Electronic supplementary information

Formation of CC-type palladacycles with assistance from an apparently innocent NH(CO) functional group

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General consideration. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with standard procedures. Starting chemicals were purchased from commercial source and used as received. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded at 300.13, 75.48, and 121.49 MHz, respectively, on a Bruker AV-300 spectrometer. Infra-red spectra were acquired from a Varian Cary 640 infra-red spectrophotometer. Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. Electrospray ionization (ESI) and atmospheric-pressure chemical ionization (APCI) mass spectrometry were performed on a Finnigan/Thermo TSQ Quantum triple quadrupole mass spectrometer.

Synthesis of L^{1}. A mixture of 1-(4-fluorobenzyl)-2-methyl-1*H*-imidazole (10.9 g, 0.0570 mol) and 2-chloro-*N*-phenylacetamide[1] (9.70 g, 0.0570 mol) in THF (30 mL) was placed in a Schlenk flask. The mixture was heated under reflux for 2 d. After cooling, the white solid was collected on a frit, washed with THF, and dried under vacuum. Yield: 15.4 g (75%). Anal. Calc. for $C_{19}H_{19}ClFN_3O$: C, 63.42; H, 5.32; N, 11.67%. Found: C, 63.42; H, 5.37; N, 11.70 %. ^{1}H NMR (DMSO-d_6): δ 2.26 (s, 3H, CH_3), 5.29 (s, 2H, CH_2), 5.50 (s, 2H, CH_2), 7.10 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, *p*-Ph-*H*), 7.25–7.46 (m, 6H, Ar-*H*, imi-*H*), 7.65 (d, $^{3}J_{HH}$ = 7.5 Hz, 2H, *o*-Ph-*H*), 7.81–7.83 (m, 2H, Ar-*H*, imi-*H*), 11.22 (s,

1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 10.3 (*C*H_3), 50.3 (N*C*H_2), 51.0 (*C*H_2CO), 116.3 (d, J_{CF} = 21.66 Hz, *C*H), 119.6, 121.7, 123.4, 124.1, 129.2, 130.6(d, J_{CF} = 8.38 Hz, *C*H), 131.2(d, J_{CF} = 3.02 Hz, *C*H), 138.9 (Ar-*C*, imi-*C*), 146.1 (N*C*N), 162.4 (d, J_{CF} = 301.6 Hz, *C*F), 163.9 (*C*O).

Synthesis of L^2. A mixture of 1-(naphthalen-1-ylmethyl)-2-phenyl-1*H*-imidazole (6.45 g, 0.0230 mol) and 2-chloro-N-phenylacetamide (3.46 g, 0.0230 mol) in dry THF (50 mL) was heated at 80ºC for 2 d. The workup procedure is similar to that of L^1. Yield: 5.11 g (49 %). M.p.: 218.9–219.4°C. Anal. Calc. for $C_{28}H_{24}ClN_3O$: C, 74.08; H, 5.32; N, 9.25 %. Found: C, 73.82; H, 5.36; N, 9.28 %. ^1H NMR (DMSO-d_6): δ 5.17 (s, 2H, NpCH_2), 5.87 (s, 2H, CH_2C=O), 7.03–7.08 (m, 2H, Ar-*H*), 7.29 (t, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 7.46 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-Ar-*H*), 7.54–7.67 (m, 9H, Ar-*H*), 7.82-7.99 (m, 3H, Ar-*H*), 8.05 (d, $^3J_{HH}$ = 1.5 Hz, 1H, imi-*H*), 8.20 (d, $^3J_{HH}$ = 1.8 Hz, 1H, imi-*H*), 11.31 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 50.1 (*C*H_2), 51.6 (*C*H_2), 119.1, 121.2, 123.0, 124.2, 124.7, 125.5, 125.8, 126.8, 127.3, 129.1, 129.4, 129.8, 130.1, 130.5, 130.6, 132.9, 133.5, 138.7 (N*C*), 146.0 (N*C*N), 163.8 (*C*O).

Synthesis of L^3. The compound was prepared with a similar procedure to that of L^1. A mixture of 1-(4-fluorobenzyl)-2-methyl-1*H*-imidazole (3.16 g, 0.0170 mol) and 2-chloro-*N*-methyl-*N*-phenylacetamide (3.04 g, 0.0170 mol) was used. A white solid was obtained. Yield: 2.73 g （77 %). M.p.: 235.8–236.2°C. Anal. Calc. for $C_{20}H_{21}ClFN_3O$: C, 64.25; H, 5.66; N, 11.23 %. Found: C, 64.51; H, 5.62; N, 11.24 %. ^1H NMR (DMSO-d_6): δ 2.56 (s, 3H, C*C*H_3), 3.21 (s, 3H, NCH_3), 7.26 (t, 2H, $^3J_{HH}$ = 8.7 Hz, Ar-*H*), 7.32–7.86 (m, 9H, Ar-*H*, imi-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 10.2 (C*C*H_3), 37.8 (N*C*H_3), 50.2 (N*C*H_2, *C*H_2CO), 116.3 (d, J_{CF} = 21.66 Hz, *C*H),

121.5, 123.5, 128.0, 128.9, 130.4 (d, J_{CF} = 8.68 Hz, *C*H), 131.3(d, J_{CF} = 3.02 Hz, *C*H),141.8 (Ar-*C*, imi-*C*), 146.2 (N*C*N), 162.4 (d, J_{CF} = 245 Hz, *C*F), 164.4 (*C*O).

Synthesis of 1. Method A: To a 50 mL Schlenk fask, $PdCl_2$ (0.0940 g, 0.530 mmol), L^1 (0.190 g, 0.530 mmol), and K_2CO_3 (0.290 g, 2.12 mmol) were added and dissolved in dry pyridine (10 mL) under nitrogen atmosphere. The solution was allowed to stir at 80°C overnight. The solvent was then completely removed under vacuum. The residue was re-dissolved in dichloromethane and washed with water. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a light orange solid. Yield: 0.190 g (66%). Method B: To a 20 mL Schlenk flask, **3** (0.0500 g, 0.092 mmol) and dry pyridine (5 mL) were added. The solution was then stirred at 80°C overnight. The solvent was removed completely under vacuum. The residue was washed with diethyl ether. The light orange solid was then filtered on a frit and dried under vacuum. Yield: 0.0490 g (97%). Mp: 142.3-144.8°C. Anal. Calc. for $C_{24}H_{22}ClFN_4OPd$: C, 53.05; H, 4.08; N, 10.31. Found: C, 52.76; H, 4.15; N, 10.05 %. ^{1}H NMR ($CDCl_3$): δ 1.97 (d, $^2J_{HH}$ = 15.3 Hz, 1H, PdCH_aH$_b$), 2.44 (d, $^2J_{HH}$ = 15.3 Hz, 1H, PdCH$_a$$H_b$), 4.89, 4.97 (ABq, $^2J_{AB}$ = 15.3 Hz, $\Delta\nu_{AB}$ = 12.3 Hz, 2H, NCH_2), 5.32 (s, 1H, C*H*C=O), 6.68–7.31 (m, 11H, Ar-*H*, imi-*H*, py-*H*), 7.62–7.72 (m, 3H, py-*H*, Ar-*H*), 8.70 (d, $^3J_{HH}$ = 5.1 Hz, 2H, *o*-py-*H*), 9.89 (s, 1H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 4.1 (Pd*C*H$_2$), 49.2 (Ar*C*H$_2$), 49.5 (*C*HC=O), 116.3 (d, J_{CF} = 21.8 Hz, *C*H), 119.1, 120.8, 122.5, 124.2, 124.7 (py-*C*), 124.9, 128.8, 129.3 (d, J_{CF} = 8.3 Hz, *C*H), 137.2 (py-C), 138.5, 150.3 (py-*C*), 152.4 (J_{CF} = 127.2 Hz, *C*F), 161.2 (N*C*N), 174.1 (*C*=O). IR (KBr/pellet, cm^{-1}): 3359 (br, w), 3160 (br, w), 2998 (br, w), 1675 (w), 1625 (s), 1521 (m), 1502 (w), 1457 (s), 1423 (s), 1319 (w), 1272 (m), 1238 (m), 1205 (m), 1166 (br, m),

1054 (m), 989 (w), 927 (w), 875 (w), 808 (m), 775 (w), 711 (s), 680 (s), 582 (w), 539 (w), 476 (w), 420 (w). ESI-MS: *m/z* 585.9 $[M - Cl + py]^+$, 548.1 $[M - Cl + CH_3CN]^+$, 507.1 $[M - Cl]^+$, 501.0 $[M - Cl - py + DMF]^+$, 469.0 $[M - Cl - py + CH_3CN]^+$.

Synthesis of 2. Method A: A mixture of **1** (0.0340 g, 0.0625 mmol) and PPh_3 (0.0164 g, 0.0625 mmol) inf dichloromethane (10 mL) was stirred at ambient temperature overnight. The solvent was removed completely under vacuum. The residue was washed thoroughly with diethyl ether to afford a yellowish solid. Yield: 0.0382 g (84 %). Method B: A mixture of **4** (0.0810 g, 0.111 mmol) in dry pyridine (5 mL) was stirred at 80°C overnight. The solvent was removed completely under vacuum. The residue was washed with diethyl ether. The solid was then filtered on a frit and dried under vacuum. Yield: 0.0702 g (87%). M.p.: 183.5–184.7ºC. Anal. Calc. for $C_{37}H_{32}ClFN_3OPPd$: C, 61.16; H, 4.43; N, 5.78 %. Found: C, 61.34; H, 4.53; N, 5.36 %. ^{1}H NMR ($CDCl_3$): δ 1.32 (dd, $^2J_{HH}$ = 16.2 Hz, $^3J_{HP}$ = 7.5 Hz, 1H, PdCH_aH$_b$), 1.77 (dd, $^2J_{HH}$ = 16.8 Hz, $^3J_{HP}$ = 7.5 Hz, 1H, PdCH$_a$$H_b$) , 4.59 (s, 2H, NC$H_2$), 5.30 (d, 1H, $^3J_{PH}$ = 11.1 Hz, C*H*CO), 6.82–7.69 (m, 26H, Ar-*H*, imi-*H*), 9.99 (s, 1H, N*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 7.6 (d, J_{PC} = 7.4 Hz, Pd*C*H$_2$), 49.5 (Ar*C*H$_2$), 60.2 (d, J_{PC} = 97.6 Hz, *C*HCO), 116.2 (d, J_{CF} = 21.8 Hz, *C*H), 119.3, 121.2. (d, J_{PC} = 3.7 Hz, Ph-*C*), 122.2, 122.5, 128.1 (d, J_{PC} = 9.5 Hz, *C*H), 128.5, 129.2, 129.6 (d, J_{CF} = 8.5 Hz, *C*H), 130.0 (d, J_{PC} = 1.9 Hz, *C*H), 131.6, 132.1, 134.5 (d, J_{PC} = 12.1 Hz, *C*H), 139.8, 161.3 (d, J_{PC} = 9.2 Hz, N*C*N), 162.7 (J_{CF} = 248.9 Hz, *C*F), 173.7 (d, J_{PC} = 3.8 Hz, *C*O). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.4. IR (KBr/pellet, cm^{-1}): 3315 (br, w), 3197 (w), 3153 (w), 3087 (w), 3016 (w), 1675 (m), 1629 (s), 1560 (s), 1519 (m), 1459 (s), 1421 (m), 1303 (w), 1272 (m), 1234 (w), 1207 (m), 1168 (m), 1118 (m), 1083 (m), 971 (w), 910 (w), 871 (w),

808 (w), 769 (m), 719 (s), 688 (m), 570 (w), 539 (m), 518 (m), 476 (m), 439 (w). APCI-MS: *m/z* 725.5 $[M + H]^+$, 690.1 $[M - Cl]^+$.

Synthesis of 3. To a 20 mL Schlenk fask, $PdCl_2$ (0.0990 g, 0.556 mmol), L^1 (0.200 g, 0.556 mmol), and K_2CO_3 (0.308 g, 2.22 mmol) were dissolved in dry pyridine (10 mL) under nitrogen atmosphere. The solution was allowed to stir at ambient temperature for 5 h. The workup procedure was similar to that of **1** (method A). A yellowish solid was obtained. Yield: 0.154 g (51%). M.p.: 176.7–178.9°C. Anal. Calc. for $C_{24}H_{22}ClFN_4OPd$: C, 53.05; H, 4.08; N, 10.31 %. Found: C, 53.20; H, 4.12; N, 10.23 %. ^{1}H NMR ($CDCl_3$): δ 2.80 (s, 3H, C*H*$_3$), 4.56 (s, 1H, PdC*H*), 5.10 (s, 2H, ArC*H*$_2$), 6.85–7.21 (m, 12H, Ar-*H*, imi-*H*, py-*H*), 7.65 (t, 1H, $^3J_{HH}$ = 7.5 Hz, py-*H*), 7.74 (s, 1H, imi-*H*), 8.52 (d, $^3J_{HH}$ = 4.8 Hz, 2H, py-*o*-*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 10.6 (*C*H$_3$), 50.0 (*C*H$_2$), 79.5 (*C*HCO), 116.1 (d, J_{CF} = 21.7 Hz, *C*H), 121.2, 121.5, 122.7, 123.2, 124.3 (py-*C*), 127.9, 130.0 (d, J_{CF} = 8.3 Hz, *C*H), 131.3, 136.5 (py-*C*), 145.3, 146.6 (N*C*N), 150.0 (py-*C*), 162.3 (J_{CF} = 244.6 Hz, *C*F), 170.7 (*C*O). IR (KBr/pellet, cm^{-1}): 3288 (br, w), 3197 (w), 1654 (s), 1594 (w), 1569 (w), 1544 (m), 1471 (s), 1438 (s), 1344 (w), 1276 (m), 1209 (m), 1130 (w), 1054 (m), 937 (w), 879 (w), 806 (m), 719 (m), 680 (m), 644 (m), 563 (w), 501 (w), 455 (s), 431 (s). ESI-MS: *m/z* 585.9 [M – Cl + py]$^+$, 543.0 $[M + H]^+$, 507.1 $[M - Cl]^+$, 466.1 [M – py + H]$^+$, 428.1 [M – Cl – py]$^+$.

Synthesis of 4. A mixture of **3** (0.0516 g, 0.0940 mmol) and PPh_3 (0.0249 g, 0.0940 mmol) in dichloromethane (10 mL) was stirred at ambient temperature overnight. The solvent was removed completely under vacuum. The residue was washed thoroughtly with diethyl ether to afford a yellowish solid. Yield: 0.0650 g (94 %). Mp: 178.6–180.5ºC. Anal. Calc. for $C_{37}H_{32}ClFN_3OPPd$: C,

61.16; H, 4.43; N, 5.78. Found: C, 61.19; H, 4.86; N, 5.31 %. ^{1}H NMR (DMSO-d_6): δ 2.32 (s, 3H, CH_3), 4.09 (s, 1H, PdC*H*), 5.09 (s, 2H, PhCH_2), 6.08 (t, 1H, $^{3}J_{HH}$ = 6.9 Hz, Ph-*H*), 7.05–7.99 (m, 25H, Ar-*H*, imi-*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 10.0 (*C*H$_3$), 31.1 (*C*HCO), 49.7 (*C*H$_2$), 116.2 (d, J_{CF} = 21.7 Hz, *C*H), 120.0, 121.2, 123.6, 127.8, 128.5 (d, J_{PC} = 10.1 Hz, Ph-*C*), 129.2 (d, J_{CF} = 11.8 Hz, *C*H), 130.7, 131.1 (d, J_{PC} = 8.5 Hz, Ph-*C*), 131.7, 131.9 (d, J_{PC} = 9.7 Hz, Ph-*C*), 132.3, 134.4 (d, J_{PC} = 11.8 Hz, Ph-*C*), 147.4 ((N*C*N), 162.5 (J_{CF} = 245.3 Hz, *C*F), 172.6 (*C*O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 28.4. IR (KBr/pellet, cm^{-1}): 3326 (br, w), 2996 (w), 1720 (m), 1654 (s), 1639 (s), 1596 (w), 1542 (s), 1500 (m), 1459 (s), 1425 (m), 1400 (m), 1342 (m), 1245 (m), 1213 (m), 1185 (m), 1081 (m), 919 (w), 800 (m), 728 (s), 676 (m), 553 (m), 522 (m), 482 (m), 447 (m), 424 (m). APCI-MS: *m/z* 726.1 [M + H$^+$], 690.1 [M – Cl]$^+$.

Synthesis of 5. Method A: The compound was prepared with a procedure similar to that of **1** (method A). A mixture of PdCl$_2$ (0.0781 g, 0.441 mmol), L^2 (0.200 g, 0.441 mmol), and K$_2$CO$_3$ (0.243 g, 1.76 mmol) was used. A yellowish solid was obtained. Yield: 0.220 g (80 %). Method B: The compound was prepared with a procedure similar to that of **1** (method B). A pyridine solution of **6** (0.0500 g, 0.0780 mmol) was used. Yield: 0.0470 g (94%). M.p.: 198.3–199.1ºC. Anal. Calc. for C$_{33}$H$_{27}$ClN$_4$OPd: C, 62.17; H, 4.26; N, 8.78. Found: C, 62.20; H, 4.42; N, 8.63 %. ^{1}H NMR (CDCl$_3$): δ 5.89, 5.98 (ABq, $^{2}J_{AB}$ = 15.9 Hz, Δν$_{AB}$ = 13.7 Hz, 2H, NCH_2), 6.10 (s, 1H, C*H*C=O), 6.78–7.96 (m, 22H, Ar-*H*, imi-*H*, py-*H*), 8.88 (d, $^{3}J_{HH}$ = 4.5 Hz, 2H, *o*-py-*H*), 9.14 (s, 1H, N*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 49.9 (N*C*H), 51.1 (*C*H$_2$), 118.1, 122.4, 122.6, 123.2, 124.9 (py-*C*), 125.8, 126.7, 127.3, 127.7, 128.9, 129.1, 129.3, 129.5, 130.1, 131.1, 132.5, 133.4, 133.7, 138.0 (py-*C*), 139.7,

149.8 (N*C*N), 152.3 (py-*C*), 153.3, 172.4 (*C*=O). IR (KBr/pellet, cm^{-1}): 3372 (br, w), 3207 (w), 3087 (w), 2979 (w), 1687 (m), 1637 (s), 1560 (s), 1508 (m), 1457 (s), 1425 (m), 1334 (w), 1276 (m), 1228 (m), 1197 (m), 1133 (br, m), 1049 (w), 991 (w), 927 (w), 827 (m), 777 (m), 736 (m), 709 (m), 680 (s), 599 (w), 547 (w), 520 (w), 491 (w), 449 (w), 426 (w). ESI-MS: *m/z* 600.9 $[M - Cl]^+$, 562.7 $[M - Cl - py + CH_3CN]^+$, 522.1 $[M - Cl - py]^+$.

Synthesis of 6. A mixture of $PdCl_2$ (0.0780 g, 0.441 mmol), L^2 (0.200 g, 0.441 mmol), and K_2CO_3 (0.240 g, 1.76 mmol) in pyridine (10 mL) was stirred at room temperature overnight. The workup procedure was similar to that of **1** (method A). A yellowish solid was obtained. Yield: 0.18 g (65 %). M.p.: = 185.8–187.1ºC. Anal. Calc. for $C_{33}H_{27}ClN_4OPd$: C, 62.17; H, 4.26; N, 8.78. Found: C, 61.60; H, 4.35; N, 8.36 %. ^{1}H NMR ($CDCl_3$): δ 4.56 (s, 1H, PdC*H*), 5.46 (s, 2H, CH_2), 6.25–7.89 (m, 22H, 8.50 (d, $^3J_{HH}$ = 4.8 Hz, 2H, *o*-py-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 49.9 (*C*H_2), 121.7, 122.0, 123.0, 123.2, 124.3 (py-*C*) , 124.7, 125.8, 126.8, 127.3, 127.9, 129.1, 129.3, 129.7, 129.9, 130.6, 130.9, 132.6, 133.4, 136.5 (py-*C*), 146.4 (N*C*N), 150.0 (py-*C*), 153.4, 171.0 (*C*=O). IR (KBr/pellet, cm^{-1}): 3293 (br, w), 3174 (w), 3143 (w), 3008 (w), 1685 (w), 1654 (w), 1608 (m), 1562 (w), 1544 (m), 1508 (s), 1473 (s), 1413 (s), 1349 (w), 1274 (w), 1226 (w), 1197 (m), 1130 (m), 1049 (m), 987 (w), 827 (m), 777 (m), 736 (m), 682 (s), 559 (w), 520 (w), 484 (w), 458 (w), 431 (w). ESI-MS: *m/z* 675.9 $[M - Cl + DMF]^+$, 638.8 $[M + H]^+$, 601.1 $[M - Cl]^+$, 594.9 $[M - Cl - py + DMF]^+$, 562.9 $[M - Cl - py + CH_3CN]^+$, 560.9 $[M - py]^+$, 522.1 $[M - Cl - py]^+$.

Synthesis of 7. The compound was prepared with a procedure similar to that of **4**. A mixture of **6** (0.0238 g, 0.0909 mmol), PPh_3 (0.0580 g, 0.0909 mmol) was used. A yellowish product was

obtained. Yield: 0.0680 g (92 %). M.p.: 178.1–181.2ºC. Anal. Calc. for $C_{46}H_{37}ClN_3OPPd$: C, 67.32; H, 4.54; N, 5.12. Found: C, 67.04; H, 4.70; N, 4.83 %. ^{1}H NMR (DMSO-d_6): δ 4.00 (s, 1H, PdC*H*), 5.59 (s, 2H, CH_2), 6.79–7.97 (m, 34H, Ar-*H*, imi-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.6 (*C*H_3), 50.0 (*C*H_2), 79.5 (*C*HC=O), 116.1 (d, J_{CF} = 21.7 Hz, *C*H), 121.2, 121.5, 122.7, 123.2, 124.3 (py-*C*), 127.9, 130.0 (d, J_{CF} = 8.3 Hz, *C*H), 131.3, 136.5 (py-*C*), 145.3, 146.6 (N*C*N), 150.0 (py-*C*), 162.3 (J_{CF} = 244.6 Hz, *C*F), 170.7 (*C*=O). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 28.3. IR (KBr/pellet, cm^{-1}): 3461 (br, w), 3056 (w), 2933 (w), 1695 (w), 1681 (w), 1621 (s), 1589 (m), 1486 (m), 1434 (m), 1363 (m), 1263 (w), 1184 (m), 1097 (m), 1027 (w), 998 (w), 879 (w), 786 (m), 750 (m), 696 (s), 534 (s), 511 (m), 451 (w), 433 (w). ESI-MS: *m/z* 860.1 $[M + K]^+$, 856.8 $[M - Cl + DMF]^+$, 824.5 $[M - Cl + CH_3CN]^+$, 820.2 $[M + H]^+$, 784.3 $[M - Cl]^+$.

Synthesis of 8. To a 20 mL Schlenk flask, $PdCl_2$ (0.0948 g, 0.534 mmol), L^3 (0.200 g, 0.534 mmol), and K_2CO_3 (0.295 g, 2.14 mmol) were added and dissolved in dry pyridine (10 mL) under nitrogen atmosphere. The solution was allowed to stir at 80°C overnight. The solvent was then completely removed under vacuum. The residue was re-dissolved in dichloromethane and washed with water. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a solid. Diethyl ether was added and the yellowish solid formed was collected on frit, washed with more diethyl ether and methanol, and dried under vacuum. Yield: 0.143 g (48 %). M.p.: 164.8–165.6°C. Anal. Calc. For $C_{25}H_{24}ClFN_4OPd$: C, 53.87; H, 4.34; N, 10.05. Found: C, 53.10; H, 4.44; N, 10.13 %. ^{1}NMR ($CDCl_3$): δ 2.82 (s, 3H, imi-CH_3), 3.38 (s, 3H, N-CH_3), 4.98, 5.18 (ABq, $^3J_{AB}$ = 15.6 Hz, $\Delta\nu_{AB}$ = 29.7 Hz, 2H, CH_2), 5.61 (s, 1H, PdC*H*), 6.57–7.29 (m, 12H, Ar-*H*, imi-*H*,

Py-H), 7.66 (t, $^{3}J_{HH}$ = 8.1 Hz, 1H, Py-*p*-H), 8.80 (d, $^{3}J_{HH}$ = 4.8 Hz, 2H, Py-*o*-H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6): δ 14.0 (*C*H$_3$), 33.3 (*C*H$_3$), 48.7 (*C*HC=O), 49.7 (*C*H$_2$), 116.0 (d, J_{CF} = 21.6 Hz, *C*H), 116.4, 123.4, 124.2, 124.6, 124.3, 129.9 (d, J_{CF} = 8.2 Hz, *C*H), 131.8, 137.6, 144.3 (N*C*N), 162.2 (J_{CF} = 244.5 Hz, *C*F), 169.7 (*C*=O). IR (KBr/pellet, cm^{-1}): 3394 (w), 3345 (w), 3318 (w), 3232 (w), 3176 (w), 3100 (w), 3018 (w), 1656 (m), 1617 (m), 1585 (s), 1544 (s), 1484 (s), 1438 (w), 1402 (m), 1319 (m), 1278 (m), 1243 (m), 1203 (s), 1139 (m), 1083 (m), 958 (m), 908 (br, m), 802 (m), 734 (m), 711 (m), 630 (w), 578 (w), 514 (w), 476 (m), 420 (w). ESI-MS: *m/z* 521.0 [M – Cl – py + 2CH$_3$CN]$^+$, 514.9 [M – Cl – py + DMF]$^+$, 482.9 [M – Cl – py + CH$_3$CN]$^+$.

Synthesis of 9. In a 20 mL Schlenk flask, a THF (5 mL) solution of **8** (0.0826 g, 0.148 mmol) was heated at 50 °C for 3 h. The solid was collected on a frit, washed with THF, and dried under vacuum. Yield: 0.0636 g (90%). M.p.: 202.1–203.0 ºC. Anal. Calc. for $C_{40}H_{38}Cl_2F_2N_6O_2Pd_2$: C, 50.22; H, 4.00; N, 8.78. Found: C, 49.97; H, 3.80; N, 8.85 %. ^{1}H NMR (DMSO-d_6): δ 2.58 (s, 6H, CC*H*$_3$), 3.20 (s, 6H, NC*H*$_3$), 5.34 (s, 4H, NC*H*$_2$), 5.52 (s, 2H, PdC*H*), 6.81–7.69 (m, 20H, Ar-*H*, imi-*H*). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6): δ 14.0 (*C*H$_3$), 33.3 (N*C*H$_3$), 48.7 (*C*HCO), 49.7 (*C*H$_2$), 116.0 (d, J_{CF} = 21.6 Hz, *C*H), 116.4, 123.4, 124.2, 124.6, 124.3, 129.9 (d, J_{CF} = 8.2 Hz, *C*H), 131.8, 137.6, 144.3 (N*C*N), 162.2 (J_{CF} = 244.5 Hz, *C*F), 169.7 (*C*O). IR (KBr/pellet, cm^{-1}): 3324 (br, w), 3180 (w), 3043 (w), 2886 (w), 1718 (m), 1685 (m), 1654 (s), 1639 (s), 1594 (s), 1560 (m), 1542 (s), 1527 (s), 1498 (s), 1475 (s), 1438 (m), 1398 (m), 1276 (w), 1245 (m), 1214 (m), 1166 (w), 1139 (m), 1083 (m), 966 (w), 889 (w), 794 (m), 765 (w), 725 (m), 632 (w), 599 (m), 499 (m), 482 (s), 464 (m), 430 (m). ESI-MS: *m/z* 920.8 [M – Cl]$^+$, 514.9 [M/2 – Cl + DMF]$^+$, 482.9 [M/2 – Cl + CH$_3$CN]$^+$.

X-ray diffraction studies. Crystal structures were collected at 150(2) K on a Bruker APEX II equipped with a CCD area detector and a graphite monochromater utilizing Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by least-squares refinement. Data collection and reduction were performed using the Bruker APEX2 and SAINT software.[2] Absorption corrections were performed using the SADABS program.[3] All the structures were solved by direct methods and refined by full-matrix least squares methods against F^2 with the SHELXTL software package.[4] All non-H atoms were refined anisotropically. All H-atoms were fixed at calculated positions and refined with the use of a riding model. In the structure of **7**·C_3H_7NO, the DMF solvent is disordered with two orientations of 50:50 occupancy ratio. The disordered molecule was successfully refined as a rigid group. The SIMU instruction is used for C47 to O2 and C47a to O2A. Crystallographic data are listed in Table 1. CCDC-850737 (**1**), -850738 (**2**), -850739 (**4**·0.5$C_4H_{10}O$·C_3H_7NO), -850740 (**5**·CH_2Cl_2), -850741 (**7**·C_3H_7NO), and -850742 (**9**·4C_3H_7NO) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details. All computational results were calculated with Gaussian 09 program.[5] Density functional theory (DFT) with B3LYP/LANL2DZ level of theory was applied for all calculations. For solvent correction, a Polarized Continuum (overlapping spheres) model (PCM) with pyridine as solvent was used. The computational results for three most stable structural isomers **S1**, **S2**, **S3** and proposed transition state **TS1** are listed in the Table 5S. As shown in the Table 5S, the solvent effect is very small (barrier reduced from 38.1 to 35.3 kcal/mole). However, this barrier reduced significantly (from 38.1 to 25.9 kcal/mole) when additional pyridine molecule is added into the system. Although the complex **TS1+Pyridine** (Figure S3) might be an intermediate instead of transition state (since the imaginary frequency is only -18 cm^{-1}), the results suggest that pyridine might play a catalytic role in the reaction.

Table S1. Crystallographic data.

	1	**2**	**4**·0.5$C_4H_{10}O$·C_3H_7NO	**5**·CH_2Cl_2	**7**·C_3H_7NO	**9**·4C_3H_7NO
empirical formula	$C_{25}H_{24}Cl_3FN_4OPd$	$C_{37}H_{32}ClFN_3OPPd$	$C_{37}H_{32}ClFN_3OPPd$ ·0.5$C_4H_{10}O$·C_3H_7NO	$C_{33}H_{27}ClN_4OPd$ ·CH_2Cl_2	$C_{46}H_{37}ClN_3OPPd$ ·C_3H_7NO	$C_{40}H_{38}Cl_2F_2N_6O_2Pd_2$ ·4C_3H_7NO
formula weight	628.23	726.48	836.13	722.36	893.70	1248.85
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.5854(5)	9.3340(4)	14.5982(11)	9.8587(2)	12.507(6)	9.4686(11)
b, Å	10.3690(6)	10.4256(4)	16.6492(13)	11.1511(3)	13.088(12)	11.5276(14)
c, Å	14.3676(7)	18.9156(8)	17.5208(15)	15.0170(4)	14.438(7)	13.1627(16)
α, deg	83.969(2)	80.502(3)	81.635(6)	80.665(2)	103.747(9)	90.963(7)
β, deg	71.762(2)	77.272(2)	70.792(5)	89.264(2)	115.434(6)	106.242(6)
γ, deg	72.577(2)	68.741(2)	82.732(4)	73.218(2)	90.425(9)	94.606(7)
V, Å^3	1293.95(12)	1665.96(12)	3964.4(5)	1558.65(7)	2057(2)	1373.8(3)
T, K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Z	2	2	4	2	2	1
no. of unique data	6602	8601	17316	8024	10604	5937
no. of params refined	316	407	954	388	550	340
R_1[a] [$I > 2\sigma(I)$]	0.0466	0.0529	0.0588	0.0631	0.0663	0.0514
wR_2[b] (all data)	0.1048	0.1013	0.1387	0.1592	0.1846	0.1371

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$

Table S2. Selected bond distances (Å) and angles (°) of **1** and **2**.

	1		**2**
Pd1—C7	2.034(4)	Pd1—C1	2.036(4)
Pd1—C8	2.059(4)	Pd1—P1	2.0373(11)
Pd1—N1	2.101(3)	Pd1—Cl1	2.3810(12)
Pd1—Cl1	2.4093(3)	Pd1—C5	2.122(4)
C7—Pd1—C8	86.02(14)	C1—Pd1—C5	83.99(18)
C8—Pd1—Cl1	96.07(10)	C5—Pd1—Cl1	90.27(13)
Cl1—Pd1—N1	89.76(8)	P1—Pd1—Cl1	95.02(4)
C7—Pd1—N1	88.16(13)	C1—Pd1—P1	90.66(13)
C8—Pd1—N1	173.63(13)	C5—Pd1—P1	171.01(13)
C7—Pd1—Cl1	177.88(11)	C1—Pd1—Cl1	174.26(14)

Table S3. Selected bond distances (Å) and angles (°) of **4**·0.5$C_4H_{10}O$·C_3H_7NO.[a]

Pd1—C2	2.018(5)	Pd2—C39	2.036(5)
Pd1—N3	2.088(4)	Pd2—N6	2.078(4)
Pd1—Cl1	2.3960(15)	Pd2—Cl2	2.4010(14)
Pd1—P1	2.2317(16)	Pd2—P2	2.2408(16)
C2—Pd1—P1	98.30(17)	C39—Pd2—P2	100.14(16)
C2—Pd1—N3	67.0(2)	C39—Pd2—N6	66.63(19)
N3—Pd1—Cl1	103.02(13)	N6—Pd2—Cl2	102.24(12)
Cl1—Pd1—P1	91.48(6)	Cl2—Pd2—P2	91.07(5)
C2—Pd1—Cl1	169.70(16)	C39—Pd2—Cl2	168.74(16)
N3—Pd1—P1	164.86(13)	N6—Pd2—P2	166.29(12)

[a] There are two independent molecules.

Table S4. Selected bond distances (Å) and angles (°) of **5**·CH_2Cl_2 and **7**·C_3H_7NO.

	5		**7**
Pd1—C26	2.035(5)	Pd1—C21	2.043(5)
Pd1—C20	2.008(5)	Pd1—N3	2.068(4)
Pd1—Cl1	2.4217(14)	Pd1—P1	2.234(2)
Pd1—N3	2.124(5)	Pd1—Cl1	2.3585(15)
C20—Pd1—C26	87.6(2)	C21—Pd1—N3	65.41(16)
C20—Pd1—N3	94.1(2)	C21—Pd1—P1	103.25(13)
C26—Pd1—Cl1	88.19(16)	N3—Pd1—N1	166.22(12)
N3—Pd1—Cl1	89.86(13)	C21—Pd1—Cl1	164.29(12)
C26—Pd1—N3	177.5(2)	N3—Pd1—Cl1	99.87(11)
C20—Pd1—Cl1	173.24(16)	P1—Pd1—Cl1	92.06(5)

Table S5. Computational results for **S1**, **S2**, **S3** and **TS1** (at B3LYP/LANL2DZ theory)

	S1	**S2**	**S3**	**TS1**
Gas Phase				
Energy (a.u.)	-1463.4543713	-1463.4630939	-1463.4533703	-1463.4023038
Rel. Energy (kcal/mol)	5.5	0	6.1	38.1
Rel. Free Energy (kcal/mol)	5.6	0	8.2	36.8
Dipole Moment (Debye)	4.4	10.5	4.0	6.2
Imaginary Frequencies (cm^{-1})	None	None	None	-110
Solution (in Pyridine, PCM, Single-Point)				
Energy (a.u.)	-1463.4861961	-1463.4950107	-1463.4836895	-1463.4386789
Rel. Energy (kcal/mol)	5.5	0	7.1	35.3
Dipole Moment (Debye)	5.3	13.2	5.6	7.8

	S1+Pyridine	**S2+Pyridine**	**S3+Pyridine**	**TS1+Pyridine**
Gas Phase				
Energy (a.u.)	-1711.6989045	-1711.7122670	-1711.7028196	-1711.6710328
Rel. Energy (kcal/mol)	8.4	0	5.9	25.9
Rel. Free Energy (kcal/mol)	8.3	0	8.4	30.3
Dipole Moment (Debye)	2.8	10.3	4.5	11.4
Imaginary Frequencies (cm^{-1})	None	None	None	-18
Solution (in Pyridine, PCM, Single-Point)				
Energy (a.u.)	-1711.7347341	-1711.7446522	-1711.7331231	-1711.7106291
Rel. Energy (kcal/mol)	6.2	0	7.2	21.3
Dipole Moment (Debye)	3.5	12.9	5.9	14.1

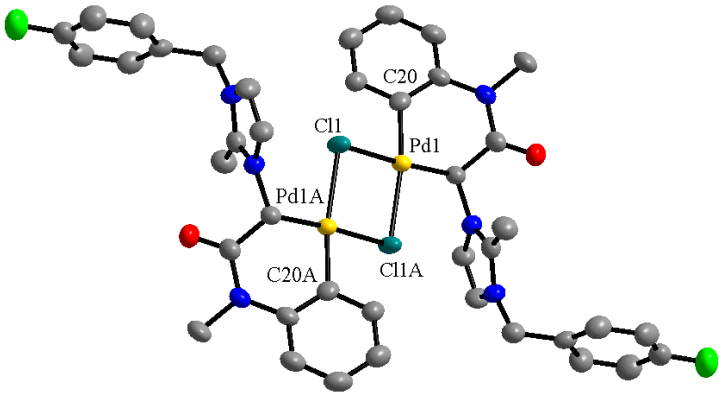

Figure S1. Molecular structures of **9**·4C_3H_7NO with 50% probability ellipsoids for non-H atoms. Hydrogen atoms and solvent molecules were omitted for clarity. The dimeric compound lies about an inversion centre. Selected bond distances (Å) and angles (deg): Pd1—C12 2.034(4), Pd1—C20 1.989(4), Pd1—Cl1 2.4295(11), Pd1—Cl1A 2.4774(11); C12—Pd1—C20 82.79(17), Cl1—Pd1—Cl1A 83.24(4), C12—Pd1—Cl1A 99.49(12), C20—Pd1—Cl1 95.11(12), Cl1A—Pd1—C20 168.93(12), C12—Pd1—Cl1 175.89(11). Symmetry code for A: 1– x. –y, 1 – z.

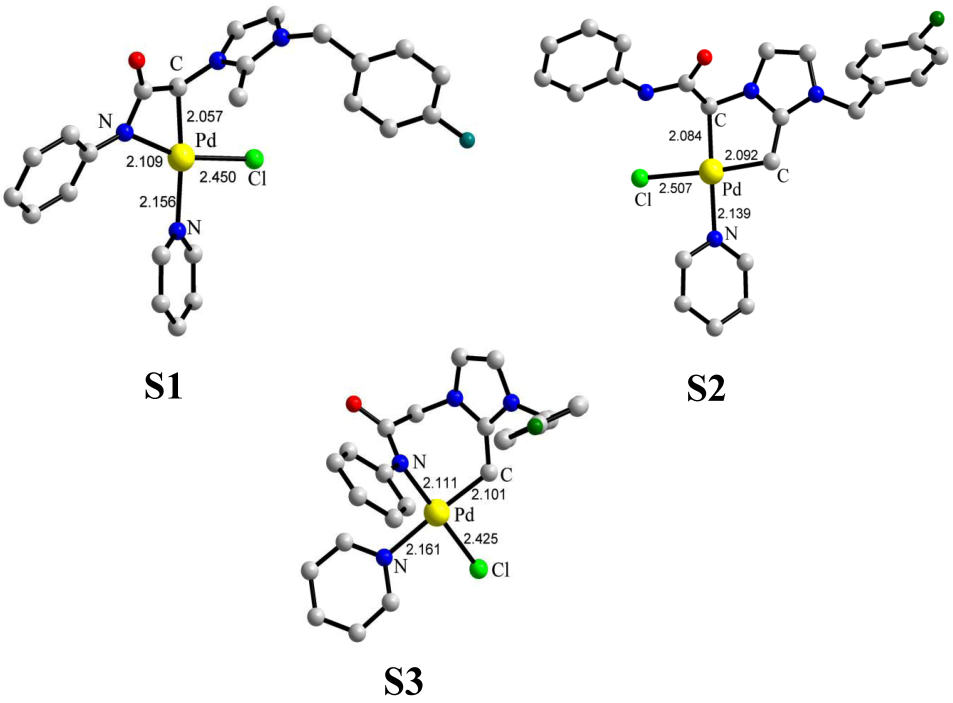

Figure S2. DFT optimized structures for **S1**—**S3**. H atoms are omitted for clarity. Selected distances (Å) are indicated.

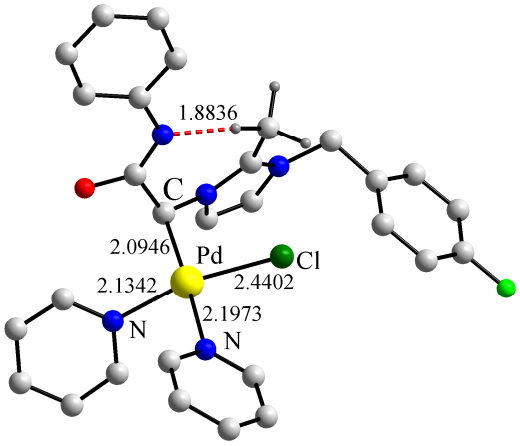

Figure S3. DFT optimized structure for **TS1** + **Pyridine**. H atoms except those on methyl group are omitted for clarity. Selected distances (Å) are indicated.

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