(26)	1.378(6)
C(25)-H(25)	0.9300
C(26)-C(27)	1.374(5)
C(26)-H(26)	0.9300
C(27)-H(27)	0.9300
Cl(1)-O(2)	1.428(3)
Cl(1)-O(3)	1.436(3)
Cl(1)-O(5)	1.437(3)
Cl(1)-O(4)	1.439(3)

C(1)-Pd(1)-N(1)	88.33(13)
C(1)-Pd(1)-N(3)	96.59(13)
N(1)-Pd(1)-N(3)	174.68(11)
C(1)-Pd(1)-O(1)	168.46(12)
N(1)-Pd(1)-O(1)	80.22(10)
N(3)-Pd(1)-O(1)	94.91(10)
C(2)-C(1)-C(6)	116.4(3)
C(2)-C(1)-Pd(1)	127.9(3)
C(6)-C(1)-Pd(1)	115.6(2)
C(1)-C(2)-C(3)	121.5(4)
C(1)-C(2)-H(2)	119.2
C(3)-C(2)-H(2)	119.2
C(4)-C(3)-C(2)	121.5(4)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(5)-C(4)-C(3)	118.5(3)
C(5)-C(4)-H(4)	120.7
C(3)-C(4)-H(4)	120.7
C(4)-C(5)-C(6)	120.7(4)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	121.3(3)
C(5)-C(6)-P(1)	122.4(3)
C(1)-C(6)-P(1)	116.3(3)
N(1)-P(1)-C(6)	102.03(15)
N(1)-P(1)-C(7)	114.08(16)
C(6)-P(1)-C(7)	110.21(16)
N(1)-P(1)-C(13)	112.92(16)
C(6)-P(1)-C(13)	111.44(16)
C(7)-P(1)-C(13)	106.25(16)
C(8)-C(7)-C(12)	120.0(3)
C(8)-C(7)-P(1)	120.7(3)
C(12)-C(7)-P(1)	118.8(3)
C(7)-C(8)-C(9)	119.6(3)
C(7)-C(8)-H(8)	120.2
C(9)-C(8)-H(8)	120.2
C(10)-C(9)-C(8)	119.7(3)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	120.5(3)
C(11)-C(10)-H(10)	119.8
C(9)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	120.7(3)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-H(11)	119.6
C(11)-C(12)-C(7)	119.5(3)
C(11)-C(12)-H(12)	120.3

C(7)-C(12)-H(12)	120.3
C(18)-C(13)-C(14)	119.0(3)
C(18)-C(13)-P(1)	118.8(3)
C(14)-C(13)-P(1)	122.1(3)
C(15)-C(14)-C(13)	120.2(3)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	120.0(4)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.4(4)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(16)-C(17)-C(18)	120.1(4)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(13)-C(18)-C(17)	120.2(3)
C(13)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(19)-N(1)-P(1)	125.0(2)
C(19)-N(1)-Pd(1)	116.6(2)
P(1)-N(1)-Pd(1)	117.20(16)
N(1)-C(19)-C(20)	109.0(3)
N(1)-C(19)-H(19A)	109.9
C(20)-C(19)-H(19A)	109.9
N(1)-C(19)-H(19B)	109.9
C(20)-C(19)-H(19B)	109.9
H(19A)-C(19)-H(19B)	108.3
O(1)-C(20)-N(2)	120.8(3)
O(1)-C(20)-C(19)	120.2(3)
N(2)-C(20)-C(19)	119.1(3)
C(20)-O(1)-Pd(1)	113.8(2)
C(20)-N(2)-C(21)	119.6(3)
C(20)-N(2)-C(22)	124.6(3)
C(21)-N(2)-C(22)	115.8(3)
N(2)-C(21)-H(21A)	109.5
N(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(2)-C(22)-H(22A)	109.5
N(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
N(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(27)-N(3)-C(23)	117.6(3)
C(27)-N(3)-Pd(1)	123.1(3)
C(23)-N(3)-Pd(1)	118.7(2)
N(3)-C(23)-C(24)	122.9(4)
N(3)-C(23)-H(23)	118.6
C(24)-C(23)-H(23)	118.6
C(25)-C(24)-C(23)	118.2(4)
C(25)-C(24)-H(24)	120.9
C(23)-C(24)-H(24)	120.9
C(24)-C(25)-C(26)	119.7(4)
C(24)-C(25)-H(25)	120.1
C(26)-C(25)-H(25)	120.1
C(27)-C(26)-C(25)	118.7(4)

C(27)-C(26)-H(26)	120.6
C(25)-C(26)-H(26)	120.6
N(3)-C(27)-C(26)	122.9(4)
N(3)-C(27)-H(27)	118.6
C(26)-C(27)-H(27)	118.6
O(2)-Cl(1)-O(3)	109.65(18)
O(2)-Cl(1)-O(5)	109.05(17)
O(3)-Cl(1)-O(5)	109.72(18)
O(2)-Cl(1)-O(4)	110.09(18)
O(3)-Cl(1)-O(4)	109.42(16)
O(5)-Cl(1)-O(4)	108.90(17)

Table S19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	12(1)	18(1)	13(1)	3(1)	3(1)	2(1)
C(1)	18(2)	22(2)	16(2)	-2(2)	7(1)	-2(2)
C(2)	20(2)	35(2)	23(2)	7(2)	6(2)	5(2)
C(3)	15(2)	51(3)	31(2)	1(2)	9(2)	6(2)
C(4)	18(2)	42(2)	26(2)	-1(2)	11(2)	-9(2)
C(5)	24(2)	30(2)	18(2)	1(2)	10(2)	-1(2)
C(6)	14(2)	18(2)	17(2)	-3(1)	6(1)	0(1)
P(1)	14(1)	16(1)	12(1)	1(1)	5(1)	0(1)
C(7)	18(2)	14(2)	16(2)	-2(1)	7(1)	-3(1)
C(8)	18(2)	20(2)	21(2)	3(2)	7(1)	-1(2)
C(9)	21(2)	21(2)	28(2)	-5(2)	13(2)	0(2)
C(10)	27(2)	27(2)	16(2)	-4(2)	8(2)	-10(2)
C(11)	20(2)	21(2)	18(2)	5(2)	-1(1)	-4(2)
C(12)	19(2)	16(2)	18(2)	2(1)	7(1)	-2(1)
C(13)	14(2)	13(2)	16(2)	0(1)	4(1)	1(1)
C(14)	23(2)	20(2)	18(2)	-1(2)	5(2)	-2(2)
C(15)	25(2)	22(2)	28(2)	8(2)	3(2)	-4(2)
C(16)	24(2)	14(2)	34(2)	0(2)	-4(2)	1(2)
C(17)	27(2)	31(2)	24(2)	-16(2)	3(2)	2(2)
C(18)	22(2)	25(2)	14(2)	-2(2)	4(1)	-1(2)
N(1)	13(1)	25(2)	16(1)	9(1)	5(1)	4(1)
C(19)	19(2)	23(2)	14(2)	2(2)	8(1)	3(2)
C(20)	17(2)	13(2)	15(2)	-4(1)	7(1)	0(1)
O(1)	15(1)	22(1)	18(1)	6(1)	6(1)	2(1)
N(2)	17(2)	20(2)	16(1)	0(1)	6(1)	-1(1)
C(21)	24(2)	23(2)	25(2)	2(2)	10(2)	-4(2)
C(22)	13(2)	38(2)	23(2)	4(2)	2(2)	4(2)
N(3)	15(2)	23(2)	19(2)	3(1)	5(1)	2(1)
C(23)	20(2)	23(2)	22(2)	1(2)	2(2)	-1(2)
C(24)	31(2)	24(2)	32(2)	9(2)	9(2)	4(2)
C(25)	28(2)	39(3)	23(2)	14(2)	0(2)	7(2)
C(26)	22(2)	33(2)	26(2)	2(2)	-2(2)	1(2)
C(27)	19(2)	22(2)	25(2)	3(2)	4(2)	-1(2)
Cl(1)	22(1)	20(1)	17(1)	-1(1)	6(1)	0(1)
O(2)	48(2)	44(2)	19(1)	6(1)	12(1)	4(2)
O(3)	25(2)	36(2)	43(2)	-11(1)	16(1)	-2(1)
O(4)	24(2)	28(2)	36(2)	-8(1)	3(1)	-1(1)
O(5)	46(2)	20(2)	28(2)	1(1)	8(1)	3(1)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for **7b**.

	x	y	z	U(eq)
H(2)	5629	828	6264	31
H(3)	6804	1453	5574	38
H(4)	6245	2510	4386	33
H(5)	4462	2900	3864	28
H(8)	3220	885	3328	23
H(9)	2352	74	2027	27
H(10)	650	566	1252	27
H(11)	-175	1859	1743	25
H(12)	671	2685	3030	21
H(14)	2483	3897	3056	24
H(15)	2266	5619	2998	31
H(16)	2027	6478	4187	32
H(17)	1911	5617	5392	34
H(18)	2153	3888	5473	25
H(19A)	634	1523	4541	21
H(19B)	760	2471	5150	21
H(21A)	448	-181	6778	35
H(21B)	-789	-24	6475	35
H(21C)	-62	720	7147	35
H(22A)	-847	1821	4952	38
H(22B)	-1361	1733	5721	38
H(22C)	-1454	838	5065	38
H(23)	3329	-1027	6652	27
H(24)	4192	-1992	7841	35
H(25)	5541	-1266	8937	38
H(26)	6008	396	8804	35
H(27)	5108	1294	7595	27

Table S21. Crystal data and structure refinement for **8**.

Empirical formula	C21 H22 Cl2 N P Pd S	
Formula weight	528.73	
Temperature	100(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.9372(5) Å	α= 90°.
	b = 16.4538(11) Å	β= 90.2140(10)°.
	c = 16.6017(11) Å	γ = 90°.
Volume	2168.1(2) Å^3	
Z	4	
Density (calculated)	1.620 Mg/m^3	
Absorption coefficient	1.279 mm^{-1}	
F(000)	1064	
Crystal size	0.16 x 0.06 x 0.05 mm^3	
Theta range for data collection	1.74 to 27.53°.	
Index ranges	-10<=h<=10, -21<=k<=20, -21<=l<=21	
Reflections collected	18890	
Independent reflections	4967 [R(int) = 0.0577]	
Completeness to theta = 27.53°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93805 and 0.7506	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4967 / 0 / 245	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.0915	
R indices (all data)	R1 = 0.0661, wR2 = 0.0999	
Largest diff. peak and hole	0.633 and -0.851 e.Å^{-3}	

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8874(1)	750(1)	8654(1)	13(1)
P(1)	7836(1)	-574(1)	7234(1)	14(1)
N(1)	9132(4)	-214(2)	7890(2)	17(1)
C(19)	10654(5)	-686(2)	8102(3)	20(1)
S(1)	11720(1)	768(1)	8678(1)	17(1)
Cl(1)	5969(1)	715(1)	8643(1)	22(1)
Cl(2)	8954(1)	1805(1)	9576(1)	23(1)
C(1)	6738(5)	255(2)	6735(2)	16(1)
C(3)	4430(5)	745(3)	5924(3)	28(1)
C(6)	7445(5)	1027(2)	6747(2)	20(1)
C(20)	12152(5)	-116(2)	8056(3)	21(1)
C(2)	5248(5)	113(3)	6322(2)	23(1)
C(5)	6601(6)	1665(3)	6361(3)	26(1)
C(18)	10081(5)	-635(2)	5978(2)	21(1)
C(7)	6294(5)	-1282(2)	7622(2)	15(1)
C(21)	12222(5)	370(3)	9662(2)	25(1)
C(14)	9239(5)	-1945(2)	6487(3)	21(1)
C(13)	9070(5)	-1102(2)	6486(2)	16(1)
C(12)	5338(5)	-1796(2)	7129(3)	20(1)
C(8)	6053(5)	-1295(2)	8454(3)	21(1)
C(4)	5107(6)	1515(3)	5945(3)	26(1)
C(9)	4844(6)	-1802(3)	8789(3)	27(1)
C(15)	10420(5)	-2311(3)	5991(3)	23(1)
C(16)	11451(5)	-1852(3)	5506(3)	24(1)
C(17)	11256(5)	-1007(3)	5491(3)	24(1)
C(11)	4132(5)	-2306(3)	7471(3)	28(1)
C(10)	3892(6)	-2299(3)	8290(3)	31(1)

Table S23. Bond lengths [Å] and angles [°] for **8**.

Pd(1)-N(1)	2.042(3)
Pd(1)-S(1)	2.2590(10)
Pd(1)-Cl(1)	2.3068(10)
Pd(1)-Cl(2)	2.3144(10)
P(1)-N(1)	1.609(3)
P(1)-C(13)	1.806(4)
P(1)-C(7)	1.810(4)
P(1)-C(1)	1.817(4)
N(1)-C(19)	1.478(5)
C(19)-C(20)	1.517(5)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
S(1)-C(21)	1.804(4)
S(1)-C(20)	1.816(4)
C(1)-C(2)	1.386(6)
C(1)-C(6)	1.389(6)
C(3)-C(4)	1.376(6)
C(3)-C(2)	1.392(6)
C(3)-H(3)	0.9500
C(6)-C(5)	1.398(6)
C(6)-H(6)	0.9500
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(2)-H(2)	0.9500
C(5)-C(4)	1.392(6)
C(5)-H(5)	0.9500
C(18)-C(17)	1.379(6)
C(18)-C(13)	1.397(5)
C(18)-H(18)	0.9500
C(7)-C(12)	1.398(5)
C(7)-C(8)	1.396(5)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(14)-C(15)	1.387(6)
C(14)-C(13)	1.393(6)
C(14)-H(14)	0.9500
C(12)-C(11)	1.396(6)
C(12)-H(12)	0.9500
C(8)-C(9)	1.389(6)
C(8)-H(8)	0.9500
C(4)-H(4)	0.9500
C(9)-C(10)	1.386(7)
C(9)-H(9)	0.9500
C(15)-C(16)	1.376(6)
C(15)-H(15)	0.9500
C(16)-C(17)	1.399(6)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(11)-C(10)	1.374(7)
C(11)-H(11)	0.9500
C(10)-H(10)	0.9500
N(1)-Pd(1)-S(1)	85.29(9)
N(1)-Pd(1)-Cl(1)	94.45(9)
S(1)-Pd(1)-Cl(1)	179.13(4)
N(1)-Pd(1)-Cl(2)	172.19(9)
S(1)-Pd(1)-Cl(2)	87.39(4)

Cl(1)-Pd(1)-Cl(2)	92.83(4)
N(1)-P(1)-C(13)	107.21(17)
N(1)-P(1)-C(7)	115.30(18)
C(13)-P(1)-C(7)	107.71(18)
N(1)-P(1)-C(1)	109.66(18)
C(13)-P(1)-C(1)	107.99(18)
C(7)-P(1)-C(1)	108.73(18)
C(19)-N(1)-P(1)	119.2(3)
C(19)-N(1)-Pd(1)	110.1(2)
P(1)-N(1)-Pd(1)	129.91(18)
N(1)-C(19)-C(20)	107.6(3)
N(1)-C(19)-H(19A)	110.2
C(20)-C(19)-H(19A)	110.2
N(1)-C(19)-H(19B)	110.2
C(20)-C(19)-H(19B)	110.2
H(19A)-C(19)-H(19B)	108.5
C(21)-S(1)-C(20)	100.5(2)
C(21)-S(1)-Pd(1)	103.21(14)
C(20)-S(1)-Pd(1)	99.86(13)
C(2)-C(1)-C(6)	120.4(4)
C(2)-C(1)-P(1)	120.4(3)
C(6)-C(1)-P(1)	119.2(3)
C(4)-C(3)-C(2)	119.7(4)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(1)-C(6)-C(5)	119.1(4)
C(1)-C(6)-H(6)	120.4
C(5)-C(6)-H(6)	120.4
C(19)-C(20)-S(1)	108.5(3)
C(19)-C(20)-H(20A)	110.0
S(1)-C(20)-H(20A)	110.0
C(19)-C(20)-H(20B)	110.0
S(1)-C(20)-H(20B)	110.0
H(20A)-C(20)-H(20B)	108.4
C(1)-C(2)-C(3)	120.3(4)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(4)-C(5)-C(6)	120.0(4)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(17)-C(18)-C(13)	120.1(4)
C(17)-C(18)-H(18)	119.9
C(13)-C(18)-H(18)	119.9
C(12)-C(7)-C(8)	119.6(4)
C(12)-C(7)-P(1)	123.1(3)
C(8)-C(7)-P(1)	117.2(3)
S(1)-C(21)-H(21A)	109.5
S(1)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
S(1)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(15)-C(14)-C(13)	119.8(4)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(14)-C(13)-C(18)	119.4(4)
C(14)-C(13)-P(1)	122.1(3)
C(18)-C(13)-P(1)	117.7(3)
C(7)-C(12)-C(11)	119.8(4)
C(7)-C(12)-H(12)	120.1

C(11)-C(12)-H(12)	120.1
C(9)-C(8)-C(7)	120.2(4)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(3)-C(4)-C(5)	120.5(4)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(10)-C(9)-C(8)	119.3(4)
C(10)-C(9)-H(9)	120.3
C(8)-C(9)-H(9)	120.3
C(16)-C(15)-C(14)	120.8(4)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(17)	119.4(4)
C(15)-C(16)-H(16)	120.3
C(17)-C(16)-H(16)	120.3
C(18)-C(17)-C(16)	120.3(4)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(10)-C(11)-C(12)	119.7(4)
C(10)-C(11)-H(11)	120.1
C(12)-C(11)-H(11)	120.1
C(9)-C(10)-C(11)	121.3(4)
C(9)-C(10)-H(10)	119.3
C(11)-C(10)-H(10)	119.3

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	12(1)	12(1)	15(1)	-2(1)	0(1)	-1(1)
P(1)	13(1)	12(1)	17(1)	-1(1)	1(1)	-1(1)
N(1)	13(2)	14(2)	23(2)	-5(1)	-2(1)	5(1)
C(19)	19(2)	13(2)	29(2)	-5(2)	-4(2)	3(2)
S(1)	14(1)	19(1)	18(1)	1(1)	0(1)	-2(1)
Cl(1)	14(1)	22(1)	30(1)	-5(1)	1(1)	1(1)
Cl(2)	27(1)	21(1)	21(1)	-6(1)	0(1)	-2(1)
C(1)	18(2)	15(2)	14(2)	1(2)	3(2)	4(2)
C(3)	19(2)	34(3)	31(2)	11(2)	0(2)	0(2)
C(6)	24(2)	17(2)	20(2)	1(2)	2(2)	0(2)
C(20)	16(2)	22(2)	25(2)	-4(2)	1(2)	2(2)
C(2)	22(2)	25(2)	23(2)	6(2)	1(2)	-2(2)
C(5)	35(3)	16(2)	27(2)	3(2)	11(2)	-2(2)
C(18)	25(2)	13(2)	24(2)	-2(2)	2(2)	-3(2)
C(7)	11(2)	13(2)	20(2)	3(2)	-1(2)	-1(2)
C(21)	21(2)	39(3)	15(2)	5(2)	-1(2)	0(2)
C(14)	18(2)	19(2)	27(2)	0(2)	5(2)	-3(2)
C(13)	13(2)	19(2)	17(2)	-2(2)	2(2)	1(2)
C(12)	17(2)	18(2)	27(2)	-4(2)	0(2)	1(2)
C(8)	21(2)	15(2)	26(2)	1(2)	-3(2)	3(2)
C(4)	29(2)	23(2)	27(2)	10(2)	9(2)	12(2)
C(9)	33(3)	26(2)	23(2)	12(2)	11(2)	7(2)
C(15)	26(2)	16(2)	27(2)	-6(2)	5(2)	-1(2)
C(16)	23(2)	24(2)	24(2)	-6(2)	9(2)	0(2)
C(17)	28(2)	22(2)	22(2)	-1(2)	12(2)	-4(2)
C(11)	21(2)	17(2)	45(3)	-3(2)	-1(2)	-2(2)
C(10)	25(2)	17(2)	51(3)	14(2)	11(2)	1(2)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8**.

	x	y	z	U(eq)
H(19A)	10800	-1144	7721	24
H(19B)	10551	-910	8653	24
H(3)	3410	646	5639	34
H(6)	8488	1121	7014	24
H(20A)	12339	54	7491	25
H(20B)	13180	-395	8252	25
H(2)	4782	-419	6310	28
H(5)	7048	2200	6382	31
H(18)	9959	-61	5967	25
H(21A)	11723	-171	9721	38
H(21B)	11769	733	10076	38
H(21C)	13448	332	9723	38
H(14)	8548	-2268	6826	25
H(12)	5510	-1797	6563	25
H(8)	6718	-957	8792	25
H(4)	4550	1948	5674	31
H(9)	4671	-1808	9355	32
H(15)	10519	-2886	5987	28
H(16)	12287	-2106	5185	28
H(17)	11935	-687	5144	29
H(11)	3479	-2656	7139	33
H(10)	3058	-2641	8519	37