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The preparation and coordination chemistry of phosphorus(III) derivatives of piperazine and homopiperazine

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Abstract

Reaction of piperazine or homopiperazine with R_2PCl [$R_2 = Ph_2$, OC_2H_4O, OC_6H_4O] gives six new bidentate phosphines. Simple bis-chelate and bridging complexes with demonstrative Mo(0), Pd(II), Pt(II) and Ru(II) centres are reported. The crystal structures of $Ph_2P(O)N(C_2H_4)_2P(O)Ph_2$, *cis*-[$PdCl_2${$Ph_2PN(C_2H_4)_2NPPh_2$}] (**7**) and *cis*-[$PtCl_2${$Ph_2PN(C_5H_{10})NPPh_2$}][$PtcodCl_2]_2$ (**15**) are reported. In $Ph_2P(O)N(C_2H_4)_2P(O)Ph_2$ the central N_2C_4 ring has a chair conformation and the P=O groups are *trans*. In **7** the piperazine backbone results in P–Pd–P bite angle of approximately 95° whilst in **15** the homopiperazine backbone enlarges the bite angle to 97°.

Keywords: Coordination chemistry; Crystal structures; Piperazine; Homopiperazine

1. Introduction

We have recently reported a number of syntheses of new monodentate and bidentate P(III) and P(V) ligands via simple P–N bond forming reactions [1–5]. Apart from systems with totally non-carbon backbones we have been able to synthesise the first six-membered true heterocycles [6] and we have developed some very electron rich [7,8] hemilabile [9–11] and chiral ligands [12,13] by this approach. One of the important roles occupied by ligands in catalytic metal complexes is to offer steric protection to the catalytically active site. In polymerisation catalysts for example, this requirement may be achieved by incorporating bulky substituent groups into the ligand which hinder the approach of the reactants and 'steer' them towards the reacting polymer chain [14]. With this in mind, we have studied the reactions of the cyclic amine compounds piperazine and homopiperazine with different chlorophosphines to ascertain the possibility of synthesising diphosphine chelates, which would offer significant steric hindrance and bite angle control by forming umbrella-like ligands around a metal centre. Here we report on the synthesis of diphosphine derivatives of piperazine and homopiperazine and their reactions with different metal compounds.

2. Experimental

General experimental conditions and instrumentation were as set out in Section 2.28 and as described previously [13]. [{$RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)$}$_2$][15] was prepared using the literature procedure and piperazine, homopiperazine, 1,2-phenylenephosphoro-chloridite and 2-chloro-1,3,2-dioxaphospholane were used without further purification.

2.1. $Ph_2PN(C_2H_4)_2NPPh_2$ (*1*)

A solution of chlorodiphenylphosphine (5.1 g, 4.2 cm^3, 24.0 mmol) in thf (20.0 cm^3) was added dropwise over a period of 30 min to a stirred solution of piperazine (1.00 g, 12.0 mmol) and triethylamine (2.40 g, 3.3 cm^3, 24.0 mmol) in thf (30 cm^3) at room temperature (r.t.). Stirring was continued for 24 h,

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during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give a white solid product. Yield: 3.92 g, 75%.

2.2. $(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$ (**2**)

A solution of 1,2-phenylenephosphoro-chloridite (4.65 g, 16.7 mmol) in thf (60.0 cm^3) was added dropwise over a period of 1 h to a stirred solution of piperazine (0.72 g, 8.3 mmol) and triethylamine (1.69 g, 2.3 cm^3, 16.7 mmol) in thf (70.0 cm^3). Stirring was continued for a further 2 h, during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give a white solid product. Yield: 2.15 g, 71%.

2.3. $(C_2H_4O_2)PN(C_2H_4)_2NP(C_2H_4O_2)$ (**3**)

A solution of 2-chloro-1,3,2-dioxaphospholane (5.69 g, 4.0 cm^3, 45.0 mmol) in thf (70.0 cm^3) was added dropwise over a period of 1 h to a stirred solution of piperazine (1.93 g, 22.5 mmol) and triethylamine (4.54 g, 6.2 cm^3, 45.0 mmol) in thf (80.0 cm^3). Stirring was continued for a further 2 h, during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give a white solid product. Yield: 4.31 g, 72%.

2.4. cis-$[PtCl_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ (**4**)

To a solution of $[PtCl_2(cod)]$ (0.100 g, 0.26 mmol) in dichloromethane (5.0 cm^3) was added solid $Ph_2PN(C_2H_4)_2NPPh_2$ (0.120 g, 0.26 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (10.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.152 g, 79%.

2.5. cis-$[PtCl_2\{(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)\}]$ (**5**)

To a solution of $[PtCl_2(cod)]$ (0.100 g, 0.26 mmol) in dichloromethane (15.0 cm^3) was added solid $(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$ (0.097 g, 0.26 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (15.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.150 g, 89%.

2.6. cis-$[PtMe_2\{(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)\}]$ (**6**)

To a solution of $[PtMe_2(cod)]$ (0.080 g, 0.24 mmol) in dichloromethane (10.0 cm^3) was added solid $(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$ (0.087 g, 0.24 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (40.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.089 g, 63%.

2.7. cis-$[PdCl_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ (**7**)

To a solution of $[PdCl_2(cod)]$ (0.100 g, 0.35 mmol) in dichloromethane (5.0 cm^3) was added solid $Ph_2PN(C_2H_4)_2NPPh_2$ (0.160 g, 0.35 mmol) and the yellow solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (10.0 cm^3) added. The yellow product was collected by suction filtration. Yield: 0.137 g, 62%.

2.8. cis-$[Mo(CO)_4\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ (**8**)

To a partially dissolved solution of $[Mo(CO)_4(pip)_2]$ (0.500 g, 1.30 mmol) in dichloromethane (20.0 cm^3) was added solid $Ph_2PN(C_2H_4)_2NPPh_2$ (0.590 g, 1.30 mmol). The solution was heated to reflux for approximately 15 min and allowed to cool to r.t. The solution was concentrated under reduced pressure to approximately 2.0 cm^3 and methanol (15.0 cm^3) added. The yellow product was collected by suction filtration. Yield: 0.635 g, 72%.

2.9. $[Ph_2P(AuCl)N(C_2H_4)_2NP(AuCl)Ph_2]$ (**9**)

To a solution of [AuCl(tht)] (0.071 g, 0.22 mmol) in dichloromethane (5.0 cm^3) was added solid $Ph_2PN(C_2H_4)_2NPPh_2$ (0.050 g, 0.11 mmol) and the colourless solution stirred for approximately 1 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (5.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.054 g, 53%.

2.10. $[(C_6H_4O_2)P(AuCl)N(C_2H_4)_2NP(AuCl)(C_6H_4O_2)]$ (**10**)

To a solution of [AuCl(tht)] (0.184 g, 0.58 mmol) in dichloromethane (15.0 cm^3) was added solid $(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$ (0.104 g, 0.29 mmol) and the colourless solution stirred for approximately 1 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (30.0

cm^3) added. The white product was collected by suction filtration. Yield: 0.205 g, 86%.

2.11. $[(C_2H_4O_2)P(AuCl)N(C_2H_4)_2$-$NP(AuCl)(C_2H_4O_2)]$ (**11**)

To a solution of [AuCl(tht)] (0.160 g, 0.50 mmol) in dichloromethane (15.0 cm^3) was added solid $(C_2H_4O_2)PN(C_2H_4)_2NP(C_2H_4O_2)$ (0.068 g, 0.25 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (30.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.140 g, 76%.

2.12. $[\{RuCl_2(\eta^6$-p-$MeC_6H_4^iPr)\}_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ (**12**)

To a solution of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}_2]$ (0.250 g, 0.40 mmol) in thf (20.0 cm^3) was added solid $Ph_2PN(C_2H_4)_2NPPh_2$ (0.185 g, 0.40 mmol) and the brown solution stirred for approximately 12 h. The solution was concentrated under reduced pressure to approximately 2.0 cm^3 and diethyl ether (10.0 cm^3) added. The red–brown product was collected by suction filtration and washed with diethyl ether (2×10.0 cm^3). Yield: 0.299 g, 69%.

2.13. $Ph_2PN(C_5H_{10})NPPh_2$ (**13**)

A solution of chlorodiphenylphosphine (6.87 g, 5.6 cm^3, 31.2 mmol) in thf (50.0 cm^3) was added dropwise over a period of 1 h to a stirred solution of homopiperazine (1.56 g, 15.6 mmol) and triethylamine (3.13 g, 4.3 cm^3, 31.3 mmol) in thf (75 cm^3) at r.t. Stirring was continued for 2 h, during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give a white solid product. Yield: 4.92 g, 68%.

2.14. $[Ph_2P\{Se\}N(C_5H_{10})N\{Se\}PPh_2]$ (**14**)

To a toluene (20 ml) solution of selenium (0.075 g, 0.904 mmol) was added $Ph_2P\{Se\}N(C_5H_{10})N\{Se\}PPh_2$ (0.207 g, 0.281 mmol). The reaction was stirred and heated to reflux for 2–3 h. The product was collected by suction filtration under nitrogen atmosphere and an off-white product was isolated. Yield: 0.123 g, 70%.

2.15. cis-$[PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$ (**15**)

To a solution of $[PtCl_2(cod)]$ (0.100 g, 0.26 mmol) in dichloromethane (10.0 cm^3) was added solid $Ph_2PN(C_5H_{10})NPPh_2$ (0.125 g, 0.26 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (40.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.180 g, 92%.

2.16. cis-$[PtMe_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$ (**16**)

To a solution of $[PtMe_2(cod)]$ (0.100 g, 0.30 mmol) in dichloromethane (10.0 cm^3) was added solid $Ph_2PN(C_5H_{10})NPPh_2$ (0.140 g, 0.30 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (30.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.130 g, 64%.

2.17. cis-$[PdCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$ (**17**)

To a solution of $[PdCl_2(cod)]$ (0.152 g, 0.53 mmol) in dichloromethane (20.0 cm^3) was added solid $Ph_2PN(C_5H_{10})NPPh_2$ (0.250 g, 0.53 mmol) and the yellow solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (40.0 cm^3) added. The yellow product was collected by suction filtration. Yield: 0.300 g, 87%.

2.18. $[Ph_2P(AuCl)N(C_5H_{10})NP(AuCl)Ph_2]$ (**18**)

To a solution of [AuCl(tht)] (0.192 g, 0.60 mmol) in dichloromethane (15.0 cm^3) was added solid $Ph_2PN(C_5H_{10})NPPh_2$ (0.140 g, 0.30 mmol) and the colourless solution stirred for approximately 1 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (35.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.214 g, 76%.

2.19. $(C_6H_4O_2)PN(C_5H_{10})NP(C_6H_4O_2)$ (**19**)

A solution of 1,2-phenylenephosphoro-chloridite (4.65 g, 16.7 mmol) in thf (55.0 cm^3) was added dropwise over a period of 1 h to a stirred solution of homopiperazine (0.84 g, 8.3 mmol) and triethylamine (1.69 g, 2.3 cm^3, 16.7 mmol) in thf (85.0 cm^3). Stirring was continued for a further 2 h, during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give a white solid product. Yield: 2.58 g, 82%.

2.20. cis-$[PtCl_2\{(C_6H_4O_2)PN(C_5H_{10})NP(C_6H_4O_2)\}]$ (**20**)

To a solution of $[PtCl_2(cod)]$ (0.179 g, 0.48 mmol) in dichloromethane (15.0 cm^3) was added solid

$(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$ (0.180 g, 0.48 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (30.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.104 g, 84%.

2.21. *cis-[PtMe$_2${(C$_6$H$_4$O$_2$)PN(C$_5$H$_{10}$)-NP(C$_6$H$_4$O$_2$)}] (**21**)*

To a solution of [$PtMe_2$(cod)] (0.100 g, 0.30 mmol) in dichloromethane (10.0 cm^3) was added solid $(C_6H_4O_2)$-$PN(C_2H_4)_2NP(C_6H_4O_2)$ (0.114 g, 0.30 mmol) and the colourless solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (35.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.120 g, 66%.

2.22. *cis-[PdCl$_2${(C$_6$H$_4$O$_2$)PN(C$_5$H$_{10}$)-NP(C$_6$H$_4$O$_2$)}] (**22**)*

To a solution of [$PdCl_2$(cod)] (0.285 g, 1.00 mmol) in dichloromethane (25.0 cm^3) was added solid $(C_6H_4O_2)$-$PN(C_5H_{10})NP(C_6H_4O_2)$ (0.378 g, 1.0 mmol) and the yellow solution stirred for approximately 2 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (30.0 cm^3) added. The yellow product was collected by suction filtration. Yield: 0.520 g, 94%.

2.23. *[(C$_6$H$_4$O$_2$)P(AuCl)N(C$_5$H$_{10}$)-NP(AuCl)(C$_6$H$_4$O$_2$)] (**23**)*

To a solution of [AuCl(tht)] (0.140 g, 0.44 mmol) in dichloromethane (15.0 cm^3) was added solid $(C_6H_4O_2)$-$PN(C_5H_{10})NP(C_6H_4O_2)$ (0.083 g, 0.22 mmol) and the colourless solution stirred for approximately 1 h. The solution was concentrated under reduced pressure to approximately 1.0 cm^3 and diethyl ether (30.0 cm^3) added. The white product was collected by suction filtration. Yield: 0.150 g, 81%.

2.24. *(C$_2$H$_4$O$_2$)PN(C$_5$H$_{10}$)NP(C$_2$H$_4$O$_2$) (**24**)*

A solution of 2-chloro-1,3,2-dioxaphospholane (5.69 g, 4.0 cm^3, 45.0 mmol) in thf (55.0 cm^3) was added dropwise over a period of 1 h to a stirred solution of homopiperazine (2.25 g, 22.5 mmol) and triethylamine (4.54 g, 6.2 cm^3, 45.0 mmol) in thf (100.0 cm^3). Stirring was continued for a further 2 h, during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give a white solid product. Yield: 4.91 g, 78%.

2.25. *^{i}Pr$_2$PN(C$_5$H$_{10}$)NP^{i}Pr$_2$ (**25**)*

A solution of diisopropylphosphinechloride (1.61 ml, 0.01 g, 10.0 mmol) in thf (20 cm^3) was added dropwise to a stirred solution of homopiperazine (0.49 g, 4.89 mmol) and degassed Et_3N (1.40 ml, 0.01 g, 10.0 mmol) in thf (20 cm^3) at r.t. The reaction mixture was stirred for a further 2 h, during which time triethylammonium hydrochloride separated from the colourless solution. This precipitate was removed by suction filtration and the filtrate evaporated to dryness in vacuo to give an oily colourless product.

2.26. *[^{i}Pr$_2$P{Se}N(C$_5$H$_{10}$)N{Se}P^{i}Pr$_2$] (**26**)*

To a toluene (10 ml) solution of selenium (0.105 g, 1.330 mmol) was added solid ligand L^3 (0.212 g, 0.638 mmol). The reaction was stirred and heated to reflux for 2–3 h under reflux. The product was collected by suction filtration under nitrogen atmosphere and an off-white product was isolated. Yield: 0.146 g, 47%.

2.27. *cis-[PtCl$_2${^{i}Pr$_2$PN(C$_5$H$_{10}$)NP^{i}Pr$_2$}] (**27**)*

To a solution of [$PtCl_2$(cod)] (0.202 g, 0.541 mmol) in dichloromethane (10 ml) was added solid ligand L^3 (0.180 g, 0.541 mmol). The mixture reaction was stirred for 2 h then diethyl ether (5 ml) was added to solubilise the cod moiety whilst the complex is insoluble and was precipitated as a white solid. After 15 min in the ultrasonic bath, the sample was filtered, the white solid was washed with diethyl ether. Yield: 0.324 g, 50%.

2.28. *Crystallography*

Crystallography was performed using a Bruker SMART diffractometer; full hemisphere of data with 0.3° 'slices', r.t., Mo Kα radiation and empirical absorption corrections. All of the other non-H atoms were refined anisotropically with the hydrogen atoms being refined in idealised geometries. All calculations employed the SHELXTL program system [16].

Compound **7**: $C_{28}H_{28}Cl_2N_2P_2Pd$ $M = 631.8$, monoclinic, space group $P2_1/n$, $a = 11.223(1)$, $b = 27.882(3)$, $c = 17.936(2)$ Å. $\beta = 96.646(3)°$ $U = 5575$ Å^3, $Z = 8$ (two independent molecules), $D_{calc} = 1.51$ g cm^{-3}, $F(000) = 2560$, μ(Mo Kα) = 1.62 mm^{-1}. Of 24 012 measured data, 7949 were unique and observed [$I > 2.0\sigma(I)$] to give $R = 0.080$ and $wR_2 = 0.1421$.

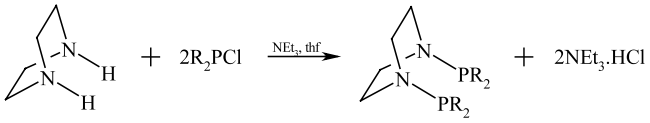
Compound **15**: $C_{47}H_{58}Cl_{10}N_2P_2Pt3$ $M = 1652.7$, orthorhombic, space group $Pca2(1)$, $a = 16.556(1)$, $b = 9.814(1)$, $c = 33.1291(1)$. $U = 5383$ Å^3, $Z = 4$, $D_{calc} = 2.04$ g cm^{-3}, $F(000) = 3152$, μ(Mo Kα) = 8.37 mm^{-1}. Of 21 988 measured data 7523 were unique and observed [$I > 2.0\sigma(I)$] to give $R = 0.0291$ and $wR_2 = 0.0712$. The

H atoms on one of the solvent molecules was not included in the refinement.

$Ph_2(O)PNC_4H_8NP(O)Ph_2 \cdot H_2O$: $C_{28}H_{30}N_2O_3P_2$ $M = 504.5$, monoclinic, space group $P2_1/n$, $a = 9.736(1)$, $b = 12.868(3)$, $c = 10.940(2)$ Å. $\beta = 111.89(1)^\circ$ $U = 1272$ Å^3, $Z = 2$, $D_{calc} = 1.32$ g cm^{-3}, $F(000) = 532$, μ(Mo Kα) = 0.204 mm^{-1} (there was considerable decomposition during data collection and no absorption correction was applied). Of 2560 measured data 1414 were unique and observed [$I > 2.0\sigma(I)$] to give $R = 0.0376$ and $wR_2 = 0.0858$.

3. Results and discussion

Reaction of piperazine with 2 equiv. of the chlorophosphines Ph_2PCl, $R_2 = Ph_2$ (**1**), $C_6H_4O_2$ (**2**) and OC_2H_4O (**3**)



$R_2 = Ph_2$ (**1**), $C_6H_4O_2$ (**2**) and OC_2H_4O (**3**)

(1)

$(C_6H_4O_2)PCl$ and $(C_2H_4O_2)PCl$, in the presence of NEt_3, proceeds in thf to give **1**, **2** and **3** respectively (Eq. (1)).

Addition of the chlorophosphine in thf to a solution of piperazine in thf, at r.t., results in the immediate precipitation of $[Et_3NH]Cl$ as the reaction proceeds. Removal of the ammonium salt by filtration, reduction of the volume of thf in vacuo and addition of diethyl ether gives the new species in 70–80% yield. The $^{31}P\{^1H\}$ NMR spectrum of **1** comprises a singlet at δ(P) 62.9. The possibility of this peak representing the mono-substituted amine was rejected after performing in situ ^{31}P NMR studies. Monitoring of the reaction mixture at regular intervals, immediately after completion of the chlorodiphenylphosphine addition, shows a phosphorus-containing species, with a chemical shift of δ(P) 35.1, to be the initial reaction product. This is assumed to be the mono-substituted amine and gradually decreases in intensity as the reaction proceeds, to leave **1** as the only phosphorus containing compound. The $^{31}P\{^1H\}$ NMR spectrum of **2** and **3** are singlets at δ(P) 144.2 and 137.9 ppm respectively; the large downfield shift when compared with **1** reflecting the close proximity of the phosphorus centre to the strongly electronegative oxygen atoms. Although stable for short periods in the solid state in solution **1**–**3** oxidise readily in solution in air. Crystals of **1O$_2$** were obtained from a CH_2Cl_2 solution of **1** and the structure is shown in Fig. 1

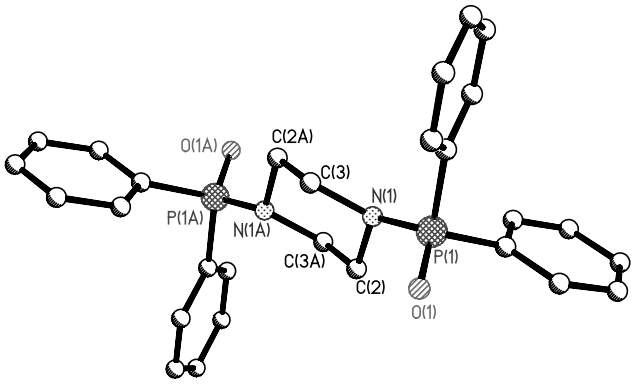
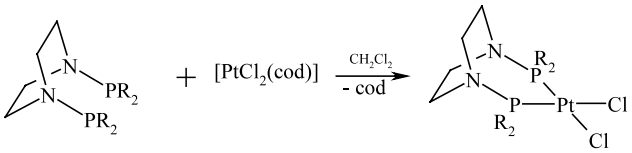


Fig. 1. Solid state structure of $Ph_2P(O)N(C_2H_4)NP(O)Ph_2$.

with selected bond lengths and angles in Table 2. The piperazine ring adopts a chair conformation with the P=O groups being on opposite sides of the molecule.

Reaction of **1** and **2** with equimolar quantities of $[PtCl_2(cod)]$ in dichloromethane (Eq. (2)) to yield the seven-membered, *P,P′* chelates **4** and **5**.



$R_2 = Ph_2$ (**4**), $C_6H_4O_2$ (**5**)

(2)

The $^{31}P\{^1H\}$ NMR spectra of both compounds are singlets with satellites from coupling to ^{195}Pt, the nature of the substituent groups on the phosphorus being reflected in the positions of the chemical shifts (δ(P) 53.5 and 99.6 ppm, respectively) and the magnitude of the $^1J(^{195}Pt-^{31}P)$ coupling constants (3972 and 5480 Hz, respectively) which are in accord with values previously reported for similarly substituted phosphines when *trans* to a chloride in a Pt(II) complex **2** [5,17,18] also reacts with $[PtMe_2(cod)]$, in dichloromethane, to produce the *P,P′* chelate *cis*-$[PtMe_2\{(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)\}]$ (**6**).

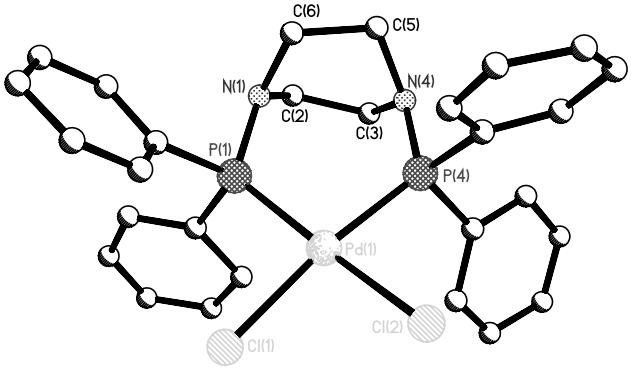


Fig. 2. Solid state structure of *cis*-$[PdCl_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ (**7**).

Table 1
Elemental analysis and selected spectroscopic data

	Formula	δ ^{31}P (ppm)/^{1}J(Pt–P) (Hz)	*m/e*	ν(CN)	ν(PN)	C	H	N
1	$Ph_2PN(C_2H_4)_2NPPh_2$	62.9	455	1478	930	73.8(74.0)	6.2(6.2)	5.5(6.2)
2	$(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$	144.2	362	1479	918	53.2(53.0)	4.3(4.4)	7.3(7.7)
3	$(C_2H_4O_2)PN(C_2H_4)_2NP(C_2H_4O_2)$	137.9	266	1438	952	35.6(36.1)	6.2(6.0)	9.9(10.5)
4	*cis*-$[PtCl_2\{Ph_2PN(C_2H_4)_2NPPh_2]$	53.5/3972	720	1435	960	46.9(46.7)	3.7(3.9)	3.2(3.9)
5	*cis*-$[PtCl_2\{(C_6H_4O_2)_2PN(C_2H_4)_2NP(C_6H_4O_2)_2\}]$	99.6/5480	597[-Cl]	1477	966	30.4(30.6)	2.8(2.6)	4.3(4.5)
6	*cis*-$[PtMe_2\{(C_6H_4O_2)_2PN(C_2H_4)_2NP(C_6H_4O_2)_2\}]$	154.9/2977	587	1480	966	36.3(36.8)	3.9(3.8)	4.6(4.8)
7	*cis*-$[PdCl_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$	101.7	632	1435	959	52.9(53.3)	4.5(4.5)	4.3(4.4)
8	*cis*-$[Mo(CO)_4\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ [a]	97.2	634	1435	959	57.6(58.0)	3.9(4.3)	3.8(4.2)
9	$[Ph_2P\{AuCl\}N(C_2H_4)_2NP\{AuCl\}Ph_2]$	80.7	883[−Cl]	1434	966	36.4(36.6)	2.8(3.1)	2.4(3.1)
10	$[(C_6H_4O_2)_2P\{AuCl\}N(C_2H_4)_2NP\{AuCl\}(C_6H_4O_2)_2]$	136.4	827	1445	966	23.2(23.2)	1.9(1.9)	3.3(3.4)
11	$[(C_2H_4O_2)_2P\{AuCl\}N(C_2H_4)_2NP\{AuCl\}(C_2H_4O_2)_2]$	131.7	695[−Cl]	1445	967	13.3(13.1)	2.2(2.2)	3.8(3.8)
12	$[\{RuCl_2(\eta^6\text{-}p\text{-}Me\text{-}C_6H_4^iPr)\}_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$	69.8	1066	1432	953	54.1(54.0)	5.3(5.3)	2.2(2.6)
13	$Ph_2PN(C_5H_{10})NPPh_2$	65.7	468	1431	921	74.4(74.3)	6.1(6.4)	5.8(5.9)
14	$Ph_2P(Se)N(C_5H_{10})NP(Se)Ph_2$	71.9/753	629	1455	912	55.9(55.6)	4.7(4.8)	4.3(4.5)
15	$[PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$	64.1/4092	734	1436	936	47.4(47.5)	3.9(4.1)	3.4(3.8)
16	$[PtMe_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$	89.1/2231	678[$-CH_3$]	1435	925	53.1(53.6)	4.9(5.2)	3.8(4.0)
17	$[PdCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$	92.6	646	1432	953	54.3(54.0)	4.8(4.7)	4.2(4.4)
18	$[Ph_2P\{AuCl\}N(C_5H_{10})NP\{AuCl\}Ph_2]$	78.7	897[−Cl]	1433	903	37.6(37.4)	3.2(3.2)	2.7(3.0)
19	$(C_6H_4O_2)PN(C_5H_{10})NP(C_6H_4O_2)$	148.3	376	1459	916	53.8(54.3)	4.3(4.8)	6.9(7.4)
20	$[PtCl_2\{(C_6H_4O_2)PN(C_5H_{10})NP(C_6H_4O_2)\}]$	102.3/5466	606[-Cl]	1478	951	31.5(31.8)	2.9(2.8)	3.9(4.4)
21	$[PtMe_2\{(C_6H_4O_2)PN(C_5H_{10})NP(C_6H_4O_2)\}]$	156.9/2937	586[$-CH_3$]	1480	919	37.6(37.9)	3.9(4.0)	4.5(4.7)
22	$[PdCl_2\{(C_6H_4O_2)PN(C_5H_{10})NP(C_6H_4O_2)\}]$	125.6	553	1459	916	36.9(36.8)	3.6(3.3)	4.6(5.0)
23	$[(C_6H_4O_2)P\{AuCl\}N(C_5H_{10})NP\{AuCl\}(C_6H_4O_2)]$	139.9	805[−Cl]	1441	908	23.8(24.3)	2.1(2.1)	3.2(3.3)
24	$(C_2H_4O_2)PN(C_5H_{10})NP(C_2H_4O_2)$	143.8	280	1450	931	38.8(38.6)	6.8(6.4)	10.4(10.0)
25	$^iPr_2PN(C_5H_{10})N^iPPr_2$	96.0	215[−Pr2P]	1463	919	60.3(61.4)	12.7(11.6)	8.6(8.4)
26	$^iPr_2P(Se)N(C_5H_{10})N^iP(Se)Pr_2$	101.5/753	629	1455	912	55.9(55.6)	4.71(4.8)	4.3(4.5)
27	*cis*-$PtCl_2[(^iPr_2PN(C_5H_{10})N^iPPr_2)]$	87.6/4020	597	1459	900	34.7(34.1)	6.9(6.4)	4.6(4.7)

NMR in $CDCl_3$. Microanalyses, calculated values in brackets. FAB MS data; values are for parent ions except where indicated otherwise.
[a] ν(CO) 2021, 1917, 1901, 1888 cm^{-1}.

Similarly, the reaction of **1** with an equimolar quantity of $[PdCl_2(cod)]$ in thf results in the bidentate, *P*,*P*′ chelate complex *cis*-$[PdCl_2\{Ph_2PN(C_2H_4)_2NPPh_2]$ (**7**). The X-ray structure of **7** contains two crystallographically independent molecules and shows the product to have the expected square-planar geometry about the Pd centre (Table 2, Fig. 2). The bidentate nature of the co-ordination to the metal results in the formation of two seven-membered Pd–P–N–C–C–N–P ring systems The $N(C_2H_4)_2N$ backbone of the ligand adopts a boat conformation and forms an 'umbrella-like' structure around the Pd centre. The structure also reveals that the square-planar palladium centre is some-

Table 2
Selected comparative bond lengths (Å) and angles (°) in $Ph_2P(O)N(C_2H_4N)P(O)Ph_2$ and $^iPr_2P(Se)N(C_5H_{10})NP(Se)^iPr_2$

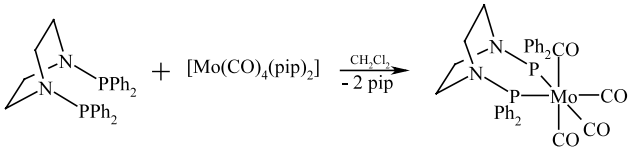
	$Ph_2P(O)N$-$(C_2H_4N)P(O)Ph_2$	$^iPr_2P(Se)N$-$(C_5H_{10})NP(Se)^iPr_2$
Bond lengths		
P(1)–E(1)	1.475(2)	2.115(5)
P(4)–E(4)		2.118(5)
P(1)–N(1)	1.646(3)	1.655(13)
P(4)–N(4)		1.688(14)
Bond angles		
E(1)–P(1)–N(1)	117.4(1)	114.8(5)
E(4)–P(4)–N(4)		111.9(5)

Table 3
Selected comparative bond lengths (Å) and angles (°) in $\{[Pt(cod)Cl_2]_2\cdot[PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]\}$, $[PdCl_2\{Ph_2PN(C_2H_4)_2NPPh_2\}]$ (**7**) and *cis*-$[PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$ (**15**)

Bond	$[PdCl_2\{Ph_2PN$-$(C_2H_4)_2NPPh_2\}]$ (**7**)	*cis*-$[PtCl_2\{Ph_2PN$-$(C_5H_{10})NPPh_2\}]$ (**15**)
Bond lengths		
M(1)–P(1)	2.246(5) [2.265(5)]	2.255(6)
M(1)–P(4)	2.256 (5) [2.246(5)]	2.215(6)
M(1)–Cl(1)	2.391 (4) [2.363(4)]	2.358(7)
M(1)–Cl(2)	2.381 (5) [2.388(5)]	2.388(5)
P(1)–N(1)	1.697 (13) [1.680(12)]	1.70(2)
P(4)–N(4)	1.666 (13) [1.704(14)]	1.64(2)
Bond angles		
P(1)–M(1)–P(4)	93.9(2) [94.7(2)]	97.3(1)
Cl(1)–M(1)–Cl(2)	92.1(2) [91.9(2)]	89.1(1)
M(1)–P(1)–N(1)	120.1(5) [121.8(6)]	119.0(8)
M(1)–P(4)–N(2)	123.3(5) [121.2(6)]	125.0(8)

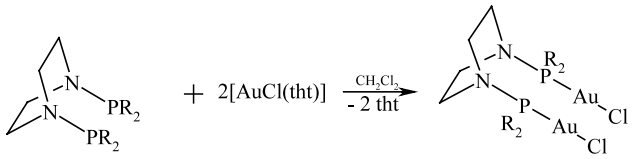
N.B. The values in parentheses are for the second crystallographically independent molecule.

what distorted and in both of the two independent molecules the bite angle of the piperazine is larger than the ideal 90° [94.0 (2°) and 94.7 (2°)] and the Cl–Pd–Cl angles are also greater than 90° [92.1 (2°) and 92.0 (2°)]. The mean deviations of PdP_2Cl_2 from the plane are 0.14 Å for one of the molecules and 0.02 Å for the second. In both molecules the P–N, Pd–P and P–Cl bond lengths are all typical of single bonds.



(3)

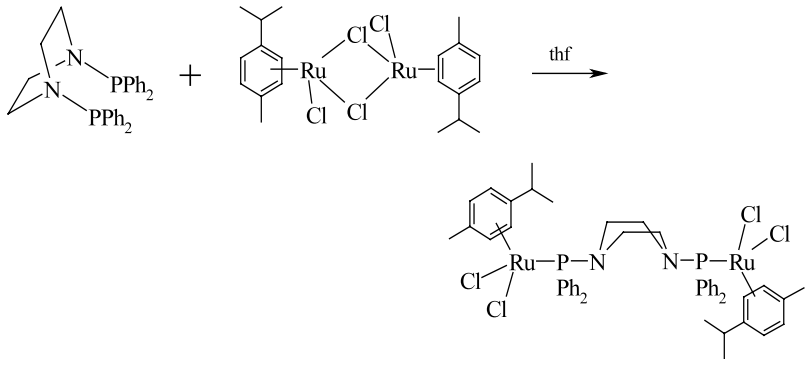
form seven-membered metallacycles. Reactions with compounds containing Au(I) and Ru(II) show that **1**–**3** can also act as a bridging ligands between two metal centres (Eq. (4)).



R = Ph (**9**), $C_6H_4O_2$ (**10**) OC_2H_4O (**11**)

(4)

Analogous ligands to **1**–**3** can be synthesised by reacting the same chlorophosphines with homopiperazine which differs from piperazine by containing an extra CH_2 group, therefore, forming a seven-membered nitrogen–carbon ring system. Reaction of homopiperazine with 2 equiv. of Ph_2PCl, $(C_6H_4O_2)PCl$ and $(C_2H_4O_2)PCl$, in the presence of NEt_3, proceeds in thf to give **13, 19** and **24.** Reaction of $^{i}Pr_2PCl$ with homopiperazine yields the analogous ^{i}Pr derivative **25**. The δ_P values of all three aryl ligands are slightly downfield from the values observed for the analogous piperazine derivatives, **1**–**3**, suggesting that the addition



The reaction of **1** with $[Mo(CO)_4(pip)_2]$ in dichloromethane proceeds, with displacement of the piperidines, to give **8** (Eq. (3)). The $^{31}P\{^{1}H\}$ NMR spectrum of **8** displays a singlet at δ(P) 97.2, a downfield shift of around 35 ppm upon complexation whilst its IR spectrum contains four strong bands due to ν(CO) (2021, 1917, 1901 and 1888 cm^{-1}), confirming the *cis* structure. Compounds **4**–**8** demonstrate the ability of $Ph_2PN(C_2H_4)_2NPPh_2$ and $(C_6H_4O_2)PN(C_2H_4)_2NP(C_6H_4O_2)$ to act as bidentate chelating ligands and

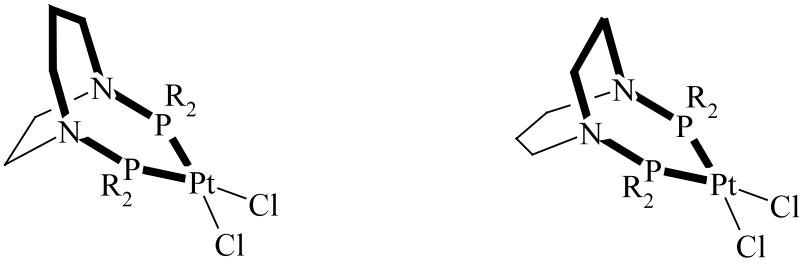


Fig. 3. Different ring sizes in complexes containing the homopiperazine based ligands.

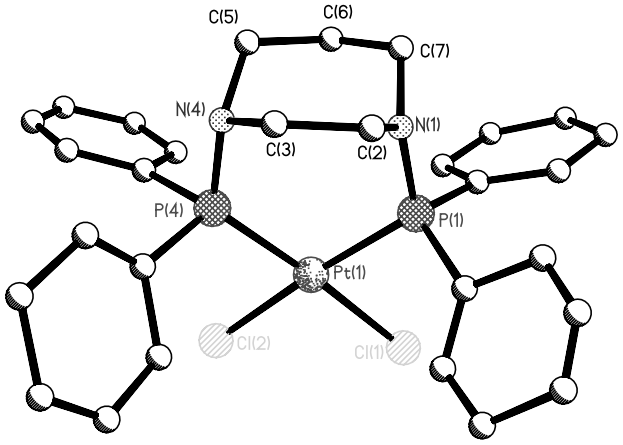


Fig. 4. The structure of $[PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$ in the crystal structure of $[Pt(cod)Cl_2]_2 \cdot [PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}]$.

of an extra CH_2 group into the ligand backbone causes a slight deshielding of the phosphorus centres. The homopiperazine derivatives form complexes in an analogous fashion to their piperazine analogues. Spectroscopic data for the new compounds are summarised in Tables 1–3.

The Pt(II), Pd(II) and Mo(0) complexes of **13**, **19** and **24** contain seven- and eight-membered (Figs. 3 and 4) chelate rings. The spectroscopic data for derivatives of the two amines, which incorporate the same phosphorus substituents, are very similar suggesting that the extra CH_2 in the homopiperazine ligands has little effect on the electronic properties of the ligands and resulting complexes.

The X-ray structure of *cis*-$[PtCl_2\{Ph_2PN(C_5H_{10})NPPh_2\}][PtcodCl_2]_2$ was obtained. It reveals that the P–Pt–P bite angle is expanded to 97° as a consequence of the homopiperazine backbone.

This work clearly demonstrates the usefulness of simple organic nitrogen containing rings in the formation of large bite angle phosphines.

4. Supplementary material

Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic data centre, CCDC Nos. 176413–176415. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

[1] P. Bhattacharyya, J.D. Woollins, Polyhedron 14 (1995) 3367.
[2] T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451.
[3] J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 2893.
[4] A.M.Z. Slawin, M.B. Smith, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 4575.
[5] P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, D.J. Williams, J.D. Woollins, J. Chem. Soc., Dalton Trans. (1996) 3647.
[6] T.Q. Ly, A.M.Z. Slawin, J.D. Woollins, Angew. Chem., Int. Ed. Engl. 37 (1998) 2501.
[7] M.L. Clarke, D.J. Cole-Hamilton, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Chem. Commun. (2000) 2065.
[8] M. Rodriguez i Zubiri, M.L. Clarke, D.F. Foster, D.J. Cole-Hamilton, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2001) 969.
[9] S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, J. Organomet. Chem. 582 (1999) 83.
[10] S.M. Aucott, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2000) 2559.
[11] T.Q. Ly, A.M.Z. Slawin, J.D. Woollins, Polyhedron 18 (1999) 1761.
[12] Q. Zhang, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc., Dalton Trans. (2001) 3598.
[13] A.M.Z. Slawin, J.D. Woollins, Q. Zhang, J. Chem. Soc., Dalton Trans. (2001) 621.
[14] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 428.
[15] M.A. Bennett, T.N. Huang, T.W. Matheson, A.R. Smith, Inorg. Synth. 21 (1982) 74.
[16] SHELXTL, Bruker AXS, Madison, WI, 1999.
[17] A. Sen, Acc. Chem. Res. 26 (1993) 303.
[18] V.S. Reddy, K.V. Katti, C.L. Barnes, Chem. Ber. 127 (1994) 1355.