

IR,  $^{31}\text{P}$  NMR and analytical data for **1-5**. IR spectra were obtained in dichloromethane solution, and  $^{31}\text{P}$  NMR in  $\text{CDCl}_3$  at 121.42 MHz and referenced to external  $\text{H}_3\text{PO}_4$ .

| Compound | $\nu(\text{C}\equiv\text{C}) / \text{cm}^{-1}$ | $\delta(^{31}\text{P})$<br>( $^1J_{\text{PtP}} / \text{Hz}$ ) | Formula   | Analytical data (%) |              |              |
|----------|--|---|---|---------------------|--------------|--------------|
|          |  |   |   | Found (Calc.)       |              |              |
|          |  |   |   | C                   | H            | N            |
| <b>1</b> | 2113   | 9.30<br>(2298)  | $\text{C}_{20}\text{H}_{34}\text{NIO}_2\text{P}_2\text{Pt}$ | 34.2<br>(34.1)      | 4.8<br>(4.9) | 1.9<br>(2.0) |
| <b>2</b> | 2115 <sup>a</sup>                              | 9.24<br>(2294)  | $\text{C}_{21}\text{H}_{34}\text{NIP}_2\text{Pt}$           | 37.2<br>(36.9)      | 4.7<br>(5.0) | 2.3<br>(2.1) |
| <b>3</b> | 2098   | 11.90<br>(2344)   | $\text{C}_{28}\text{H}_{38}\text{NIO}_2\text{P}_2\text{Pt}$ | 42.0<br>(41.8)      | 4.6<br>(4.8) | 1.9<br>(1.7) |
| <b>4</b> | 2099 <sup>b</sup>                              | 11.83<br>(2348)   | $\text{C}_{29}\text{H}_{38}\text{NIP}_2\text{Pt}$           | 44.3<br>(44.4)      | 4.9<br>(4.9) | 1.6<br>(1.8) |
| <b>5</b> | 2101   | 12.03<br>(2384)   | $\text{C}_{28}\text{H}_{38}\text{I}_2\text{P}_2\text{Pt}$   | 37.9<br>(38.0)      | 4.5<br>(4.3) | -            |

<sup>a</sup> Also shows  $\nu(\text{C}\equiv\text{N})$  at  $2226 \text{ cm}^{-1}$ .

<sup>b</sup> Also shows  $\nu(\text{C}\equiv\text{N})$  at  $2225 \text{ cm}^{-1}$ .

### Synthetic procedures

**[PtI(PEt<sub>3</sub>)<sub>2</sub>(-C≡C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>)] 1.** [Pt(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub>] (0.095 g, 0.138 mmol), *p*-nitrophenylacetylide (0.022 g, 0.149 mmol) and copper iodide (10 mg) were dissolved in toluene (10 cm<sup>3</sup>) and diisopropylamine (0.5 cm<sup>3</sup>) was added to give a yellow solution. This solution was then stirred under nitrogen at room temperature for 1 h. After removal of the solvent under vacuum, the product was redissolved in toluene and filtered through celite. The product was then purified by silica column chromatography with toluene as eluent. The first yellow band eluted was unreacted Pt(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub> (0.009 g, 0.013 mmol), and the second was the desired product PtI(PEt<sub>3</sub>)<sub>2</sub>(-C≡C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>), which following removal of the solvent was isolated as a yellow oil (0.072 g, 0.125 mmol, 82 %). Recrystallisation from hexane gave an analytical sample as yellow crystals.

**[PtI(PEt<sub>3</sub>)<sub>2</sub>(-C≡C-C<sub>6</sub>H<sub>4</sub>CN)] 2.** [Pt(PEt<sub>3</sub>)<sub>2</sub>I<sub>2</sub>] (0.200 g, 0.291 mmol), *p*-ethynylbenzotrile (0.038 g, 0.299 mmol) and copper iodide (10 mg) were dissolved in toluene (10 cm<sup>3</sup>) and diisopropylamine (0.5 cm<sup>3</sup>), giving a yellow solution. This solution was then stirred under nitrogen at room temperature for 2 h. After removal of the solvent under vacuum, the product was redissolved in toluene and filtered

through celite. The product was then purified by silica column chromatography with 8:1 toluene:dichloromethane as eluent. The first (yellow) band eluted was unreacted  $\text{Pt}(\text{PEt}_3)_2\text{I}_2$  (0.043 g, 0.062 mmol), and the second (yellow-green) band (eluted with 5:1 toluene:dichloromethane) was the desired product  $\text{PtI}(\text{PEt}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CN})$ , which following removal of the solvent was isolated as a yellow-green oil (0.112 g, 0.163 mmol, 56 %). Recrystallisation from hexane gave an analytical sample as yellow-green needles.

**[Pt(PEt<sub>3</sub>)<sub>2</sub>(C≡C-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>)(C≡C-C<sub>6</sub>H<sub>4</sub>-I)] 3.** 0.044 g (0.062 mmol) of  $\text{PtI}(\text{PEt}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{NO}_2)$ , 0.022 g (0.088 mmol) of *p*-iodophenylacetylene and 5 mg of CuI were stirred for 24 h in a mixture of 10 cm<sup>3</sup> of toluene and 0.5 cm<sup>3</sup> of diisopropylamine, giving a yellow solution. After removal of the solvent under vacuum, the product was redissolved in toluene and filtered through celite. Following evaporation to dryness, the product was then purified by alumina column chromatography with 1:1 toluene:dichloromethane as eluent. Collection and evaporation of the first yellow band gave 0.039 g of  $\text{Pt}(\text{PEt}_3)_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{NO}_2)(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{I})$  as a yellow solid (0.048 mmol, 77 %), which was recrystallised as yellow crystals from a refrigerated diethyl ether / hexane mixture.

**[Pt(PEt<sub>3</sub>)<sub>2</sub>(-C≡C-C<sub>6</sub>H<sub>4</sub>-CN)(-C≡C-C<sub>6</sub>H<sub>4</sub>-I)] 4.** 0.100 g of  $\text{PtI}(\text{PEt}_3)_2(-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CN})$  (0.146 mmol), 0.035 g of *p*-iodophenylacetylide (0.153 mmol) and copper iodide (10 mg) were dissolved in toluene (10 cm<sup>3</sup>) and diisopropylamine (0.5 cm<sup>3</sup>) to give a pale yellow solution. This solution was then stirred under nitrogen at room temperature for 2 h. The solvent was removed under vacuum and the product was redissolved in toluene and filtered. Following evaporation to dryness, the product was then purified by alumina column chromatography with 1:1 toluene:dichloromethane as eluent, collecting the first yellow band visible. Evaporation of the solvent and recrystallisation from diethyl ether / hexane gave yellow / orange crystals of the product (0.052 g, 0.066 mmol, 45 %).

**[Pt(PEt<sub>3</sub>)<sub>2</sub>(-C≡C-C<sub>6</sub>H<sub>4</sub>-I)<sub>2</sub>] 5.**  $\text{Pt}(\text{PEt}_3)_2\text{I}_2$  (0.100 g, 0.15 mmol), *p*-iodophenylacetylide, (0.097 g, 0.42 mmol) and copper iodide (10 mg) were dissolved in toluene (10 cm<sup>3</sup>) and diisopropylamine (0.5 cm<sup>3</sup>) to give a pale yellow solution.

This solution was then stirred under nitrogen at room temperature overnight. The solvent was removed under vacuum and the product was redissolved in toluene and filtered. Following removal of the solvent, the residual solid was recrystallised from ethyl acetate to give an off-white crystalline solid (0.036 g, 0.038 mmol, 26 %).