Supplementary Information

The Synthesis and Characterization of, and Dynamic Processes Occurring in Pd(II) Chelate Complexes of 2-pyridyldiphenylphosphine

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Supplementary Figure 1. The $^{31}$P{¹H} NMR spectrum recorded at 293 K of isolated product from the reaction of [Pd(PhCN)$_2$Cl$_2$] with 1 equivalent of Ph$_2$Ppy in CH$_2$Cl$_2$.

Supplementary Figure 2. (a) $^{31}$P{¹H} NMR spectrum of 3[X], (X = Cl, BF$_4$, OTf, MeSO$_3$) in CH$_2$Cl$_2$/MeOH recorded at 233 K (top) and 3(Cl) at 293 K (bottom).

(b) ¹H NMR spectra of 3[X], (X = Cl, BF$_4$, OTf, MeSO$_3$) in CH$_2$Cl$_2$/MeOH recorded at 233 K.

Supplementary Figure 3. Aromatic region of the ¹H NMR spectra of 4[OTf] in CD$_2$Cl$_2$ recorded at 233 K (top) and 293 K (bottom).

Supplementary Figure 4. $^{31}$P{¹H} NMR spectrum of “[Pd($\kappa^2$-Ph$_2$Ppy)($\kappa^1$-Ph$_2$Ppy) (CH$_3$CN)][BF$_4$]$_2$“ (5) in CH$_2$Cl$_2$:CH$_3$CN (20:1) solution recorded at 193 K.

Supplementary Figure 5. (a) $^{31}$P{¹H} NMR spectrum of 8[X], (X = OTf, CF$_3$CO$_2$, MeSO$_3$) in CH$_2$Cl$_2$ recorded at 193 K.

(b) Aromatic region of the ¹H NMR spectra of 8[X], (X = OTf, CF$_3$CO$_2$, MeSO$_3$) in CH$_2$Cl$_2$ recorded at 193 K.

Supplementary Figure 6. (a) $^{31}$P{¹H} NMR spectrum of 8′[X], (X = OTf, MeSO$_3$, BF$_4$) in CH$_2$Cl$_2$ recorded at 193 K.
(b) Aromatic region of the $^1$H NMR spectra of $8[X]$, $(X = \text{OTf, MeSO}_3, \text{BF}_4)$ in CH$_2$Cl$_2$ recorded at 193 K.

**Supplementary Figure 7.** $^{31}$P{$^1$H} NMR spectrum of $[\text{Pd}(\kappa^2-\text{Ph}_2\text{Ppy})(\kappa^1-$Ph$_2\text{PpyH})(\text{MeSO}_3)][\text{MeSO}_3]_2$ recorded at 183 K in CH$_2$Cl$_2$ in the presence of excess MeSO$_3\text{H}$. The sharp resonance at ca. $\delta(\text{P}) = -10$ ppm is due to $[\text{Ph}_2\text{Ppy}][\text{MeSO}_3]$.

**Supplementary Figure 8.** (a) The $^{15}$N and (b) $^{15}$N{$^1$H} NMR spectra of Ph$_2$Ppy recorded at 293K in CH$_2$Cl$_2$; (c) the $^{15}$N and (d) $^{15}$N{$^1$H} NMR spectra of $[\text{Ph}_2\text{PpyH}][\text{MeSO}_3]$ recorded at 203K in CH$_2$Cl$_2$.

VT NMR spectra, and simulations, Eyring and Arrhenius plots.

**Supplementary Figure 9.** Experimental and simulated variable temperature $^{31}$P{$^1$H} NMR spectra of $10$ in MeOH $\text{Pd:PPh}_2\text{py:CH}_3\text{SO}_3\text{H} = 1:3.4:10.$ (sample 3)

**Supplementary Figure 10.** Eyring and Arrhenius plots for $10$ in MeOH $\text{Pd:PPh}_2\text{py:CH}_3\text{SO}_3\text{H} = 1:3.4:10.$ (sample 3)

**Supplementary Figure 11.** Experimental and simulated variable temperature $^{31}$P{$^1$H} NMR spectra of $10$ in MeOH $\text{Pd:PPh}_2\text{py:CH}_3\text{SO}_3\text{H} = 1:3.4:25.$ (sample 4)
**Supplementary Figure 12.** Eyring and Arrhenius plots for 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.4:25. (sample 4)

**Supplementary Figure 13.** Experimental and simulated variable temperature $^{31}$P{¹H} NMR spectra 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.2:15. (sample 5)

**Supplementary Figure 14.** Eyring and Arrhenius plots for 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.2:15. (sample 5)

**Supplementary Figure 15.** Experimental and simulated variable temperature $^{31}$P{¹H} NMR spectra of 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:2.9:25. (sample 6)

**Supplementary Figure 16.** Eyring and Arrhenius plots for 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:2.9:25. (sample 6)

**Supplementary Figure 17.** Experimental and simulated variable temperature $^{31}$P{¹H} NMR spectra of 10 in MeOH:CD₂Cl₂ 4:3; Pd:PPh₂py:CH₃SO₃H = 1:3.1:5. (sample 8)

**Supplementary Figure 18.** Eyring and Arrhenius plots for 10 in MeOH:CD₂Cl₂ 4:3; Pd:PPh₂py:CH₃SO₃H = 1:3.1:5. (sample 8)

**Supplementary Figure 19.** Experimental and simulated variable temperature $^{31}$P{¹H} NMR spectra of 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.1:10. (sample 1)
**Supplementary Figure 20.** Eyring and Arrhenius plots for 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.1:10. (sample 1)

**Supplementary Figure 21.** Experimental and simulated variable temperature ³¹P{¹H} NMR spectra of 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.1:10. (sample 2).

**Supplementary Figure 22.** Eyring and Arrhenius plots for 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.1:10. (sample 2).

**Supplementary Figure 23.** Experimental and simulated variable temperature ³¹P{¹H} NMR spectra of 10 in MeOH:CD₂Cl₂ (2:9) Pd:PPh₂py:CH₃SO₃H = 1:3.1:25. (sample 7)

**Supplementary Figure 24.** Eyring and Arrhenius plots for 10 in MeOH:CD₂Cl₂ (2:9) Pd:PPh₂py:CH₃SO₃H = 1:3.1:25. (sample 7)

**Supplementary Figure 25.** Experimental and simulated variable temperature ³¹P{¹H} NMR spectra of 10 in CD₂Cl₂ Pd:PPh₂py:CH₃SO₃H = 1:2.9:2. (sample 9). Impurities included to aid simulation, but not optimized.

**Supplementary Figure 26.** Eyring and Arrhenius plots for 10 in CD₂Cl₂ Pd:PPh₂py:CH₃SO₃H = 1:2.9:2. (sample 9).

**Supplementary Figure 27.** Equilibrium saturation transfer difference measurements on impure 10. The resonance of the chelating PPh₂py ligand at ca. δ(P) -48 was irradiated throughout the recovery delay (3 s). Top set sample of Supp Fig 13.- 10 in MeOH
Fig 15.- Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.2:15); bottom set sample of Supp. (sample 2)

Significant saturation transfer is seen to the other PPh$_2$py ligands in 10 but not to those of other complexes.

Supplementary Figure 28. Experimental and simulated variable temperature $^{31}$P{$^1$H} NMR spectra of 3(Cl) in CD$_2$Cl$_2$ plus 0.1 mL MeOH. Note changes in ppm scale at 233, 253, 283 and 293 K.

Supplementary Figure 29. Experimental and simulated variable temperature $^{31}$P{$^1$H} NMR spectra of 3[OTf] in CD$_2$Cl$_2$ plus 0.1 mL MeOH. Note changes in ppm scale at 223, 263, and 283 K.

Supplementary Figure 30. Experimental and simulated variable temperature $^{31}$P{$^1$H} NMR spectra of 3(Cl) in CD$_2$Cl$_2$:MeOH (1:1). Note changes in ppm scale at 243, and 273 K.

Supplementary Figure 31. Experimental and simulated variable temperature $^{31}$P{$^1$H} NMR spectra of 3[OTf] in CD$_2$Cl$_2$:MeOH (1:1).

Supplementary Figure 32. Variable temperature $^{31}$P{$^1$H} NMR spectra of 4(Cl) in CD$_2$Cl$_2$:MeOH (1:1).

Supplementary Figure 33. $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 193 K.

Supplementary Figure 34. $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 213 K.
**Supplementary Figure 35.** $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 233 K.

**Supplementary Figure 36.** $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 243 K.

**Supplementary Figure 37.** $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 263 K.

**Supplementary Figure 38.** $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 273 K.

**Supplementary Figure 39.** $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 283 K.

**Supplementary Figure 40.** $^{31}$P{$^1$H} NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:2.8 to 1:4.6 as chloride or triflate salts, T = 293 K.

**Supplementary Figure 41.** Simulations of the variable temperature $^{31}$P{$^1$H} NMR spectra of 4(Cl) in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1: 4.6, together with the Eyring and Arrhenius plots.

**Supplementary Figure 42.** Simulations of the variable temperature $^{31}$P{$^1$H} NMR spectra of 4(Cl) in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1: 3.4, together with the Eyring and Arrhenius plots.

**Supplementary Figure 43.** Simulations of the variable temperature $^{31}$P{$^1$H} NMR spectra of 4(Cl) in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1: 3.03, together with the Eyring and Arrhenius plots.
Supplementary Table 1  Kinetic and thermodynamic parameters for the dynamic processes in 4(Cl)in CD2Cl2:MeOH (1:1).

X-ray crystal structures

Supplementary Table 2  Crystal data for 2b.2CH2Cl2, 2b'[MeSO3]2.2CH2Cl2, 3BF4, 4.2H2O and 7.CH2Cl2

Crystal Structure of trans-[Pd(κ1-Ph2Ppy)2Cl2] (2b)

Supplementary Figure 44. Molecular structure of trans-[Pd(κ1-Ph2Ppy)2Cl2] 2b with key atoms labelled and H atoms removed for clarity

Supplementary Table 3  Selected bond lengths (Å) and angles (°) for trans-[Pd(κ1-Ph2Ppy)2Cl2] 2b

Crystal structure of [Pd(κ1-Ph2Ppy)3Cl](Cl) (4(Cl))

Supplementary Figure 45. Molecular structure of [Pd(κ1-Ph2Ppy)3Cl](Cl) (4(Cl)) highlighting the CH...N (blue) and π-stacking interactions (red) between the phosphine ligands.

Supplementary Table 4  Selected bond lengths (Å) and angles (°) for [Pd(κ1-Ph2Ppy)3Cl](Cl) (4(Cl))
**Supplementary Figure 1.** The $^{31}P\{^1H\}$ NMR spectrum recorded at 293 K of isolated product from the reaction of [Pd(PhCN)$_2$Cl$_2$] with 1 equivalent of Ph$_2$Ppy in CH$_2$Cl$_2$. 

![NMR Spectrum](image-url)
Supplementary Figure 2. (a) $^{31}$P$^1$H NMR spectrum of 3[X], (X = Cl, BF$_4$, OTf, MeSO$_3$) in CH$_2$Cl$_2$/MeOH recorded at (top) 233 K and 3(Cl) at 293 K (bottom).
Supplementary Figure 2  Aromatic region of the $^1$H NMR spectra of 3(X), ($X = \text{Cl, BF}_4$, OTf, MeSO$_3$) in CH$_2$Cl$_2$/MeOH recorded at 233 K.
Supplementary Figure 3. Aromatic region of the $^1$H NMR spectra of 4[OTf] in CD$_2$Cl$_2$ recorded at 233 K (top) and 293 K (bottom).
Supplementary Figure 4. $^{31}$P($^1$H) NMR spectrum of "$^{[\text{Pd}(\kappa^2-\text{Ph}_{2}\text{Ppy})(\kappa^1-\text{Ph}_{2}\text{Ppy})(\text{CH}_3\text{CN})](\text{BF}_4)_2}"$ (5) in CH$_2$Cl$_2$:CH$_3$CN (20:1) solution recorded at 193 K.
Supplementary Figure 5. (a) $^{31}$P($^1$H) NMR spectrum of $8[X]$, ($X =$ OTf, CF$_3$CO$_2$, MeSO$_3$) in CH$_2$Cl$_2$ recorded at 193 K.
**Supplementary Figure 5.** (b) Aromatic region of the $^1$H NMR spectra of $8[X]$, ($X = \text{OTf}$, $\text{CF}_3\text{CO}_2$, $\text{MeSO}_3$) in $\text{CH}_2\text{Cl}_2$ recorded at 193 K.
Supplementary Figure 6.  (a) $^{31}$P($^1$H) NMR spectrum of $8'[X]$, ($X = \text{OTf, MeSO}_3, \text{BF}_4$) in CH$_2$Cl$_2$ recorded at 193 K.
Supplementary Figure 6. (b) Aromatic region of the $^1$H NMR spectra of $8'[X]$, ($X = \text{OTf}$, $\text{MeSO}_3$, $\text{BF}_4$) in $\text{CH}_2\text{Cl}_2$ recorded at 193 K.
**Supplementary Figure 7.** $^{31}$P$^{{1}H}$ NMR spectrum of [Pd($\kappa^2$-Ph$_2$Ppy($\kappa^2$-
Ph$_2$PpyH))(MeSO$_3$)][MeSO$_3$]$_2$ (8$^*$[MeSO$_3$]) recorded at 183 K in
CH$_2$Cl$_2$ in the presence of excess MeSO$_3$H. The sharp
resonance at ca. $\delta$(P) = -10 ppm is due to [Ph$_2$PpyH][MeSO$_3$].
Supplementary Figure 8.  (a) The $^{15}$N and (b) $^{15}$N($^1$H) NMR spectra of Ph$_2$Ppy recorded at 293K in CH$_2$Cl$_2$; (c) the $^{15}$N and (d) $^{15}$N($^1$H) NMR spectra of [Ph$_2$PpyH](CH$_3$SO$_3$H) recorded at 203K in CH$_2$Cl$_2$.
Supplementary Figure 9. Experimental and simulated variable temperature $^{31}\text{P}^1\text{H}$ NMR spectra of 10 in MeOH Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.4:10. (sample 3). The sharp resonance at ca. -10 ppm is due to [PPh$_2$pyH]$^+\text{[MeSO}_3\text{]}$. (sample 3).
Supplementary Figure 10. Eyring and Arrhenius plots for 10 in MeOH. Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.4:10. (sample 3)

**Arrhenius plot k1**

- Intercept: 22.6
- Gradient: -3911
- $R^2 = 0.993$

**Arrhenius plot k2**

- Intercept: 22.75
- Gradient: -4579
- $R^2 = 0.9985$

**Eyring plot k1**

- Intercept: 22.6
- Gradient: -3911.1
- $R^2 = 0.9899$

**Eyring plot k2**

- Intercept: 22.75
- Gradient: -4579.1
- $R^2 = 0.9985$

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- $h = 6.63 \times 10^{-34} \text{ J s}^{-1}$
- $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$
- $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

**Eyring**

- $k_1$
  - Intercept: 22.6
  - Gradient: -3911
  - $R^2 = 0.993$

- $k_2$
  - Intercept: 22.75
  - Gradient: -4579
  - $R^2 = 0.9985$

**Arrhenius**

- Eact: 35
  - $E_{\text{act}}$: 40 \text{ kJ mol}^{-1}

- gradEyr
  - $\Delta H$: 33
  - $\Delta S$: -10
  - $-8 \text{ J K}^{-1} \text{ mol}^{-1}$

- gradAhr
  - $-4216$
  - $-4822$
Supplementary Figure 11. Experimental and simulated variable temperature $^{31}$P($^1$H)

NMR spectra of 10 in MeOH Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.4:25.

The resonance at ca. -10 ppm is due to [PPh$_2$pyH]$^+$(MeSO$_3$).

(sample 4)

\[ T = 183 \text{ K} \]
\[ k_i = 660 \text{ s}^{-1} \]
\[ k_s < 300 \text{ s}^{-1} \]

\[ T = 208 \text{ K} \]
\[ k_i = 1.07 \times 10^4 \text{ s}^{-1} \]
\[ k_s = 460 \text{ s}^{-1} \]

\[ T = 233 \text{ K} \]
\[ k_i = 7.86 \times 10^4 \text{ s}^{-1} \]
\[ k_s = 7.85 \times 10^3 \text{ s}^{-1} \]

\[ T = 243 \text{ K} \]
\[ k_i = 1.27 \times 10^5 \text{ s}^{-1} \]
\[ k_s = 1.90 \times 10^4 \text{ s}^{-1} \]

\[ T = 253 \text{ K} \]
\[ k_i = 2.29 \times 10^5 \text{ s}^{-1} \]
\[ k_s = 3.43 \times 10^4 \text{ s}^{-1} \]

\[ T = 263 \text{ K} \]
\[ k_i = 5.14 \times 10^5 \text{ s}^{-1} \]
\[ k_s = 5.71 \times 10^4 \text{ s}^{-1} \]
Supplementary Figure 12. Eyring and Arrhenius plots for 10% MeOH - PdPPh2_2:CH3SO3H, 1:3.4:25. (sample 4)

**Eyring**

- $k_1$: intercept = 20.756, gradient = -3515
- $k_2$: intercept = 19.798, gradient = -4654

**Arrhenius**

- $E_{act}$: 31 kJ mol$^{-1}$
- $\Delta S$: -25 J K$^{-1}$ mol$^{-1}$
- $\Delta H$: 29-39 kJ mol$^{-1}$

**Constants**

- $h$: 6.63E-34 J s$^{-1}$
- $k_B$: 1.38E-23 J K$^{-1}$
- $R$: 8.314 J mol$^{-1}$ K$^{-1}$
Supplementary Figure 13. Experimental and simulated variable temperature $^{31}\text{P}[^1\text{H}]$ NMR spectra of 10 in MeOH Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.2:15.

(sample 5)
Supplementary Figure 14. Eyring and Arrhenius plots for 10 in MeOH Pd:PPh₂py:CH₃SO₃H = 1:3.2:15. (sample 5).

**Eyring and Arrhenius plots**

- **Arrhenius plot** k1:
  - $y = -3733.9x + 24.531$
  - $R^2 = 0.9903$

- **Arrhenius plot** k2:
  - $y = -4104.4x + 23.596$
  - $R^2 = 0.9951$

- **Eyring plots** k1:
  - $y = -3499.6x + 20.722$
  - $R^2 = 0.9891$

- **Eyring plots** k2:
  - $y = -3953.6x + 20.095$
  - $R^2 = 0.9941$

**Parameters**

- $h = 6.63 \times 10^{-34}$ J s⁻¹
- $k_B = 1.38 \times 10^{-23}$ J K⁻¹
- $R = 8.314$ J mol⁻¹ K⁻¹

**Eyring**

- $k_1$ intercept: 20.72
- $k_2$ intercept: 19.74
- $\text{grad}E_y$: -3500, -3857
- $\Delta H$: 29, 32 kJ mol⁻¹
- $\Delta S$: -25, -33 J K⁻¹ mol⁻¹

**Arrhenius**

- $E_{act}$: 31, 34 kJ mol⁻¹
- $\text{grad}A_{hr}$: -3734, -4104
NMR spectra of 10 in MeOH Pd:PPPh2py:CH3SO3H = 1:2.9:25. (sample 6).
Supplementary Figure 16. Eyring and Arrhenius plots for 10 in MeOH:PAH:py:CH₃SO₃H = 1:2.9:25. (sample 6).

\[
h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1}
\]
\[
k_B = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}
\]
\[
R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
\]

Eyring

\[
\text{k}_1 \quad \text{k}_2
\]

intercept 21.7 20.75
gradEy -3736 -4101

\[
\Delta H = 31 \text{ kJ mol}^{-1}
\]
\[
\Delta S = -17 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\]

Arrhenius

\[
E_{\text{act}} = 34 \text{ kJ mol}^{-1}
\]

gradAhr -4046 -3719

Eyring plot k1
\[
y = -3656.1x + 21.309
\]
\[
R^2 = 0.9898
\]

Eyring plot k2
\[
y = -4100.6x + 20.748
\]
\[
R^2 = 0.9922
\]
Supplementary Figure 17. Experimental and simulated variable temperature $^{31}P\{^1H\}$ NMR spectra of 10 MeOH:CD$_2$Cl$_2$ 4:3; Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3:1:5. (sample 8)

- **T = 183 K**
  - $k_1 = 4630$ s$^{-1}$
  - $k_2 = 518$ s$^{-1}$

- **T = 193 K**
  - $k_1 = 1.20 \times 10^4$ s$^{-1}$
  - $k_2 = 407$ s$^{-1}$

- **T = 198 K**
  - $k_1 = 1.57 \times 10^4$ s$^{-1}$
  - $k_2 = 462$ s$^{-1}$

- **T = 203 K**
  - $k_1 = 1.85 \times 10^4$ s$^{-1}$
  - $k_2 = 555$ s$^{-1}$

- **T = 208 K**
  - $k_1 = 2.22 \times 10^4$ s$^{-1}$
  - $k_2 = 925$ s$^{-1}$

- **T = 213 K**
  - $k_1 = 4.18 \times 10^4$ s$^{-1}$
  - $k_2 = 1480$ s$^{-1}$
Supplementary Figure 18. Eyring and Arrhenius plots for 10 MeOH:CDCl₃:CH₃SO₃H = 1:3.1:5. (sample 8)

Eyring k1 k2
intercept 21.38 20.71
gradEy -2905 -3684
ΔH 24 31 kJ mol⁻¹
ΔS -20 -25 J K⁻¹ mol⁻¹

Arrhenius
Eact 28 33 kJ mol⁻¹
gradAhr -3323 -3978

h 6.63E-34 J s⁻¹
kB 1.38E-23 J K⁻¹
R 8.314 J mol⁻¹ K⁻¹
Supplementary Figure 19. Experimental and simulated variable temperature $^{31}\text{P}[^1\text{H}]$ NMR spectra of 10 in MeOH. Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.1:10. (Sample 1)

- T = 183 K
  - $k_1$ = 1144 s$^{-1}$
  - $k_0$ = <300 s$^{-1}$

- T = 198 K
  - $k_1$ = 7245 s$^{-1}$
  - $k_0$ = <300 s$^{-1}$

- T = 203 K
  - $k_1$ = 9150 s$^{-1}$
  - $k_0$ = 380 s$^{-1}$

- T = 208 K
  - $k_1$ = 1.14 $\times$ 10$^4$ s$^{-1}$
  - $k_0$ = 610 s$^{-1}$

- T = 213 K
  - $k_1$ = 15.2 $\times$ 10$^3$ s$^{-1}$
  - $k_0$ = 1015 s$^{-1}$

- T = 218 K
  - $k_1$ = 2.64 $\times$ 10$^4$ s$^{-1}$
  - $k_0$ = 1650 s$^{-1}$

- T = 223 K
  - $k_1$ = 3.68 $\times$ 10$^4$ s$^{-1}$
  - $k_0$ = 2540 s$^{-1}$
Supplementary Figure 20. Eyring and Arrhenius plots for 10 in MeOH. Pd:Ph₃py:CH₃SO₃H = 1:3:1:10. (sample 1)

Eyring

\[ y = -3712.6x + 22.009 \quad R^2 = 0.9918 \]

Arrhenius

\[ y = -4676.4x + 26.359 \quad R^2 = 0.9978 \]

\[ h = 6.63 \times 10^{-34} \quad \text{J s}^{-1} \]

\[ k_B = 1.38 \times 10^{-23} \quad \text{J K}^{-1} \]

\[ R = 8.314 \quad \text{J mol}^{-1} \text{K}^{-1} \]

Eyring

<table>
<thead>
<tr>
<th>k1</th>
<th>k2</th>
</tr>
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<tbody>
<tr>
<td>intercept 22.01</td>
<td>22.41</td>
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<tr>
<td>gradEyr -3713</td>
<td>-4435</td>
</tr>
<tr>
<td>ΔH 31</td>
<td>37 kJ mol⁻¹</td>
</tr>
<tr>
<td>ΔS -15</td>
<td>-11 kJ mol⁻¹ K⁻¹</td>
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Arrhenius

<table>
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<tr>
<th>Eact</th>
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<tr>
<td>33</td>
<td>-3943</td>
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<td>39 kJ mol⁻¹</td>
<td>-4676</td>
</tr>
</tbody>
</table>

\[ y = -4434.8x + 22.406 \quad R^2 = 0.9974 \]
Supplementary Figure 21. Experimental and simulated variable temperature \(^{31}\)P\(^{(1)}\)H\) NMR spectra of 10 in MeOH Pd:PPh\(_2\)py:CH\(_3\)SO\(_3\)H = 1:3:1:10. (sample 2).
Supplementary Fig 21 continued

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\begin{align*}
T &= 233 \text{ K} \\
k_i &= 6.77 \times 10^4 \text{ s}^{-1} \\
k_0 &= 5.999 \times 10^4 \text{ s}^{-1}
\end{align*}

\begin{align*}
T &= 243 \text{ K} \\
k_i &= 1.54 \times 10^5 \text{ s}^{-1} \\
k_0 &= 1.37 \times 10^4 \text{ s}^{-1}
\end{align*}

\begin{align*}
T &= 253 \text{ K} \\
k_i &= 3.07 \times 10^5 \text{ s}^{-1} \\
k_0 &= 2.69 \times 10^4 \text{ s}^{-1}
\end{align*}

\begin{align*}
T &= 273 \text{ K} \\
k_i &= 9.23 \times 10^5 \text{ s}^{-1} \\
k_0 &= 1.08 \times 10^5 \text{ s}^{-1}
\end{align*}

\begin{align*}
T &= 283 \text{ K} \\
k_i &= 1.85 \times 10^6 \text{ s}^{-1} \\
k_0 &= 2.00 \times 10^5 \text{ s}^{-1}
\end{align*}

\begin{align*}
T &= 293 \text{ K} \\
k_i &= 2.92 \times 10^5 \text{ s}^{-1} \\
k_0 &= 2.92 \times 10^5 \text{ s}^{-1}
\end{align*}
Supplementary Figure 22. Eyring and Arrhenius plots for Pd(PPh2)2/py:CH3SO3H = 1:3.1:10 (sample 2).

Eyring plot k1
\[ y = \frac{-3850.3x + 22.277}{1/T} \]
\[ R^2 = 0.9924 \]

Arrhenius plot k1
\[ y = -4095.1x + 26.063 \]
\[ R^2 = 0.9946 \]

Eyring plot k2
\[ y = \frac{-4712x + 26.071}{1/T} \]
\[ R^2 = 0.998 \]

Arrhenius plot k2
\[ y = -4469.8x + 22.307 \]
\[ R^2 = 0.9977 \]

- \( h = 6.63 \times 10^{-34} \, \text{J} \, \text{s}^{-1} \)
- \( k_B = 1.38 \times 10^{-23} \, \text{J} \, \text{K}^{-1} \)
- \( R = 8.314 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1} \)

Eyring
- \( k_1 \) intercept: 22.277
- \( \text{grad}E_y \) (Eyring): -3850

Arrhenius
- \( E_{\text{act}} \): 34
- \( \Delta H \): 32
- \( \Delta S \): -12
- \( \text{grad}A_{\text{hr}} \): -4095

- \( k_2 \) intercept: 22.301
- \( \text{grad}A_{\text{hr}} \) (Arrhenius): -4470

- \( \Delta H \): 37
- \( \Delta S \): -12

Electronic Supplementary Information for Dalton Transactions
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Supplementary Figure 23. Experimental and simulated variable temperature $^{31}$P($^1$H) NMR spectra of 10 in MeOH:CD$_2$Cl$_2$ (2:9) Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.1:25. (sample 7).
Supplementary Figure 24. Eyring and Arrhenius plots for 3b in MeOH-CD$_2$Cl$_2$ (3:1) PAPPP, pyCH$_3$SO$_3$H = 1:3.1:25. (sample 7).

\[
y = -2996.6x + 23.195 \\
R^2 = 0.9856
\]

Arrhenius plot $k_1$

\[
y = -2625.8x + 18.779 \\
R^2 = 0.972
\]

Eyring plot $k_1$

\[
y = -4102.8x + 23.688 \\
R^2 = 0.9874
\]

Arrhenius plot $k_2$

\[
y = -3860.8x + 19.926 \\
R^2 = 0.9851
\]

Eyring plot $k_2$

- $h$ = $6.63\times10^{-34}$ J s$^{-1}$
- $k_B$ = $1.38\times10^{-23}$ J K$^{-1}$
- $R$ = 8.314 J mol$^{-1}$ K$^{-1}$

Eyring $k_1$ $k_2$
- intercept $18.78$ $19.93$
- gradEy $-2626$ $-3861$
- $\Delta H$ $22$ $32$ kJ mol$^{-1}$
- $\Delta S$ $-41$ $-32$ J K$^{-1}$ mol$^{-1}$

Arrhenius
- $E_{act}$ $25$ $34$ kJ mol$^{-1}$
- gradAhr $-2997$ $-4103$
Supplementary Figure 25. Experimental and simulated variable temperature $^{31}\text{P}$$^{(1}\text{H})$ NMR spectra of 10 in CD$_2$Cl$_2$ Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:2.9:2. (sample 9). Impurities included to aid simulation, but not optimized.
Supplementary Figure 26. Eyring and Arrhenius plots for 10 in CD$_2$Cl$_2$. Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:2.9:2. (sample 9).

Eyring k1, k2
intercept 23.25 21.23
gradEy -4022 -4166

Arrhenius
Eact 35 37 kJ mol$^{-1}$
gradAhr -4183 -4412

\[ y = -4183.4x + 28.037 \quad R^2 = 0.9877 \]

\[ y = -4412.1x + 26.397 \quad R^2 = 0.9826 \]

\[ y = -4021.8x + 23.254 \quad R^2 = 0.9828 \]

\[ y = -4165.5x + 21.231 \quad R^2 = 0.97 \]

- $h = 6.63 \times 10^{-34}$ J s$^{-1}$
- $k_B = 1.38 \times 10^{-23}$ J K$^{-1}$
- $R = 8.314$ J mol$^{-1}$ K$^{-1}$
Supplementary Figure 27. Equilibrium saturation transfer difference measurements on impure 10. The resonance of the chelating PPh$_2$py ligand at ca. $\delta$(P) -48 was irradiated throughout the recovery delay (3 s). Top set sample 5 - 10 in MeOH Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:3.2:15; bottom set sample 6.- Pd:PPh$_2$py:CH$_3$SO$_3$H = 1:2.9:10.

Significant saturation transfer is seen to the other PPh$_2$py ligands in 10 but not to those of other complexes.
Supplementary Figure 28. Experimental and simulated variable temperature $^{31}\text{P}^{1\text{H}}$ NMR spectra of 3(Cl) in CD$_2$Cl$_2$:MeOH (8:1). Note changes in ppm scale at 233, 253, 283 and 293 K.

- T = 193 K, $k = <11$ s$^{-1}$
- T = 203 K, $k = 22.5$ s$^{-1}$
- T = 213 K, $k = 64.6$ s$^{-1}$
- T = 223 K, $k = 135$ s$^{-1}$
- T = 233 K, $k = 281$ s$^{-1}$
- T = 243 K, $k = 618$ s$^{-1}$
- T = 253 K, $k = 1146$ s$^{-1}$
- T = 263 K, $k = 1966$ s$^{-1}$
- T = 273 K, $k = 2800$ s$^{-1}$
- T = 283 K, $k = 4719$ s$^{-1}$

- T = 293 K, $k = 6742$ s$^{-1}$
**Supplementary Figure 29.** Experimental and simulated variable temperature $^{31}$P($^1$H) NMR spectra of $3[\text{OTf}]$ in CD$_2$Cl$_2$:MeOH (8:1). Note changes in ppm scale at 223, 263, and 283 K.
Supplementary Figure 30. Experimental and simulated variable temperature $^{31}$P($^1$H) NMR spectra of 3(Cl) in CD$_2$Cl$_2$:MeOH (1:1). Note changes in ppm scale at 243, and 273 K.
Supplementary Figure 31. Experimental and simulated variable temperature $^{31}$P($^1$H) NMR spectra of 3[OTf] in CD$_2$Cl$_2$:MeOH (1:1).
Supplementary Figure 32. Variable temperature $^{31}\text{P}[^1\text{H}]$ NMR spectra of 4(Cl) in CD$_2$Cl$_2$:MeOH (1:1).
Supplementary Figure 33. $^{31}\text{P}^{(1\text{H})}$ NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 193 K.
Supplementary Figure 34. $^{31}$P($^1$H) NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 213 K.

$^{31}$P($^1$H) NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 213 K.
Supplementary Figure 35. $^{31}\text{P}^{(1)}\text{H}$ NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 233 K.
Supplementary Figure 36. $^{31}\text{P}^{(1\text{H})}$ NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 243 K.

T = 243 K

4[OTf] xss PN

4[OTf] Stoichiometric PN

4[OTf] deficiency PN

4(Cl) 1.6 eq xss PN

4(Cl) 0.4 eq xss PN

4(Cl) Stoichiometric PN

4(Cl) 10% deficiency PN
Supplementary Figure 37. $^{31}\text{P}^{(1\text{H})}$ NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 263 K.
Supplementary Figure 38. $^{31}\text{P}^{(1\text{H})}$ NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 273 K.
Supplementary Figure 39. $^{31}$P($^1$H) NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); $T = 283$ K.
Supplementary Figure 40. $^{31}$P($^1$H) NMR spectra of 4 in CD$_2$Cl$_2$:MeOH (1:1); T = 293 K.
Supplementary Figure 41. Simulations of the variable temperature $^{31}\text{P}^1\text{H}$ NMR spectra of 4(Cl)in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:4.6, together with the Eyring and Arrhenius plots.

Eyring plot Pd:P = 3.4

Arrhenius Plot
**Supplementary Figure 42.** Simulations of the variable temperature $^{31}\text{P}^1\text{H}$ NMR spectra of 4(Cl)in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1: 3.4, together with the Eyring and Arrhenius plots.
Supplementary Figure 43. Simulations of the variable temperature $^{31}$P{$^1$H} NMR spectra of 4(Cl)in CD$_2$Cl$_2$:MeOH (1:1), Pd:P = 1:3.03, together with the Eyring and Arrhenius plots.

Eyring plot Pd:P = 3.4

Arrhenius Plot
**Supplementary Table 1**  Kinetic and thermodynamic parameters for the dynamic processes in 4(Cl) in CD_2Cl_2:MeOH (1:1).

<table>
<thead>
<tr>
<th>P:Pd</th>
<th>k_{intra}^{253 \text{ a}} / s^{-1}</th>
<th>k_{inter}^{253 \text{ a}} / s^{-1}</th>
<th>\Delta S_{intra}^{\dagger b} \text{ J mol}^{-1} \text{ K}^{-1}</th>
<th>\Delta S_{inter}^{\dagger b} \text{ J mol}^{-1} \text{ K}^{-1}</th>
<th>\Delta H_{intra}^{\dagger c} \text{ kJ mol}^{-1}</th>
<th>\Delta H_{inter}^{\dagger c} \text{ kJ mol}^{-1}</th>
<th>E_{act}^{\text{ intra c}} \text{ kJ mol}^{-1}</th>
<th>E_{act}^{\text{ inter c}} \text{ kJ mol}^{-1}</th>
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</thead>
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<tr>
<td>3.03</td>
<td>950</td>
<td>670</td>
<td>-14</td>
<td>-24</td>
<td>43</td>
<td>42</td>
<td>45</td>
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<tr>
<td>3.4</td>
<td>950</td>
<td>385</td>
<td>-21</td>
<td>-26</td>
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<td>42</td>
<td>43</td>
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<tr>
<td>4.6</td>
<td>565</td>
<td>370</td>
<td>-32</td>
<td>6\text{ d}</td>
<td>41</td>
<td>50</td>
<td>41</td>
<td>52</td>
</tr>
</tbody>
</table>

Estimated errors: \(^{\text{ a}} \sim +/- 10\%;^{\text{ b}} \sim +/- 10 \text{ J mol}^{-1} \text{ K}^{-1};^{\text{ c}} \Delta H^{\dagger} \text{ and } E_{act}^{\text{ c}} \sim +/- 10\%;^{\text{ d}} \sim +/- 20 \text{ J mol}^{-1} \text{ K}^{-1}.\)
X-Ray Crystallography.

Crystallographic data were recorded on a Bruker Smart Apex diffractometer using Mo Kα-radiation (λ = 0.71073 Å) at T = 100 K. Structures were solved by Direct Methods and refined by full-matrix least squares against F² using all data (SHELXTL). All non-H atoms were refined anisotropically with the exception of disordered atoms. H-atoms were fixed in calculated positions at parent C and N atoms, respectively. The pyridyl-N atom in 1 is disordered over two pyridyl rings (N1 and C8). The C/N site occupancies for these two positions refined to 0.5/0.5 (equivalent xyz and adp constraints were applied). The CH₂Cl₂ molecule of 7.CH₂Cl₂ is disordered over two positions. The disordered atoms were split on two positions and refined using similar distance and similar U restraints. Semi-empirical absorption corrections based upon equivalent and redundant reflections was applied to the data of 2b.CH₂Cl₂, 3[BF₄] and 7.CH₂Cl₂.
**Supplementary Table 2**  
Crystal data for 2b.2CH$_2$Cl$_2$, 2b'([MeSO$_3$])$_2$.2CH$_2$Cl$_2$, 3[BF$_4$], 4(Cl).2H$_2$O and 7.CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th></th>
<th>2b.2CH$_2$Cl$_2$</th>
<th>2b'([MeSO$_3$])$_2$.2CH$_2$Cl$_2$</th>
<th>3[BF$_4$]</th>
<th>4(Cl).2H$_2$O</th>
<th>7.CH$_2$Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>chem formula</td>
<td>C$<em>{36}$H$</em>{32}$Cl$_6$N$_2$P$_2$Pd</td>
<td>C$<em>{36}$H$</em>{40}$Cl$_6$N$_2$O$_6$P$_2$PdS$_2$</td>
<td>C$<em>{34}$H$</em>{28}$BCl$_4$N$_2$O$_6$P$_2$Pd</td>
<td>C$<em>{54}$H$</em>{46}$Cl$_2$N$_2$O$_6$P$_3$Pd</td>
<td>C$<em>{48}$H$</em>{38}$Cl$_2$N$_2$O$_2$P$_3$Pd</td>
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<tr>
<td>fw</td>
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<td>755.18</td>
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<td>space group</td>
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<td>Pbca</td>
<td>P2$_1$/n</td>
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<td>17.704(2)</td>
<td>11.8634(16)</td>
<td>8.5706(9)</td>
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<td>b, Å</td>
<td>7.9187(4)</td>
<td>10.0239(14)</td>
<td>18.156(2)</td>
<td>11.1293(15)</td>
<td>9.5072(10)</td>
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<td>c, Å</td>
<td>22.9503(12)</td>
<td>18.270(3)</td>
<td>20.149(3)</td>
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<tr>
<td>α, deg</td>
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<td>90</td>
<td>90</td>
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<td>β, deg</td>
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<td>80.784(2)</td>
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<tr>
<td>γ, deg</td>
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<td>90</td>
<td>90</td>
<td>90</td>
<td>78.237(2)</td>
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<tr>
<td>V, Å$^3$</td>
<td>3634.8(3)</td>
<td>4369.6(10)</td>
<td>6476.4(14)</td>
<td>4722.0(11)</td>
<td>1778.1(3)</td>
</tr>
<tr>
<td>Z</td>
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<td>4</td>
<td>8</td>
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<td>2</td>
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<tr>
<td>$\rho_{\text{calc}}$, g cm$^{-1}$</td>
<td>1.597</td>
<td>1.620</td>
<td>1.549</td>
<td>1.411</td>
<td>1.543</td>
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<tr>
<td>$\mu$, mm$^{-1}$</td>
<td>1.070</td>
<td>1.008</td>
<td>0.805</td>
<td>0.651</td>
<td>0.802</td>
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<tr>
<td>Reflections (total)</td>
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<td>21748</td>
<td>38516</td>
<td>23535</td>
<td>9230</td>
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<tr>
<td>Reflections (unique)</td>
<td>4310</td>
<td>7680</td>
<td>7687</td>
<td>6163</td>
<td>50.0</td>
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<tr>
<td>2θ(max), deg</td>
<td>56.5</td>
<td>50.0</td>
<td>56.5</td>
<td>50.0</td>
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<tr>
<td>R(F) [I &gt; 2σ(I)]</td>
<td>0.023</td>
<td>0.063</td>
<td>0.024</td>
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<tr>
<td>wR2(F$^2$) (all data)</td>
<td>0.058</td>
<td>0.168</td>
<td>0.064</td>
<td>0.171</td>
<td>0.164</td>
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</table>
Crystal Structure of trans-[Pd(κ¹⁻Ph₂Ppy)₂Cl₂] (2b)

Yellow crystals, suitable for an X-ray crystal structure determination were obtained by layering a dichloromethane solution of a mixture of cis and trans isomers 2a/b with diethyl ether. Visually, there appeared to be only one type of crystal present. The X-ray determination showed that these crystals contained the trans isomer 2b (Figure 1). Selected bond lengths and angles are given in Table 3.

Supplementary Figure 44. Molecular structure of trans-[Pd(κ¹⁻Ph₂Ppy)₂Cl₂] 2b with key atoms labelled and H atoms removed for clarity

The coordination about the palladium centre is square planar, with a centre of inversion at the palladium centre. Both Ph₂Ppy ligands are coordinated to palladium through phosphorus and are mutually trans, two terminal chloride ligands complete the
coordination sphere (Figure 1). The position of nitrogen in one of the Ph$_2$Ppy ligands was split exactly between two phenyl rings so that each of the two rings were refined with C8 50% occupancy and N1 50% occupancy, no further refinement was attempted. The M-P bond lengths [2.3125(4) Å] are typical for Pd(II) complexes and are comparable to those reported for trans-[Pd($\kappa^1$-Ph$_2$Ppy)$_2$(CO$_2$CH$_3$)Cl] [2.3315 Å]$^1$ and trans-[Pd($\kappa^1$-Ph$_2$Ppy)$_2$(PhC=CH$_2$)(CF$_3$CO$_2$)] [2.340(2) Å]$^2$. Bond angles between P1-Pd-P2 and Cl1-Pd-Cl2 are 180°, but P-Pd-Cl bond angles deviate slightly from the ideal 90°, Supplementary Table 2.

**Supplementary Table 3.** Selected bond lengths (Å) and angles (°) for trans-[Pd($\kappa^1$-Ph$_2$Ppy)$_2$Cl$_2$] (2b)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-P1</td>
<td>2.3125(4)</td>
</tr>
<tr>
<td>Pd-P2</td>
<td>2.3125(4)</td>
</tr>
<tr>
<td>P1-Pd-P1a</td>
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<tr>
<td>Cl1-Pd-Cl1a</td>
<td>180.000</td>
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<tr>
<td>Pd-Cl1</td>
<td>2.2973(4)</td>
</tr>
<tr>
<td>Pd-Cl2</td>
<td>2.2973(4)</td>
</tr>
<tr>
<td>P1-Pd-Cl1</td>
<td>92.988(13)</td>
</tr>
<tr>
<td>P1a-Pd-Cl1a</td>
<td>87.012(13)</td>
</tr>
</tbody>
</table>
Crystal structure of \[\text{Pd}(\kappa^1-\text{Ph}_2\text{Ppy})_3\text{Cl}](\text{Cl}) \ (4(\text{Cl}))

Crystals of 4 suitable for an X-ray crystal structure determination were obtained by slow removal of solvent from a saturated dichloromethane/MeOH solution in vacuo. Supplementary Figure 49 shows the molecular structure of 4 and selected bond lengths and angles are given in Supplementary Table 4. The complex is approximately square planar at the palladium centre with three purely monodentate pyridylphosphine ligands bonded through phosphorus and one chloride ligand completing the coordination sphere. The distortion from ideal geometry can be attributed to the steric bulk of the phosphine ligands. The Pd-P bond trans to the chloride is significantly shorter, 2.267(5) Å, as compared to the average Pd-P bond length cis to the Cl⁻ ligand, 2.3515(13) Å. The average Cl-Pd-P cis and P cis-P-P trans bond angles were found to be 84.44(6)° and 96.65(6)° respectively, whereas the P cis-P-P cis bond angle was determined to be 161.50(6)°. Within the monocationic complex the pyridyl and phenyl groups are packed effectively via pi-stacking interactions and CH..N contacts, Supplementary Figure 45.

**Supplementary Table 4.** Selected bond lengths (Å) and angles (°) for \[[\text{Pd}(\kappa^1-\text{Ph}_2\text{Ppy})_3\text{Cl}](\text{Cl}).2\text{H}_2\text{O}\] (4(\text{Cl}).2\text{H}_2\text{O}).

<table>
<thead>
<tr>
<th>Bond Lengths (Å)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-P1</td>
<td>2.3515(13)</td>
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<tr>
<td>Pd-P2</td>
<td>2.3515(13)</td>
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<tr>
<td>P1-Pd-P2</td>
<td>161.51(5)</td>
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<tr>
<td>P1-Pd-P3</td>
<td>96.62(5)</td>
</tr>
<tr>
<td>P2-Pd-P3</td>
<td>96.65(5)</td>
</tr>
</tbody>
</table>
Supplementary Figure 45. Molecular structure of \([\text{Pd}(\kappa^1-\text{Ph}_2\text{Ppy})_3\text{Cl}](\text{Cl})\cdot2\text{H}_2\text{O}\) (4(Cl).2H_2O) highlighting the CH...N (blue) and π-stacking interactions (red) between the phosphine ligands.
References