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Synthesis and coordination of 7-diphenylphosphinoazaindole (dppai)

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Abstract

7-diphenylphosphinoazaindole has been synthesised and coordinated as a P,N bidentate ligand. Reaction of dppai with [PtCl₂(cod)], [PtClMe(cod)] and [PtClPh(cod)] in dichloromethane gives [PtCl₂(dppai-P,N)], [PtClMe(dppai-P,N)] and [PtClPh(dppai-P,N)] respectively.

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Hemilabile ligands continue to illicit great interest. The chemistry of dppap has been thoroughly explored by Aucott et al. [1], furthermore we have studied a range of phosphines obtained by P–N bond formations [2–7]. Here we report on the chemistry of an analogue of dppap which has the rotational freedom about the amine functionality removed by addition of a second ring thus providing a stabilising influence. The synthesis of 7-diphenylphosphinoazaindole (dppai, 1) proceeds straightforwardly (Eq. (1)) to give 1 in 36% yield.



This colourless solid is moderately air stable, it will completely degrade when exposed to air for a few days, it is however very soluble in all common laboratory solvents. The ³¹P NMR (CDCl₃) displays a singlet at δ (P) 33.2 ppm, which is similar to dppap (26.4 ppm). The pyC[6] proton is observed at δ (H) 8.4 ppm as a double doublet, (J_{H-H} 5 and 2 Hz). The v(P–N) vibration is observed at 983 cm⁻¹ and the v(C–N) in the pyridyl ring is at 1589 cm⁻¹.

Reaction of dppai with [PtCl₂(cod)] in dichloromethane gives [PtCl₂(dppai-P,N)], **2** with δ (P) 55 ppm, and ${}^{1}J_{Pt-P}$ of 4160 Hz. This NMR data is consistent with a phosphorus *trans*- to a chloride but is significantly larger coupling constant than the average value

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seen in dppap (3576 Hz) for the equivalent reaction. ¹ The ¹H NMR is also enlightening with respect to the pyC[6] proton, as we predict that on chelation this pro-

¹ 7-diphenylphosphinoazaindole (dppai) (1): Chlorodiphenylphosphine (3.80 cm³, 21.1 mmol) was added to a solution of 1H-indole (2.5 g, 21.1 mmol), triethylamine (3.10 ml, 22.2 mmol) and DMAP (259 mg, 2.1 mmol) in THF (100 cm³) and refluxed overnight. The reaction mixture was filtered to remove a white solid (Et₃NHCl) and washed with THF (50 cm³). The solvent was removed in vacuo leaving a pale yellow solid. This solid was recrystallised by cooling a concentrated diethyl ether solution in a fridge overnight (yield: 2.3 g, 36%). v_{max}/cm^{-1} : 1589, 1405, 983. ³¹P NMR (109.3 MHz, CDCl₃), δ 33.2. ¹H NMR (270 MHz, CDCl₃), 8.4 (1H, dd, J = 5 Hz, 2 Hz, aromatic), 7.9 (1H, dt, J = 8 Hz, 1 Hz, aromatic), 7.4–7.3 (10H, m, aromatic), 7.1 (1H, dd, J = 8 Hz, 5 Hz, aromatic), 7.0 (1H, dd, J = 4 Hz, 2Hz, aromatic), 6.5 (1H, dd, J = 4 Hz, 1 Hz, aromatic).

[*PtCl*₂(*dppai-P,N*)] (2): Dppai (81 mg, 0.268 mmol) and [PtCl₂(cod)] (100 mg, 0.268 mmol) were weighed into a schlenk type flask and DCM (5 cm³) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was isolated after addition of Et₂O then filtered and washed with further ether (yield: 56 mg, 37%). C₁₉H₁₅N₂PCl₂Pt requires: C, 40.1; H, 2.66; N, 4.93. Found: C, 40.7; H, 2.68; N, 4.86%. v_{max}/cm^{-1} : 1648, 1438, 1107, 996. ³¹P NMR (109.3 MHz, CDCl₃), δ 55.4 (J_{P-Pt} = 4160 Hz). ¹H NMR (270 MHZ, CDCl₃), 9.4 (1H, m, J_{P-H} = 6 Hz, J_{Pt-H} = 43 Hz, pyC[6]H), 8.1 (2H, m, aromatic), 7.8 (3H, m, aromatic), 7.5 (5H, m, aromatic), 7.2 (4H, m, aromatic).

[PdCl₂(dppai-P,N)] (3): As 2. Dppai (106 mg, 0.35 mmol), and [PdCl₂(cod)] (100 mg, 0.35 mmol) gave a yellow solid (yield: 133 mg, 79%). C₁₉H₁₅N₂PCl₂Pd requires: C, 47.5; H, 3.15; N, 5.84. Found: C, 47.0; H, 2.63; N, 5.95%. v_{max}/cm^{-1} : 1438, 1104, 994, 344, 312. ³¹P NMR (109.3 MHz, CDCl₃), δ 80.5. ¹H NMR (270 MHz, CDCl₃), 9.2 (1H, dd, $J_{P-H} = 6$ Hz, pyC[6]H), 8.1 (1H, m, aromatic), 7.8 (4H, m, aromatic), 7.7–7.6 (2H, m, aromatic), 7.6–7.5 (4H, m, aromatic), 7.3 (1H, dd, aromatic), 7.2 (1H, m, aromatic), 7.0 (1H, m, aromatic).

Compounds 4 and 5 were prepared by similar procedures.

Crystal data: Single crystal X-ray diffraction studies on crystals were performed using a Bruker SMART diffractometer with graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, the non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were fixed. Structural refinements were by the full-matrix least-squares method on F^2 using SHELXTL [8].

2 C₁₉H₁₅N₂PCl₂Pt, M = 568.29, orthorhombic, a = 9.0694(15) Å, b = 15.250(3) Å, c = 26.813(5) Å, $\beta = 92.036(3)^{\circ}$. U = 3708.3(11) Å³, T = 125 K, space group *Pbca* Z = 8, μ (Mo-K α) = 7.946 mm⁻¹. Of 14,950 measured data, 2658 were unique, to give $R_1[I > 2\sigma(I)] =$ 0.0241, wR 0.0448.

3 C₁₉H₁₅N₂PCl₂Pd, M = 479.60, monoclinic, a = 9.8511(10) Å, b = 15.5407(16) Å, c = 12.3756(12) Å, $\beta = 111.174(2)^{\circ}$. U = 1766.7(3) Å³, T = 125 K, space group P2(1)/c, Z = 4, μ (Mo-K α) = 1.477 mm⁻¹. Of 7581 measured data, 2527 were unique to give $R_1[I > 2\sigma(I)] = 0.0228$, wR 0.0574.

4 C₂₀H₁₈N₂PClPt, M = 547.87, triclinic, a = 9.584(3) Å, b = 10.289(3) Å, c = 10.965(4) Å, $\alpha = 88.925(5)$, $\beta = 77.471(5)$, $\gamma = 62.072(4)^{\circ}$. U = 928.3(5) Å³, T = 125 K, space group $P\bar{I}$, Z = 2, μ (Mo-K α) = 7.792 mm⁻¹. Of 4703 measured data, 2632 were unique to give $R_1[I > 2\sigma(I)] = 0.0395$, $wR \ 0.1027$. Crystallographic Data for the structural analyses has been deposited with the Cambridge Crystallographic data centre, CCDC No. 240298–240300. Copies of this information may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax: +44 1223 336 033 or E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk. ton would show a considerable shift. The proton is found at $\delta(H)$ 9.4 ppm as a doublet (${}^{2}J_{H-H} = 6$ Hz) with platinum satellites giving a ${}^{3}J_{Pt-H} = 43$ Hz, this is confirmation that **2** is a chelate complex. The v(C-N) stretch in **2** is found at 1648 cm⁻¹, this is a considerable shift from the value for the free ligand and provides further support for our proposed structure. Furthermore, there are two v(M-Cl) stretches observed in the spectrum at 339 and 318 cm⁻¹, the presence of two peaks again indicates two chlorides bound *cis* to the metal centre.



M = Pt (2) or Pd (3)

The X-ray structure of **2** is shown (Fig. 1) confirms the square planar geometry and chelation of the ligand. Using Pd(COD)Cl₂ we formed [PdCl₂(dppai-P,N] (3), δ (P) 81 ppm which is structurally very similar to **2**.

When dppai was reacted with [PtClMe(cod)] and [PtClPh(cod)] the expected bidentate complex was formed, giving [PtClMe(dppai-P,N)] (4) and [PtClPh (dppai-P,N)] (5), respectively. The ³¹P NMR in both cases showed peaks consistent with the earlier platinum



Fig. 1. Crystal structure of $[PtCl_2(dppai-P,N)]$ (2), $[PdCl_2(dppai-P,N)]$ (3) has a similar structure and is not illustrated. Selected bond lengths (Å) and angles (°): P(1)–M(1) 2.1998(11), Pt(1)–Cl(1) 2.3381(11), Pt(1)–Cl(2) 2.3068(11), P(1)–N(2) 1.716(3), N(2)–C(10) 1.373(5), N(9)– C(10) 1.326(5), P(1)–M(1)–Cl(1) 176.70(4), P(1)–M(1)–Cl(2) 91.04(4), M(1)–N(9) 85.93(10), M(1)–P(1)–N(2) 99.73(12).



Fig. 2. Crystal Structure of [PtClMe(dppai-P,N)] (4), selected bond lengths (Å) and angles (°) P(1)–Pt(1) 2.168(2), Pt(1)–Cl(1) 2.349(2), Pt(1)–N(9) 2.145(7), P(1)–N(2) 1.730(6), Pt(1)–C(30) 2.042(8), N(2)–C(10) 1.369(10), N(9)–C(10) 1.333(11), P(1)–Pt(1)–Cl(1) 177.37(6), P(1)–Pt(1)–C(30) 93.7(3), P(1)–Pt(1)–N(9) 85.35(19), Pt(1)–P(1)–N(2) 101.1(2).

examples with resonances observed at $\delta(P)$ 60.9 ppm, and 58.5 ppm for **4** and **5**, respectively, with ${}^{1}J_{Pt-P} =$ 5070 Hz for **4** and 4960 Hz for **5**.

The X-ray structure of **4** (Fig. 1) shows similar features to **2** and **3** though the P–N bond is slightly longer in this example, being 1.730(6) Å [cf. 1.719(2) and 1.716(4) Å] whilst **4** has a Pt–N bond length of 2.145(7) Å compared to 2.039(3) Å for **2** reflecting the change of *trans* ligands (see Fig. 2).

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