Electronic Supplementary Information for Dalton Transactions

Supporting Information

Modular Synthesis of Chiral and Achiral *C,N*-Chelated Pd(II)-Pyridinylidenes

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1. General Considerations

All reactions were carried out under nitrogen atmosphere using standard Schlenk line and glove box techniques. Unless otherwise noted, chemicals were obtained commercially and used as supplied. The Pd(0) precursor $Pd_2(dba)_3 \cdot CHCl_3$ (dba = dibenzylideneacetone) was prepared according to a standard literature procedure.[1] ^1H and $^{13}C\{^1H\}$ NMR spectra were collected using a Varian Mercury 400 spectrometer (400.085 MHz for ^1H and 100.602 MHz for ^{13}C) or a Varian INOVA 400 spectrometer (399.762 MHz for ^1H and 100.520 MHz for ^{13}C). All spectra were recorded at r.t., with the exception of compounds those of **4** and **5**, which were recorded at 25 °C. Residual solvent proton (relative to external $SiMe_4$, δ 0.00) or solvent carbon (relative to external $SiMe_4$, δ 0.00) was used as an internal reference. Coupling constants are given in Hz. Unless otherwise noted, spectra were measured for samples dissolved in CD_3CN due to the limited solubility of the Pd(II) pyridinylidenes in less polar solvents. Coordinated CH_3CN ligands were not observed spectroscopically due to rapid exchange with bulk CD_3CN. High resolution mass spectrometry data were provided by Mr. Doug Hairsine (UWO) and were collected using a Finningan MAT 8200 instrument. Elemental analyses were provided by Guelph Chemical Laboratories Ltd. All of the metal complexes showed high affinity for Et_2O that in some cases could not be driven off despite prolonged exposure to vacuum at elevated temperatures.

[1] Ukai, T. Kawazura, H., Ishii, Y., Bonnet, J. J., Ibers, J. A. *J. Organomet. Chem.*, 1974, **65**, 253-266.

2. Syntheses

2-chloro-3-formyl-1-methylpyridinium triflate, [1–Cl][OTf]. Methyl triflate (2.23 g, 13.6 mmol, 1.53 mL) was added dropwise over several minutes to an orange suspension of 2-chloro-3-formylpyridine (1.6 g, 11.3 mmol) in Et_2O (50 mL). The reaction mixture was stirred at r.t. for *ca*. 3 h, during which time the product precipitated. The title pyridinium was isolated as an off-white powder by evaporation of the solvent. Yield: 2.8 g (82 %). ^{1}H NMR (CD_3CN): δ 4.37 (s, 3H, NC*H*$_3$), 8.09 (dd, 1H, py*H*, $^3J_{HH}$ = 6.1, $^3J_{HH}$ = 7.7), 8.83 (dd, 1H, py*H*, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.7), 8.97 (dd, 1H, py*H*, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 1.6), 10.31 (s, 1H, C*H*O). ^{13}C{^{1}H} NMR (CD_3CN): δ 47.9, 126.4, 132.8, 146.1, 151.7, 169.0, 185.7. ^{19}F{^{1}H} NMR (CD_3CN): δ -79.5. HRMS calcd. for C_7H_7ClNO (found): 156.02107 (155.02187).

[Pd(1)(Cl)(CH$_3$CN)$_2$][OTf], 2. Solid $Pd_2(dba)_3{\cdot}CHCl_3$ (0.93 g, 0.90 mmol) was added to a solution of **[1–Cl][OTf]** (0.55 g, 1.8 mmol) in CH_3CN (30 mL) to give a dark brown suspension that was heated to 60-70 °C for *ca*. 1 h. A small quantity of insoluble Pd black was removed by centrifuge and the solvent was evaporated, leaving an yellow-orange powder. Residual dba was removed by washing the solid with Et_2O (5 × 10 mL), and the product was dried under vacuum. Yield: 0.80 g (90 %). ^{1}H NMR (CD_3CN): δ 4.93 (s, 3H, NC*H*$_3$), 7.67, (dd, 1H, py*H*, $^3J_{HH}$ = 6.2, $^3J_{HH}$ = 7.7), 8.34 (dd, 1H, py*H*, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.6), 8.69 (dd, 1H, py*H*, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 1.5), 11.06 (s, 1H, C*H*O). ^{13}C{^{1}H} NMR (CD_3CN): δ 53.9, 123.5, 140.5, 141.8, 149.9, 171.4, 190.9. ^{19}F{^{1}H} NMR (CD_3CN): δ –79.6.

[Pd(1)(CH$_3$CN)$_3$][OTf]$_2$, 3. *Method 1.* The dication **3** was prepared by addition of either AgOTf (0.24 g, 0.94 mmol) or Me_3SiOTf (0.17 mL, 0.94 mmol) to a CH_3CN (12 mL) solution containing equimolar **2** (0.46 g, 0.94 mmol). The reaction mixture was stirred at r.t. for a

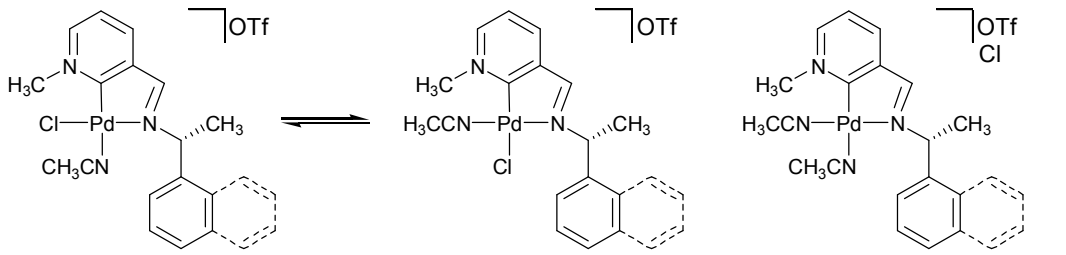
minimum of 1 h. When AgOTf was used as the halide abstractor, filtration was necessary prior to evaporation of the solvent in order to remove the insoluble AgCl salt. When Me_3SiOTf was used, the product was isolated directly by removal of the solvent to give **3** as an orange powder. Yield: 0.56 g, 99 %. *Method 2*. Compound **3** could also be prepared directly from [**1**□**Cl][OTf]** (0.24 g, 0.78 mmol) without isolation of **2** by successive reaction with $Pd_2(dba)_3{\cdot}CHCl_3$ (0.41 g, 0.39 mmol) and, after *ca*. 45 min at 60-70°C and centrifugation to remove a small quantity of Pd black, Me_3SiOTf (0.17 g, 0.78 mmol). During this addition the solution changed from yellow to dark orange. The reaction mixture was stirred at r.t. for *ca*. 2 h. The solvent was evaporated and the orange residue was washed with Et_2O (4 × 10 mL) to remove free dba and then dried under vacuum, leaving **3** as an orange powder. Yield: 0.45 g (94 %). ^{1}H NMR (CD_3CN): δ 4.83 (s, 3H, NC*H*$_3$), 7.80 (dd, 1H, py*H*, $^3J_{HH}$ = 6.2, $^3J_{HH}$ = 7.8), 8.44 (dd, 1H, py*H*, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.6), 8.72 (dd, 1H, py*H*, $^3J_{HH}$ = 6.2, $^4J_{HH}$ = 1.6), 10.36 (s, 1H, C*H*O). ^{13}C{^{1}H} NMR (CD_3CN): δ 54.2, 125.4, 142.3, 145.2, 151.2, 161.5, 162.0. ^{19}F{^{1}H} NMR (CD_3CN): δ –79.7. X-ray quality crystals were grown by slow diffusion of Et_2O into a concentrated solution of **3** in CH_3CN at □ 20 °C.

[Pd(*C*,*N*-1^{Ph})(Cl)(CH_3CN)][OTf], 4. (*R*)-(+)-α-methylbenzylamine (0.059 g, 0.49 mmol, 62 μL) was added to a solution of **2** (0.20 g, 0.40 mmol) in CH_3CN (5 mL) containing several grains of 4 Å molecular sieves. The yellow reaction mixture was stirred at r.t. for *ca*. 12 h. Sieve fragments were removed by filtration through Celite. The solvent was then evaporated and the yellow solid residue was washed with Et_2O (2 × 3 mL) to remove excess amine and the remaining yellow solid was dried under vacuum to give **4** as a bright yellow powder. Yield: 0.24 g (93 %). Spectroscopically, **4** presented as an equilibrium mixture of major and minor isomers (**4**^{maj} and **4**^{min}) in CD_3CN solution at –25 °C. Presumably, these corresponded to the

geometrical isomers **4a** and **4b** (Chart S1), but they could not be assigned definitively. The bis(acetonitrile) adduct (**4c**) was excluded by comparison of the ^{1}H NMR spectrum of **4** to that of the independently prepared compound **6** (below). ^{1}H NMR (CD_3CN): $\mathbf{4}^{maj}$ – δ 4.48 (s, 3H, NC*H*$_3$), 5.33 (m, 1H, NC*H*CH_3), 8.47 (s, 1H, N=C*H*); $\mathbf{4}^{min}$ – δ 4.24 (s, 3H, NC*H*$_3$), 6.04 (m, 1H, NC*H*CH_3). Doublets arising from the NHCHC*H*$_3$ protons of $\mathbf{4}^{maj}$ and $\mathbf{4}^{min}$ were overlapped and appeared as a broad peak at δ 1.69. The aromatic protons and the imine proton of $\mathbf{4}^{min}$ were overlapped and could not be unambiguously assigned. They were: δ 7.31 (m, Ph), 7.38 (m, Ph), 7.44 (m, Ph), 7.63 (m, py*H*), 8.18 (m, py*H*), 8.32 (m, py*H* and N=C*H*). ^{13}C{^{1}H} NMR (CD_3CN, $\mathbf{4}^{maj}$ & $\mathbf{4}^{min}$): δ 20.8, 20.9, 52.5, 53. 6, 65.4, 67.3, 122.4, 123.7, 126.7, 126.9, 127.8, 128.0, 128.5, 128.9, 139.6, 139.9, 140.4, 147.1, 148.2, 149.4, 172.8, 174.8. ^{19}F {^{1}H} NMR (CD_3CN): δ –79.6. HRMS calcd $C_{17}H_{19}N_3PdCl$ (found): 404.0308 (404.0294). Anal calcd. for $C_{18}H_{19}N_3O_3ClF_3PdS$: C, 38.86; H, 3.44; N, 7.55 %; Found: C, 38.87; H, 3.16; N, 7.39 %.

[Pd(*C,N*-1^{Np})(Cl)(CH_3CN)][OTf], 5. This compound was made using the same procedure described for the synthesis of **4**. Reaction of (*R*)-(+)-1-(1-naphthyl)ethylamine (0.13 g, 0.77 mmol, 0.12 mL) with **2** (0.38 g, 0.77 mmol) in CH_3CN (10 mL) gave **5** as a pale yellow powder. Yield: 0.32 g (70 %). As in the previous case, **5** presented as an equilibrium mixture of major and minor isomers ($\mathbf{5}^{maj}$ and $\mathbf{5}^{min}$) in CD_3CN solution at –25 °C. Presumably, these corresponded to the geometrical isomers **5a** and **5b** (Chart S1), but they could not be assigned definitively. The bis(acetonitrile) adduct (**5c**) was excluded by comparison of the ^{1}H NMR spectrum of **5** to that of the independently prepared compound **7** (below). ^{1}H NMR (CD_3CN, –25 °C): $\mathbf{5}^{maj}$ – δ 4.18 (s, 3H, NC*H*$_3$), 6.69 (m, 1H, NC*H*CH_3); $\mathbf{5}^{min}$ – δ 4.44 (s, 3H, NC*H*$_3$), 5.93 (m, 1H, NC*H*CH_3). Doublets arising from the NHCHC*H*$_3$ protons of $\mathbf{5}^{maj}$ and $\mathbf{5}^{min}$ were overlapped, appearing as a broad peak at δ 1.79. The peaks attributed to the aromatic protons

and the imine protons could not be assigned definitively to **5**^{maj} or **5**^{min}. They were: δ 7.30 (d, Np, $^2J_{HH}$ = 7.0), 7.40 (pt, Np, $^2J_{HH}$ = 6.6), 7.45-7.60 (m, Np), 7.63 (d, Np, $^2J_{HH}$ = 7.0), 7.74 (d, Np, 7.4), 7.90 (d, Np, $^2J_{HH}$ = 8.2), 7.96 (d, py*H*, $^2J_{HH}$ = 7.8), 8.07 (m, py*H*), 8.13 (d, py*H*, $^2J_{HH}$ = 8.6), 8.21 (d, py*H*, $^2J_{HH}$ = 5.6), 8.25 (m, py*H*), 8.39 (s, N=C*H*). $^{13}C\{^1H\}$ NMR (CD_3CN, –25 °C, **5**^{maj} & **5**^{min}): δ 19.4, 19.8, 52.5, 53.7, 61.2, 65.4, 119.3, 122.4, 122.9, 124.1, 125.5, 126.2, 127.2, 128.9, 129.4, 129.7, 130.6, 133.9, 134.1, 134.9, 136.3, 139.4, 146.6, 147.1, 147.8, 149.4, 172.8, 174.4, 175.3, 177.1. $^{19}F\{^1H\}$ NMR (CD_3CN): δ –79.7. HRMS calcd (found): 456.0459 (454.0452).



4a (phenyl), **5a** (naphthyl) **4b** (phenyl), **5b** (naphthyl) **4c** (phenyl), **5c** (naphthyl)

Chart S1. Isomers of **4** and **5** in CD_3CN solution.

[Pd(*C*,*N*-1^{Ph})(CH_3CN)$_2$][OTf]$_2$, 6. The title compound was made using a procedure similar to that described for the synthesis of **4**. Thus, reaction of (*R*)-(+)-α-methylbenzylamine (0.12 g, 0.99 mmol, 0.13 mL) and **3** (0.50 g, 0.82 mmol) gave **6** as a bright yellow powder. Yield: 0.41 g (70 %). ^1H NMR (CD_3CN): δ 1.72 (d, 3H, NCHC*H*$_3$, $^2J_{HH}$ = 6.6), 4.23 (s, 3H, NC*H*$_3$), 5.20 (m, 1H, NC*H*CH_3), 7.28–7.54 (m, 5H, Ph), 7.73 (pt, 1H, py*H*, $^2J_{HH}$ = 7.2), 8.22 (d, 1H, py*H*, $^2J_{HH}$ = 7.5), 8.35 (d, 1H, py*H*, $^2J_{HH}$ = 6.2), 8.38 (s, 1H, N=C*H*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 21.5, 52.2, 64.5, 119.5, 122.7, 123.6, 124.5, 125.8, 126.9, 128.3, 128.6, 128.8, 129.0, 129.2, 146.9, 170.1. $^{19}F\{^1H\}$ NMR (CD_3CN): δ –79.8. HRMS calcd. for $C_{19}H_{22}N_4Pd$ (found): 404.0308 (404.0294).

Anal calcd. for $C_{21}H_{22}N_4O_6F_6PdS_2 \bullet 0.2C_4H_{10}O$: C, 36.03; H, 3.31; N, 7.74 %; Found: C, 35.93; H, 3.49; N, 7.63 %.

[Pd(*C*,*N*-1^{Np})(CH$_3$CN)$_2$][OTf]$_2$, 7. Using the same method described for the synthesis of **4**, reaction of (*R*)-(+)-1-(1-naphthyl)ethylamine (0.068 g, 0.39 mmol, 63 μL) and **3** (0.20 g, 0.32 mmol) furnished **7** as a bright yellow powder. Yield: 0.23 g (92 %). ^{1}H NMR (CD$_3$CN): δ 1.90 (d, 3H, NCHC*H*$_3$, $^3J_{HH}$ = 6.55), 4.32 (s, 3H, NC*H*$_3$), 6.05 (m, 1H, NC*H*CH$_3$), 7.45 (d, 1H, Ar*H*, $^3J_{HH}$ = 7.0), 7.63 (m, 2H, Np*H*), 7.75 (m, 2H, Np*H*), 8.04 (m, 2H, Np*H*), 8.14 (d, 1H, py*H*, $^3J_{HH}$ = 8.6), 8.25 (d, 1H, py*H*, $^3J_{HH}$ = 7.6), 8.43 (m, 2H, py*H* and N=C*H*). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 19.9, 52.7, 64.8, 122.8, 123.0, 124.4, 125.2, 126.5, 127.6, 129.4, 129.5, 130.0, 134.3, 135.5, 140.9, 147.4, 149.0, 175.9. ^{19}F{^{1}H} NMR (CD$_3$CN): δ –79.8. X-ray quality crystals were grown by slow diffusion of Et$_2$O into a concentrated solution of **7** in CH$_3$CN at - 20 °C.

[Pd(*C*,*N*-1$^{p\text{-MeOPh}}$)(Cl)(CH$_3$CN)][OTf], 8. Using the method described for the synthesis of **4**, condensation of *para*-anisidine (0.087 g, 0.71 mmol) with **2** (0.35 g, 0.71 mmol) gave **8** as a dark yellow powder. Yield: 0.33 g (83 %). ^{1}H NMR (CD$_3$CN): δ 3.87 (s, 3H, OC*H*$_3$), 4.64 (s, 3H, NC*H*$_3$), 7.06 (d, 2H, Ar*H*, $^3J_{HH}$ = 7.7), 7.44 (d, 2H, Ar*H*, $^3J_{HH}$ = 8.1), 7.63 (pt, 1H, py*H*, $^3J_{HH}$ = 7.0), 8.24 (d, 1H, py*H*, $^3J_{HH}$ = 7.7), 8.36 (d, 1H, py*H*, $^3J_{HH}$ = 6.1), 8.46 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 53.6, 55.7, 114.4, 124.1, 124.7, 128.7, 129.3, 130.8, 139.8, 143.0, 147.4, 160.6. ^{19}F{^{1}H} NMR (CD$_3$CN): δ –79.8. HRMS calcd. for $C_{16}H_{17}ClN_3OPd$ (found): 408.0108 (408.0078). Anal calcd. for $C_{17}H_{17}ClF_3N_3O_4PdS$: C, 36.57; H, 3.07; N, 7.53 %; Found: C, 36.21; H, 2.82; N, 7.29 %. X-ray quality crystals were grown by slow diffusion of Et$_2$O into a concentrated solution of **8** in CH$_3$CN at - 20 °C.

3-chloro-4-formyl-1-methylpyridinium triflate, [9–Cl][OTf]. Using the method described for the synthesis of [**1–Cl][OTf]**, CH_3OTf (0.23 g, 1.4 mmol) was reacted with 3-chloro-4-formylpyridine (0.20 g, 1.4 mmol) to give [**9–Cl][OTf]** as an off-white powder. Yield: 0.35 g (81 %). ^{1}H NMR (CD_3CN): δ 4.34 (s, 3H, NC*H*$_3$), 8.25 (m, 1H, py*H*), 8.74 (d, 1H, py*H*, $^3J_{HH}$ = 6.2), 9.01 (s, 1H, py*H*), 10.37 (s, 1H, C*H*O). ^{13}C{^{1}H} NMR (CD_3CN): δ 49.0, 122.5, 126.3, 135.7, 145.4, 148.1, 186.2. ^{19}F{^{1}H} NMR (CD_3CN): δ - 79.3. HRMS calcd. for C_7H_7ClNO (found): 156.0216 (156.0202).

[9$^{p\text{-MeOPh}}$–Cl][OTf], 10. *Para*-anisidine (0.061 g, 0.49 mmol) was added to a solution of **[9–Cl][OTf]** (0.13 g, 0.41 mmol) in CH_3CN (6 mL) containing several grains of 4 Å molecular sieves, whereupon the colour changed from pale yellow to red. The reaction mixture was stirred at r.t. for *ca*. 3 h. Molecular sieve fragments were removed by filtration and the solvent was removed by evaporation. Excess amine was removed by washing with Et_2O (3 × *ca.* 4 mL). The remaining orange solid residue was dried under vacuum. Yield: 0.17 g (100 %). ^{1}H NMR (CD_3CN): δ 3.85 (s, 3H, OC*H*$_3$), 4.28 (s, 3H, NC*H*$_3$), 7.05 (d, 2H, Ar*H*, $^3J_{HH}$ = 8.9), 7.55 (d, 2H, Ar*H*, $^3J_{HH}$ = 8.8), 8.56 (d, 1H, py*H*, $^3J_{HH}$ = 6.3), 8.60 (d, 1H, py*H*, $^3J_{HH}$ = 6.3), 8.85 (s, 1H, py*H*), 8.98 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR (CD_3CN): δ 48.5, 55.7, 115.1, 124.9, 134.4, 147.7, 148.2, 161.6. ^{19}F{^{1}H} NMR (CD_3CN): δ –79.6. HRMS calcd. for $C_{14}H_{14}ClN_2O$ (found): 261.0789 (261.0800).

[Pd(*C*,*N*-9$^{p\text{-MeOPh}}$)(Cl)(CH$_3$CN)][OTf], 11. A solution of **10** (0.11 g, 0.27 mmol) in CH_3CN (4 mL) was added to $Pd_2(dba)_3{\cdot}CHCl_3$ (0.14 g, 0.14 mmol) that was partially dissolved in toluene (4 mL). The resultant dark-coloured slurry was stirred at r.t. for *ca*. 12 h. A small amount of Pd black deposited during the reaction and was removed by filtration through Celite. The solvent was evaporated to give a yellow-orange solid, from which residual dba was removed by

successive washings with Et_2O (4 × *ca.* 5 mL). The yellow solid was dried under vacuum. Yield: 0.13 g (87 %). ^{1}H NMR (CD_3CN): δ 3.88 (s, 3H, OC*H*$_3$), 4.25 (s, 3H, NC*H*$_3$), 7.09 (d, 2H, Ar*H*, $^3J_{HH}$ = 8.7), 7.49 (d, 2H, Ar*H*, $^3J_{HH}$ = 8.8), 7.87 (d, 1H, py*H*, $^3J_{HH}$ = 6.0), 8.39 (d, 1H, py*H*, $^3J_{HH}$ = 5.9), 8.51 (s, 1H, py*H*), 8.81 (s, 1H, N=C*H*). ^{13}C{^{1}H} NMR (CD_3CN): δ 48.5, 55.5, 114.2, 124.2, 124.4, 128.2, 141.3, 142.4, 142.5, 147.4, 160.8, 172.5. ^{19}F{^{1}H} NMR (CD_3CN): δ –79.7. HRMS calcd. for $C_{16}H_{17}ClN_3OPd$ (found): 406.0100 (406.0085). Anal calcd. for $C_{17}H_{17}ClF_3N_3O_4PdS$: C, 36.57; H, 3.07; N, 7.53 %; Found: C, 36.30; H. 2.97; 7.24 %.

[Pd(9$^{p\text{-MeOPh}}$)(CH_3CN)$_2$][OTf]$_2$, 12. A small excess of Me_3SiOTf (0.057 g, 0.26 mmol) was added to a solution of **11** (0.12 g, 0.22 mmol) in CH_3CN (6 mL). The reaction mixture was stirred at r.t. for *ca.* 2.5 h, during which time the colour changed from yellow to dark orange. The solvent was evaporated and the remaining orange powder was washed with Et_2O (*ca.* 4 mL) and dried under vacuum. Yield: 0.14 g (93 %). ^{1}H NMR (CD_3CN): δ 3.81 (s, 3H, OC*H*$_3$), 4.24 (s, 3H, NC*H*$_3$), 7.04 (d, 2H, Ph, $^3J_{HH}$ = 9.4), 7.39 (d, 2H, Ph, $^3J_{HH}$ =9.0), 7.87 (d, 1H, py*H*, $^3J_{HH}$ = 6.3), 8.27 (s, 1H, py*H*), 8.34 (s, 1H, N=C*H*), 8.46 (d, 1H, py*H*, $^3J_{HH}$ = 6.3). ^{13}C{^{1}H} NMR (CD_3CN): δ 48.9, 55.8, 114.6, 124.8, 125.3, 141.0, 144.9, 146.7, 161.5, 175.8. ^{19}F{^{1}H} NMR (CD_3CN): δ –79.8. Anal calcd. for $C_{20}H_{20}F_6N_4O_7PdS_2$: C, 33.69; H, 2.83; N, 7.86 %; Found: C, 33.89; H, 2.78; N, 7.36 %.

[Pd(*C*,*N*-1^{Np})(η^3-allyl)][OTf], 13. The allyl complex **13** was prepared by addition of (allyl)$SnBu_3$ (0.060 g, 0.18 mmol) to a solution of **5** (0.11 g, 0.18 mmol) in CH_3CN (6 mL). The reaction mixture was stirred at r.t. for *ca.* 12 h, during which time the colour changed from light yellow to dark orange. The title compound was isolated by evaporation of the solvent to give a light brown powder that was purified by washing with Et_2O (5 × 3 mL) and dried under vacuum. Yield: 0.097 g (89 %). ^{1}H NMR (CD_3CN): δ 1.89 (m, 2H, NCHC*H*$_3$), 2.88 (d, 2H, C*H*$_2$CHCH$_2$,

$^3J_{HH}$ = 14.1), 3.96 (d, 2H, CH_2CHCH_2, $^3J_{HH}$ = 29.7), 4.31 (s, 3H, NCH_3), 5.45 (m, 1H, CH_2CHCH_2), 6.14 (m, 1H, $NCHCH_3$), 7.56 (m, 5H, Np*H*), 7.96 (d, 1H, Np*H*, $^3J_{HH}$ = 7.8), 8.01 (d, 1H, Np*H*, $^3J_{HH}$ = 8.2), 8.09 (m, 2H, N=C*H* and py*H*), 8.51 (d, 1H, py*H*, $^3J_{HH}$ = 5.7), 8.63 (d, 1H, py*H*, $^3J_{HH}$ = 11.7). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 20.18, 51.0, 65.6, 72.9, 119.8, 123.2, 123.5, 123.6, 125.7, 126.4, 127.2, 129.2, 129.4, 134.5, 138.1, 145.5, 149.5, 171.9. $^{19}F\{^1H\}$ NMR (CD_3CN): δ –79.7. HRMS calcd. for $C_{22}H_{23}N_2OPd$ (found): 419.0901 (419.0894). Anal calcd. for $C_{23}H_{23}F_3N_2O_3PdS$: C, 48.39; H, 4.06; N, 4.91 %; Found: C, 48.12; H, 3.92; N, 4.93 %.

[Pd(*C*,*N*-9$^{p\text{-MeOPh}}$)(η^3-allyl)][OTf], 14. The allyl complex **14** was made using the procedure given above for the synthesis of **13**. Accordingly, equimolar reaction of **11** (0.080 g, 0.14 mmol) with (allyl)$SnBu_3$ (0.047 g, 0.14 mmol) gave the title compound as an intensely coloured orange powder. Yield: 0.074 g (99 %). ^1H NMR (CD_3CN): δ 3.52 (d, 2H, CH_2CHCH_2, $^3J_{HH}$ = 14.1), 3.89 (s, 3H, OCH_3), 4.14 (d, 2H, CH_2CHCH_2, $^3J_{HH}$ = 7.8), 4.20 (s, 3H, NCH_3), 5.65 (m, 1H, CH_2CHCH_2), 7.02 (d, 2H, Ph, $^3J_{HH}$ = 9.0), 7.67 (d, 2H, Ph, $^3J_{HH}$ = 9.0), 7.95 (d, 1H, py*H*, $^3J_{HH}$ = 5.9), 8.33 (dd, 1H, py*H*, $^3J_{HH}$ = 6.0, $^4J_{HH}$ = 1.2), 8.67 (s, 1H, py*H*), 8.82 (s, 1H, N=C*H*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 46.0, 47.5, 55.8, 73.5, 114.7, 119.3, 124.8, 142.5, 143.6, 150.6, 161.2, 167.0, 169.5. $^{19}F\{^1H\}$ NMR (CD_3CN): δ –79.8. Anal calcd. for $C_{18}H_{19}F_3N_2O_4PdS$: C, 41.35; H, 3.66; N, 5.36 %; Found: C, 41.68; H, 3.65; N, 5.37 %.