Orthopalladation of (*Z*)-2-Aryl-4-Arylidene-5(4*H*)-Oxazolones. Structure and Functionalization

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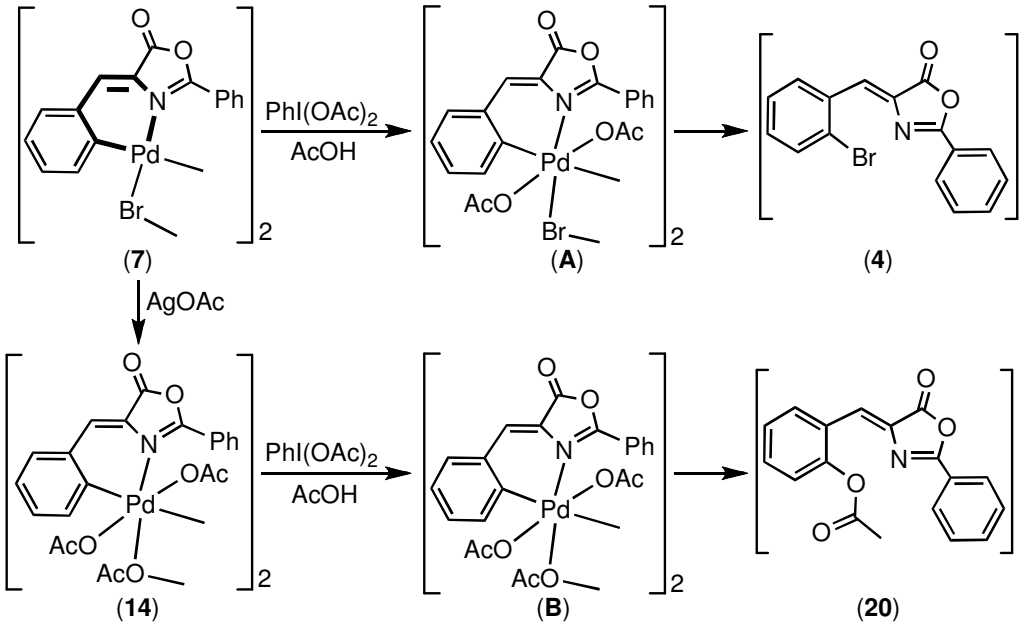
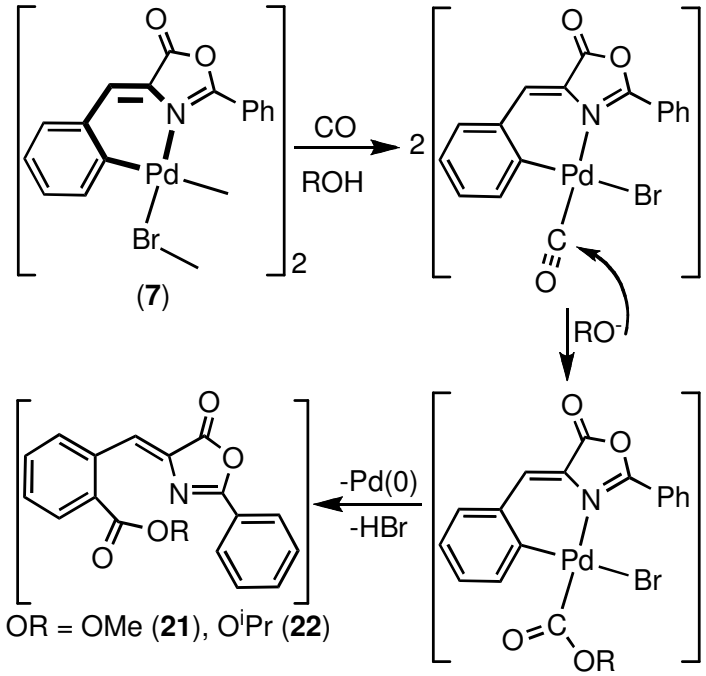
Supporting Information



Scheme S1. Proposed reaction pathway for synthesis of **4** and **20** from **7** and **14.**



Scheme S2. Proposed reaction pathway for the synthesis of **21** and **22** from **7.**

General Methods. Solvents were dried and distilled using standard procedures before use. Elemental analyses (CHNS) were carried out on a Perkin-Elmer 2400-B microanalyser. Infrared spectra (4000-380 cm^{-1}) were recorded on a Perkin-Elmer Spectrum One IR spectrophotometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions at 25 ºC on a Bruker AV400 spectrometer (δ

in ppm, *J* in Hz) at ^{1}H operating frequency of 400.13 MHz. ^{1}H and ^{13}C spectra were referenced using the solvent signal as internal standard, while ^{31}P spectra were externally referenced to H_3PO_4 (85%). DOSY experiments were carried out in spinning $CDCl_3$ solutions (averaged concentration 2 mM), at a strictly constant temperature (300 K), using optimized values of gradient strenght (little delta δ) and diffusion time (big delta Δ) for each sample. ESI (ESI+) mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) 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. The mass spectra (MALDI+) were recorded from $CHCl_3$ solutions on a MALDI-TOF Microflex (Bruker) spectrometer (DCTB as matrix).

Preparation of *N*-2-bromobenzoylglycine (2): glycine (0.948 g, 12.628 mmol) was dissolved in water (50 mL), and then 2-bromobenzoyl chloride (0.649 g, 2.957 mmol) and a an aqueous NaOH solution (0.380 g, 9.500 mmol) were added in portions at the same time to this solution, to keep the pH of the mixture slightly basic. The mixture was stirred vigorously after the addition of each portion. Crushed ice was added to the solution and then concentrated HCl was added dropwise until the mixture was acidified (pH 2–3). The mixture was subsequently cooled down in the fridge, then it was filtered and the precipitate washed several times with water to remove excess of glycine and then dried under vacuum to obtain **2** as a white crystalline solid (Yield 0.565 g, 74%). ^{1}H NMR (400 MHz, *DMSO-d₆*) δ: 3.90 (d, ^{3}J = 6.0 Hz, 2H, CH_2), 7.34-7.49 (m, 3H, H_6, H_5, H_4), 7.66 (dd, ^{3}J = 7.9 Hz, ^{4}J = 0.8 Hz, 1H, H_3), 8.75 (t, ^{3}J = 5.9 Hz, 1H, NH), 12.64 (broad s, 1H, COOH). ^{13}C NMR (101 MHz, *DMSO-d₆*) δ: 40.84 (1C, CH_2), 118.85 (1C, C_2), 127.47, 128.95, 131.02 (3C, C_6, C_5, C_4), 132.78 (1C, C_3), 138.31 (1C, C_1), 167.43 (1C, CO), 170.82 (1C, COOH). IR ν = 3256 cm^{-1} vs (NH), 1727 cm^{-1} vs (C=O). MS (ESI +) *m/z*: 257.8, 259.8 $[MH]^+$, 279.8, 281.7 $[MNa]^+$. Anal Calc. for $C_9H_8BrNO_3$: C, 41.89; H, 3.12; N, 5.43. Found: C, 41.56; H, 3.44; N, 5.23.

Preparation of *N*-2-iodobenzoylglycine (3): glycine (2.431 g, 32.383 mmol), iodobenzoyl chloride (2.157 g, 8.950 mmol) and NaOH (0.712 g, 17.800 mmol) were reacted, as described for **2**, to give **3** as

a white crystalline solid (Yield 1.531 g, 62%). ^{1}H NMR (400 MHz, *DMSO-d$_6$*) δ: 3.90 (d, ^{3}J = 6.0 Hz, 2H, CH_2), 7.19 (td, ^{3}J = 7.7 Hz, ^{4}J = 1.7 Hz, 1H, H_4), 7.36 (dd, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 1H, H_6), 7.47 (td, ^{3}J = 7.5 Hz, ^{4}J = 1.1 Hz, 1H, H_5), 7.90 (dd, ^{3}J = 7.9 Hz, ^{4}J = 0.9 Hz, 1H, H_3), 8.71 (t, ^{3}J = 5.9 Hz, 1H, NH), 12.65 (broad s, 1H, COOH). ^{13}C NMR (101 MHz, *DMSO-d$_6$*) δ: 40.89 (1C, CH_2), 93.30 (1C, C_2), 127.90, 128.23 (2C, C_5, C_6), 130.95 (1C, C_4), 139.24 (1C, C_3), 142.03 (1C, C_1), 168.99 (1C, CO), 170.86 (1C, COOH). IR ν = 3269 cm^{-1} vs (NH), 1726, 1702 cm^{-1} vs (C=O). MS (ESI+) *m/z*: 305.8 $[MH]^+$, 327.8 $[MNa]^+$. Anal. Calc. for $C_9H_8INO_3$: C, 35.43; H, 2.64; N, 4.59. Found: C, 35.54; H, 2.76; N, 4.83.

Preparation of (*Z*)-2-(2-bromophenyl)-4-benzylidene-5(4*H*)-oxazolone (5): benzaldehyde (2.830 g, 26.679 mmol), anhydrous sodium acetate (2.188 g, 26.679 mmol), *N*-2-bromobenzoylglycine **2** (6.880 g, 26. 679 mmol), and acetic anhydride (8.170 g, 80.000 mmol) were added to a 100 mL round-bottom flask. The mixture was heated for 2h at 100 ^{o}C and then allowed to cool at room temperature to solidify. The solid formed was disaggregated with a mixture of ethanol and water, cooled down for 30 minutes and then filtered. Compound (**5**) was obtained as a yellow solid after recrystallization from EtOH (Yield 6.650 g, 76%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 7.34 (s, 1H, $H_{7''}$), 7.38-7.44 (td, 1H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, $H_{4'}$), 7.45-7.49 (m, 4H, $H_{5'}$, $H_{3''}$, $H_{4''}$, $H_{5''}$), 7.81 (dd, ^{3}J = 8.0 Hz, ^{4}J = 1.20 Hz, 1H, $H_{3'}$), 8.08 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.7 Hz, 1H, $H_{6'}$), 8.21-8.29 (m, 2H, $H_{2''}$, $H_{6''}$). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ: 122.51, 125.85, 133.28 (3C, $C_{2'}$, $C_{1'}$, C_2), 127.54 (1C, $C_{5'}$), 128.99 (2C, $C_{3''}$, $C_{5''}$), 131.56 (1C, $C_{4''}$), 132.05 (1C, $C_{6'}$), 132.60 (2C, $C_{2''}$, $C_{6''}$), 132.68 (1C, $C_{1''}$), 133.29 (1C, $C_{4'}$), 133.41 (1C, $C_{7''}$), 135.48 (1C, $C_{3'}$), 161.85 (1C, C_1), 167.18 (1C, C_3). MS (MALDI +) *m/z*, (rel. int. %): 328.0 (10.0%) $[MH]^+$. IR ν = 1789, 1767 cm^{-1} vs (C=O), 1651 cm^{-1} vs (C=N). Anal. Calc. for $C_{16}H_{10}BrNO_2$: C, 58.56; H, 3.07; N, 4.27. Found: C, 58.63; H, 3.34; N, 4.37.

Preparation of (*Z*)-2-(2-iodophenyl)-4-benzylidene-5(4*H*)-oxazolone (6): benzaldehyde (0.536 g, 5.050 mmol), anhydrous sodium acetate (0.415 g, 5.050 mmol), *N*-2-iodobenzoylglycine **3** (1.542 g,

5.050 mmol) and acetic anhydride (1.548 g, 15.160 mmol) were reacted, as described for **5**, to give (*Z*)-2-(2-iodophenyl)-4-benzylidene-5(4*H*)-oxazolone **6** as a yellow solid (Yield 1.365 g, 72%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 7.22 (td, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, $H_{4'}$), 7.35 (s, 1H, $H_{7''}$), 7.44-7.53 (m, 4H, $H_{5'}$, $H_{3''}$, $H_{5''}$, $H_{4''}$), 8.04 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H, $H_{6'}$), 8.17 (dd, ^3J = 8.0 Hz, ^4J = 1.1 Hz, 1H, $H_{3'}$), 8.28-8.34 (m, 2H, $H_{2''}$, $H_{6''}$). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ: 94.15 (1C, $C_{2'}$), 128.28 (1C, $C_{5'}$), 128.49, 132.49, 133.18 (3C, $C_{1'}$, $C_{1''}$, C_2), 128.99 (2C, $C_{3''}$, $C_{5''}$), 131.58, 131.75 (2C, $C_{5'}$, $C_{4''}$), 132.59 (2C, $C_{2''}$, $C_{6''}$), 133.25 (1C, $C_{4'}$), 133.44 (1C, $C_{7''}$), 142.74 (1C, $C_{3'}$), 162.27 (1C, C_1), 167.22 (1C, C_3). MS (ESI+) *m/z*: 398.1 $[MNa]^+$. IR ν = 1787, 1767 cm^{-1} vs (C=O), 1649 cm^{-1} vs (C=N). Anal. Calc. for $C_{16}H_{10}INO_2$: C, 51.22; H, 2.69; N, 3.73. Found: C, 51.32; H, 2.78; N, 3.98.

Synthesis of 7: $Pd_2(dba)_3{\cdot}CHCl_3$ (0.300 g, 0.328 mmol) and **4** (0.163 g, 0.655 mmol) were suspended in toluene or CH_2Cl_2 (30 mL) under an Ar atmosphere, and this deep violet mixture was stirred at 25 ºC for 24 h. The resulting suspension was centrifugated and the solid obtained was washed two times with CH_2Cl_2 (20 mL) and Et_2O (10 mL) to afford **7** as a green solid (Yield 0.248 g, 87%). IR ν = 1784 cm^{-1} vs (C=O), 1633 cm^{-1} vs (C=N). MS (MALDI+) *m/z*, (rel. int. %): 788.9 (100%) $[M\text{-}Br]^+$. Anal. Calc. for. $C_{32}H_{20}Br_2N_2O_4Pd_2$: C, 44.22; H, 2.32; N, 3.22. Found C, 44.48; H, 2.65; N, 3.67.

Synthesis of 8: To a stirred suspension of **7** (0.231 g, 0.266 mmol) in CH_2Cl_2 (10 mL) under Ar atmosphere, PPh_2Me (0.212 g, 1.058 mmol) was added. The initial suspension gradually dissolved. After stirring for 1 hour at 25 ºC the resulting solution was filtered through Celite and evaporated to afford **8** as a yellow solid (Yield 0.256 g, 76%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 1.80 (t, ^4J = 3.4 Hz, 6H, $2CH_3$), 6.60 (t, ^3J = 7.3 Hz, 1H, $H_{5''}$), 6.75 (t, ^3J = 7.5 Hz, 1H, $H_{4''}$), 7.09 (d, ^3J = 6.4 Hz, 1H, $H_{6''}$), 7.19-7.34 (m, 12H, $4H_{o\text{-}PPh2Me}$, $8H_{m\text{-}PPh2Me}$), 7.40-7.44 (m, 8H, $H_{o\text{-}PPh2Me}$), 7.50 (t, ^3J = 7.5 Hz, 2H, $H_{3'}$, $H_{5'}$), 7.54-7.59 (m, 1H, $H_{4'}$) 7.72 (s, 1H, $H_{7''}$), 8.10 (d, ^3J = 7.2 Hz, 2H, $H_{2'}$, $H_{6'}$), 8.18 (d, ^3J = 8.0 Hz, 1H, $H_{3''}$). ^{31}P NMR (162 MHz, *CDCl$_3$*) δ: 7.29 (s, 2P, $2PPh_2CH_3$). MS (MALDI+) *m/z*, (rel. int. %): 554.1 (6.7%) $[M/2\text{-}Br]^+$, 448.2 (100%) $[M/2\text{-}Br\text{-}Pd]^+$. IR ν = 1783 cm^{-1} vs (C=O), 1636 cm^{-1} vs (C=N).

Anal. Calc. for $C_{29}H_{23}BrNO_2PPd$: C, 54.87; H, 3.65; N, 2.21. Found: C, 54.61; H, 3.75; N, 2.43.

Synthesis of 9: Complex **9** was prepared following the same procedure as that reported for **8**. Therefore, **7** (0.159 g, 0.183 mmol) was reacted with PPh_3 (0.096 g, 0.366 mmol) in CH_2Cl_2 (10 mL) to give **9** as a yellow solid (Yield 0.217 g, 85%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 6.78-6.89 (m, 2H, $H_{4''}$, $H_{5''}$), 7.10-7.39 (m, 6H, $H_{m\text{-}PPh3}$), 7.37-7.65 (m, 12H, $6H_{o\text{-}PPh3}$, $3H_{p\text{-}PPh3}$, $H_{6''}$, $H_{3'}$, $H_{4'}$, $H_{5'}$), 8.12-8.16 (m, 2H, $H_{2'}$, $H_{6'}$), 8.30 (d, ^3J = 7.30 Hz, 1H, $H_{3''}$), 8.58 (s, 1H, $H_{7''}$). ^{31}P NMR (162 MHz, *CDCl$_3$*) δ: 24.04 (s, PPh_3). IR ν= 1783 cm^{-1} vs (C=O), 1643 cm^{-1} vs (C=N). MS (MALDI+) *m/z*, (rel. int. %): 616.0 (37.0%) $[M/2\text{-}Br]^+$, 509.9 (100%) $[M/2\text{-}Br\text{-}Pd]^+$. Anal. Calc. for: $C_{68}H_{50}Br_2N_2O_4P_2Pd_2$: C, 58.60; H, 3.62; N, 2.01. Found: C, 58.58; H, 3.53; N, 1.71.

Synthesis of 10. Method A: To a stirred suspension of **7** (0.205 g, 0.236 mmol) in MeOH, PPh_3 (0.247 g, 0.943 mmol) was added and then the solution was refluxed for 1 h. The color of the suspension turned to greenish black. The mixture was then filtered and dried to afford **10** as a yellow solid (Yield 0.326 g, 72%). **Method B**: To a stirred suspension of **9** (0.232 g, 0.166 mmol) in MeOH, PPh_3 (0.087 g, 0.333 mmol) was added and then the solution was refluxed for 1 h. The mixture was then filtered and dried to afford **10** as a yellow solid (Yield 0.278 g, 87%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 6.31 (t, ^3J = 7.7 Hz, 1H, $H_{5''}$), 6.51 (t, ^3J = 7.4 Hz, 1H, $H_{4''}$), 6.99 (d, ^3J = 8.0 Hz, 1H, $H_{6''}$), 7.14-7.25 (m, 18H, $12H_{m\text{-}PPh3}$, $6H_{p\text{-}PPh3}$), 7.40-7.49 (m, 15H, $12H_{o\text{-}PPh3}$, $H_{3'}$, $H_{4'}$, $H_{5'}$), 7.73 (d, ^3J = 7.8 Hz, 1H, $H_{3''}$), 7.98 (d, ^3J = 7.1 Hz, 2H, $H_{2'}$, $H_{6'}$), 8.00 (s, 1H, $H_{7''}$). ^{31}P NMR (162 MHz, *CDCl$_3$*) δ: 24.04 (s, PPh_3). IR ν = 1788, 1770 cm^{-1} vs (C=O), 1644 cm^{-1} vs (C=N). MS (MALDI+) *m/z*, (rel. int. %): 615.7 (11.2%) $[M\text{-}Br\text{-}PPh_3]^+$, 509.7 (100%) $[M\text{-}Br\text{-}PPh_3\text{-}Pd]^+$. Anal. Calc. for: $C_{52}H_{40}BrNO_2P_2Pd$: C, 65.12; H, 4.20; N, 1.46. Found: C, 65.26; H, 4.41; N, 1.67.

Synthesis of 11: To a stirred suspension of **7** (0.134 g, 0.154 mmol) in 10 mL of anhydrous CH_2Cl_2, Tl(acac) (0.094 g, 0.308 mmol) was added. The resulting suspension was stirred for 2 h at room temperature, then filtered through celite. The resulting yellow solution was evaporated to dryness,

affording **11** as a yellow solid (Yield 0.119 g, 85%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 1.21 (s, 3H, CH_3, acac), 2.04 (s, 3H, CH_3, acac), 5.20 (s, 1H, CH, acac), 7.16 (t, ^{3}J = 7.3 Hz, 1H, $H_{5''}$), 7.26-7.32 (m, 2H, $H_{4''}$, $H_{6''}$), 7.50 (t, ^{3}J = 7.7 Hz, 2H, $H_{3'}$, $H_{5'}$), 7.60-7.64 (m, 2H, $H_{7''}$, $H_{4''}$), 7.78 (d, ^{3}J = 8.6 Hz, 1H, $H_{3''}$), 8.42 (d, ^{3}J = 7.6 Hz, 2H, $H_{2'}$, $H_{6'}$). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ: 26.52, 27.54 (2C, CH_3, acac), 99.93 (1C, CH, acac), 99.97, 124.24, 132.72, 145.82 (4C, $C_{1''}$, $C_{2''}$, $C_{1'}$, C_2), 125.34 (1C, $C_{5''}$), 127.93 (2C, $C_{3'}$, $C_{5'}$), 130.64 (2C, $C_{2'}$, $C_{6'}$), 131.02, 132.89 (2C, $C_{4''}$, $C_{6''}$), 133.88 (1C, $C_{4'}$), 134.83 (1C, $C_{3''}$), 140.62 (1C, $C_{7''}$), 161.81 (1C, C_1), 166.28 (1C, C_3), 186.08, 187.11 (2C, CO, acac). MS (MALDI+) *m/z*, (rel. int. %): 354.0 (37.9%) $[M\text{-acac}]^+$. IR ν= 1791 cm^{-1} vs (C=O), 1663 cm^{-1} vs (C=N), 1570 cm^{-1}, 1507 vs (acac). Anal. Calc. for $C_{21}H_{17}NO_4Pd$: C, 55.58; H, 3.78; N, 3.09. Found: C, 55.32; H, 3.61; N, 3.31.

Synthesis of 12: Complex **12** was prepared following the same procedure as that reported for **8**. Therefore, **7** (0.159 g, 0.183 mmol) was reacted with pyridine (0.029 g, 0.366 mmol) in CH_2Cl_2 (10 mL) to afford **12** as a yellow solid. (Yield 0.152 g, 81%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 6.52 (d, ^{3}J = 7.8 Hz, 1H, $H_{6''}$), 6.96 (t, ^{3}J = 7.6 Hz, 1H, $H_{5''}$), 7.09 (t, ^{3}J = 7.2 Hz, 1H, $H_{4''}$), 7.28-7.33 (m, 3H, $2H_{m\text{-}Py}$, $H_{3''}$), 7.57-7.62 (m, 3H, $H_{3'}$, $H_{5'}$, $H_{7''}$), 7.71 (t, ^{3}J = 6.8 Hz, 1H, $H_{4'}$), 7.77 (t, ^{3}J = 7.6 Hz, 1H, $H_{p\text{-}Py}$), 8.61 (d, ^{3}J = 7.4 Hz, 2H, $H_{2'}$, $H_{6'}$), 8.67 (d, ^{3}J = 5.1 Hz, 2H, $H_{o\text{-}Py}$). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ: 124.14, 133.02, 136.57, 140.67 (4C, $C_{1'}$, $C_{1''}$, C_2, $C_{2''}$), 125.13 (2C, $2C_{m\text{-}Py}$), 125.41 (1C, $C_{4''}$), 128.33 (2C, $C_{3'}$, $C_{5'}$), 131.39 (1C, $C_{5''}$), 131.55 (1C, $C_{2'}$, $C_{6'}$), 131.96 (1C, $C_{3''}$), 134.77 (1C, $C_{4'}$), 136.82 (1C, $C_{6''}$), 138.05 (2C, $2C_{p\text{-}Py}$), 139.49 (1C, $C_{7''}$), 153.57 (2C, $C_{o\text{-}Py}$), 161.57 (1C, C_1), 168.56 (1C, C_3). MS (MALDI+) *m/z*, (rel. int. %): 432.7 (11.3%) $[M\text{-py}]^+$, 353.6 (100%) $[M/2\text{-Br-py}]^+$. IR ν= 1785 cm^{-1} vs (C=O), 1638 cm^{-1} vs (C=N). Anal. Calc. for $C_{21}H_{15}ClN_2O_2Pd$: C, 53.75; H, 3.22; N, 5.97. Found: C, 53.91; H, 3.49; N, 5.65.

Synthesis of 13: To a stirred suspension of **7** (0.145 g, 0.236 mmol) in MeOH, pyridine (0.053 g, 0.667 mmol) was added and the solution was stirred for 1 h. Any remaining insoluble solids were then

filtered through celite. The resulting solution was evaporated to dryness to afford **13** as a white solid (Yield 0.148 g, 71%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 3.95 (s, 3H, $COOCH_3$), 6.81 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.2 Hz, 1H, $H_{5''}$), 6.87 (td, ^{3}J = 7.6 Hz, ^{4}J = 1.6 Hz, 1H, $H_{4''}$), 7.20-7.26 (m, 5H, $4H_{m\text{-}Py}$, $H_{6''}$), 7.42 (t, ^{3}J = 7.6 Hz, 2H, $H_{3'}$, $H_{5'}$), 7.47-7.53 (m, 2H, $H_{3''}$, $H_{4'}$), 7.67 (tt, ^{3}J = 7.7 Hz, ^{3}J = 1.6 Hz, 2H, $2H_{p\text{-}Py}$), 7.74 (d, ^{3}J = 7.2 Hz, 2H, $H_{2'}$, $H_{6'}$), 8.47 (s, 1H, $H_{7''}$), 8.86 (d, ^{3}J = 5.1 Hz, 4H, $4H_{o\text{-}Py}$). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ: 52.93 (1C, $COOCH_3$), 122.61, 133.77, 138.10 (3C, $C_{1'}$, $C_{1''}$, $C_{2''}$), 124.04 (1C, $C_{5''}$), 124.76 (4C, $4C_{m\text{-}Py}$), 127.30 (2C, $C_{2'}$, $C_{6'}$), 127.79 (1C, $C_{4''}$), 128.03 (1C, $C_{6''}$), 128.64 (2C, $C_{3'}$, $C_{5'}$), 132.01 (1C, $C_{4'}$), 133.13 (1C, $C_{7''}$), 134.05 (1C, $C_{3''}$), 137.63 (2C, $2C_{p\text{-}Py}$), 153.67 (4C, $4C_{o\text{-}Py}$), 165.19, 166.15 (2C, C_1, C_3). IR ν= 3240 cm^{-1} broad, vs (NH), 1714 cm^{-1} vs (C=O). MS (MALDI+) *m/z*, (rel. int. %): 465.4 (73.5%) $[M\text{-}2Py]^+$, 386.3 (100%) $[M\text{-}2py\text{-}Br]^+$. Anal. Calc. for $C_{27}H_{24}BrN_3O_3Pd$: C, 51.90; H, 3.87; N, 6.73. Found: C, 51.61; H, 3.54; N, 6.34.

Synthesis of 14: To a suspension of **7** (0.258 g, 0.297 mmol) in 10 mL of CH_2Cl_2, silver acetate (0.149 g, 0.893 mmol) was added. The color of the suspension changed from greenish to brown reddish. This suspension was stirred overnight at 25 ºC with exclusion of light. After the reaction time the suspension was filtered through celite and the reddish solution was evaporated to dryness affording **14** as a red solid (Yield 0.204 g, 83%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 1.04 (s, 3H, CH_3), 7.15-7.25 (m, 2H, $H_{4''}$, $H_{5''}$), 7.31 (dd, ^{3}J = 7.3 Hz, ^{4}J = 2.0 Hz, 1H, $H_{6''}$), 7.38-7.45 (m, 3H, $H_{3''}$, $H_{3'}$, $H_{5'}$), 7.49 (s, 1H, $H_{7''}$), 7.55 (t, ^{3}J = 7.2 Hz, 1H, $H_{4'}$), 7.85 (d, ^{3}J = 7.3 Hz, 2H, $H_{2'}$, $H_{6'}$). ^{13}C NMR (101 MHz, *CDCl$_3$*) δ: 22.72 (1C, $\underline{C}H_3COO$), 123.12, 123.49, 130.23, 140.35 (4C, $C_{1'}$, $C_{1''}$, C_2, $C_{2''}$), 125.57 (1C, $C_{4''}$), 127.94 (2C, $C_{3'}$, $C_{5'}$), 130.40 (1C, $C_{5''}$), 131.10 (2C, $C_{2'}$, $C_{6'}$), 133.48 (1C, $C_{4'}$), 133.72 (1C, $C_{6''}$), 134.64 (1C, $C_{3''}$), 139.68 (1C, $C_{7''}$), 161.34 (1C, C_1), 167.34 (1C, C_3), 179.99 (1C, $CH_3\underline{C}OO$). MS (MALDI +): *m/z*, (rel. int. %): 768.9 (20.0%) $[M\text{-}CH_3COO^-]^+$, 354.0 (100%) $[M/2\text{-}CH_3COO^-]^+$. IR ν= 1791 cm^{-1} vs (C=O), 1663 vs (C=N). Anal. Calc for: $C_{36}H_{26}N_2O_8Pd_2$: C, 52.26; H, 3.17; N, 3.39. Found: C, 52.18; H, 3.34; N, 3.56.

Synthesis of 15: To a stirred suspension of **7** (0.244 g, 0.281 mmol) in NCMe (10 mL) under argon, silver perchlorate (0.116 g, 0.562 mmol) was added. The mixture was stirred at 25 ºC for 30 min with exclusion of light. After that time the suspension was filtered through celite, and the resulting solution evaporated to a small volume (2 mL). By addition of Et_2O (20 mL) **15** was obtained as a yellow solid (Yield 0.223 g, 74%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 2.12 (broad s, 6H, CH_3CN), 7.24-7.32 (m, 2H, $H_{4''}$, $H_{5''}$,), 7.60 (dd, ^3J = 7.0 Hz, ^4J = 2.2 Hz, 1H, $H_{3''}$), 7.51 (broad s, 1H, $H_{6''}$), 7.78-7.85 (m, 3H, $H_{3'}$, $H_{5'}$, $H_{7''}$), 7.89 (t, ^3J = 7.5 Hz, 1H, $H_{4'}$), 8.50 (d, ^3J = 7.2 Hz, $H_{2'}$, $H_{6'}$). ^{13}C NMR (101 MHz, *DMSO-d$_6$*) δ: 127.43 (1C, $H_{4''}$), 130.09 (2C, $C_{3'}$, $C_{5'}$), 131.63 (2C, $C_{2'}$, $C_{6'}$), 132.21 (1C, $C_{5''}$), 132.93 (1C) 133.85 (1C, $C_{3''}$), 136.32 (1C, $C_{4'}$), 138.53 (1C, $C_{7''}$), 149.82 (1C), 152.22 (1C), 159.08 (1C), 161.27 (1C). MS (MALDI+) *m/z* 354.0 (47.7%) $[M-ClO_4-2CH_3CN]^+$. IR ν= 2320 vs (CN), 1793 cm^{-1} vs (C=O), 1648 cm^{-1} vs (C=N). Anal. Calc. for $C_{20}H_{16}ClN_3O_6Pd$: C, 44.80; H, 3.01; N, 7.84. Found: C, 44.87; H, 3.20; N, 7.93.

Synthesis of 16: A deep violet suspension of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.618 g, 0.675 mmol) in toluene (30 mL) under Ar was treated with PPh_3 (1.416 g, 5.400 mmol). The color of the solution turned in a few minutes to deep yellow. The mixture was stirred for 15 min at 25 ºC and then (*Z*)-2-(2-iodophenyl)-4-benzylidene-5(4*H*)-oxazolone **6** (0.506 g, 1.350 mmol) was added. The resulting suspension was stirred at 25 ºC for additional 2h, while a yellow-green solid was formed. After the reaction time the solid was filtered, washed twice with CH_2Cl_2 (20 mL) and once with acetone (10 mL) and Et_2O (5 mL) to afford **16** as a yellow-greenish solid (Yield 0.733 g, 73%). IR ν = 1781 cm^{-1} vs (C=O), 1637 cm^{-1} vs (C=N). MS (MALDI+) *m/z*, (rel. int. %): 616.2 (76.4%) $[M/2-I]^+$, 510.3 (75.4%) $[M/2-I-Pd]^+$. MS (ESI+) *m/z*: 963.5 $[M-2PPh_3]^+$. Anal. Calc. for $C_{68}H_{50}I_2N_2O_4P_2Pd_2$: C, 54.90; H, 3.39; N, 1.88. Found: C, 55.02; H, 3.15; N, 1.75.

Synthesis of 17: To a stirred suspension of **16** (0.246 g, 0.165 mmol) in $CHCl_3$ (10 mL), PPh_3 (0.173 g, 0.661 mmol) was added. The initial suspension gradually became a solution and was stirred for 10 min

at 25 ºC. The resulting solution was then filtered through celite and evaporated to afford **17** as a yellow solid (Yield 0.253 g, 76%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ: 6.48 (t, ^{3}J = 7.3 Hz, 1H, $H_{4'}$), 6.53 (t, ^{3}J = 7.1 Hz, 1H, $H_{5'}$), 6.99 (t, ^{3}J = 7.7 Hz, 13H, 12$H_{m\text{-}PPh3}$, $H_{6'}$), 7.17 (t, ^{3}J = 7.1 Hz, 6H, 6$H_{p\text{-}PPh3}$), 7.19-7.29 (m, 2H, $H_{7''}$, $H_{3'}$), 7.40-7.47 (m, 13H, 12$H_{o\text{-}PPh3}$, $H_{4''}$), 7.59 (t, ^{3}J = 8.0 Hz, 2H, $H_{3''}$, $H_{5''}$), 8.57 (d, ^{3}J = 7.6 Hz, 2H, $H_{2''}$, $H_{6''}$). ^{31}P NMR *(*162 MHz, *CDCl$_3$*) δ: 19.66 (s, 2P, 2PPh_3). IR ν= 1782 cm^{-1} vs (C=O), 1638 cm^{-1} vs (C=N). MS (MALDI+) *m/z*, (rel. int. %): 616.3 (7.1%) [M-I-PPh_3]$^{+}$, 510.3 (25.9%) [M-I-Pd-PPh_3]$^{+}$. Anal. Calc. for $C_{52}H_{41}INO_2P_2Pd$ C, 62.01; H, 4.10; N, 1.39. Found: C, 61.89; H, 3.88; N, 1.10.

Reactivity of 7 with PhI(OAc)$_2$. Synthesis of 4. To a suspension of **7** (0.160 g, 0.185 mmol) in AcOH (10 mL) PhI(OAc)$_2$ (0.248 g, 0.74 mmol) was added. The resulting brown mixture was stirred for 16h at room temperature affording an orange suspension which was filtered, giving a solid and a solution which were treated separately. The solid obtained is a mixture in which **4** can be identified. This solid was dissolved in CH_2Cl_2 (3 mL), washed with H_2O (5 mL) and the organic phase was dried on anhydrous $MgSO_4$, filtered, and evaporated to dryness to afford **4** was as pale yellow solid (30.1 mg). On the other hand, the orange solution was evaporated to dryness. The residue was dissolved in chloroform (17 mL) and washed with Na_2SO_3 10% (4×10 mL) and with saturated NaCl solution (3×10 mL). The organic phase was dried on anhydrous $MgSO_4$, filtered, and evaporated to dryness. The yellow residue was purified by silica gel chromatography using ethyl acetate/hexane (2:8) as eluent. The yellow band was collected and evaporated to dryness yielding **4** as a pale yellow solid (29.8 mg). (Total yield: 50 %). These solids were characterized as **4** by comparison of their spectral data with those of an authentic sample.

Synthesis of 18. PhI(OAc)$_2$ (0.229 g, 0.693 mmol) was added to a suspension of **7** (0.152 g, 0.173 mmol) in MeOH (15 mL) and the mixture was stirred for 18h at room temperature. After the reaction time the brown-orange solution was evaporated to dryness. The brown-yellow residue was purified by

as described for **4** by $CHCl_3$ solution, washing with Na_2SO_3 and brine, and silica gel chromatography using ethyl acetate/hexane (1:9) as eluent. The yellow band was collected and evaporated to dryness yielding **18** as a yellow solid (Yield 41.2 mg, 42%).

Synthesis of 19. Compound **19** was prepared similar to **18**, starting from **7** (0.152 g, 0.173 mmol) and $PhI(OAc)_2$ (0.231 g, 0.717 mmol) in ethanol (25 mL). The orange/brown residue was purified by silica gel chromatography using ethyl acetate/hexane (2:8) as eluent. The yellow band was collected and evaporated to dryness yielding compound **19** as a yellow solid (Yield: 10.7 mg, 9.2 %). ^{1}H NMR (400 MHz, *CDCl₃*): δ = 1.50 (t, 3H, ^3J = 7.0 Hz, CH_3), 4.14 (q, 2H, OCH_2), 6.92 (d, 1H, ^2J = 8.4 Hz, $H_{3''}$), 7.09 (t, 1H, ^2J = 8.1 Hz, $H_{5''}$), 7.42 (td, 1H, ^4J = 1.6 Hz, $H_{4''}$), 7.54 (t, 2H, ^2J = 7.8 Hz, $H_{3'}$, $H_{5'}$), 7.68 (t, 1H, $H_{4'}$), 7.90 (s, 1H, $H_{7''}$), 8.17 (dd, 2H, ^4J = 1.4 Hz, $H_{2'}$, $H_{6'}$), 8.89 (dd, 1H, ^4J = 1.7 Hz, $H_{6''}$). IR ν = 1787cm^{-1} vs (C=O), 1645 cm^{-1} vs (C=N). MS (ESI +) *m/z*: 587.1(100%) [2M+H$^+$].

Synthesis of 20. $PhI(OAc)_2$ (0.191g, 0.58 mmol) was added to a suspension of **14** (0.191 g, 0.58 mmol) in AcOH (6 mL). The resulting mixture was stirred for 18h at room temperature, and the brown-orange solution was evaporated to dryness. The resulting residue was dissolved in chloroform (17 mL) and washed with Na_2SO_3 10% (4×10 mL) and with saturated NaCl solution (3×10 mL). The organic phase was dried on anhydrous $MgSO_4$, filtered, and evaporated to dryness. The yellow residue was purified by silica gel chromatography using ethyl acetate/hexane (3:8) as eluent. The yellow band was collected and evaporated to dryness yielding **20** as a yellow solid (Yield 50.2 mg, 56.5 %). ^{1}H NMR (400 MHz, *CDCl₃*): δ = 2.42 (s, 3H, CH_3), 7.18 (dd, 1H, ^2J = 8.1 Hz, ^3J = 1.2 Hz, $H_{3''}$), 7.36 (s, 1H, $H_{7''}$), 7.40 (t, 1H, ^2J = 8.1 Hz, $H_{5''}$), 7.48 (td, 1H, ^3J = 1.7 Hz, $H_{4''}$), 7.54 (t, 2H, ^2J = 7.8 Hz, $H_{3'}$, $H_{5'}$), 7.63 (tt, 1H, ^4J = 1.3 Hz, $H_{4'}$), 8.18 (dd, 2H, $H_{2'}$, $H_{6'}$), 8.93 (dd, 1H, $H_{6''}$). ^{13}C{1H} NMR (101 MHz, *CDCl₃*): δ = 20.10 (1C, CH_3), 121.74 (1C, $C_{3''}$), 122.64 (s, $C_{7''}$), 124.36, 125.10, 133.22, (3C, $C_{1'}$, $C_{1''}$, C_2), 125.38 (1C, $C_{5''}$), 127.48 (2C, $C_{2'}$, $C_{6'}$), 127.97 (2C, $C_{3'}$, $C_{5'}$), 131.08 (1C, $C_{4''}$), 131.72 (1C, $C_{6''}$), 132.58 (1C, $C_{4'}$), 149. 48 (1C, $C_{2''}$), 163.13 (1C, C_1), 166.35 (1C, C_3), 168.15 (1C, CO). IR ν = 1789, 1761 cm^{-1} vs

(C=O), 1648 cm^{-1} vs (C=N). Anal. Calc. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.55. Found: C, 70.41; H, 4.44; N, 4.49. MS (ESI +) *m/z*: 308 (100%) [$M+H^+$].

Synthesis of 21. A suspension of **7** (0.130 g, 0.150 mmol) in methanol (10 mL) was stirred under CO atmosphere for 14 h. During this time, a clear decomposition is observed. After the reaction time the black suspension was filtered through a plug of celite to remove Pd(0), and the resulting yellow solution was evaporated to dryness. The residue was dissolved in dichloromethane (15 mL), the light suspension was still filtered through a pad of celite and the resulting yellow solution was evaporated to dryness in vacuo to afford **21** as a pale yellow solid (Yield 39.1 mg, 43.1%). ^{1}H NMR (400 MHz, *CDCl₃*): δ = 3.47 (s, 3H, OMe), 7.40 – 7.42 (m, 3H, $H_{4'}$, $H_{3'}$, $H_{5'}$), 7.44 (s, 1H, $H_{7''}$), 7.61 – 7.68 (m, 3H, $H_{2'}$, $H_{6'}$, $H_{5''}$), 7.79 (d, 2H, ^2J = 4.7 Hz, $H_{4''}$, $H_{3''}$), 8.42 (d, 1H, ^2J = 8.0 Hz, $H_{6''}$). ^{13}C{1H} NMR (101 MHz, *CDCl₃*): δ = 50.80 (s, OMe), 107.90 (s, $C_{7''}$), 125.77, 128.82, 134.19, 135.75 (4C, $C_{1'}$, $C_{1''}$, C_2, $C_{2''}$), 126.35 (2C, $C_{2'}$, $C_{6'}$), 128.48 (2C, $C_{3'}$, $C_{5'}$), 128.50 (1C, $C_{6''}$), 128.90 (1C, $C_{4''}$), 130.26 (1C, $C_{5''}$), 130.41 (1C, $C_{4'}$), 133.66 (1C, $C_{3''}$), 157.77 (1C, C_1), 160.66 (1C, C_3). The signal assigned to the CO of the carboxylate group was not observed. IR ν = 1784, 1678 cm^{-1} vs (C=O), 1646 cm^{-1} vs (C=N). MS (ESI +) *m/z*: 308.1(100%) [MH^+].

Synthesis of 22. Compound **22** was prepared similar to **21**, starting from **7** (0.138 g, 0.160 mmol) and CO (1 atm) in 2-propanol (12 mL). The mixture was stirred for 16 h at room temperature, filtered through a plug of Celite, and the resulting orange solution evaporated to dryness. The residue was purified by silica gel chromatography using ethylacetate/ hexane (3:8) as eluent. The colorless band was collected and evaporated to dryness affording the compound **22** as a white solid. (Yield: 40.1 mg, 37.4%). ^{1}H NMR (400 MHz, *CDCl₃*): δ = 1.24 (d, 3H, ^3J = 6.2 Hz, CH_3), 1.38 (d, 3H, ^3J = 6.1 Hz CH_3), 3.99 (m, CH), 7.39 – 7.40 (m, 3H, $H_{4'}$, $H_{3'}$, $H_{5'}$), 7.42 (s, 1H, $H_{7''}$), 7.61 – 7.67 (m, 3H, $H_{2'}$, $H_{6'}$, $H_{5''}$), 7.78 (m, 2H, $H_{4''}$, $H_{3''}$), 8.41 (dd, 1H, ^3J = 8.0 Hz, ^4J = 0.7 Hz, $H_{6''}$). ^{13}C{^{1}H} NMR (101 MHz, *CDCl₃*): δ = 22.85 (1C, CH_3), 23.87 (1C, CH_3), 69.1 (1C, CH), 107.50 (s, $C_{7''}$), 126.16, 129.03, 135.01, 135.72 (4C, $C_{1'}$, $C_{1''}$, C_2, $C_{2''}$), 126.37 (2C, $C_{2'}$, $C_{6'}$), 128.37 (2C, $C_{3'}$, $C_{5'}$), 128.52 (1C, $C_{6''}$), 128.82

(1C, $C_{4''}$), 130.10 (1C, $C_{5''}$), 130.20 (1C, $C_{4'}$), 133.53 (1C, $C_{3''}$), 157.90 (1C, C_1), 160.84 (1C, C_3). The signal assigned to the CO of the carboxylate group was not observed. IR ν = 1785, 1675 cm^{-1} vs (C=O), 1648 cm^{-1} vs (C=N). Anal. Calc. for $C_{20}H_{17}NO_4$: C, 71.66; H, 5.11; N, 4.18. Found: C, 71.15; H, 5.37; N, 4.12. MS (ESI +) *m/z*: 336.1 (22.6%) [MH^+].

Table 1. Crystal Data and Structure Refinement for **9·CHCl$_3$**, **14**, **15** and **17**

	9 CHCl$_3$	**14**	**15**	**17**
empirical formula	$C_{69}H_{50}Br_2Cl_3N_2O_4P_2Pd_2$	$C_{36}H_{26}N_2O_8Pd_2$	$C_{20}H_{16}ClN_3O_6Pd$	$C_{52}H_{40}INO_2P_2Pd$
fw	1512.02	827.39	536.21	1006.1
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*C*2/c	*I*2/a	$P2_12_12_1$	$P2_1$/n
a [Å]	27.885(17)	14.642(3)	7.8948(3)	10.7843(2)
b [Å]	16.233(2)	10.676(2)	11.6296(5)	32.5694(6)
c [Å]	19.01(3)	20.021(4)	21.1963(9)	12.1887(2)
β [°]	129.77(14)	92.61(3)	Flack: -0.020(19)	95.104(2)
V [Å^3]	6615(18)	3126.5(11)	2037.92(14)	4264.16(13)
Z	4	4	4	4
D_{calc} [Mgm^{-3}]	1.518	1.758	1.748	1.567
μ [mm^{-1}]	1.969	1.209	1.086	1.277
cryst. size	0.22×0.18×0.06	0.18×0.15×0.06	0.63×0.14×0.07	0.13×0.09×0.06
reflns. collected	24616	14242	10095	68817
reflns. independent	5810, R_{int} = 0.0688	3614, R_{int} = 0.0188	4566, R_{int} = 0.0236	7513, R_{int} = 0.1343
data/restr./param.	5810/0/397	3614/0/270	4566/0/282	7513/0/532
R_1, wR2 [I > 2σ(I)]	0.0476, 0.0959	0.0203, 0.0537	0.0233, 0.0453	0.0449, 0.0751
R_1, wR2 [all data]	0.0949, 0.1006	0.0213, 0.0542	0.0291, 0.0464	0.0822, 0.0821
gof	1.006	1.042	0.966	1.011
largest diff peak, hole (e·Å^{-3})	1.104, -0.513	0.636, -0.763	0.479, -0.329	0.703, -0.493
temp [K]	150(1)	293(1)	150(1)	150(1)
Radiation [λ, Å]	0.71073	0.71073	0.71073	0.71073

Table S1. Crystal data and structure refinement for $9CHCl_3$.

Empirical formula	$C_{69}H_{50}Br_2Cl_3N_2O_4P_2Pd_2$	
Formula weight	1512.02	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 27.885(17) Å	α= 90º.
	b = 16.233(2) Å	β= 129.77(14)º.
	c = 19.01(3) Å	γ = 90º.
Volume	6615(18) $Å^3$	
Z	4	
Density (calculated)	1.518 Mg/m^3	
Absorption coefficient	1.969 mm^{-1}	
F(000)	3012	
Crystal size	0.22 x 0.18 x 0.06 mm^3	
Theta range for data collection	2.56 to 25.00°.	
Index ranges	-33<=h<=30, -19<=k<=19, -20<=l<=22	
Reflections collected	24616	
Independent reflections	5810 [R(int) = 0.0688]	
Completeness to theta = 25.00º	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.888 and 0.862	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5810 / 0 / 397	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.0959	
R indices (all data)	R1 = 0.0949, wR2 = 0.1006	
Largest diff. peak and hole	1.104 and -0.513 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 9.$CHCl_3$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	709(1)	437(1)	5274(1)	40(1)
Br(1)	449(1)	-665(1)	5946(1)	56(1)
P(1)	1753(1)	344(1)	6351(1)	40(1)
N(1)	886(2)	3917(4)	5383(4)	61(2)
O(1)	822(2)	4182(3)	6489(4)	82(2)
O(2)	808(3)	2894(4)	6922(4)	101(2)
C(1)	833(2)	1236(4)	4597(4)	42(2)
C(2)	823(3)	931(4)	3901(5)	55(2)
C(3)	851(3)	1479(6)	3367(5)	72(2)
C(4)	885(3)	2310(5)	3527(5)	71(2)
C(5)	896(3)	2615(4)	4209(5)	61(2)
C(6)	869(2)	2096(4)	4758(5)	42(2)
C(7)	882(2)	2391(4)	5462(4)	47(2)
C(8)	880(3)	3158(4)	5715(5)	53(2)
C(9)	837(3)	3324(5)	6417(6)	68(2)
C(10)	841(3)	4485(5)	5833(6)	67(2)
C(11)	811(3)	5363(5)	5758(7)	81(3)
C(12)	767(3)	5856(5)	6303(7)	119(4)
C(13)	710(4)	6670(8)	6167(10)	142(5)
C(14)	702(5)	7009(6)	5486(10)	139(7)
C(15)	751(5)	6524(7)	4939(7)	138(5)
C(16)	808(4)	5701(6)	5097(7)	117(4)
C(17)	2219(2)	1223(4)	6507(4)	45(2)
C(18)	2350(3)	1314(4)	5920(4)	59(2)
C(19)	2700(3)	2000(6)	6033(6)	86(3)
C(20)	2898(4)	2575(5)	6723(7)	96(3)
C(21)	2753(3)	2487(4)	7283(6)	77(2)
C(22)	2426(3)	1816(4)	7173(5)	54(2)
C(23)	2002(3)	200(3)	7493(4)	42(2)
C(24)	1689(3)	607(4)	7723(5)	53(2)
C(25)	1888(3)	557(4)	8600(6)	68(2)
C(26)	2406(4)	89(5)	9240(6)	85(3)
C(27)	2707(4)	-323(5)	9011(6)	85(2)
C(28)	2507(3)	-276(4)	8142(5)	62(2)
C(29)	2071(3)	-514(4)	6169(4)	50(2)
C(30)	1703(4)	-1169(5)	5669(5)	85(3)
C(31)	1949(5)	-1863(5)	5556(7)	121(4)
C(32)	2563(5)	-1879(7)	5945(7)	107(4)
C(33)	2923(4)	-1225(7)	6409(6)	95(3)
C(34)	2691(3)	-554(5)	6544(4)	70(2)
C(35)	227(11)	4851(11)	7470(20)	155(11)
Cl(1)	-159(4)	5727(3)	7123(4)	165(3)
Cl(2)	996(3)	4918(5)	8447(4)	177(3)
Cl(3)	-182(2)	4099(4)	7560(4)	117(2)

Table S3. Bond lengths [Å] and angles [º] for 9CHCl$_3$.

Pd(1)-C(1)	2.007(6)
Pd(1)-P(1)	2.249(5)
Pd(1)-Br(1)#1	2.522(6)
Pd(1)-Br(1)	2.5582(15)
Br(1)-Pd(1)#1	2.522(6)
P(1)-C(29)	1.799(7)
P(1)-C(17)	1.823(6)
P(1)-C(23)	1.823(7)
N(1)-C(10)	1.318(9)
N(1)-C(8)	1.389(8)
O(1)-C(10)	1.373(8)
O(1)-C(9)	1.402(8)
O(2)-C(9)	1.232(8)
C(1)-C(2)	1.396(8)
C(1)-C(6)	1.417(8)
C(2)-C(3)	1.391(9)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.373(9)
C(3)-H(3A)	0.9300
C(4)-C(5)	1.370(9)
C(4)-H(4A)	0.9300
C(5)-C(6)	1.380(8)
C(5)-H(5A)	0.9300
C(6)-C(7)	1.402(8)
C(7)-C(8)	1.336(8)
C(7)-H(7A)	0.9300
C(8)-C(9)	1.439(10)
C(10)-C(11)	1.429(10)
C(11)-C(16)	1.366(13)
C(11)-C(12)	1.376(12)
C(12)-C(13)	1.335(13)
C(12)-H(12A)	0.9300
C(13)-C(14)	1.395(16)
C(13)-H(13A)	0.9300
C(14)-C(15)	1.378(16)
C(14)-H(14A)	0.9300
C(15)-C(16)	1.356(12)
C(15)-H(15A)	0.9300
C(16)-H(16A)	0.9300
C(17)-C(18)	1.386(8)
C(17)-C(22)	1.388(8)
C(18)-C(19)	1.403(9)
C(18)-H(18A)	0.9300
C(19)-C(20)	1.403(11)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.366(11)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.349(8)
C(21)-H(21A)	0.9300
C(22)-H(22A)	0.9300
C(23)-C(24)	1.368(8)
C(23)-C(28)	1.372(8)
C(24)-C(25)	1.382(9)
C(24)-H(24A)	0.9300
C(25)-C(26)	1.376(10)
C(25)-H(25A)	0.9300
C(26)-C(27)	1.345(10)

C(26)-H(26A)	0.9300
C(27)-C(28)	1.366(9)
C(27)-H(27A)	0.9300
C(28)-H(28A)	0.9300
C(29)-C(30)	1.356(9)
C(29)-C(34)	1.389(9)
C(30)-C(31)	1.405(10)
C(30)-H(30A)	0.9300
C(31)-C(32)	1.364(12)
C(31)-H(31A)	0.9300
C(32)-C(33)	1.334(11)
C(32)-H(32A)	0.9300
C(33)-C(34)	1.371(10)
C(33)-H(33A)	0.9300
C(34)-H(34A)	0.9300
C(35)-Cl(1)	1.646(18)
C(35)-Cl(2)	1.72(3)
C(35)-Cl(3)	1.748(16)

C(1)-Pd(1)-P(1)	88.52(19)
C(1)-Pd(1)-Br(1)#1	87.72(18)
P(1)-Pd(1)-Br(1)#1	175.28(5)
C(1)-Pd(1)-Br(1)	173.01(17)
P(1)-Pd(1)-Br(1)	96.52(10)
Br(1)#1-Pd(1)-Br(1)	87.47(8)
Pd(1)#1-Br(1)-Pd(1)	92.53(8)
C(29)-P(1)-C(17)	104.4(3)
C(29)-P(1)-C(23)	105.7(3)
C(17)-P(1)-C(23)	102.6(3)
C(29)-P(1)-Pd(1)	112.7(2)
C(17)-P(1)-Pd(1)	117.9(2)
C(23)-P(1)-Pd(1)	112.2(2)
C(10)-N(1)-C(8)	106.9(7)
C(10)-O(1)-C(9)	104.2(6)
C(2)-C(1)-C(6)	120.6(6)
C(2)-C(1)-Pd(1)	118.0(5)
C(6)-C(1)-Pd(1)	121.1(5)
C(3)-C(2)-C(1)	119.2(7)
C(3)-C(2)-H(2A)	120.4
C(1)-C(2)-H(2A)	120.4
C(4)-C(3)-C(2)	119.6(7)
C(4)-C(3)-H(3A)	120.2
C(2)-C(3)-H(3A)	120.2
C(3)-C(4)-C(5)	121.5(7)
C(3)-C(4)-H(4A)	119.3
C(5)-C(4)-H(4A)	119.2
C(4)-C(5)-C(6)	121.0(7)
C(4)-C(5)-H(5A)	119.5
C(6)-C(5)-H(5A)	119.5
C(5)-C(6)-C(7)	122.2(6)
C(5)-C(6)-C(1)	118.0(6)
C(7)-C(6)-C(1)	119.8(6)
C(8)-C(7)-C(6)	131.3(7)
C(8)-C(7)-H(7A)	114.4
C(6)-C(7)-H(7A)	114.4
C(7)-C(8)-N(1)	131.2(8)
C(7)-C(8)-C(9)	122.0(7)
N(1)-C(8)-C(9)	106.7(7)
O(2)-C(9)-O(1)	117.7(9)

O(2)-C(9)-C(8)	134.7(8)
O(1)-C(9)-C(8)	107.6(7)
N(1)-C(10)-O(1)	114.5(7)
N(1)-C(10)-C(11)	131.1(9)
O(1)-C(10)-C(11)	114.4(9)
C(16)-C(11)-C(12)	120.5(8)
C(16)-C(11)-C(10)	117.2(10)
C(12)-C(11)-C(10)	122.2(11)
C(13)-C(12)-C(11)	119.1(12)
C(13)-C(12)-H(12A)	120.4
C(11)-C(12)-H(12A)	120.4
C(12)-C(13)-C(14)	119.9(14)
C(12)-C(13)-H(13A)	120.0
C(14)-C(13)-H(13A)	120.0
C(15)-C(14)-C(13)	121.7(12)
C(15)-C(14)-H(14A)	119.2
C(13)-C(14)-H(14A)	119.2
C(16)-C(15)-C(14)	116.7(12)
C(16)-C(15)-H(15A)	121.7
C(14)-C(15)-H(15A)	121.7
C(15)-C(16)-C(11)	122.1(11)
C(15)-C(16)-H(16A)	119.0
C(11)-C(16)-H(16A)	119.0
C(18)-C(17)-C(22)	119.4(6)
C(18)-C(17)-P(1)	118.7(5)
C(22)-C(17)-P(1)	121.8(5)
C(17)-C(18)-C(19)	118.4(7)
C(17)-C(18)-H(18A)	120.8
C(19)-C(18)-H(18A)	120.8
C(18)-C(19)-C(20)	119.4(8)
C(18)-C(19)-H(19A)	120.3
C(20)-C(19)-H(19A)	120.3
C(21)-C(20)-C(19)	121.5(7)
C(21)-C(20)-H(20A)	119.2
C(19)-C(20)-H(20A)	119.2
C(22)-C(21)-C(20)	118.2(8)
C(22)-C(21)-H(21A)	120.9
C(20)-C(21)-H(21A)	120.9
C(21)-C(22)-C(17)	123.1(7)
C(21)-C(22)-H(22A)	118.5
C(17)-C(22)-H(22A)	118.5
C(24)-C(23)-C(28)	118.8(6)
C(24)-C(23)-P(1)	119.0(5)
C(28)-C(23)-P(1)	122.2(5)
C(23)-C(24)-C(25)	120.7(6)
C(23)-C(24)-H(24A)	119.6
C(25)-C(24)-H(24A)	119.6
C(26)-C(25)-C(24)	118.9(7)
C(26)-C(25)-H(25A)	120.6
C(24)-C(25)-H(25A)	120.6
C(27)-C(26)-C(25)	120.5(8)
C(27)-C(26)-H(26A)	119.8
C(25)-C(26)-H(26A)	119.8
C(26)-C(27)-C(28)	120.4(8)
C(26)-C(27)-H(27A)	119.8
C(28)-C(27)-H(27A)	119.8
C(27)-C(28)-C(23)	120.7(7)
C(27)-C(28)-H(28A)	119.7
C(23)-C(28)-H(28A)	119.7

C(30)-C(29)-C(34)	117.2(6)
C(30)-C(29)-P(1)	119.9(5)
C(34)-C(29)-P(1)	122.9(5)
C(29)-C(30)-C(31)	120.9(8)
C(29)-C(30)-H(30A)	119.6
C(31)-C(30)-H(30A)	119.6
C(32)-C(31)-C(30)	119.9(9)
C(32)-C(31)-H(31A)	120.0
C(30)-C(31)-H(31A)	120.0
C(33)-C(32)-C(31)	119.6(9)
C(33)-C(32)-H(32A)	120.2
C(31)-C(32)-H(32A)	120.2
C(32)-C(33)-C(34)	120.8(9)
C(32)-C(33)-H(33A)	119.6
C(34)-C(33)-H(33A)	119.6
C(33)-C(34)-C(29)	121.5(7)
C(33)-C(34)-H(34A)	119.3
C(29)-C(34)-H(34A)	119.3
Cl(1)-C(35)-Cl(2)	115.0(14)
Cl(1)-C(35)-Cl(3)	110.1(11)
Cl(2)-C(35)-Cl(3)	112.5(15)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for 9CHCl$_3$. 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)	31(1)	38(1)	44(1)	2(1)	20(1)	-6(1)
Br(1)	36(1)	52(1)	62(1)	19(1)	22(1)	-6(1)
P(1)	33(1)	48(1)	37(1)	-2(1)	21(1)	-3(1)
N(1)	42(3)	51(4)	60(4)	-4(3)	19(3)	-10(3)
O(1)	78(4)	65(4)	82(4)	-33(3)	42(3)	-12(3)
O(2)	140(5)	91(4)	79(5)	-20(3)	73(4)	-21(4)
C(1)	35(4)	58(4)	36(4)	-2(3)	23(3)	-8(3)
C(2)	42(4)	72(5)	55(5)	-8(4)	33(4)	-14(3)
C(3)	48(4)	121(7)	53(5)	-11(5)	36(4)	-28(5)
C(4)	70(5)	83(6)	58(6)	3(5)	40(5)	-32(4)
C(5)	53(5)	68(5)	54(5)	4(4)	30(4)	-15(4)
C(6)	32(4)	42(4)	45(4)	2(4)	22(3)	-9(3)
C(7)	45(4)	42(4)	43(5)	-4(3)	22(4)	-4(3)
C(8)	45(4)	55(5)	40(5)	-1(4)	18(4)	-10(3)
C(9)	68(5)	52(6)	54(6)	-2(4)	26(5)	-12(4)
C(10)	46(4)	72(6)	52(5)	-1(5)	17(4)	-15(4)
C(11)	44(4)	29(5)	95(7)	-4(5)	10(5)	-5(3)
C(12)	65(6)	35(5)	177(11)	-35(6)	40(6)	-6(4)
C(13)	54(6)	101(11)	173(14)	-52(9)	28(8)	-14(6)
C(14)	57(6)	38(6)	187(15)	-17(8)	16(8)	-9(5)
C(15)	142(10)	70(8)	111(9)	-13(7)	39(8)	-39(7)
C(16)	96(7)	44(6)	115(9)	1(6)	23(7)	-11(5)
C(17)	28(3)	67(4)	38(4)	-2(4)	20(3)	-14(3)
C(18)	48(4)	88(5)	45(5)	-9(4)	31(4)	-18(4)
C(19)	59(5)	126(8)	92(7)	18(6)	56(5)	-17(5)
C(20)	65(6)	68(6)	136(9)	-9(6)	55(6)	-31(4)
C(21)	79(6)	72(6)	102(7)	-23(5)	68(6)	-36(4)
C(22)	45(4)	73(5)	54(5)	-7(4)	36(4)	-14(4)
C(23)	32(4)	48(4)	47(4)	-6(3)	26(4)	-10(3)
C(24)	51(4)	65(5)	47(5)	-3(4)	33(4)	0(3)
C(25)	69(5)	84(6)	73(6)	-14(5)	56(5)	-12(4)
C(26)	93(7)	120(7)	52(6)	2(5)	51(6)	-11(6)
C(27)	77(6)	123(7)	55(6)	21(5)	43(5)	25(5)
C(28)	56(5)	84(5)	43(5)	9(4)	31(4)	12(4)
C(29)	49(4)	66(5)	28(4)	-9(4)	21(3)	-3(4)
C(30)	72(6)	88(6)	87(7)	-13(5)	47(5)	16(5)
C(31)	143(10)	68(6)	125(9)	-37(6)	73(8)	11(6)
C(32)	112(9)	128(9)	85(8)	18(7)	64(7)	68(7)
C(33)	68(6)	142(9)	55(6)	-6(6)	31(5)	32(6)
C(34)	52(5)	100(6)	41(5)	-11(4)	22(4)	19(4)
C(35)	160(30)	48(11)	280(30)	42(17)	150(30)	6(12)
Cl(1)	171(8)	102(4)	118(6)	10(3)	45(6)	41(4)
Cl(2)	97(4)	315(9)	88(4)	-39(5)	46(4)	18(5)
Cl(3)	106(5)	135(4)	135(5)	-3(4)	88(4)	7(3)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for $9CHCl_3$.

	x	y	z	U(eq)
H(2A)	797	367	3796	66
H(3A)	848	1283	2904	86
H(4A)	900	2673	3164	86
H(5A)	923	3181	4304	74
H(7A)	894	1982	5815	57
H(12A)	776	5626	6760	143
H(13A)	676	7010	6527	170
H(14A)	663	7576	5398	167
H(15A)	746	6750	4484	166
H(16A)	846	5356	4745	141
H(18A)	2210	929	5463	71
H(19A)	2799	2073	5655	104
H(20A)	3132	3027	6800	115
H(21A)	2877	2879	7727	93
H(22A)	2334	1747	7562	65
H(24A)	1340	920	7285	63
H(25A)	1676	835	8755	81
H(26A)	2549	58	9835	102
H(27A)	3054	-642	9447	102
H(28A)	2715	-570	7990	74
H(30A)	1283	-1158	5397	102
H(31A)	1693	-2311	5217	145
H(32A)	2731	-2344	5886	129
H(33A)	3335	-1225	6645	114
H(34A)	2956	-115	6893	85

Table S6. Crystal data and structure refinement for 14.

Empirical formula	$C_{36}H_{26}N_2O_8Pd_2$	
Formula weight	827.39	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 14.642(3) Å	α= 90°.
	b = 10.676(2) Å	β= 92.61(3)°.
	c = 20.021(4) Å	γ = 90°.
Volume	3126.5(11) $Å^3$	
Z	4	
Density (calculated)	1.758 Mg/m^3	
Absorption coefficient	1.209 mm^{-1}	
F(000)	1648	
Crystal size	0.183 x 0.153 x 0.059 mm^3	
Theta range for data collection	2.04 to 27.57°.	
Index ranges	-18<=h<=19, -13<=k<=13, -26<=l<=25	
Reflections collected	14242	
Independent reflections	3614 [R(int) = 0.0188]	
Completeness to theta = 27.57°	99.8 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3614 / 0 / 270	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0203, wR2 = 0.0537	
R indices (all data)	R1 = 0.0213, wR2 = 0.0542	
Extinction coefficient	0.00059(7)	
Largest diff. peak and hole	0.636 and -0.763 e.$Å^{-3}$	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 14. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1662(1)	2656(1)	375(1)	14(1)
O(3)	2343(1)	1403(1)	990(1)	18(1)
N(1)	1007(1)	3864(1)	-273(1)	16(1)
O(4)	1552(1)	1074(1)	-269(1)	17(1)
O(2)	874(1)	6767(1)	-1073(1)	28(1)
O(1)	518(1)	4718(1)	-1244(1)	21(1)
C(1)	1783(1)	3957(2)	1074(1)	18(1)
C(11)	177(1)	2549(2)	-1137(1)	19(1)
C(17)	2996(1)	781(1)	758(1)	17(1)
C(8)	1187(1)	5154(2)	-231(1)	17(1)
C(7)	1535(1)	5780(2)	304(1)	18(1)
C(9)	877(1)	5723(2)	-862(1)	21(1)
C(15)	-668(1)	646(2)	-994(1)	25(1)
C(3)	2107(1)	4423(2)	2247(1)	28(1)
C(6)	1776(1)	5256(2)	949(1)	18(1)
C(2)	1939(1)	3572(2)	1734(1)	23(1)
C(10)	600(1)	3673(2)	-856(1)	17(1)
C(5)	1967(1)	6111(2)	1470(1)	22(1)
C(12)	106(1)	2395(2)	-1828(1)	25(1)
C(16)	-212(1)	1671(2)	-719(1)	20(1)
C(13)	-343(1)	1359(2)	-2097(1)	30(1)
C(14)	-731(1)	490(2)	-1681(1)	30(1)
C(4)	2134(1)	5701(2)	2115(1)	28(1)
C(18)	3256(1)	-419(2)	1111(1)	25(1)

Table S8. Bond lengths [Å] and angles [°] for 14.

Pd(1)-C(1)	1.9741(16)
Pd(1)-N(1)	2.0378(14)
Pd(1)-O(3)	2.0455(11)
Pd(1)-O(4)	2.1268(11)
Pd(1)-Pd(1)#1	2.9357(8)
O(3)-C(17)	1.2688(19)
N(1)-C(10)	1.302(2)
N(1)-C(8)	1.404(2)
O(4)-C(17)#1	1.246(2)
O(2)-C(9)	1.192(2)
O(1)-C(10)	1.3618(19)
O(1)-C(9)	1.405(2)
C(1)-C(2)	1.393(2)
C(1)-C(6)	1.409(2)
C(11)-C(12)	1.392(3)
C(11)-C(16)	1.394(2)
C(11)-C(10)	1.452(2)
C(17)-O(4)#1	1.246(2)
C(17)-C(18)	1.505(2)
C(8)-C(7)	1.343(2)
C(8)-C(9)	1.456(2)
C(7)-C(6)	1.438(2)
C(15)-C(16)	1.384(2)
C(15)-C(14)	1.384(3)
C(3)-C(2)	1.385(2)
C(3)-C(4)	1.390(3)
C(6)-C(5)	1.404(2)
C(5)-C(4)	1.376(3)
C(12)-C(13)	1.383(3)
C(13)-C(14)	1.387(3)
C(1)-Pd(1)-N(1)	91.71(6)
C(1)-Pd(1)-O(3)	90.49(6)
N(1)-Pd(1)-O(3)	177.42(5)
C(1)-Pd(1)-O(4)	172.16(5)
N(1)-Pd(1)-O(4)	95.54(5)
O(3)-Pd(1)-O(4)	82.34(5)
C(1)-Pd(1)-Pd(1)#1	108.22(5)
N(1)-Pd(1)-Pd(1)#1	93.11(4)
O(3)-Pd(1)-Pd(1)#1	84.92(3)
O(4)-Pd(1)-Pd(1)#1	74.43(3)
C(17)-O(3)-Pd(1)	118.50(10)
C(10)-N(1)-C(8)	106.49(13)
C(10)-N(1)-Pd(1)	130.85(11)
C(8)-N(1)-Pd(1)	120.13(10)
C(17)#1-O(4)-Pd(1)	130.31(10)
C(10)-O(1)-C(9)	107.07(12)
C(2)-C(1)-C(6)	117.29(15)
C(2)-C(1)-Pd(1)	118.03(12)
C(6)-C(1)-Pd(1)	124.57(12)
C(12)-C(11)-C(16)	120.14(16)
C(12)-C(11)-C(10)	119.57(16)
C(16)-C(11)-C(10)	120.15(16)
O(4)#1-C(17)-O(3)	126.30(14)
O(4)#1-C(17)-C(18)	116.76(14)
O(3)-C(17)-C(18)	116.93(14)
C(7)-C(8)-N(1)	126.80(15)

C(7)-C(8)-C(9)	125.22(15)
N(1)-C(8)-C(9)	107.89(14)
C(8)-C(7)-C(6)	126.27(16)
O(2)-C(9)-O(1)	121.75(15)
O(2)-C(9)-C(8)	133.88(16)
O(1)-C(9)-C(8)	104.36(13)
C(16)-C(15)-C(14)	119.90(17)
C(2)-C(3)-C(4)	120.63(17)
C(5)-C(6)-C(1)	120.59(15)
C(5)-C(6)-C(7)	116.51(15)
C(1)-C(6)-C(7)	122.83(15)
C(3)-C(2)-C(1)	121.70(17)
N(1)-C(10)-O(1)	114.10(14)
N(1)-C(10)-C(11)	130.27(15)
O(1)-C(10)-C(11)	115.51(14)
C(4)-C(5)-C(6)	120.73(17)
C(13)-C(12)-C(11)	119.64(18)
C(15)-C(16)-C(11)	119.78(17)
C(12)-C(13)-C(14)	120.06(18)
C(15)-C(14)-C(13)	120.46(17)
C(5)-C(4)-C(3)	118.99(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y,-z

Table S9. Anisotropic displacement parameters (Å^{2}x 10^3) for 14. 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)	14(1)	11(1)	16(1)	0(1)	0(1)	1(1)
O(3)	21(1)	13(1)	19(1)	1(1)	-1(1)	3(1)
N(1)	16(1)	13(1)	20(1)	0(1)	1(1)	0(1)
O(4)	17(1)	14(1)	20(1)	-2(1)	-1(1)	0(1)
O(2)	36(1)	16(1)	31(1)	8(1)	-7(1)	-2(1)
O(1)	24(1)	17(1)	21(1)	4(1)	-4(1)	-2(1)
C(1)	16(1)	16(1)	21(1)	-2(1)	1(1)	1(1)
C(11)	16(1)	17(1)	23(1)	-1(1)	-3(1)	0(1)
C(17)	18(1)	12(1)	20(1)	-1(1)	-4(1)	-2(1)
C(8)	15(1)	13(1)	23(1)	3(1)	1(1)	1(1)
C(7)	18(1)	13(1)	24(1)	0(1)	2(1)	1(1)
C(9)	19(1)	18(1)	25(1)	1(1)	-1(1)	-1(1)
C(15)	20(1)	21(1)	35(1)	3(1)	-3(1)	-3(1)
C(3)	43(1)	23(1)	19(1)	-1(1)	-4(1)	5(1)
C(6)	16(1)	16(1)	21(1)	-2(1)	1(1)	0(1)
C(2)	31(1)	16(1)	22(1)	0(1)	0(1)	4(1)
C(10)	15(1)	17(1)	20(1)	2(1)	0(1)	1(1)
C(5)	27(1)	15(1)	25(1)	-2(1)	-2(1)	1(1)
C(12)	27(1)	25(1)	23(1)	1(1)	-1(1)	-2(1)
C(16)	16(1)	20(1)	23(1)	1(1)	-3(1)	1(1)
C(13)	32(1)	34(1)	25(1)	-7(1)	-5(1)	-1(1)
C(14)	25(1)	25(1)	39(1)	-8(1)	-7(1)	-4(1)
C(4)	40(1)	20(1)	23(1)	-6(1)	-4(1)	2(1)
C(18)	30(1)	17(1)	28(1)	6(1)	4(1)	6(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for 14.

	x	y	z	U(eq)
H(4)	2234(15)	6260(20)	2450(10)	25(5)
H(2)	1935(18)	2740(20)	1815(13)	33(6)
H(14)	-1035(14)	-210(20)	-1871(10)	27(5)
H(16)	-191(14)	1780(20)	-272(11)	24(5)
H(13)	-407(15)	1270(20)	-2550(11)	29(5)
H(7)	1597(14)	6620(20)	252(10)	28(6)
H(12)	360(15)	2990(20)	-2082(11)	25(5)
H(5)	1965(15)	6960(20)	1364(11)	30(6)
H(15)	-926(14)	100(20)	-710(10)	25(5)
H(19)	2775(16)	-730(20)	1351(11)	31(6)
H(20)	3422(19)	-1020(30)	796(13)	53(8)
H(18)	3740(20)	-250(30)	1405(14)	59(8)
H(21)	2168(15)	4120(20)	2679(11)	25(5)

Table S11. Crystal data and structure refinement for 15.

Empirical formula	$C_{20}H_{16}ClN_3O_6Pd$	
Formula weight	536.21	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.8948(3) Å	α= 90°.
	b = 11.6296(5) Å	β= 90°.
	c = 22.1963(9) Å	γ = 90°.
Volume	2037.92(14) $Å^3$	
Z	4	
Density (calculated)	1.748 Mg/m^3	
Absorption coefficient	1.086 mm^{-1}	
F(000)	1072	
Crystal size	0.63 x 0.14 x 0.07 mm^3	
Theta range for data collection	2.74 to 28.83°.	
Index ranges	-5<=h<=9, -15<=k<=14, -27<=l<=27	
Reflections collected	10095	
Independent reflections	4566 [R(int) = 0.0236]	
Completeness to theta = 28.83°	88.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0722 and 0.9222	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4566 / 0 / 282	
Goodness-of-fit on F^2	0.966	
Final R indices [I>2sigma(I)]	R1 = 0.0233, wR2 = 0.0453	
R indices (all data)	R1 = 0.0291, wR2 = 0.0464	
Absolute structure parameter	-0.020(19)	
Largest diff. peak and hole	0.479 and -0.329 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 15. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	-9325(1)	-1121(1)	-652(1)	17(1)
C(1)	-9956(3)	-1359(2)	207(1)	20(1)
C(2)	-10347(3)	-424(2)	569(1)	25(1)
C(3)	-10582(4)	-542(3)	1183(1)	31(1)
C(4)	-10424(4)	-1599(3)	1459(1)	31(1)
C(5)	-10087(3)	-2543(3)	1112(1)	26(1)
C(6)	-9866(3)	-2449(2)	485(1)	18(1)
C(7)	-9704(3)	-3514(2)	157(1)	21(1)
C(8)	-9861(3)	-3623(2)	-440(1)	20(1)
C(9)	-9987(3)	-4713(2)	-762(1)	25(1)
O(1)	-9846(2)	-5694(2)	-627(1)	34(1)
O(2)	-10396(2)	-4383(2)	-1358(1)	25(1)
N(1)	-10112(3)	-2733(2)	-852(1)	18(1)
C(10)	-10456(3)	-3213(2)	-1369(1)	19(1)
C(11)	-10887(3)	-2704(2)	-1946(1)	19(1)
C(12)	-11706(3)	-1641(2)	-1973(1)	20(1)
C(13)	-12120(3)	-1181(3)	-2526(1)	27(1)
C(14)	-11704(4)	-1766(3)	-3053(1)	30(1)
C(15)	-10889(4)	-2819(2)	-3024(1)	31(1)
C(16)	-10492(3)	-3288(2)	-2473(1)	24(1)
N(2)	-8367(3)	414(2)	-431(1)	24(1)
C(17)	-7759(3)	1274(2)	-322(1)	21(1)
C(18)	-7020(4)	2377(2)	-179(1)	27(1)
N(3)	-8363(3)	-855(2)	-1533(1)	21(1)
C(19)	-7684(3)	-754(2)	-1974(1)	21(1)
C(20)	-6794(4)	-648(3)	-2550(1)	34(1)
Cl(1)	-3692(1)	-8592(1)	-1422(1)	25(1)
O(3)	-3529(3)	-8564(2)	-2064(1)	45(1)
O(4)	-5110(3)	-9280(2)	-1256(1)	48(1)
O(5)	-2199(3)	-9071(2)	-1162(1)	49(1)
O(6)	-3923(3)	-7442(2)	-1204(1)	41(1)

Table S13. Bond lengths [Å] and angles [°] for 15.

Pd(1)-C(1)	1.991(3)
Pd(1)-N(2)	2.000(2)
Pd(1)-N(1)	2.024(2)
Pd(1)-N(3)	2.120(2)
C(1)-C(2)	1.386(4)
C(1)-C(6)	1.412(4)
C(2)-C(3)	1.383(4)
C(3)-C(4)	1.379(4)
C(4)-C(5)	1.368(4)
C(5)-C(6)	1.406(4)
C(6)-C(7)	1.442(4)
C(7)-C(8)	1.337(3)
C(8)-N(1)	1.396(3)
C(8)-C(9)	1.459(4)
C(9)-O(1)	1.185(3)
C(9)-O(2)	1.415(3)
O(2)-C(10)	1.361(3)
N(1)-C(10)	1.305(3)
C(10)-C(11)	1.451(3)
C(11)-C(16)	1.389(3)
C(11)-C(12)	1.397(4)
C(12)-C(13)	1.378(4)
C(13)-C(14)	1.392(4)
C(14)-C(15)	1.385(4)
C(15)-C(16)	1.375(4)
N(2)-C(17)	1.135(3)
C(17)-C(18)	1.446(4)
N(3)-C(19)	1.123(3)
C(19)-C(20)	1.464(4)
Cl(1)-O(4)	1.425(2)
Cl(1)-O(5)	1.426(2)
Cl(1)-O(3)	1.431(2)
Cl(1)-O(6)	1.434(2)
C(1)-Pd(1)-N(2)	89.06(10)
C(1)-Pd(1)-N(1)	90.27(10)
N(2)-Pd(1)-N(1)	175.30(9)
C(1)-Pd(1)-N(3)	173.48(9)
N(2)-Pd(1)-N(3)	87.72(9)
N(1)-Pd(1)-N(3)	92.46(8)
C(2)-C(1)-C(6)	117.5(2)
C(2)-C(1)-Pd(1)	120.1(2)
C(6)-C(1)-Pd(1)	122.05(19)
C(3)-C(2)-C(1)	121.6(3)
C(4)-C(3)-C(2)	121.0(3)
C(5)-C(4)-C(3)	118.8(3)
C(4)-C(5)-C(6)	121.3(3)
C(5)-C(6)-C(1)	119.7(3)
C(5)-C(6)-C(7)	116.3(2)
C(1)-C(6)-C(7)	123.7(2)
C(8)-C(7)-C(6)	125.0(2)
C(7)-C(8)-N(1)	126.3(2)
C(7)-C(8)-C(9)	125.1(2)
N(1)-C(8)-C(9)	108.2(2)
O(1)-C(9)-O(2)	121.2(3)
O(1)-C(9)-C(8)	135.0(3)
O(2)-C(9)-C(8)	103.8(2)

C(10)-O(2)-C(9)	107.2(2)
C(10)-N(1)-C(8)	106.8(2)
C(10)-N(1)-Pd(1)	130.78(18)
C(8)-N(1)-Pd(1)	119.93(16)
N(1)-C(10)-O(2)	113.8(2)
N(1)-C(10)-C(11)	130.6(2)
O(2)-C(10)-C(11)	115.6(2)
C(16)-C(11)-C(12)	120.0(2)
C(16)-C(11)-C(10)	119.4(2)
C(12)-C(11)-C(10)	120.5(2)
C(13)-C(12)-C(11)	119.5(3)
C(12)-C(13)-C(14)	120.1(3)
C(15)-C(14)-C(13)	120.2(3)
C(16)-C(15)-C(14)	119.9(3)
C(15)-C(16)-C(11)	120.3(3)
C(17)-N(2)-Pd(1)	176.7(2)
N(2)-C(17)-C(18)	178.7(3)
C(19)-N(3)-Pd(1)	172.2(2)
N(3)-C(19)-C(20)	178.9(3)
O(4)-Cl(1)-O(5)	108.95(15)
O(4)-Cl(1)-O(3)	109.91(14)
O(5)-Cl(1)-O(3)	109.74(14)
O(4)-Cl(1)-O(6)	109.68(14)
O(5)-Cl(1)-O(6)	109.49(14)
O(3)-Cl(1)-O(6)	109.06(13)

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2$x 10^3) for 15. 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)	15(1)	16(1)	1(1)	1(1)	-1(1)
C(1)	14(1)	24(2)	20(1)	1(1)	0(1)	0(1)
C(2)	26(2)	20(1)	30(2)	0(1)	2(1)	5(1)
C(3)	33(2)	36(2)	24(2)	-9(1)	6(1)	4(2)
C(4)	33(2)	41(2)	18(1)	-2(1)	4(1)	-1(1)
C(5)	23(1)	33(2)	22(2)	5(1)	-1(1)	-7(1)
C(6)	16(1)	21(1)	19(1)	1(1)	1(1)	-1(1)
C(7)	22(2)	19(1)	21(1)	4(1)	0(1)	-2(1)
C(8)	21(1)	18(2)	22(1)	1(1)	2(1)	-1(1)
C(9)	30(1)	22(2)	24(2)	2(1)	3(1)	1(1)
O(1)	58(1)	14(1)	30(1)	3(1)	3(1)	1(1)
O(2)	39(1)	14(1)	21(1)	-1(1)	-1(1)	0(1)
N(1)	21(1)	18(1)	14(1)	2(1)	1(1)	0(1)
C(10)	19(2)	15(1)	22(1)	0(1)	-1(1)	0(1)
C(11)	19(1)	19(1)	19(1)	0(1)	0(1)	-3(1)
C(12)	16(1)	20(1)	23(1)	-3(1)	-1(1)	-1(1)
C(13)	21(1)	29(2)	30(2)	3(2)	-4(1)	0(2)
C(14)	34(2)	35(2)	22(2)	4(1)	-3(1)	-1(1)
C(15)	39(2)	33(2)	20(1)	-2(1)	2(1)	5(2)
C(16)	29(2)	20(1)	23(1)	-1(1)	1(1)	2(1)
N(2)	30(1)	22(1)	20(1)	1(1)	3(1)	-3(1)
C(17)	24(1)	23(2)	18(1)	2(1)	4(1)	3(1)
C(18)	31(2)	17(1)	34(2)	-4(1)	3(1)	-2(1)
N(3)	21(1)	21(1)	22(1)	2(1)	0(1)	-2(1)
C(19)	18(1)	19(1)	26(2)	4(1)	-4(1)	-1(1)
C(20)	34(2)	42(2)	25(2)	5(1)	8(1)	3(2)
Cl(1)	30(1)	25(1)	21(1)	-2(1)	3(1)	-3(1)
O(3)	68(2)	47(2)	18(1)	-5(1)	5(1)	-3(1)
O(4)	43(1)	46(2)	54(2)	2(1)	9(1)	-21(1)
O(5)	42(1)	55(2)	51(2)	1(1)	-12(1)	12(1)
O(6)	61(2)	24(1)	37(1)	-6(1)	5(1)	0(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for 15.

	x	y	z	U(eq)
H(2A)	-10455	315	391	30
H(3A)	-10855	115	1418	37
H(4A)	-10548	-1670	1884	37
H(5A)	-10001	-3277	1297	31
H(7A)	-9469	-4190	383	25
H(12A)	-11977	-1238	-1614	23
H(13A)	-12689	-462	-2548	32
H(14A)	-11981	-1442	-3433	36
H(15A)	-10604	-3216	-3384	37
H(16A)	-9944	-4014	-2454	28
H(17A)	-5980	2484	-414	33
H(17B)	-6751	2407	252	33
H(17C)	-7827	2989	-278	33
H(20A)	-6069	-1322	-2611	41
H(20B)	-6096	49	-2546	41
H(20C)	-7622	-599	-2878	41

Table S16. Crystal data and structure refinement for 17.

Empirical formula	$C_{52}H_{40}INO_2P_2Pd$	
Formula weight	503.05	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.7843(2) Å	α= 90°.
	b = 32.5694(6) Å	β= 95.104(2)°.
	c = 12.1887(2) Å	γ = 90°.
Volume	4264.16(13) $Å^3$	
Z	8	
Density (calculated)	1.567 Mg/m^3	
Absorption coefficient	1.277 mm^{-1}	
F(000)	2016	
Crystal size	0.13 x 0.09 x 0.06 mm^3	
Theta range for data collection	2.64 to 25.00°.	
Index ranges	-12<=h<=12, -38<=k<=38, -14<=l<=14	
Reflections collected	68817	
Independent reflections	7513 [R(int) = 0.1343]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9273 and 0.8515	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7513 / 0 / 532	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.0751	
R indices (all data)	R1 = 0.0822, wR2 = 0.0821	
Largest diff. peak and hole	0.703 and -0.493 $e.Å^{-3}$	

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 17. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	11457(1)	1453(1)	2385(1)	12(1)
I(1)	9044(1)	1643(1)	2290(1)	22(1)
P(1)	11482(1)	1327(1)	4270(1)	14(1)
P(2)	11715(1)	1694(1)	613(1)	14(1)
N(1)	11866(4)	574(1)	1984(3)	14(1)
O(1)	13067(3)	-427(1)	2069(3)	28(1)
O(2)	13694(3)	232(1)	2280(3)	18(1)
C(1)	13287(4)	1352(1)	2593(4)	15(1)
C(2)	14086(4)	1678(2)	2879(4)	17(1)
C(3)	15368(5)	1622(2)	3086(4)	25(1)
C(4)	15870(4)	1237(2)	2990(4)	23(1)
C(5)	15116(4)	910(2)	2707(4)	20(1)
C(6)	13821(4)	962(2)	2507(4)	14(1)
C(7)	13055(4)	603(1)	2240(4)	15(1)
C(8)	12806(5)	-68(2)	2056(4)	19(1)
C(9)	11627(5)	152(2)	1850(4)	19(1)
C(10)	10562(5)	-54(2)	1591(4)	21(1)
C(11)	9285(4)	78(2)	1333(4)	18(1)
C(12)	8910(5)	486(2)	1331(4)	20(1)
C(13)	7679(5)	588(2)	1057(4)	24(1)
C(14)	6810(5)	294(2)	775(4)	27(1)
C(15)	7164(5)	-111(2)	775(5)	35(2)
C(16)	8386(5)	-219(2)	1056(4)	29(1)
C(17)	11588(4)	1813(2)	4999(4)	18(1)
C(18)	11384(5)	2172(2)	4420(5)	27(1)
C(19)	11439(5)	2549(2)	4958(5)	38(2)
C(20)	11704(6)	2569(2)	6068(6)	43(2)
C(21)	11928(5)	2215(2)	6657(5)	40(2)
C(22)	11881(5)	1836(2)	6137(4)	28(1)
C(23)	12770(4)	1025(2)	4933(4)	15(1)
C(24)	13911(5)	1206(2)	5242(4)	20(1)
C(25)	14905(5)	974(2)	5683(4)	24(1)
C(26)	14770(5)	558(2)	5838(4)	27(1)
C(27)	13656(5)	377(2)	5540(4)	28(1)
C(28)	12654(5)	604(2)	5087(4)	23(1)
C(29)	10145(4)	1045(1)	4711(4)	16(1)
C(30)	9645(5)	1114(2)	5703(4)	21(1)
C(31)	8724(5)	856(2)	6016(4)	24(1)
C(32)	8318(5)	528(2)	5370(4)	25(1)
C(33)	8808(5)	462(2)	4385(4)	28(1)
C(34)	9718(4)	723(2)	4050(4)	20(1)
C(35)	12922(4)	1481(1)	-188(4)	16(1)
C(36)	14171(5)	1506(2)	196(4)	22(1)
C(37)	15085(5)	1332(2)	-383(4)	26(1)
C(38)	14762(5)	1128(2)	-1350(4)	27(1)
C(39)	13533(5)	1100(2)	-1741(4)	28(1)
C(40)	12621(5)	1275(2)	-1172(4)	22(1)
C(41)	10322(4)	1661(2)	-343(4)	14(1)
C(42)	9905(5)	1982(2)	-1023(4)	22(1)
C(43)	8828(5)	1936(2)	-1722(4)	28(1)
C(44)	8162(5)	1571(2)	-1741(4)	24(1)
C(45)	8585(5)	1251(2)	-1085(4)	23(1)
C(46)	9660(5)	1294(2)	-393(4)	21(1)

C(47)	12023(4)	2245(1)	644(4)	16(1)
C(48)	11189(5)	2492(2)	1170(4)	20(1)
C(49)	11265(5)	2912(2)	1117(4)	23(1)
C(50)	12188(5)	3092(2)	575(4)	24(1)
C(51)	13018(5)	2856(2)	76(4)	25(1)
C(52)	12938(5)	2434(2)	105(4)	20(1)

Table S18. Bond lengths [Å] and angles [°] for 17.

Pd(1)-C(1)	1.994(5)
Pd(1)-P(1)	2.3306(13)
Pd(1)-P(2)	2.3389(12)
Pd(1)-I(1)	2.6682(5)
P(1)-C(17)	1.812(5)
P(1)-C(29)	1.830(5)
P(1)-C(23)	1.831(5)
P(2)-C(41)	1.821(5)
P(2)-C(47)	1.824(5)
P(2)-C(35)	1.832(5)
N(1)-C(7)	1.296(6)
N(1)-C(9)	1.407(6)
O(1)-C(8)	1.203(5)
O(2)-C(8)	1.378(6)
O(2)-C(7)	1.389(5)
C(1)-C(2)	1.392(6)
C(1)-C(6)	1.403(6)
C(2)-C(3)	1.395(7)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.376(7)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.365(7)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.407(6)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.453(6)
C(8)-C(9)	1.460(7)
C(9)-C(10)	1.343(6)
C(10)-C(11)	1.450(7)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.386(7)
C(11)-C(16)	1.391(7)
C(12)-C(13)	1.381(7)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.363(7)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.372(7)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.377(7)
C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500
C(17)-C(18)	1.376(7)
C(17)-C(22)	1.397(7)
C(18)-C(19)	1.391(7)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.359(8)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.367(8)
C(20)-H(20A)	0.9500
C(21)-C(22)	1.387(7)
C(21)-H(21A)	0.9500
C(22)-H(22A)	0.9500
C(23)-C(24)	1.386(7)
C(23)-C(28)	1.391(6)
C(24)-C(25)	1.381(7)
C(24)-H(24A)	0.9500
C(25)-C(26)	1.378(7)

C(25)-H(25A)	0.9500
C(26)-C(27)	1.358(7)
C(26)-H(26A)	0.9500
C(27)-C(28)	1.382(7)
C(27)-H(27A)	0.9500
C(28)-H(28A)	0.9500
C(29)-C(34)	1.376(7)
C(29)-C(30)	1.385(6)
C(30)-C(31)	1.382(7)
C(30)-H(30A)	0.9500
C(31)-C(32)	1.375(7)
C(31)-H(31A)	0.9500
C(32)-C(33)	1.371(7)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.388(7)
C(33)-H(33A)	0.9500
C(34)-H(34A)	0.9500
C(35)-C(40)	1.387(7)
C(35)-C(36)	1.389(7)
C(36)-C(37)	1.384(6)
C(36)-H(36A)	0.9500
C(37)-C(38)	1.370(7)
C(37)-H(37A)	0.9500
C(38)-C(39)	1.372(7)
C(38)-H(38A)	0.9500
C(39)-C(40)	1.376(7)
C(39)-H(39A)	0.9500
C(40)-H(40A)	0.9500
C(41)-C(42)	1.384(6)
C(41)-C(46)	1.390(6)
C(42)-C(43)	1.386(7)
C(42)-H(42A)	0.9500
C(43)-C(44)	1.390(7)
C(43)-H(43A)	0.9500
C(44)-C(45)	1.367(7)
C(44)-H(44A)	0.9500
C(45)-C(46)	1.379(7)
C(45)-H(45A)	0.9500
C(46)-H(46A)	0.9500
C(47)-C(52)	1.378(6)
C(47)-C(48)	1.403(6)
C(48)-C(49)	1.373(7)
C(48)-H(48A)	0.9500
C(49)-C(50)	1.372(7)
C(49)-H(49A)	0.9500
C(50)-C(51)	1.363(7)
C(50)-H(50A)	0.9500
C(51)-C(52)	1.378(7)
C(51)-H(51A)	0.9500
C(52)-H(52A)	0.9500

C(1)-Pd(1)-P(1)	85.51(13)
C(1)-Pd(1)-P(2)	88.56(13)
P(1)-Pd(1)-P(2)	167.76(5)
C(1)-Pd(1)-I(1)	173.81(14)
P(1)-Pd(1)-I(1)	90.54(3)
P(2)-Pd(1)-I(1)	94.41(3)
C(17)-P(1)-C(29)	108.1(2)
C(17)-P(1)-C(23)	103.9(2)

C(29)-P(1)-C(23)	100.8(2)
C(17)-P(1)-Pd(1)	108.98(16)
C(29)-P(1)-Pd(1)	115.92(16)
C(23)-P(1)-Pd(1)	118.11(15)
C(41)-P(2)-C(47)	102.1(2)
C(41)-P(2)-C(35)	102.8(2)
C(47)-P(2)-C(35)	104.3(2)
C(41)-P(2)-Pd(1)	114.33(15)
C(47)-P(2)-Pd(1)	110.38(16)
C(35)-P(2)-Pd(1)	120.86(15)
C(7)-N(1)-C(9)	105.4(4)
C(8)-O(2)-C(7)	105.9(4)
C(2)-C(1)-C(6)	117.4(4)
C(2)-C(1)-Pd(1)	119.4(3)
C(6)-C(1)-Pd(1)	123.2(3)
C(1)-C(2)-C(3)	121.8(5)
C(1)-C(2)-H(2A)	119.1
C(3)-C(2)-H(2A)	119.1
C(4)-C(3)-C(2)	119.7(5)
C(4)-C(3)-H(3A)	120.2
C(2)-C(3)-H(3A)	120.2
C(5)-C(4)-C(3)	120.1(5)
C(5)-C(4)-H(4A)	119.9
C(3)-C(4)-H(4A)	119.9
C(4)-C(5)-C(6)	120.7(5)
C(4)-C(5)-H(5A)	119.6
C(6)-C(5)-H(5A)	119.6
C(1)-C(6)-C(5)	120.3(4)
C(1)-C(6)-C(7)	121.2(4)
C(5)-C(6)-C(7)	118.5(4)
N(1)-C(7)-O(2)	115.1(4)
N(1)-C(7)-C(6)	129.9(4)
O(2)-C(7)-C(6)	115.0(4)
O(1)-C(8)-O(2)	121.8(5)
O(1)-C(8)-C(9)	132.6(5)
O(2)-C(8)-C(9)	105.5(4)
C(10)-C(9)-N(1)	131.3(5)
C(10)-C(9)-C(8)	120.6(5)
N(1)-C(9)-C(8)	108.1(4)
C(9)-C(10)-C(11)	132.6(5)
C(9)-C(10)-H(10A)	113.7
C(11)-C(10)-H(10A)	113.7
C(12)-C(11)-C(16)	117.9(5)
C(12)-C(11)-C(10)	123.8(5)
C(16)-C(11)-C(10)	118.3(4)
C(13)-C(12)-C(11)	120.4(5)
C(13)-C(12)-H(12A)	119.8
C(11)-C(12)-H(12A)	119.8
C(14)-C(13)-C(12)	121.0(5)
C(14)-C(13)-H(13A)	119.5
C(12)-C(13)-H(13A)	119.5
C(13)-C(14)-C(15)	119.4(5)
C(13)-C(14)-H(14A)	120.3
C(15)-C(14)-H(14A)	120.3
C(14)-C(15)-C(16)	120.4(5)
C(14)-C(15)-H(15A)	119.8
C(16)-C(15)-H(15A)	119.8
C(15)-C(16)-C(11)	120.9(5)
C(15)-C(16)-H(16A)	119.5

C(11)-C(16)-H(16A)	119.5
C(18)-C(17)-C(22)	118.3(5)
C(18)-C(17)-P(1)	119.4(4)
C(22)-C(17)-P(1)	122.2(4)
C(17)-C(18)-C(19)	120.8(5)
C(17)-C(18)-H(18A)	119.6
C(19)-C(18)-H(18A)	119.6
C(20)-C(19)-C(18)	120.5(6)
C(20)-C(19)-H(19A)	119.8
C(18)-C(19)-H(19A)	119.8
C(19)-C(20)-C(21)	119.7(6)
C(19)-C(20)-H(20A)	120.1
C(21)-C(20)-H(20A)	120.1
C(20)-C(21)-C(22)	120.8(6)
C(20)-C(21)-H(21A)	119.6
C(22)-C(21)-H(21A)	119.6
C(21)-C(22)-C(17)	119.9(5)
C(21)-C(22)-H(22A)	120.1
C(17)-C(22)-H(22A)	120.1
C(24)-C(23)-C(28)	118.1(5)
C(24)-C(23)-P(1)	120.7(4)
C(28)-C(23)-P(1)	121.1(4)
C(25)-C(24)-C(23)	120.8(5)
C(25)-C(24)-H(24A)	119.6
C(23)-C(24)-H(24A)	119.6
C(26)-C(25)-C(24)	120.2(5)
C(26)-C(25)-H(25A)	119.9
C(24)-C(25)-H(25A)	119.9
C(27)-C(26)-C(25)	119.4(5)
C(27)-C(26)-H(26A)	120.3
C(25)-C(26)-H(26A)	120.3
C(26)-C(27)-C(28)	121.2(5)
C(26)-C(27)-H(27A)	119.4
C(28)-C(27)-H(27A)	119.4
C(27)-C(28)-C(23)	120.2(5)
C(27)-C(28)-H(28A)	119.9
C(23)-C(28)-H(28A)	119.9
C(34)-C(29)-C(30)	119.9(4)
C(34)-C(29)-P(1)	116.2(4)
C(30)-C(29)-P(1)	123.6(4)
C(31)-C(30)-C(29)	119.2(5)
C(31)-C(30)-H(30A)	120.4
C(29)-C(30)-H(30A)	120.4
C(32)-C(31)-C(30)	121.0(5)
C(32)-C(31)-H(31A)	119.5
C(30)-C(31)-H(31A)	119.5
C(33)-C(32)-C(31)	119.7(5)
C(33)-C(32)-H(32A)	120.1
C(31)-C(32)-H(32A)	120.1
C(32)-C(33)-C(34)	119.9(5)
C(32)-C(33)-H(33A)	120.0
C(34)-C(33)-H(33A)	120.0
C(29)-C(34)-C(33)	120.3(5)
C(29)-C(34)-H(34A)	119.9
C(33)-C(34)-H(34A)	119.9
C(40)-C(35)-C(36)	117.7(4)
C(40)-C(35)-P(2)	121.5(4)
C(36)-C(35)-P(2)	120.8(4)
C(37)-C(36)-C(35)	121.2(5)

C(37)-C(36)-H(36A)	119.4
C(35)-C(36)-H(36A)	119.4
C(38)-C(37)-C(36)	119.9(5)
C(38)-C(37)-H(37A)	120.0
C(36)-C(37)-H(37A)	120.0
C(37)-C(38)-C(39)	119.6(5)
C(37)-C(38)-H(38A)	120.2
C(39)-C(38)-H(38A)	120.2
C(38)-C(39)-C(40)	120.6(5)
C(38)-C(39)-H(39A)	119.7
C(40)-C(39)-H(39A)	119.7
C(39)-C(40)-C(35)	120.9(5)
C(39)-C(40)-H(40A)	119.5
C(35)-C(40)-H(40A)	119.5
C(42)-C(41)-C(46)	119.0(4)
C(42)-C(41)-P(2)	122.9(4)
C(46)-C(41)-P(2)	118.1(4)
C(41)-C(42)-C(43)	119.8(5)
C(41)-C(42)-H(42A)	120.1
C(43)-C(42)-H(42A)	120.1
C(42)-C(43)-C(44)	120.4(5)
C(42)-C(43)-H(43A)	119.8
C(44)-C(43)-H(43A)	119.8
C(45)-C(44)-C(43)	119.9(5)
C(45)-C(44)-H(44A)	120.0
C(43)-C(44)-H(44A)	120.0
C(44)-C(45)-C(46)	119.8(5)
C(44)-C(45)-H(45A)	120.1
C(46)-C(45)-H(45A)	120.1
C(45)-C(46)-C(41)	121.0(5)
C(45)-C(46)-H(46A)	119.5
C(41)-C(46)-H(46A)	119.5
C(52)-C(47)-C(48)	118.5(5)
C(52)-C(47)-P(2)	124.4(4)
C(48)-C(47)-P(2)	116.8(4)
C(49)-C(48)-C(47)	120.4(5)
C(49)-C(48)-H(48A)	119.8
C(47)-C(48)-H(48A)	119.8
C(50)-C(49)-C(48)	119.7(5)
C(50)-C(49)-H(49A)	120.1
C(48)-C(49)-H(49A)	120.1
C(51)-C(50)-C(49)	120.5(5)
C(51)-C(50)-H(50A)	119.7
C(49)-C(50)-H(50A)	119.7
C(50)-C(51)-C(52)	120.4(5)
C(50)-C(51)-H(51A)	119.8
C(52)-C(51)-H(51A)	119.8
C(51)-C(52)-C(47)	120.3(5)
C(51)-C(52)-H(52A)	119.8
C(47)-C(52)-H(52A)	119.8

Symmetry transformations used to generate equivalent atoms:

Table S19. Anisotropic displacement parameters ($Å^2$x 10^3) for 17. 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)	10(1)	14(1)	13(1)	0(1)	3(1)	0(1)
I(1)	15(1)	26(1)	25(1)	1(1)	5(1)	2(1)
P(1)	13(1)	16(1)	14(1)	-1(1)	3(1)	0(1)
P(2)	12(1)	16(1)	13(1)	1(1)	3(1)	2(1)
N(1)	15(2)	13(2)	15(2)	-2(2)	2(2)	-2(2)
O(1)	22(2)	19(2)	41(2)	-5(2)	-5(2)	4(2)
O(2)	13(2)	15(2)	25(2)	-3(2)	-5(2)	4(2)
C(1)	13(3)	22(3)	10(2)	4(2)	-2(2)	-5(2)
C(2)	18(3)	17(3)	15(3)	7(2)	2(2)	-2(2)
C(3)	25(3)	30(3)	20(3)	-2(3)	7(2)	-13(3)
C(4)	6(3)	42(4)	21(3)	2(3)	0(2)	-4(3)
C(5)	10(3)	28(3)	22(3)	-2(2)	5(2)	6(2)
C(6)	8(3)	22(3)	12(3)	1(2)	2(2)	4(2)
C(7)	16(3)	17(3)	11(3)	0(2)	5(2)	6(2)
C(8)	22(3)	19(3)	17(3)	2(2)	-1(2)	-2(3)
C(9)	18(3)	19(3)	18(3)	-3(2)	1(2)	3(2)
C(10)	25(3)	14(3)	23(3)	-3(2)	4(2)	1(2)
C(11)	17(3)	16(3)	22(3)	0(2)	4(2)	-1(2)
C(12)	20(3)	22(3)	17(3)	2(2)	5(2)	-5(2)
C(13)	23(3)	24(3)	26(3)	-1(2)	2(2)	7(3)
C(14)	16(3)	35(4)	30(3)	-2(3)	-4(2)	-3(3)
C(15)	25(3)	36(4)	43(4)	2(3)	-1(3)	-12(3)
C(16)	30(3)	18(3)	37(3)	-3(3)	-4(3)	1(3)
C(17)	11(3)	22(3)	22(3)	1(2)	3(2)	-7(2)
C(18)	24(3)	26(3)	32(3)	-7(3)	7(3)	-2(3)
C(19)	32(4)	32(4)	51(4)	-5(3)	9(3)	-7(3)
C(20)	44(4)	24(4)	62(5)	-21(3)	15(4)	-12(3)
C(21)	32(4)	59(5)	32(4)	-26(3)	10(3)	-7(3)
C(22)	29(3)	28(3)	27(3)	-8(3)	6(3)	-1(3)
C(23)	14(3)	22(3)	10(3)	1(2)	7(2)	1(2)
C(24)	21(3)	25(3)	14(3)	1(2)	5(2)	-5(2)
C(25)	10(3)	40(4)	23(3)	3(3)	0(2)	-3(3)
C(26)	17(3)	34(4)	31(3)	1(3)	1(2)	8(3)
C(27)	29(3)	23(3)	32(3)	8(3)	-2(3)	8(3)
C(28)	19(3)	22(3)	28(3)	-2(2)	3(2)	-4(2)
C(29)	11(3)	17(3)	19(3)	8(2)	2(2)	3(2)
C(30)	28(3)	17(3)	18(3)	2(2)	8(2)	1(2)
C(31)	24(3)	30(3)	20(3)	2(3)	15(2)	5(3)
C(32)	22(3)	28(3)	27(3)	8(3)	11(2)	-10(3)
C(33)	27(3)	28(3)	28(3)	-8(3)	0(3)	-7(3)
C(34)	19(3)	23(3)	19(3)	-3(2)	5(2)	-5(2)
C(35)	17(3)	16(3)	16(3)	5(2)	7(2)	3(2)
C(36)	21(3)	29(3)	16(3)	4(2)	6(2)	4(2)
C(37)	21(3)	36(4)	22(3)	5(3)	7(2)	8(3)
C(38)	29(3)	28(3)	27(3)	5(3)	18(3)	10(3)
C(39)	36(4)	23(3)	25(3)	-8(3)	6(3)	1(3)
C(40)	24(3)	20(3)	24(3)	-1(2)	7(2)	0(2)
C(41)	9(2)	16(3)	18(3)	-2(2)	5(2)	1(2)
C(42)	26(3)	19(3)	21(3)	5(2)	-2(2)	-6(2)
C(43)	31(3)	25(3)	25(3)	3(3)	-11(3)	5(3)
C(44)	17(3)	31(4)	22(3)	-7(3)	-7(2)	0(3)
C(45)	24(3)	23(3)	24(3)	-6(3)	5(2)	-7(3)
C(46)	21(3)	22(3)	19(3)	1(2)	4(2)	2(3)

C(47)	13(3)	17(3)	18(3)	0(2)	-5(2)	1(2)
C(48)	22(3)	21(3)	19(3)	3(2)	5(2)	-1(2)
C(49)	23(3)	18(3)	28(3)	-5(2)	-4(2)	5(2)
C(50)	27(3)	15(3)	29(3)	5(2)	-5(3)	-3(3)
C(51)	24(3)	25(3)	27(3)	5(3)	6(2)	-11(3)
C(52)	20(3)	22(3)	20(3)	2(2)	8(2)	-1(2)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 17.

	x	y	z	U(eq)
H(2A)	13750	1946	2934	20
H(3A)	15891	1849	3293	29
H(4A)	16744	1198	3120	28
H(5A)	15469	645	2645	24
H(10A)	10665	-344	1573	25
H(12A)	9504	695	1519	24
H(13A)	7434	868	1064	29
H(14A)	5967	368	581	33
H(15A)	6563	-318	581	42
H(16A)	8617	-500	1059	35
H(18A)	11203	2163	3643	32
H(19A)	11290	2795	4547	46
H(20A)	11733	2827	6432	51
H(21A)	12119	2230	7432	48
H(22A)	12048	1593	6554	33
H(24A)	14009	1494	5150	24
H(25A)	15685	1102	5880	29
H(26A)	15450	399	6151	33
H(27A)	13563	90	5644	34
H(28A)	11883	471	4881	27
H(30A)	9931	1337	6162	25
H(31A)	8367	905	6689	29
H(32A)	7700	348	5604	30
H(33A)	8524	238	3931	34
H(34A)	10049	680	3363	24
H(36A)	14402	1644	869	26
H(37A)	15936	1354	-111	31
H(38A)	15387	1007	-1748	33
H(39A)	13308	958	-2410	33
H(40A)	11774	1255	-1458	27
H(42A)	10356	2233	-1010	27
H(43A)	8544	2156	-2192	33
H(44A)	7414	1543	-2209	29
H(45A)	8138	999	-1105	28
H(46A)	9953	1070	57	25
H(48A)	10568	2368	1565	25
H(49A)	10682	3078	1454	28
H(50A)	12248	3382	547	29
H(51A)	13654	2983	-294	30
H(52A)	13518	2272	-248	24