

Electronic Supplementary Information for Dalton Trans.

A Novel Fluorene-Containing κ^4 - P_2N_2 -Tetradentate Platinum(II) Complex

Mark R. J. Elsegood, Andrew J. Lake and Martin B. Smith*

Department of Chemistry, Loughborough University, Loughborough,

Leicestershire, UK, LE11 3TU

* To whom correspondence should be addressed. E-mail: m.b.smith@lboro.ac.uk. Tel: +44 (0)1509 222553. Fax: +44 (0)1509 223925.

Experimental Section

Materials. Reactions were carried out under aerobic conditions unless otherwise stated. Dichloromethane was previously distilled over CaH₂ and diethyl ether over sodium/benzophenone. HPLC grade acetone, methanol and other chemicals were obtained from commercial suppliers and used without further purification. The starting materials Ph₂PCH₂OH and PtCl₂(cod) were prepared according to literature procedures.^{1,2}

Instrumentation. FT–IR spectra were recorded as pressed KBr pellets over the range 4000–200 cm⁻¹ using a Perkin-Elmer system 2000 FT spectrometer. ¹H NMR and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) reported relative to external TMS or 85% H₃PO₄. Coupling constants (*J*) in Hz. All NMR spectra were recorded in CDCl₃ solutions at *ca.* 298 K. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Compound **2** was analysed by low-resolution EI and CI (positive ion mode only) using CH₂Cl₂/CH₃OH as the solvent. Compound **3** was analysed (Finnigan MAT 95XP instrument) by low-resolution FAB (LSIMS) in positive ionisation mode using CH₂Cl₂ as the solvent and a NOBA matrix whereas compound **4** was analysed (Micromass ZQ4000 instrument) by electrospray (ES) in both positive and negative ionisation modes using CH₂Cl₂/CH₃OH as the solvent and CH₃OH/H₂O as the liquid flow in which samples were introduced into the source.

Preparation of Ph₂PCH₂NHN=CC₁₂H₈, 1. The solids H₂NN=CC₁₂H₈ (0.750 g, 3.86 mmol) and Ph₂PCH₂OH (1.045 g, 4.83 mmol) in CH₃OH (HPLC grade, 30 cm³) were refluxed, under a nitrogen atmosphere, for *ca.* 24 h. The yellow suspension was left to cool to ambient temperature and the volume concentrated, under reduced pressure, to *ca.* 10–15 cm³. The solid was filtered, washed with a small portion of CH₃OH and dried *in vacuo*. Yield: 1.402 g, 93%. Selected spectroscopic data for **1**: δ_P (161.8 MHz: CDCl₃) –16.0 ppm. δ_H (400 MHz: CDCl₃) 7.71–7.20 (18H, m, arom. H), 6.55 (1H, br, NH), 4.37 (2H, d, ²J_{PH} 6 Hz, CH₂) ppm. δ_C (100.6 MHz: CDCl₃) 141.04 (s, CN); 136.09 (d, ¹J_{CP} 14.1 Hz), 133.24, 133.06, 129.04, 128.82, 128.76 (all PC₆H₅); 140.83, 137.86, 137.73, 130.14, 128.94, 127.72, 127.68, 127.32, 124.36, 120.61, 120.35, 119.41 (all C₁₂H₈); 51.4 (d, ¹J_{CP} 16.1 Hz, CH₂) ppm. FT–IR (KBr) ν_{NH} 3284 cm⁻¹. Found: C, 79.69; H, 5.04; N, 6.68; C₂₆H₂₁N₂P requires C, 79.56; H, 5.40; N, 7.14.

Preparation of Ph₂P(O)CH₂NHN=CC₁₂H₈, 2: To an acetone (HPLC grade, 10 cm³) solution of **1** (0.101 g, 0.257 mmol) was added aq. H₂O₂ (27.5%, 0.1 cm³). After stirring for *ca.* 90 min the solution was evaporated to dryness. The residue was extracted into CH₂Cl₂ (1 cm³) and addition of diethyl ether (20 cm³) and hexanes (10 cm³) gave **2** which was collected by suction filtration and dried *in vacuo*. Yield: 0.079 g, 75%. Selected spectroscopic data for **2**: δ_P (161.8 MHz: CDCl₃) 28.6 ppm. δ_H (400 MHz: CDCl₃) 7.81–7.13 (18H, m, arom. H), 6.90 (1H, br, NH), 4.40 (2H, s, CH₂) ppm. FT–IR (KBr) ν_{NH} 3244, ν_{PO} 1210 cm⁻¹. EI–MS 408 [M]⁺. Found: C, 76.27; H, 5.15; N, 7.12; C₂₆H₂₁N₂PO requires C, 76.45; H, 5.19; N, 6.86.

Suitable crystals of **2** for X-ray crystallography were grown by the slow evaporation of a CH₃OH/C₇H₈ solution of the tertiary phosphine **1**.

Preparation of cis-PtCl₂(Ph₂PCH₂NHN=CC₁₂H₈)₂, **3:** To a CH₂Cl₂ (10 cm³) solution of PtCl₂(cod) (0.077 g, 0.206 mmol) was added **1** (0.164 g, 0.418 mmol) as a solid in one portion. The yellow solution was stirred for 15 min and concentrated, under reduced pressure, to approx. 2 cm³. Addition of diethyl ether (20 cm³) gave solid **3** which was collected by suction filtration and dried *in vacuo*. Yield: 0.214 g, 99%. Selected spectroscopic data for **3**: δ_P (161.8 MHz: CDCl₃) 9.6 ppm, ¹J_{PtP} 3721 Hz. δ_H (400 MHz: CDCl₃) 8.34 (2H, d, arom. H), 8.22 (2H, t, NH), 7.72–6.88 (34H, m, arom. H), 4.65 (4H, d, ²J_{PH} 5.6 Hz, CH₂) ppm. δ_C (100.6 MHz: CDCl₃) 140.66 (s, CN); 133.51, 129.24, 128.29 (all PC₆H₅); 140.36, 137.95, 137.87, 131.16, 129.97, 128.64, 127.66, 127.31, 125.36, 120.30, 120.14, 119.44 (all C₁₂H₈); 55.9 (m, ¹J_{CP} 44.2 Hz, CH₂) ppm. FT-IR (KBr) ν_{NH} 3358, ν_{PtCl} 314, 292 cm⁻¹. FAB-MS 1015 [M-Cl]⁺. Found: C, 59.55; H, 4.53; N, 4.96; C₅₂H₄₂N₄P₂PtCl₂ requires C, 59.43; H, 4.04; N, 5.33. Suitable crystals for X-ray crystallography were grown by vapour diffusion of Et₂O into a CDCl₃ solution of **3**.

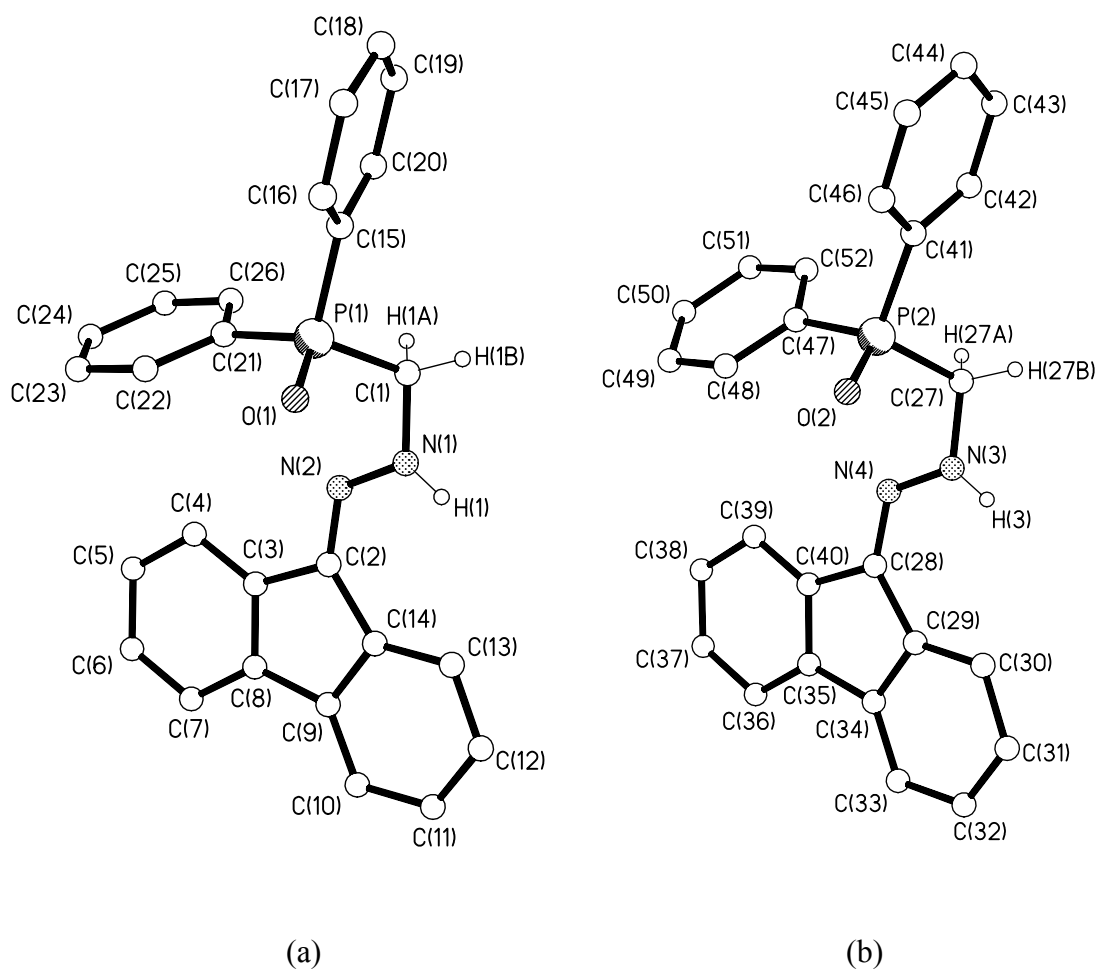
Preparation of Pt(κ⁴-P₂N₂-Ph₂PCH=NNCC₁₂H₈)₂, **4:** A suspension of **3** (0.300 g, 0.285 mmol) and ^tBuOK (0.071 g, 0.633 mmol) in CH₃OH (HPLC grade, 20 cm³) were refluxed, under a nitrogen atmosphere, for 4 h. The suspension was allowed to cool, the volume reduced by *ca.* half and the solid isolated by filtration under vacuum. Yield: 0.177 g, 64%. Selected spectroscopic data for **4**: δ_P (161.8 MHz: CDCl₃) 55.3 ppm, ¹J_{PtP} 3300 Hz. δ_H (400 MHz, 298 K: CDCl₃) 8.30 (4H, br, arom. H), 7.42–7.26 (20H, m, arom. H), 7.00 (4H, br, arom. H), 6.70 (4H, br, arom. H), 6.20 (4H, br, arom. H), 5.75 (2H, d, ²J_{PH} 32 Hz, CH₂) ppm. δ_C (100.6 MHz: CDCl₃) 92.5 (t, ²J_{CPt} 51.8 Hz, CH) ppm. ES-MS 977 [M-H]⁺. Found: C, 60.54; H, 3.63; N, 4.07; C₅₂H₃₈N₄P₂Pt·3H₂O requires C, 60.63; H, 4.31; N, 5.44. Suitable crystals for X-ray crystallography were grown by vapour diffusion of Et₂O into a CH₂Cl₂/C₇H₈ solution of **4**.

References

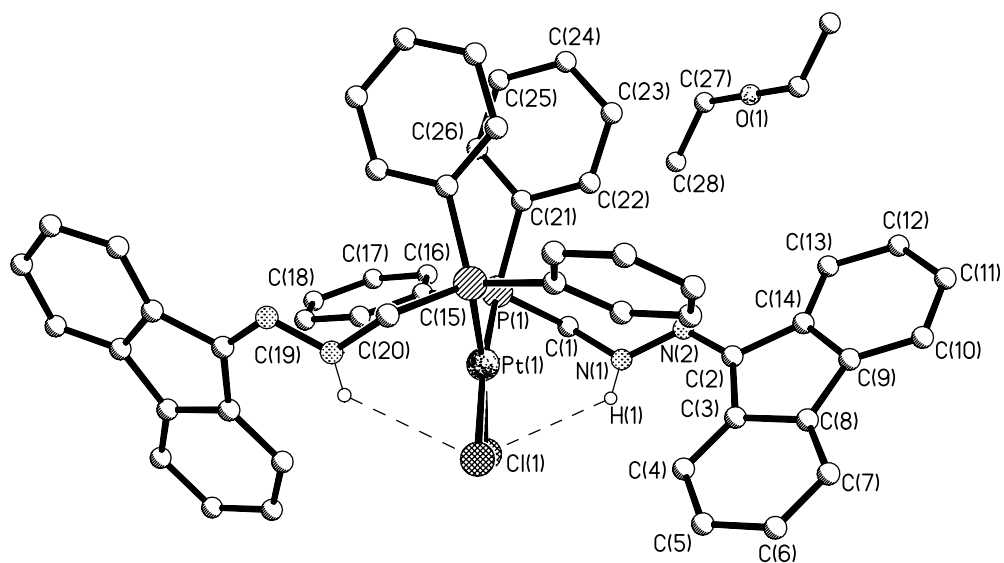
1. H. Hellmann, J. Bader, H. Birkner and O. Schumacher, *Justus Liebigs Ann. Chem.*, 1962, **659**, 49.
2. J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

Additional X-ray Figures (for 2–4) and Variable Temperature ^1H NMR spectra (for 4)

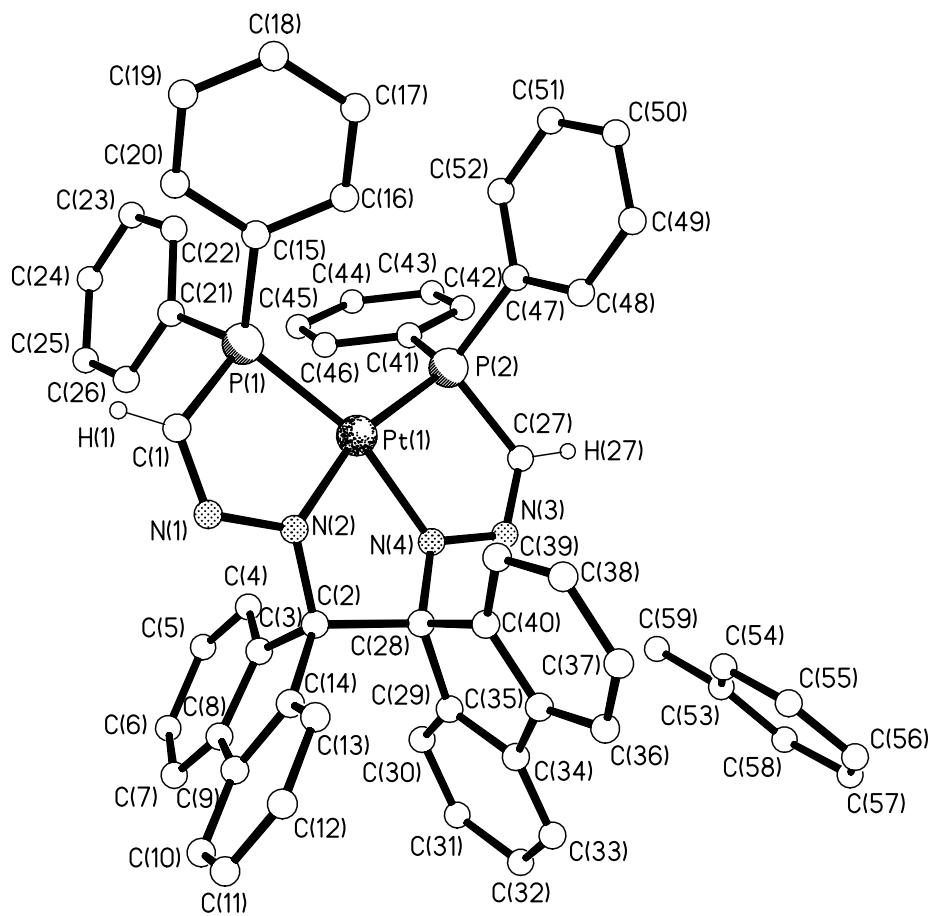
ESIFIG1 for **2** showing the full atom numbering scheme for both independent molecules.



ESIFIG2 for 3 showing the full atom numbering scheme.



ESIFIG3 for 4 showing the full atom numbering scheme.



ESIFIG4 for **4** showing the variable temperature ^1H NMR spectra (CDCl_3) in the range 20 -
-40 °C.

