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A Novel Fluorene-Containing $\kappa^4$-$P_2N_2$-Tetradeentate Platinum(II) Complex

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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: δₚ (161.8 MHz: CDCl₃) −16.0 ppm. δₜ (400 MHz: CDCl₃) 7.71–7.20 (18H, m, arom. H), 6.55 (1H, br, NH), 4.37 (2H, d, 2JₚH 6 Hz, CH₂) ppm. δₐ (100.6 MHz: CDCl₃) 141.04 (s, CN); 136.09 (d, 1JₚC 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, 1JₚC 16.1 Hz, CH₂) ppm. FT–IR (KBr) νₕ 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: δₚ (161.8 MHz: CDCl₃) 28.6 ppm. δₛ (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) νₕ 3244, νₚₔ 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 CH$_3$OH/C$_7$H$_8$ solution of the tertiary phosphine 1.

**Preparation of cis-PtCl$_2$(Ph$_2$PCH$_2$NHN=CC$_{12}$H$_8$)$_2$, 3:** To a CH$_2$Cl$_2$ (10 cm$^3$) solution of PtCl$_2$(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 cm$^3$. Addition of diethyl ether (20 cm$^3$) 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: CDCl$_3$) 9.6 ppm, $^1$J$_{PtP}$ 3721 Hz. δ$_H$ (400 MHz: CDCl$_3$) 8.34 (2H, d, arom. H), 8.22 (2H, t, NH), 7.72–6.88 (34H, m, arom. H), 4.65 (4H, d, $^2$J$_{PH}$ 5.6 Hz, CH$_2$) ppm. δ$_C$ (100.6 MHz: CDCl$_3$) 140.66 (s, CN); 133.51, 129.24, 128.29 (all PC$_6$H$_5$); 140.36, 137.95, 137.87, 131.16, 129.97, 128.64, 127.66, 127.31, 125.36, 120.30, 119.44 (all C$_{12}$H$_8$); 55.9 (m, $^1$J$_{CP}$ 44.2 Hz, CH$_2$) 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; C$_{52}$H$_{42}$N$_4$P$_2$PtCl$_2$ requires C, 59.43; H, 4.04; N, 5.33. Suitable crystals for X-ray crystallography were grown by vapour diffusion of Et$_2$O into a CDCl$_3$ solution of 3.

**Preparation of Pt(κ$_4$-P$_2$N$_2$-Ph$_2$PCH=NNCC$_{12}$H$_8$)$_2$, 4:** A suspension of 3 (0.300 g, 0.285 mmol) and $t$BuOK (0.071 g, 0.633 mmol) in CH$_3$OH (HPLC grade, 20 cm$^3$) 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: CDCl$_3$) 55.3 ppm, $^1$J$_{PtP}$ 3300 Hz. δ$_H$ (400 MHz, 298 K: CDCl$_3$) 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), 6.20 (4H, br, arom. H), 5.75 (2H, d, $^2$J$_{PH}$ 32 Hz, CH$_2$) ppm. δ$_C$ (100.6 MHz: CDCl$_3$) 92.5 (t, $^2$J$_{CP}$ 51.8 Hz, CH) ppm. ES–MS 977 [M–H]$^+$. Found: C, 60.54; H, 3.63; N, 4.07; C$_{52}$H$_{38}$N$_4$P$_2$Pt$_3$H$_2$O requires C, 60.63; H, 4.31; N, 5.44. Suitable crystals for X-ray crystallography were grown by vapour diffusion of Et$_2$O into a CH$_2$Cl$_2$/C$_7$H$_8$ solution of 4.

**References**
Additional X-ray Figures (for 2–4) and Variable Temperature $^1$H 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 $^1$H NMR spectra (CDCl$_3$) in the range 20 - 40 ºC.