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The preparation and complexation of 5,10-bis(diphenylphosphino)phenazine

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Abstract

Reaction of 5,10-dihydrophenazine with two equivalents of Ph_2PCl, in the presence of *n*-BuLi at −78 °C in thf gives $Ph_2PN(C_6H_4)(C_6H_4)NPPh_2$ (**1**) [1] which can be oxidised with selenium to $Ph_2P(Se)N(C_6H_4)(C_6H_4)NP(Se)Ph_2$ (**2**) [2] or coordinated with Pt(II) in *cis*-$[PtCl_2\{Ph_2PN(C_6H_4)(C_6H_4)NPPh_2\}]$ (**3**) [3] The structure of 3 reveals a severely distorted (non-planar) phenazine backbone.

Keywords: X-ray crystallography; Synthesis; Structure

Phosphine ligands have many important applications in organometallic chemistry and catalysis [1–4]. We have recently demonstrated that phosphines derived from two N-bound pyrrolidine groups and one alkyl or aryl group are amongst the strongest σ-donor ligands, and surprisingly are even more electron rich than tris(*N*-pyrrolidinyl)phosphine [5]. We have also examined the ability of P–N containing phosphines to function as catalysts [6] and recently studied structural facets including cone angle effects [7]. We have now extended our studies to investigate the properties of the new phosphine formed from 5,10-dihydrophenazine – in part to establish if it possible to distort the phenazine backbone sufficiently to obtain bidentate coordination – and since

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[1] ***$Ph_2PN(C_6H_4)(C_6H_4)NPPh_2$* (1)**. To a −78 °C thf (40 ml) solution of 5,10-dihydrophenazine (1.053 g, 5.78 mmol) was added dropwise a hexane solution of BuLi (4.8 ml, 2.5 mol dm^{-3}, 12.08 mmol). The mixture was stirred at −78 °C for 1 h and another 30 min at room temperature. The reaction solution was cooled to −78 °C again and to it was added dropwise a solution of diphenylchlorophosphine (2.1 ml, 2.613 g, 11.84 mmol) in thf (10 ml) over 40 min. Stirring was continued for another 1 h at −78 °C and overnight at room temperature. The solution was evaporated to dryness in vacuo and dichloromethane (30 ml) was added. Lithium chloride, which precipitated, was removed by filtration under nitrogen and then the volatiles were evaporated in vacuo to leave a yellow solid. Yield: 2.896 g, 91%; Microanalysis: Found (Calcd) C 78.5 (78.5), H 5.1 (5.1), N 4.8 (5.1)%; $^{31}P–\{H\}$ NMR ($CDCl_3$): 61.0 (s) ppm; Selected IR data (KBr): *v*(PN) 951 cm^{-1}; FAB^+ MS: *m*/*z* 550 [M], 551 $[M+H^+]$, 573 $[M+Na^+]$.

[2] ***$Ph_2P(Se)N(C_6H_4)(C_6H_4)NP(Se)Ph_2$* (2)**. To a dry and degassed toluene (10 ml) solution of selenium (0.029 g, 0.36 mmol) was added solid $Ph_2PN(C_6H_4)(C_6H_4)NPPh_2$ (0.100 g, 0.18 mmol). The solution was heated to reflux for ca. 2–3 h and allowed to cool to room temperature. The solution was evaporated to dryness in vacuo and the solid was dissolved in dichloromethane (2 ml). The dichloromethane solution was filtered through Celite and diethyl ether (20 ml) was added. The white product was collected by suction filtration and washed with diethyl ether (2 × 10 ml). Yield: 0.112 g, 88%; Microanalysis: Found (Calcd) C 60.3 (61.0), H 3.8 (4.0), N 3.8 (4.0)%; $^{31}P–\{H\}$NMR ($CDCl_3$): 58.5 (s) ppm, $^1J(^{77}Se–^{31}P)$ 832 Hz; selected IR data (KBr): *v*(PN) 973 cm^{-1}, *v*(PSe) 565 cm^{-1}; FAB^+ MS: *m*/*z* 708 [M], 709 $[M+H]^+$.

[3] ***cis*-*$[PtCl_2\{Ph_2PN(C_6H_4)(C_6H_4)NPPh_2\}]$* (3)**. To a dichloromethane (5 ml) solution of $[PtCl_2(cod)]$ (0.068 g, 0.18 mmol) was added solid $Ph_2PN(C_6H_4)(C_6H_4)NPPh_2$ (0.100 g, 0.18 mmol) and the colourless solution stirred for ca. 2–3 h. The solution was concentrated under reduced pressure to ca. 1 ml and diethyl ether (10 ml) added. The white product was collected by suction filtration and washed with diethyl ether (2 × 10 ml). Yield: 0.118 g, 80%; Microanalysis: Found (Calcd) C 53.0 (53.0), H 3.4 (3.5), N 3.3 (3.4)%; $^{31}P–\{H\}$ NMR ($CDCl_3$): 43.3 (s) ppm, $^1J(^{195}Pt–^{31}P)$ 3854.6 Hz; selected IR data (KBr): *v*(PN) 949 cm^{-1}, *v*(PtCl) 311 and 291 cm^{-1}; FAB^+MS: *m*/*z* 781 $[M–Cl^-]$, 839 $[M+Na^+]$, 816 [M].

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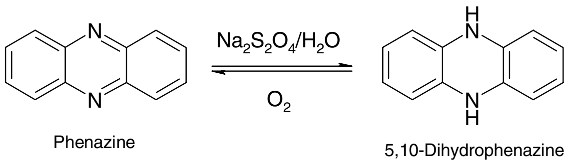
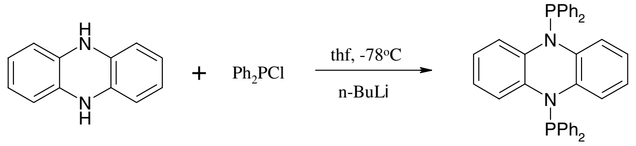
we also have an interest in the ease of distortion of planar aromatic systems [8].



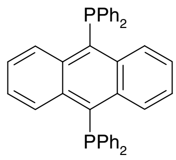
(1)

5,10-Dihydrophenazine (Eq. 1) was reacted with two equivalents of Ph_2PCl, in the presence of *n*-BuLi at −78 °C, in thf to give **1** in 91% yield (Eq. 2). [4]



(2)

The $^{31}P\text{–}\{^1H\}$NMR spectrum of **1** consists of a singlet at $\delta(P)$ 61.0 ppm – the large downfield shift when compared to its P–C relative [9,10] (**PAnP**, $\delta(P) = -21.9$ ppm) reflecting the substitution of the carbon centres in **PAnP** by nitrogen atoms in **1** (it should be noted that **PanP** is the aromatic analogue of **1** there is no direct carbon analogue).



(PAnP)

FAB$^+$ mass spectrometry confirms the proposed identity of the ligand **1** with the expected parent-ion peaks (*m/z* 550 [M], 551 [M + H$^+$] and 573 [M + Na$^+$]) whilst its IR spectrum shows a band that can be assigned to ν(P–N) (951 cm^{-1}) and elemental analysis data are in agreement with calculated values. **1** is soluble in both thf and dichloromethane and air- and moisture-stable for short periods in the solid state but oxidises readily in solution in air.

1 was oxidised to the P(V) diselenide **2** by stirring at reflux in toluene with selenium. Alternatively, reaction of **1** with $PtCl_2$(cod) gives *cis*-$[PtCl_2\{Ph_2PN(C_6H_4)(C_6H_4)NPPh_2\}]$ (**3**). The $^{31}P\text{–}\{^1H\}$ NMR spectrum of **3** is a singlet with satellites due to coupling to ^{195}Pt ($\delta(P)$ 43.3 ppm, $^1J\{^{195}Pt\text{–}^{31}P\}$ 3855 Hz); it has the expected parent-ion (*m/z* 818,816) and fragmentation patterns consistent with the loss of one chloride [*m/z* 781 [M–Cl$^-$]). Elemental analysis data are in agreement with calculated values and the IR spectrum shows bands due to ν(P–N) (949 cm$^-$) and ν(PtCl) (311 cm^{-1}).

The molecular structure of **3** confirms that the ligand is bidentate and in a *cis* geometry and that the chloride ligands are mutually *cis*. The complex contains two seven-membered Pt–P–N–C–C–N–P rings and the metal adopts the expected square planar geometry. The square-planar platinum centre is distorted and the bite angle of the ligand is larger than the ideal 90° with P(1)–Pt(1)–P(6) 99.90(3)° whilst Cl–Pt–Cl is 90.37(3)°. The backbone of the ligand forms an 'umbrella-like' structure about the platinum centre with the $C_{12}N_2$ tricyclic ring adopting a butterfly geometry with the aryl rings being inclined by 122° to each other and the N(2) and N(5) atoms lying 0.45 and 0.50 Å above the C(3)–C(4)–C(11)–C(16) mean plane, and C–N–C angles of ca. 109° as appropriate for sp^3 hybridised nitrogen atoms. The P–N bond lengths in **3** are at the upper end of the range we have observed in P–N containing phosphines [11].

We tested the usefulness of **1** for the catalytic hydroformylation of oct-1-ene using a batch autoclave and similar conditions to previously [6] – it proved to be fairly active with a similar initial rate of reactivity to the homopiperazine ligand $Ph_2PN(C_3H_6)(C_2H_4)NPPh_2$ (**4**) (2.45×10^{-3} of CO uptake in **1** versus 2.98×10^{-3} mol dm^{-3} in the piperazine) and a rather better linear:branched ratio of the aldehyde produce (2.5:1 in **1** versus 1.7:1 in **4**) which suggest that **1** may have some potential in catalytic applications – and certainly that it is robust enough to behave as a supporting ligand under hydroformylation conditions. According to simple molecular modelling studies although **1** and **4** have different natural bite angles [ca. 90° and 110°, respectively) they have similar flexibility ranges in their bite angles and this may be the most significant feature in relating their similarity in catalytic behaviour. Further work is in progress.

Supplementary data

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic

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[4] ***Catalytic studies*** (**1**) The ligand (0.03 mmol, 0.005 mol dm^{-3}), $[Rh(CO)_2(acac)]$ (5.16×10^{-3} g, 0.02 mmol, 0.004 mol dm^{-3}) and toluene (4 ml) were charged into a Schlenk tube and stirred until complexation of the rhodium complex with the phosphine species (total dissolution). The phosphine/rhodium ratio used was 3/2. This solution was placed in a glass lined steel autoclave, CO/H_2 added until 20 bar pressure, the autoclave was heated to 100 °C for the appropriate reaction time and stirred magnetically.

Single crystal X-ray diffraction studies on crystals were performed using a Bruker SMART diffractometer with graphite-monochromated Mo Kα 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 [12].

(**3**) $C_{36}H_{28}N_2P_2Cl_2Pt$, $M = 816.5$, monoclinic, $a = 10.7076(17)$, $b = 15.392(3)$, $c = 19.078(3)$ Å, $\beta = 92.036(3)°$. $U = 1138$ Å^3, $T = 125$ K, space group $P2(1)/n$, $Z = 4$, μ(Mo Kα) = 4.77 mm^{-1}. Of 13,327 measured data, 4479 were unique ($R_{int} = 0.0308$), to give R_1 $[I > 2\sigma(I)] = 0.0201$.

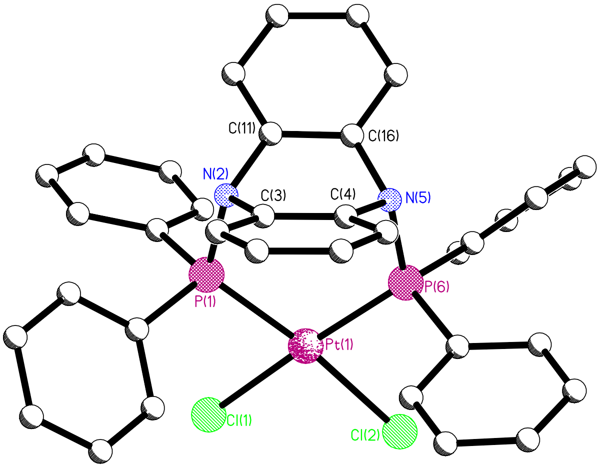

Fig. 1. Solid state structure of *cis*-[$PtCl_2\{Ph_2PN(C_6H_4)(C_6H_4)NPPh_2\}$] **3**, selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.2305 (9), Pt(1)–P(6) 2.2307 (8), Pt(1)–Cl(1), 2.3515 (5), Pt(1)–Cl(2) 2.3608 (8), P(1)–N(2) 1.726 (2), P(6)–N(5) 1.733 (2), P(1)–Pt(1)–P(6) 99.90 (3), Cl(1)–Pt(1)–Cl(2) 90.37 (3), Pt(1)–P(1)–N(2) 118.66 (9), Pt(1)–P(6)–N(5), 120.05 (9), C(11)–N(2)–P(1), 113.63 (18), C(3)–N(2)–P(1), 114.07 (19), C(3)–N(2)–C(11) 110.6 (2), C(4)–N(5)–P(6), 113.86 (18), C(16)–N(5)–P(6), 114.91 (19), C(4)–N(5)–C(16) 109.1 (2).

data centre, CCDC No. 220833. 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 http://www.ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk (see Fig. 1).

Acknowledgements

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