Supplementary Material (ESI) for Chemical Communications

Experimental

Synthesis of $[PhCH_2PPh_3]_2[PdCl_4]$

To a solution of potassium tetrachloropalladate (0.412g, 1.262×10^{-3}mol) in distilled water (50ml) was added benzyltriphenylphosphonium chloride (0.9837g, 2.530×10^{-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, 1.028×10^{-3}mol, 81.5%).

*Synthesis of $[4\text{-picolinium}]_2[PtCl_4]$, **1***

To a solution of bis-benzyltriphenylphosphonium tetrachloroplatinate(II) (1.001g, 9.60×10^{-4}mol) in dichloromethane (50ml) was added, dropwise with stirring, a solution of 4-picolinium tetrafluoroborate (0.365g, 2.02×10^{-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, 7.83×10^{-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 $[4\text{-picolinium}]_2[PdCl_4]$, **2**.*

To a solution of bis-benzyltriphenylphosphonium tetrachloropalladate(II) (1.005g, 1.05×10^{-3}mol) in dichloromethane (50ml) was added, dropwise with stirring, a solution of 4-picolinium tetrafluoroborate (0.399g, 2.21×10^{-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, 8.37×10^{-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 $[4\text{-picolinium}][(4\text{-picoline})PtCl_3]$, **3**.*

Solid $[4\text{-picolinium}]_2[PtCl_4]$ (0.411g, 7.83×10^{-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, 5.60×10^{-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-$[PtCl_2(4\text{-picoline})_2]$, **4**.*

Solid **3** (0.251g, 5.15×10^{-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, 5.08×10^{-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*-$[PtCl_2(4\text{-picoline})_2]$ (C Tessier, F.D. Rochon. *Inorg. Chim. Acta*, 1999, **295**, 25).

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*Thermolysis of **2**.*

*Synthesis of trans-[$PdCl_2$(4-picoline)$_2$], **5**.*

Solid [4-picolinium]$_2$[$PdCl_4$] (0.365g, 8.37×10^{-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 (0.287g, 7.90×10^{-4}mol, 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.