Experimental

**Synthesis of \([\text{PhCH}_2\text{PPh}_3]_2[\text{PdCl}_4]\)**

To a solution of potassium tetrachloropalladate (0.412g, 1.262x10^{-3}mol) in distilled water (50ml) was added benzyltriphenylphosphonium chloride (0.9837g, 2.530x10^{-3}mol). Dichloromethane (100ml) was added and the resulting mixture stirred overnight. The dichloromethane layer was separated and the water layer extracted with dichloromethane (3 x 50ml). The dichloromethane fractions were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure leaving the product as a dark orange powder (0.982g, 1.028x10^{-3}mol, 81.5%).

**Synthesis of \([4\text{-picolinium}]_2[\text{PtCl}_4]\), 1**

To a solution of bis-benzyltriphenylphosphonium tetrachloroplatinate(II) (1.001g, 9.60x10^{-4}mol) in dichloromethane (50ml) was added, dropwise with stirring, a solution of 4-picolinium tetrafluoroborate (0.365g, 2.02x10^{-3}mol) in dichloromethane (20ml). Immediately upon addition a red/brown precipitate was observed which was isolated by filtration, washed with dichloromethane (2x20ml) and dried at the pump (0.411g, 7.83x10^{-4}mol, 81.6%). Microanalytical data (%). Found: C, 27.31; H, 2.97; N, 5.23. Calc.: C, 27.44; H, 3.07; N, 5.33.

**Synthesis of \([4\text{-picolinimum}]_2[\text{PdCl}_4]\), 2.**

To a solution of bis-benzyltriphenylphosphonium tetrachloropalladate(II) (1.005g, 1.05x10^{-3}mol) in dichloromethane (50ml) was added, dropwise with stirring, a solution of 4-picolinium tetrafluoroborate (0.399g, 2.21x10^{-3}mol) in dichloromethane (20ml). Immediately upon addition a red brown precipitate was formed which was isolated by filtration, washed with dichloromethane (2x10ml) and dried at the pump (0.365g, 8.37x10^{-4}mol, 79.5%). Microanalytical data (%). Found: C, 32.07; H, 3.38; N, 6.05. Calc.: C, 33.02; H, 3.69; N, 6.42.

**Thermolysis of 1.**

**A: Synthesis of \([4\text{-picolininium}][(\text{4-picoline})\text{PtCl}_3]\), 3.**

Solid \([4\text{-picolininium}]_2[\text{PtCl}_4]\) (0.411g, 7.83x10^{-4}mol) was heated, with stirring, under a flow of N\(_2\) at 160°C for 90 minutes to give a pale orange/yellow powder (0.273g, 5.60x10^{-4}mol, 71.6%). Microanalytical data (%). Found: C, 29.62; H, 3.03; N, 5.37. Calc.: C, 29.49; H, 3.09; N, 5.73. Crystals suitable for X-ray diffraction study were grown by recrystallisation from dichloromethane/hexane.

**B: Synthesis of trans-[\text{PtCl}_2(\text{4-picoline})_2], 4.**

Solid 3 (0.251g, 5.15x10^{-4}mol) was heated, with stirring under a flow of N\(_2\) at 160°C for 40 minutes to give a yellow/orange powder (0.2297g, 5.08x10^{-4}mol, 98.6%). Microanalytical data (%). Found: C, 31.10; H, 3.24; N, 5.78. Calc.: C, 31.87; H, 3.12; N, 6.19. X-ray powder diffraction confirmed the structure of the product phase to be identical to that published for trans-[\text{PtCl}_2(\text{4-picoline})_2] (C Tessier, F.D. Rochon. Inorg. Chim. Acta, 1999, 295, 25).
Thermolysis of 2.

Synthesis of trans-[PdCl₂(4-picoline)₂], 5.

Solid [4-picolinium]₂[PdCl₄] (0.365g, 8.37x10⁻⁴mol) was heated with stirring under a flow of N₂ at 160°C for 90 minutes to give a pale orange/yellow powder (0.287g, 7.90x10⁻⁴mol, 94.4%). Crystals suitable for X-ray diffraction study were grown from dichloromethane/hexane. Microanalytical data (%). Found: C, 39.21; H, 3.72; N, 7.04. Calc.: C, 39.69; H, 3.88; N, 7.70.