DALTON
FULL PAPER

Novel chiral phosphine ligands and complexes from amino acid esters

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Received 13th November 2000, Accepted 17th January 2001
First published as an Advance Article on the web 15th February 2001

N-Diphenylphosphinoamino acid methyl/ethyl esters RCH(NHPPh$_2$)CO$_2$R′ **1a–1e** were prepared in high yield from equimolar amounts of amino acid methyl/ethyl ester hydrochloride and chlorodiphenylphosphine. The reaction proceeds with configurational retention. Oxidation of **1a** (R = R′ = CH$_3$) with H$_2$O$_2$ or S$_8$ leads to the *N*-diphenylphosphinoylalanine methyl ester **2a** or *N*-diphenylthiophosphinoylalanine methyl ester **3a**. **1a–1e** function as monodentate ligands to [PtCl$_2$(cod)], [RhCl(cod)]$_2$ and [AuCl(tht)] to give *cis*-[PtCl$_2$(**1**-*P*)$_2$], [RhCl(cod)(**1**-*P*)] and [AuCl(**1**-*P*)]. Two equivalents of chlorodiphenylphosphine react with alanine methyl ester hydrochloride in CH$_2$Cl$_2$ to give *N,N*-bis(diphenylphosphino)alanine methyl ester, bdppal. This is an excellent bidentate ligand, the chelate complexes [MCl$_2$(bdppal-*P*,*P*′)] (M = Pd or Pt) being prepared and studied by X-ray analysis. Oxidation at one P atom in bdppal with either H$_2$O$_2$ or S$_8$ gives *N*-diphenylphosphino-*N*-diphenylphosphinoylalanine methyl ester, bdppalO, and *N*-diphenylphosphino-*N*-diphenylthiophosphinoylalanine methyl ester, bdppalS, respectively. bdppalO is very difficult to isolate but does react *in situ* with [PdCl$_2$(cod)] to give [PdCl$_2$(bdppalO-*O*,*P*)]. bdppalS reacts with [MCl$_2$(cod)] (M = Pd or Pt) giving [MCl$_2$(bdppalS-*P*,*S*)]. The dioxidised product *N*,*N*-bis(diphenylphosphinoyl)-alanine methyl ester, bdppalO$_2$, does not react with [MCl$_2$(cod)] (M = Pd or Pt), whereas *N*,*N*-bis(diphenylthio-phosphinoyl)alanine methyl ester, bdppalS$_2$, reacts with [PdCl$_2$(cod)] to give [PdCl$_2$(bdppal-*S*,*S*′)]. All the compounds are chiral and have been fully characterised by microanalysis, IR, ^{31}P-{^{1}H}, ^{1}H NMR, and FAB$^+$ mass spectroscopies, and in several cases structures are confirmed by X-ray analysis. The crystal structures described and those previously determined reveal the configurational retention of the reactions.

Introduction

Chiral complexes are very important in catalytic asymmetric synthesis. As natural and readily available chiral compounds, amino acids are often employed as starting materials for chiral ligands.[1–4] There are several reports[5–9] which involve *N*,*N*-bis(diphenylphosphino)amino esters, but no *N*-mono(diphenylphosphino)amino esters complexes apart from one report[10] about the stereoselective synthesis of the *N*-phosphorus(V) substituted amino acids *via* the *N*-phosphorus(III) derivatives of amino acids. We found no reports on semi-oxidised *N,N*-bis(diphenylphosphino)amino esters. In our preliminary publication[11] we reported two crystal structures of (*R*)-*N*-diphenylphosphinoalanine methyl ester complexes. Here we describe several other complexes of this type of ligand. Although *N*,*N*-bis(diphenylphosphino)amino esters have previously been reported,[5–9] no crystal structures of their palladium/platinum complexes have been published, while *N*,*N*-bis(diphenylphosphino)alanine methyl ester itself (bdppal) has only been mentioned in one reference.[3] In this work we prepared bdppal and obtained the crystal structures of [PdCl$_2$(bdppal-*P*,*P*′)] and [PtCl$_2$(bdppal-*P*,*P*′)]. Since complexes containing hybrid ligands with soft (phosphorus) and hard (oxygen) donor atoms have been shown to be useful in homogeneous catalysis,[12] the oxidation of bdppal by H$_2$O$_2$/sulfur and the corresponding co-ordination behaviour were also investigated. All the compounds are chiral and have been fully characterised by microanalysis, IR, multinuclear NMR and FAB$^+$ mass spectroscopy techniques, and several complexes were structurally characterised by X-ray analysis.

Experimental

All solvents and reagents were purchased from Aldrich and Lancaster. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Diethyl ether and tetrahydrofuran were purified by reflux over sodium and distillation under nitrogen. 4-(Dimethylamino)pyridine (DMAP) was purified by recrystallisation from toluene. (*S*)- or (*R*)-α-amino ester hydrochlorides (97–99%) were used as received. Ligand preparations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Co-ordination reactions and work-up were performed in common solvents as received. [MCl$_2$(cod)] (M = Pd or Pt, cod = cycloocta-1,5-diene),[13] [RhCl(cod)]$_2$[14] and [AuCl(tht)] (tht = tetrahydrothiophene)[15] were prepared using literature procedures.

Infrared spectra were recorded from KBr discs or film on KBr plates on a Perkin-Elmer system 2000 spectrometer, ^{31}P-{^{1}H} NMR spectra on either a JEOL FX90Q operating at 36.21 MHz or a Bruker AC 250FT spectrometer at 101.3 MHz with δ referenced to external H$_3$PO$_4$ and ^{1}H NMR spectra (250 or 300 MHz) on either a Bruker AC250FT or Varian Gemini 2000 spectrometer. Microanalyses were performed by the University Service within this Department and fast atom bombardment (FAB) or chemical ionisation (CI) mass spectra by the Swansea Mass Spectrometer Service. Optical rotations were measured on an Optical Activity Polaar 2001 spectrometer in CHCl$_3$ or CH$_2$Cl$_2$ (g per 100 cm^3) in a 25 cm cell. Precious metal salts were provided on loan by Johnson Matthey PLC.

Preparations

(*S*)-*N*-Diphenylphosphinoalanine methyl ester (dppal) 1a. To a solution of (*S*)-alanine methyl ester hydrochloride (1.402 g, 10.04 mmol) in CH$_2$Cl$_2$ (60 cm^3) was added Et$_3$N (3 cm^3, 21.0 mmol) and DMAP (163 mg, 1.3 mmol). A CH$_2$Cl$_2$ (40 cm^3) solution of Ph$_2$PCl (1.95 cm^3, 10.86 mmol) was added dropwise at 0–5 °C. Stirring was continued for 3 h. The reaction mixture was evaporated to dryness *in vacuo* and THF (100 cm^3) added.

DOI: 10.1039/b009074n

The solution was filtered through a sintered frit under N_2 and the residue washed with THF (2×20 cm^3). The filtrate was evaporated to dryness *in vacuo* and the light yellow oil washed with cold MeOH (3×10 cm^3) and diethyl ether (3×10 cm^3) to give a white solid in a yield of 2.18 g (76%).

(*S*)-*N*-Diphenylphosphinoglutamic acid diethyl ester (dppgl) 1b. To a solution of (*S*)-glutamic acid diethyl ester hydrochloride (2.4 g, 10 mmol) in CH_2Cl_2 (80 cm^3) was added Et_3N (2.78 cm^3, 20 mmol) and DMAP (123 mg, 1 mmol). A CH_2Cl_2 (20 cm^3) solution of Ph_2PCl (1.95 cm^3, 2.4 g, 10.88 mmol) was added dropwise at 0–5 °C. Stirring was continued for 3 h. The reaction mixture was evaporated to dryness *in vacuo* and Et_2O (80 cm^3) added. The solution was filtered through a sintered frit under N_2 and the residue washed with Et_2O (2×30 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a milk-like oil in a crude yield of 3.49 g (90%).

(*S*)-*N*-Diphenylphosphinovaline methyl ester (dppval) 1c. To a solution of (*S*)-valine methyl ester hydrochloride (0.633 g, 3.8 mmol) and DMAP (60 mg, 488 μmol) in CH_2Cl_2 (60 cm^3) was added Et_3N (1.1 cm^3, 7.9 mmol). A CH_2Cl_2 (20 cm^3) solution of Ph_2PCl (0.68 cm^3, 0.829 g, 3.8 mmol) was added dropwise at 0–5 °C. Stirring was continued for 2 h. The reaction mixture was evaporated to dryness i*n vacuo* and Et_2O (30 cm^3) added. The solution was filtered through a cannel needle under N_2 and the residue washed with Et_2O (2×10 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a milk-like oil in a crude yield of 1.05 g (89%).

(*S*)-*N*-Diphenylphosphinophenylalanine methyl ester (dpppal) 1d. To a solution of (*S*)-phenylalanine methyl ester hydrochloride (2.206 g, 10 mmol) and DMAP (123 mg, 1 mmol) in CH_2Cl_2 (100 cm^3) was added Et_3N (2.8 cm^3, 20.1 mmol). A CH_2Cl_2 (40 cm^3) solution of Ph_2PCl (1.8 cm^3, 10.03 mmol) was added dropwise at 0–5 °C. Stirring was continued for 3 h. The reaction mixture was evaporated to dryness *in vacuo* and Et_2O (80 cm^3) added. The solution was filtered through a sintered frit under N_2 and the residue washed with Et_2O (2×30 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a milk-like oil in a crude yield of 3.58 g (98%).

(*S*)-*N*-Diphenylphosphinomethionine methyl ester (dppmet) 1e. To a solution of (*S*)-methionine methyl ester hydrochloride (1.00 g, 5 mmol) and DMAP (61 mg, 0.5 mmol) in CH_2Cl_2 (50 cm^3) was added Et_3N (1.4 cm^3, 10.06 mmol). A CH_2Cl_2 (20 cm^3) solution of Ph_2PCl (0.9 cm^3, 5.01 mmol) was added dropwise at 0–5 °C. Stirring was continued for 3 h. The reaction mixture was evaporated to dryness *in vacuo* and Et_2O (50 cm^3) added. The solution was filtered through a sintered frit under N_2 and the residue washed with Et_2O (2×10 cm^3). The filtrate was evaporated to dryness *in vacuo* to give a milk-like oil in a crude yield of 1.6 g (93%).

(*S*)-*N*-Diphenylphosphinoylalanine methyl ester (dppalO) 2a. To a solution of compound **1a** (*S* configuration, 2.88 g, 10 mmol) in THF (80 cm^3) at room temperature was added aqueous H_2O_2 (30%, 1.2 cm^3, 10.6 mmol) dropwise. $MgSO_4$ was added and stirred overnight. The reaction mixture was filtered and the residue washed with THF (2×20 cm^3). Removal of the solvent gave the product as a white powder in yield of 2.75 g (90%). Slow evaporation of THF solution gave crystals suitable for X-ray analysis.

(*S*)-*N*-Diphenylthiophosphinoylalanine methyl ester (dppalS) 3a. To a THF (25 cm^3) solution of compound **1a** (1.161 g, 4.04 mmol) was added sulfur (134 mg, 4.12 mmol). The reaction mixture was stirred under N_2 with reflux overnight. The solution was dried *in vacuo* to give a sticky gum. Separation of the crude product by column chromatography (silica gel, ethyl acetate–light petroleum (bp 40–60 °C) 1 : 1) afforded a white solid in yield of 0.411 g (32%).

***cis*-[PtCl$_2$(dppal-*P*)$_2$] 4a.** To a solution of [PtCl$_2$(cod)] (39 mg, 104 μmol) in CH_2Cl_2 (10 cm^3) was added compound **1a** (50 mg, 209 μmol). The reaction mixture was stirred for 30 min. The solvent was removed by rotatory evaporation and the product washed with Et_2O (3×3 cm^3) to give a white solid in yield of 87 mg (87%).

***cis*-[PtCl$_2$(dppgl-*P*)$_2$] 4b.** To a solution of [PtCl$_2$(cod)] (115 mg, 307 μmol) in CH_2Cl_2 (20 cm^3) was added compound **1b** (246 mg, 635 μmol). The reaction mixture was stirred for 20 min and then concentrated *in vacuo* to about 1 cm^3. The semisolid product was washed with Et_2O (2×10 cm^3) and then concentrated *in vacuo* to dryness to give a white flaky solid in yield of 255 mg (80%).

***cis*-[PtCl$_2$(dppval-*P*)$_2$] 4c.** To a round bottom flask (100 cm^3) were added compound **1c** (120 mg, 380 μmol) and [PtCl$_2$(cod)] (68 mg, 182 μmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 30 min. The solvent was removed by rotatory evaporation and the product washed with Et_2O (3×3 cm^3) to give a white powder in yield of 131 mg (80%).

***cis*-[PtCl$_2$(dpppal-*P*)$_2$] 4d.** To a round bottom flask (100 cm^3) were added compound **1d** (138 mg, 380 μmol) and [PtCl$_2$(cod)] (68 mg, 182 μmol). CH_2Cl_2 (20 cm^3) was added. The reaction mixture was stirred for 30 min. The solvent was removed by rotatory evaporation and then Et_2O (10 cm^3) and THF (two drops) were added. The white powder was filtered off and washed with Et_2O (3×3 cm^3) to give a white powder in yield of 148 mg (82%).

***cis*-[PtCl$_2$(dppmet-*P*)$_2$] 4e.** To a solution of compound **1e** (200 mg, 575 μmol) in CH_2Cl_2 (20 cm^3) was added [PtCl$_2$(cod)] (100 mg, 267 μmol). The reaction mixture was stirred for 30 min and then concentrated by rotatory evaporation to about 0.5 cm^3. Cold Et_2O (3 cm^3) was added and the mixture stood for about 10 min until a slightly yellow oil appeared at the bottom of the flask. The solvent was pipetted out and cold Et_2O (2×3 cm^3) added to wash the oil. The solvent was pipetted out and the oil dried *in vacuo* to give a light-yellow floppy solid in yield of 203 mg (79%).

[RhCl(dppal-*P*)] 5a. To a solution of [RhCl(cod)]$_2$ (91 mg, 184 μmol) in CH_2Cl_2 (10 cm^3) was added dropwise a solution of compound **1a** (106 mg, 369 μmol) in CH_2Cl_2 (10 cm^3). The solution was stirred for 30 min and then concentrated *in vacuo* to about 0.5 cm^3. Separation with column chromatography (silica gel, solvent Et_2O) and removal of solvent *in vacuo* afforded an orange flaky solid in yield of 179 mg (90%).

[RhCl(dppgl-*P*)] 5b. To a solution of [RhCl(cod)]$_2$ (91 mg, 184 μmol) in CH_2Cl_2 (10 cm^3) was added dropwise a solution of compound **1b** (143 mg, 369 μmol) in CH_2Cl_2 (10 cm^3). Treatment as for complex **5a** afforded an orange flaky solid in yield of 205 mg (88%).

[RhCl(dppval-*P*)] 5c. To a solution of compound **1c** (126 mg, 399 μmol) in CH_2Cl_2 (10 cm^3) was added [RhCl(cod)]$_2$ (94 mg, 191 μmol). Treatment as for **5a** afforded an orange flaky solid in yield of 192 mg (90%).

[RhCl(dpppal-*P*)] 5d. To a solution of compound **1d** (103 mg, 283 μmol) in CH_2Cl_2 (10 cm^3) was added [RhCl(cod)]$_2$ (68 mg, 138 μmol). Treatment as for **5a** afforded an orange flaky solid in yield of 164 mg (95%).

[RhCl(dppmet-*P*)] 5e. To a solution of compound **1e** (110 mg, 319 µmol) in CH_2Cl_2 (10 cm^3) was added $[RhCl(cod)]_2$ (74 mg, 150 µmol). The solution was stirred for 20 min and then concentrated *in vacuo* to about 0.5 cm^3. Separation with column chromatography (silica gel, solvent Et_2O) and removal of solvent *in vacuo* afforded an orange flaky solid in yield of 66 mg (37%).

[AuCl(dppal-*P*)] 6a. To a solution of compound **1a** (78 mg, 274 µmol) in CH_2Cl_2 (20 cm^3) was added [AuCl(tht)] (86 mg, 268 µmol). The reaction mixture was stirred in darkness for 30 min and then concentrated *in vacuo* to dryness. Addition of Et_2O (1 cm^3) and filtration in darkness gave a pink powder (56 mg). Addition of light petroleum (3 cm^3) to the filtrate afforded another portion of product (67 mg). The total yield was 123 mg (88%).

(*S*)-*N*,*N*-Bis(diphenylphosphino)alanine methyl ester (bdppal) 7. To a solution of (*S*)-alanine methyl ester hydrochloride (5.230 g, 37 mmol) in CH_2Cl_2 (100 cm^3) was added Et_3N (16 cm^3, 115 mmol). A CH_2Cl_2 (50 cm^3) solution of Ph_2PCl (13.3 cm^3, 74 mmol) was added dropwise. Stirring was continued for 3 h. The solution was concentrated *in vacuo* to dryness. 100 cm^3 of THF were added. The THF solution was filtered through a sintered frit and the residue washed with THF (3 × 30 cm^3). The filtrate was rotatory evaporated to dryness to give a slightly yellow sticky oil. 2 cm^3 of MeOH were added and a white solid precipitated. This was filtered off, washed with cold MeOH (3 × 10 cm^3) and cold Et_2O (3 × 3 cm^3) and dried *in vacuo*. Yield: 11.0 g (63%).

***cis*-[PdCl$_2$(bdppal-*P*,*P*′)] 8.** To a solution of $[PdCl_2(cod)]$ (33 mg, 116 µmol) in CH_2Cl_2 (5 cm^3) was added compound **7** (55 mg, 117 µmol). The reaction mixture was stirred for 20 min and then concentrated to *ca.* 1 cm^3. Addition of Et_2O (5 cm^3) led to a light green powder which was filtered off, washed with Et_2O (3 × 0.5 cm^3), light petroluem (bp 40–60 °C, 3 × 1 cm^3), Et_2O (3 × 0.5 cm^3) and dried *in vacuo* to give a yield of 75 mg (100%). Slow diffusion of light petroleum into the CH_2Cl_2 solution in three days gave pale yellow crystals suitable for X-ray analysis.

***cis*-[PtCl$_2$(bdppal-*P*,*P*′)] 9.** To a solution of compound **7** (64 mg, 135 µmol) in CH_2Cl_2 (50 cm^3) was added $[PtCl_2(cod)]$ (50 mg, 134 µmol). The reaction mixture was stirred for 2 h and then concentrated to *ca.* 1 cm^3. Addition of Et_2O (5 cm^3) led to a white powder (102 mg). The crude product was dissolved in THF (50 cm^3). Slow evaporation of THF in 20 days gave crystals suitable for X-ray analysis, yield 90 mg (90.5%).

(*S*)-*N*-(Diphenylphosphino)-*N*-(diphenylthiophosphinoyl)-alanine methyl ester (bdppalS) 11. To a solution of compound **7** (1.544 g, 3.278 mmol) in THF (20 cm^3) was added 213 mg (6.74 mmol) of sulfur. The solution was stirred overnight at room temperature and then concentrated *in vacuo* to dryness. Et_2O (20 cm^3) was added and unchanged sulfur removed by filtration. The filtrate was concentrated *in vacuo* to dryness. Addition of Et_2O (2 cm^3) to the floppy solid afforded a white powder in yield of 0.653 g (40%). Slow diffusion of light petroleum into the CH_2Cl_2 solution in two days gave colourless crystals suitable for X-ray analysis.

(*S*)-*N*,*N*-Bis(diphenylphosphinoyl)alanine methyl ester (bdppalO$_2$) 12. To a solution of compound **7** (3.088 g, 6.556 mmol) in THF (80 cm^3) was added anhydrous $MgSO_4$ and H_2O_2 (30%, 1.5 cm^3, 13.2 mmol). The solution was stirred at 0 °C for two hours and then filtered. The filtrate was dried *in vacuo* to give a sticky gum. Addition of Et_2O (2 cm^3) afforded a white powder. The powder was filtered and dried *in vacuo* to give a yield of 2.97 g (90%). Slow diffusion of light petroleum into the CH_2Cl_2 solution for one week gave colourless crystals suitable for X-ray analysis.

(*S*)-*N*,*N*-Bis(diphenylthiophosphinoyl)alanine methyl ester (bdppalS$_2$) 13. To a solution of compound **7** (1.063 g, 2.257 mmol) in THF (80 cm^3) was added sulfur (145 mg, 4.52 mmol). The solution was stirred under N_2 at reflux for 8 days. The reaction mixture was concentrated to *ca.* 0.5 cm^3. Separation with column chromatography (silica gel, ethyl acetate–light petroleum (bp 60–80 °C) 1 : 1) and removal of the solvent *in vacuo* afforded a white floppy solid in yield of 0.882 g (73%).

(*S*)-*N*-(Diphenylphosphino)-*N*-(diphenylphosphinoyl) alanine methyl ester (bdppalO) 10 and *cis*-[PdCl$_2$(bdppalO-*P*,*O*)] 14. To a solution of compound **7** (99 mg, 210 µmol) in THF (5 cm^3) was added H_2O_2 (30%, 0.036 cm^3, 315 µmol). The solution was stirred at 0 °C for about 25 min and then stood at room temperature until the ^{31}P-$\{^1H\}$ NMR spectrum showed no peak at δ 55.0 for **7**. The dioxidised compound **12** (δ_P 31.0 in THF) was unavoidable but it did not affect the co-ordination of **10** with $[PdCl_2(cod)]$. 25 mg (88 µmol) of $[PdCl_2(cod)]$ was added. The reaction mixture was stirred for 30 min and then light petroleum (40 cm^3) was carefully layered. Its slow diffusion into the THF solution in 10 h afforded orange crystals of complex **14** in yield of 32 mg (55%). Compound **10** cannot be isolated from the reaction mixture but can be observed as an intermediate by the ^{31}P-$\{^1H\}$ NMR spectrum (δ 45.8(d, P^{III}), 33.1 (d, P=O), $^2J_{PP}$ 80 Hz). Slow evaporation of the $CDCl_3$ solution gave red crystals suitable for X-ray analysis.

***cis*-[PdCl$_2$(bdppalS-*P*,*S*)] 15.** To a solution of compound **11** (73 mg, 145 µmol) in CH_2Cl_2 (5 cm^3) were added 40 mg (141 µmol) of $[PdCl_2(cod)]$. The reaction mixture was stirred for 30 min and then concentrated in a rotatory evaporator to *ca.* 1 cm^3. Et_2O (5 cm^3) was added to give a light brown powder. The product was filtered off, washed with Et_2O (3 × 1 cm^3) and then dried *in vacuo* to give a yield of 95 mg (99%).

***cis*-[PtCl$_2$(bdppalS-*P*,*S*)] 16.** To a solution of compound **11** (69 mg, 137 µmol) in CH_2Cl_2 (5 cm^3) were added 51 mg (136 µmol) of $[PtCl_2(cod)]$. The reaction mixture was stirred for 2 h and then concentrated in a rotatory evaporator to *ca.* 0.5 cm^3. Et_2O (5 cm^3) was added to give a green-yellow powder. The product was filtered off, washed with Et_2O (3 × 1 cm^3) and then dried *in vacuo* to give a yield of 101 mg (98%).

***cis*-[PdCl$_2$(bdppalS$_2$-*S*,*S*′)] 17.** To a solution of compound **13** (78 mg, 145 µmol) in CH_2Cl_2 (5 cm^3) were added 40 mg (141 µmol) of $[PdCl_2(cod)]$. The reaction mixture was stirred for 2 h and then concentrated in a rotatory evaporator to *ca.* 0.5 cm^3. Et_2O (5 cm^3) was added to give a brown powder. The product was filtered off, washed with Et_2O (3 × 1 cm^3) and then dried *in vacuo* to give a yield of 100 mg (100%).

X-Ray crystallography

Details of the data collections and refinements are summarised in Table 12. Data were collected at room temperature using Mo-Kα radiation with a SMART system. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[16] There was some disorder in complex **14**. C(4) was refined anisotropically in two 50% occupancy sites.

CCDC reference numbers 152782–152787.

See http://www.rsc.org/suppdata/dt/b0/b009074n/ for crystallographic data in CIF or other electronic format.

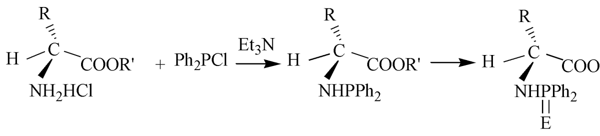
Table 1 Spectroscopic data for *N*-mono(diphenylphosphino)amino acid methyl esters

Compound	^{31}P-{^{1}H} NMR δ	^{1}H NMR		IR (cm^{-1})	Microanalysis (%) Found (Calculated)	FAB$^+$ or CIMS (*m*/*z*)	$[\alpha]_D^{25}$ (*c*) in CHCl$_3$
		δ	*J*/Hz				
1a	40.0	7.44–7.31 (m, 10H, Ar H)		3358s (ν_{N-H})	C: 66.88 (66.89)	288 [M$^+$]	+2.98
		3.84 (m, 1H, CH)	$^3J_{CHCH}$ 7.0	1739vs ($\nu_{C=O}$)	H: 6.50 (6.31)		(9.8)
		3.53 (s, 3H, OCH$_3$)	$^3J_{PNCH}$ 7.0	849m (ν_{P-N})	N: 4.50 (4.87)		
		2.56 (br d, 1H, NH)	$^3J_{CHNH}$ 10.4				
		1.37 (d, 3H, CH$_3$)					
1b	42.0	7.35–7.18 (m, 10H, Ar H)		3352m (ν_{N-H})	C: 64.42 (65.10)	389 [M + H]$^+$	+6.8
		400 (q, 2H, OCH$_2$)		1732vs ($\nu_{C=O}$)	H: 6.83 (6.83)		(11.0)
		3.86 (q, 2H, OCH$_2$)		852m (ν_{P-N})	N: 3.62 (4.06)		
		3.68 (m, 1H, CH)	$^3J_{PNCH}$ 7.2				
		2.52 (dd, 1H, NH)	$^3J_{CHNH}$ 13.0				
		2.30 (t, 2H, CHCH$_2$CH_2)	$^2J_{PNH}$ 3.0				
		1.91 (m, 2H, CHCH_2CH$_2$)	$^3J_{CHCH}$ 7.2				
		1.12 (t, 3H, OCH$_2$CH_3)	$^2J_{CHH}$ 17.5				
		1.02 (t, 3H, OCH$_2$CH_3)					
1c	43.8	7.33–7.09 (m, 10H, Ar H)		3362 (ν_{N-H})	C: 67.71 (68.58)	316 [M + H]$^+$	+22.6
		3.47 (m, 1H, CH)	$^3J_{PNCH}$ 9.0	1736vs ($\nu_{C=O}$)	H: 6.96 (7.03)		(3.7)
		3.35 (s, 3H, OCH$_3$)	$^3J_{CHCH}$ 6.8	852m (ν_{P-N})	N: 4.70 (4.44)		
		2.46 (dd, 1H, NH)	$^3J_{CHNH}$ 10.5				
		1.88 (m, 1H, CH(CH$_3$)$_2$)	$^2J_{PNH}$ 5.5				
		0.78 (d, 6H, CH(CH_3)$_2$)					
1d	42.3	7.37–7.10 (m, 15H, Ar H)	$^3J_{CHCH}$ 7.1	3363m (ν_{N-H})	C: 71.65 (72.71)	364 [M + H]$^+$	+14.3
		4.04 (m, 1H, CH)	$^3J_{PNCH}$ 7.1	1739vs ($\nu_{C=O}$)	H: 6.01 (6.10)		(10.0)
		3.38 (s, 3H, OCH$_3$)	$^2J_{CHH}$ 12.0	803m (ν_{P-N})	N: 4.16 (3.85)		
		3.00 (dd, 2H, CH_2Ph)	$^3J_{NHCH}$ 10.6				
		2.40 (dd, 1H, NH)	$^2J_{PNH}$ 1.5				
1e	42.0	7.37–7.16 (m, 10H, Ar H)		3355m (ν_{N-H})	C: 62.16 (62.25)	348 [M + H]$^+$	+2.0
		3.82 (m, 1H, CH)	$^3J_{CHCH}$ 6.8	1737vs ($\nu_{C=O}$)	H: 6.61 (6.38)		(10.0)
		3.42 (s, 3H, OCH$_3$)	$^3J_{PNCH}$ 8.4	864m (ν_{P-N})	N: 4.77 (4.03)		
		2.51 (dd, 1H, NH)	$^3J_{NHCH}$ 10.5				
		2.42 (t, 2H, SCH$_2$)	$^2J_{PNH}$ 3.1				
		1.90 (s, 3H, SCH$_3$)					
		1.83 (m, 2H, CHCH_2)	$^2J_{CHH}$ 13.0				
2a	20.0	8.30 (br s, 1H, NH)					
		8.07–7.43 (m, 10H, Ar H)		3205m (ν_{N-H})	C: 63.06 (63.36)	304 [M + H]$^+$	−24.1
		3.91 (m, 1H, CH)	$^3J_{CHCH}$ 6.3	1743vs ($\nu_{C=O}$)	H: 6.07 (5.93)		(9.0)
		3.71 (s, 3H, OCH$_3$)	$^3J_{NHCH}$ 9.0	861m (ν_{P-N})	N: 4.73 (4.62)		
		1.44 (d, 3H, CH$_3$)		1183vs ($\nu_{P=O}$)			
3a	59.5	8.02–7.26 (m, 10H, Ar H)	$^3J_{CHCH}$ 7.0	3285m (ν_{N-H})	C: 59.37 (60.21)	320 [M + H]$^+$	−23.8
		4.10 (m, 1H, CH)	$^3J_{NHCH}$ 10.0	1745vs ($\nu_{C=O}$)	H: 5.64 (5.59)		(3.2)
		3.71 (s, 1H, CH)	$^3J_{PNCH}$ 12.0	858m (ν_{P-N})	N: 4.19 (4.39)		
		3.33 (br dd, 1H, NH)					
		1.39 (d, 3H, CH$_3$)	$^2J_{PNH}$ 4.0	629s ($\nu_{P=S}$)			

Results and discussion

N-Diphenylphosphinoamino acid methyl/ethyl ester and derivatives

Like other phosphinoamines developed by our group,[17,18] (*S*)-*N*-diphenylphosphinoamino acid methyl/ethyl esters, dppam, **1a**–**1e** were easily prepared by reaction of equivalents of an *S*-α-amino methyl/ethyl ester hydrochloride and chlorodiphenylphosphine in the presence of triethylamine in dichloromethane at room temperature (eqn. 1). **1a**–**1e** were obtained as white solids or oils in yields of up to 90% under anaerobic conditions. **1a** proves to be air sensitive. In fact, work-up of the anaerobic reaction mixture of alanine methyl ester and chlorodiphenylphosphine using methanol and diethyl ether in air gave no **1a** but 75% of *N*-diphenylphosphinoylalanine methyl ester, dppalO **2a**, and a trace of alanine methyl ester-diphenylphosphinic acid salt, $CH_3CH(NH_2)CO_2CH_3$-Ph_2PO_2H, which shows typical absorption at 2735, 2618 and 2193 cm^{-1} for amino-carboxyl salts and $\nu_{(C=O)}$ at 1758 cm^{-1} and $\nu_{(P=O)}$ at 1168 cm^{-1} in the IR spectra. The structure of this salt was confirmed by X-ray analysis and will be reported elsewhere. **2a** can also be obtained by H_2O_2 (30%) oxidation of **1a** in tetrahydrofuran in 90% yield. Oxidation of **1a** by elemental sulfur in tetrahydrofuran at reflux overnight gave *N*-diphenylthiophosphinoylalanine methyl ester, dppalS **3a**. **1b**–**1e** are more air sensitive than **1a**.



(1)

1 **2a, 3a**

1a	dppal	R = CH$_3$, R' = CH$_3$
1b	dppgl	R = CH$_2$CH$_2$CO$_2$CH$_2$CH$_3$, R' = CH$_2$CH$_3$
1c	dppval	R = CH(CH$_3$)$_2$, R' = CH$_3$
1d	dpppal	R = CH$_2$Ph, R' = CH$_3$
1e	dppmet	R = CH$_2$CH$_2$SCH$_3$, R' = CH$_3$
2a	dppalO	E = O, R = CH$_3$, R' = CH$_3$
3a	dppalS	E = S, R = CH$_3$, R' = CH$_3$

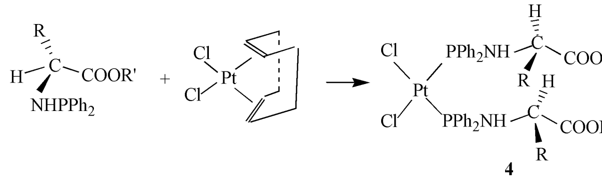
As seen in Table 1, compounds **1a**, **2a** and **3a** give satisfactory microanalysis and show the expected parent and fragment ions in the positive-ion FAB or CI mass spectra. **1a** displays a singlet at δ 40.0 in the ^{31}P-{^{1}H} NMR spectrum, **2a** and **3a** display singlets at δ 22.6 and 59.5, respectively, and are shifted by around 20 ppm to lower frequency from P^{III} to P=O and 20 ppm to higher frequency from P^{III} to P=S. The ^{1}H NMR spectrum of **1a** displays the anticipated multiplets at δ 7.44–7.31 for the aryl protons, a broad doublet at δ 2.56 for NH, a multiplet at δ 3.84 for CH, a singlet at δ 3.53 for OCH$_3$ of the ester, and a doublet at δ 1.37 for CH$_3$ [$^3J_{CHCH}$ = 7.0 Hz]. By selective irradiation at CH$_3$, NH, and CH resonances respectively, the coupling constants can be obtained [$^3J_{PNCH} = 7.0$, $^3J_{NHCH} = 10.4$ Hz], while $^2J_{NHP}$ was not observed. In the spectrum of **3a** a multiplet at δ 8.02–7.26 for aryl protons, a multiplet at δ 4.10 [$^3J_{CHCH} = 7.0$, $^3J_{PNCH} = 12.0$, $^3J_{NHCH} = 10.0$, $^2J_{PNH} = 4.0$ Hz] for CH, a singlet at δ 3.71 for OCH_3 and a doublet at δ 1.39 for CH_3 and a broad doublet of doublets at δ 3.33 for NH are observed. In the spectrum of **2a** the resonances are observed at δ 7.43–8.07 as multiplets for aryl protons, at δ 3.71 as a singlet for OCH_3, at δ 1.44 as a doublet for CH_3 and at δ 3.91 as a multiplet for CH. However, the resonance of NH is shifted *ca.* 8.30 ppm to higher frequency as a broad single peak, suggesting hydrogen bonding in this compound.

In the IR spectra, we can identify $\nu_{(N\text{-}H)}$ at 3358, 3205, 3285 cm^{-1}, $\nu_{(C=O)}$ at 1739, 1743, 1745 cm^{-1} and $\nu_{(P\text{-}N)}$ at 849, 861, 858 cm^{-1} for **1a**, **2a**, **3a**, respectively. We can also find $\nu_{(P=O)}$ at 1183 cm^{-1} for **2a** and $\nu_{(P=S)}$ at 629 cm^{-1} for **3a**. The $\nu_{(N\text{-}H)}$ vibration of **1a** at 3358 cm^{-1} was very sharp, while $\nu_{(N\text{-}H)}$ 3205 and 3285 cm^{-1} for **2a** and **3a** are relatively broad and low frequency-shifted by 153 and 73 cm^{-1} from that of **1a**, respectively, implying hydrogen bonding in compounds **2a** and **3a**. In fact the hydrogen bonding has been confirmed by the crystal structure of **2a**.[11] The IR spectra of **1b**–**1e** are quite similar to that of **1a**: showing $\nu_{(N\text{-}H)}$ at 3352–3363 cm^{-1}, $\nu_{(C=O)}$ at 1732–1739 cm^{-1} and $\nu_{(P\text{-}N)}$ at 803–864 cm^{-1}.

Microanalyses and CI-MS spectra for compounds **1b**–**1e** were satisfactory. Like **1a**, **1b**–**1e** display singlets at δ *ca.* 42 in the $^{31}P\text{-}\{^1H\}$ NMR spectra. Their ^1H NMR spectra show the following common features: multiplets at about δ 7.40–7.10 for the resonance of phenyl protons, a doublet of doublets at approximately δ 2.5 assigned as the NH resonance, a singlet at *ca.* δ 3.40 due to OCH_3 and a multiplet at δ *ca.* 3.80 for CH. The coupling constants are as follows: $^2J_{PNH} \approx 3$, $^3J_{NHCH} \approx 11$, and $^3J_{PNCH} \approx {}^3J_{CHCH} \approx 7$ Hz. In the case of **1b**, two triplets due to the two $OCCH_3$ groups are observed at δ 1.12 and 1.02 and two quartets at δ 4.00 and 3.86 are ascribed to the two OCH_2. The chiral centre at the α-carbon renders the two β-H atoms magnetically non-equivalent [$^2J_{H\text{-}H} = 17.5$ Hz]. In the ^1H NMR spectrum of **1d** a similar influence of the chiral carbon on β-H is also observed [$^2J_{HH} = 12.0$ Hz].

Compounds **1a**–**1e** react with $[PtCl_2(cod)]$, $[RhCl(cod)]_2$ and [AuCl(tht)] to give *cis*-$[PtCl_2(dppam\text{-}P)_2]$ **4a**–**4e**, [RhCl(dppam-*P*)] **5a**–**5e** and [AuCl(dppal-*P*)] **6a** as expected (eqns. 2–4).

(2)

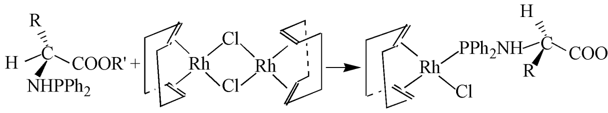


4

4a $R = CH_3$, $R' = CH_3$
4b $R = CH_2CH_2CO_2CH_2CH_3$
$R' = CH_2CH_3$

4c $R = CH(CH_3)_2$, $R' = CH_3$
4d $R = CH_2Ph$, $R' = CH_3$
4e $R = CH_2CH_2SCH_3$, $R' = CH_3$

(3)

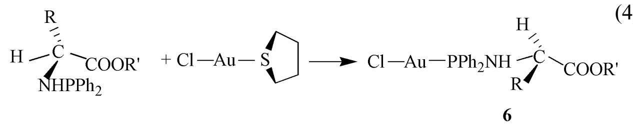


5

5a $R = CH_3$, $R' = CH_3$
5b $R = CH_2CH_2CO_2CH_2CH_3$
$R' = CH_2CH_3$

5c $R = CH(CH_3)_2$, $R' = CH_3$
5d $R = CH_2Ph$, $R' = CH_3$
5e $R = CH_2CH_2SCH_3$, $R' = CH_3$

(4)



6

6a $R = CH_3$, $R' = CH_3$

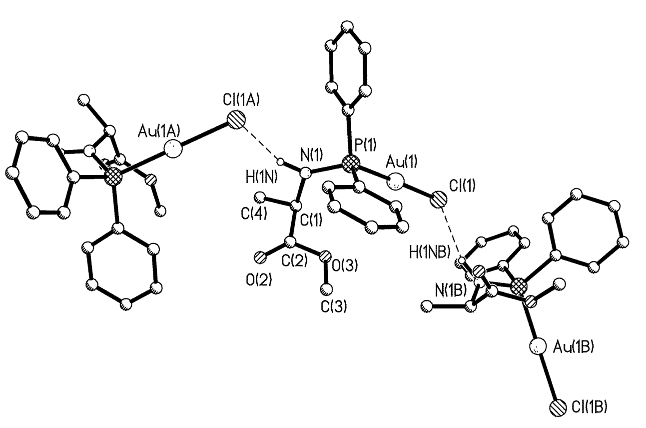


Fig. 1 The crystal structure of complex **6a**.

Tables 2 and 3 contain $^{31}P\text{-}\{^1H\}$, ^1H NMR and IR spectropic data for these complexes. In the $^{31}P\text{-}\{^1H\}$ NMR spectra the phosphorus resonances for the platinum complexes are slightly shifted to lower frequency (*ca.* 8 ppm), the coupling constant $^1J_{PtP}$ 3940 Hz is consistent with a *cis* geometry, while for the rhodium and gold species the resonances are shifted to higher frequency by *ca.* 20 and *ca.* 24 ppm, respectively. In the ^1H NMR spectra of the platinum and rhodium complexes the NH resonances are significantly different from those of the "free" ligands. They are shifted to higher frequency and change from a doublet or doublet of doublets to a triplet. The $^2J_{PNH}$ also increase from *ca.* 3 Hz for the "free" ligands to *ca.* 11 Hz for platinum and *ca.* 13 Hz for rhodium species. The higher frequency shift of δ NH suggests that relatively strong hydrogen bonding is present in these complexes. The crystal structure[11] of **4a** confirms the *cis* geometry and the *cis* N–H ··· Cl intramolecular hydrogen bonding. The rhodium species have a relatively high solubility in organic solvents, and attempts to obtain single crystals failed. However, from the similarity of the NH resonance to that of the platinum species similar hydrogen bonding can be assumed.

Gold(I) complexes of dppam are very light sensitive; only [AuCl(dppal-*P*)] **6a** was isolated as a pink powder. Slow diffusion of light petroleum into a CH_2Cl_2 solution of it gives colorless crystals. Other [AuCl(dppam-*P*)] can only be observed at about $\delta_{(P)}$ 68 in the reaction mixture. The ^1H NMR spectrum of **6a** closely resembles that of the "free" ligand; the NH resonance is a broad doublet at δ 3.08, and like **1a** the $^2J_{PNH}$ coupling is not observed. The crystal structure of **6a** (obtained from *R*-alanine methyl ester) is shown in Fig. 1 and selected bond lengths and angles are listed in Table 4. The Cl(1)–Au(1)–P(1) angle 178.90(9)° is not remarkable and the Au(1)–Cl(1) length 2.304(2) Å is comparable to that of the related gold complexes.[19,20] The molecules form zigzag shaped infinite chains within the crystal lattice by intramolecular N–H ··· Cl hydrogen bonding [H ··· Cl 2.41 Å, N(1)–H(1n) ··· Cl(1) 155.87°, Au ··· Au 3.0332(7) Å]. This hydrogen bonding is responsible for the higher frequency shift of the NH resonance in the ^1H NMR spectrum.

In the IR spectra of the above complexes the $\nu_{(N\text{-}H)}$ vibrations are shifted to lower frequency by around 50–100 cm^{-1}, whilst the $\nu_{(C=O)}$ stretches at about 1740 cm^{-1} are quite similar to those of the "free" ligands. This is consistent with the presence of the prevailing N–H ··· Cl intra/intermolecular hydrogen bonding in the complexes and the absence or rather weak N–H ··· O=C interaction. All the complexes gave satisfactory microanalysis. The anticipated parent/fragment ions and abundance distribution in the positive FAB mass spectra were observed.

Since it has been noted in $Ph_2PC_5H_4N\text{-}2$ complexes of palladium that the pyridyl nitrogen atom is believed to be essential because it can stabilise coordinatively unsaturated intermediates by weak chelate coordination and can also act as a proton relay, accepting protons during the activation of methanol and delivering the proton in the product releasing step,[21] the *cis*-N–H ··· Cl intramolecular interactions in **4** and **5**

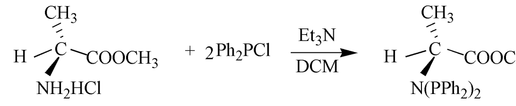
Table 2 Spectroscopic data for *cis*-[$PtCl_2$(dppam-*P*)$_2$] and [AuCl(dppal-*P*)]

Compound	^{31}P-{^{1}H} NMR		^{1}H NMR		IR (cm^{-1})	Microanalysis (%) Found (Calculated)	FAB$^+$ (*m*/*z*)	$[\alpha]_D^{25}$ (*c*) in $CHCl_3$
	δ	$^1J_{Pt-P}$/Hz	δ	*J*/Hz				
4a	35.1	3937	7.68–7.25 (m, 20H, Ar H)		3273s (ν_{N-H})	C: 46.13 (45.71)	841 [M]$^+$	
			4.53 (t, 2H, NH)	$^2J_{PNH}$ 11.0	1732vs ($\nu_{C=O}$)	H: 4.31 (4.32)	805 [M − Cl]$^+$	−13.7
			3.33 (s, 6H, OCH_3)	$^3J_{CHNH}$ 11.0	854m (ν_{P-N})	N: 3.82 (3.33)	768 [M − 2Cl]$^+$	(2.0)
			3.20 (m, 2H, CH)	$^3J_{CHCH}$ 7.0	305w (ν_{Pt-Cl})			
			1.01 (d, 6H, CH_3)	$^3J_{PNCH}$ 7.0	284w (ν_{Pt-Cl})			
4b	35.0	3945	7.90–7.08 (m, 20H, Ar H)		3269m (ν_{N-H})	C: 48.71 (48.47)	1041 [M]$^+$	+2.8
			4.89 (t, 2H, NH)	$^3J_{CHNH}$ 10.5	1734vs ($\nu_{C=O}$)	H: 4.96 (5.03)	1005 [M − Cl]$^+$	(2.8)
			4.04 (q, 4H, OCH_2)	$^2J_{PNH}$ 10.5	854m (ν_{P-N})	N: 2.91 (2.69)		
			3.72 (q, 4H, OCH_2)	$^3J_{CHCH}$ 7.1	313w (ν_{Pt-Cl})			
			3.12 (m, 2H, CH)		286w (ν_{Pt-Cl})			
			2.03 (t, 4H, $CHCH_2C\mathit{H}_2$)					
			1.65 (m, 4H, $CH\mathit{CH}_2CH_2$)	$^2J_{CHH}$ 12.6				
			1.20 (t, 6H, $OCH_2C\mathit{H}_3$)					
			0.99 (t, 6H, $OCH_2C\mathit{H}_3$)					
4c	32.9	3946	7.65–7.11 (m, 20H, Ar H)		3303m (ν_{N-H})	C: 48.52 (48.22)	897 [M]$^+$	−24.4
			5.02 (t, 2H, NH)	$^3J_{CHNH}$ 10.5	1741vs ($\nu_{C=O}$)	H: 4.83 (4.95)	861 [M − Cl]$^+$	(2.1)
			3.21 (s, 6H, OCH_3)	$^2J_{PNH}$ 10.5	875m (ν_{P-N})	N: 3.20 (3.12)	825 [M]$^+$	
			2.85 (m, 2H, CH)	$^3J_{CHCH}$ 5.2	304w (ν_{Pt-Cl})			
			1.69 (m, 2H, $C\mathit{H}(CH_3)_2$)	$^3J_{PNCH}$ 8.8	282w (ν_{Pt-Cl})			
			0.68 (d, 6H, CH_3)					
			0.60 (d, 6H, CH_3)	$^3J_{CHCH3}$ 6.8				
4d	33.9	3950	7.62–6.84 (m, 30H, Ar H)		3255m (ν_{N-H})	C: 52.10 (53.23)	1015 [M + Na]$^+$	−19.5
			4.97 (t, 2H, NH)	$^3J_{CHNH}$ 11.0	1741vs ($\nu_{C=O}$)	H: 4.44 (4.47)	993 [M]$^+$	1.5
			3.22 (s, 8H, CH + OCH_3)	$^2J_{PNH}$ 11.0	818m (ν_{P-N})	N: 2.99 (2.82)	957 [M − Cl]$^+$	
			2.64 (m, 4H, $C\mathit{H}_2Ph$)		311w (ν_{Pt-Cl})		9221 [M − 2Cl]$^+$	
					281w (ν_{Pt-Cl})			
4e	33.8	3937	7.65–7.19 (m, 20H, Ar H)		3265m (ν_{N-H})	C: 45.18 (45.01)	1098 [M]$^+$	+12.8
			4.85 (t, 2H, NH)	$^3J_{NHCH}$ 10.5	1739vs ($\nu_{C=O}$)	H: 4.44 (4.49)		(1.5)
			3.30 (s + m, 8H, OCH_3 + CH)	$^2J_{PNH}$ 10.5	855m (ν_{P-N})	N: 3.18 (2.92)		
			2.16 (m, 4H, SCH_2)	$^3J_{CHCH}$ 6.4	312w (ν_{Pt-Cl})			
			1.91 (s, 6H, SCH_3)		283w (ν_{Pt-Cl})			
			1.83 (m, 4H, $CH\mathit{CH}_2CH_2$)	$^2J_{CHH}$ 13.5				
6a	64.6		7.68–7.47 (m, 10H, Ar H)		3238s (ν_{N-H})	C: 36.31 (36.98)	1005 [2M − Cl]$^+$	−14.6
			4.13 (m, 1H, CH)	$^3J_{PNCH}$ 11.0	1740vs ($\nu_{C=O}$)	H: 3.50 (3.49)	520 [M]$^+$	(0.9)
			3.66 (s, 3H, OCH_3)		849m (ν_{P-N})	N: 2.68 (2.69)	484 [M − Cl]$^+$	
			3.08 (d, broad, 1H, NH)	$^3J_{NHCH}$ 8.5	308m (ν_{Au-Cl})			
			1.45 (d, 1H, CH_3)	$^3J_{CHCH}$ 6.8				

may be important in the catalytic utility of the platinum and rhodium complexes.

N, *N*-Bis(diphenylphosphino)alanine methyl ester and complexes

The syntheses and coordination of *N*,*N*-bis(diphenylphosphino)amino acid esters were reported by Beck's group[3–5] and Payne's group[6,7] at the end of 1970s and the beginning of the 1980s. Beck and co-workers[3–5] employed the amino methyl ester hydrochlorides, including glycine methyl ester, valine methyl ester and phenylalanine methyl ester, alanine methyl ester and methionine methyl ester hydrochloride to react with chlorodiphenylphosphine in the presence of Et_3N in $CHCl_3$ to give *N*,*N*-bis(diphenylphosphino)amino methyl esters in 40–60% yield. The complexes of some of these bidentate ligands with [$Mo(CO_6)$], [$W(CO)_5(THF)$], [$PdCl_2(NCPh)_2$], [$PtCl_2(NCPh)_2$] and [$RhCl(cod)]_2$ were studied by IR, ^{31}P-{^{1}H}, and ^{1}H NMR spectroscopy. They also used *cis*-[$MCl_2(PPh_2Cl)_2$] to react directly with lysine methyl/ethyl ester hydrochloride to give [*N*,*N*-bis(diphenylphosphino)-*N*′,*N*′-bis(diphenylphosphino)-L-lysine methyl ester]tetrachlorodipalladium. In Paynes' studies[6,7] L-alanine ethyl ester hydrochloride was employed to react with chlorodiphenylphosphine at reflux in toluene to give a 30% yield of *N*,*N*-bis(diphenylphosphino)alanine ethyl ester. This ligand was used to form platinum complexes [$Pt(CH_3)(X)$(bppal-*P,P*′)]ClO_4 (X = PPh_3, $AsPh_3$, $SbPh_3$, C_5H_5N or PPhR′R″). Almost twenty years later, Navarro and co-workers[8,9] used *N*,*N*-bis(diphenylphosphino)phenylalanine methyl ester to prepare palladium and platinum complexes containing chiral diphosphazane ligands and study the cleavage of P–N bonds by alcohols. However to date, no details of [MCl_2(bdppal-*P*,*P*′)] (M = Pd or Pt, bdppal = *N*,*N*-bis(diphenylphosphino)alanine methyl ester) have been described, nor the crystal structures of these two complexes reported. We used dichloromethane as solvent for the reaction of alanine methyl ester hydrochloride and chlorodiphenylphosphine in the presence of triethylamine. The yield of bdppal **7** was 63% (eqn. 5).



7

(5)

Compound **7** gave excellent microanalysis and the expected parent ion and fragment ions in the positive FAB mass spectrum. The ^{31}P-{^{1}H} NMR spectrum (δ 55.0) (Table 5) is in good agreement with that reported[3] (δ_P 55.5). The ^{1}H NMR spectrum shows a multiplet at δ 7.35 for the resonance of aromatic hydrogen, a multiplet at δ 4.27 for NCH [$^3J_{CHCH}$ = 7.1, $^3J_{PNCH}$ =12.0 Hz], a singlet at δ 3.52 for OCH_3 and a doublet at δ 1.44. The IR spectrum contains $\nu_{(C=O)}$ at 1733 cm^{-1} rather than two $\nu_{(C=O)}$ at 1736 and 1741 cm^{-1} as reported.[3]

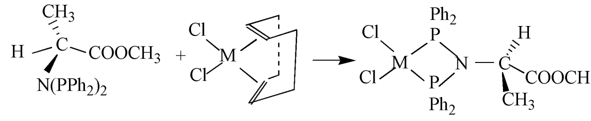
Compound **7** reacts with [MCl_2(cod)] (M = Pd or Pt) in DCM to give the chelate complexes *cis*-[$PdCl_2$(bdppal-*P*,*P*′)] **8** as a yellow-green and *cis*-[$PtCl_2$(bdppal-*P*,*P*′)] **9** as colorless solid, respectively, eqn. (6). Both **8** and **9** gave good microanalyses and the expected parent and fragment ions and appropriate abundance distribution in the positive FAB mass spectra. The phosphorus resonance of **8** at δ 35.0 is shifted to lower frequency by *ca.* 20 ppm from that of the "free" ligand, and the ^{31}P-{^{1}H} NMR spectrum of **9** shows a singlet at δ 20.5 with satellites [$^1J_{Pt-P}$ = 3308 Hz], about 30 ppm lower frequency

Table 3 Spectroscopic data for [RhCl(cod)(dppam-*P*)]

Compound	^{31}P-{^{1}H} NMR δ	^{31}P-{^{1}H} NMR $^1J_{\mathrm{Rh-P}}$/Hz	^{1}H NMR δ	^{1}H NMR J/Hz	IR (cm^{-1})	Microanalysis (%) Found (Calculated)	FAB$^+$ (m/z)	$[\alpha]_D^{25}$ (c) in CHCl$_3$
5a	60.8 (d)	158	7.85–7.33 (m, 10H, Ar H)		3288s ($\nu_{\mathrm{N-H}}$)	C: 55.07 (54.10)	556 [M + Na]$^+$	−8.2
			4.41 (dd, 1H, NH)	$^2J_{\mathrm{PNH}}$ 13.5	1741vs ($\nu_{\mathrm{C=O}}$)	H: 6.03 (5.49)	533 [M]$^+$	(1.0)
			3.53 (m, 1H, CH)	$^3J_{\mathrm{CHNH}}$ 12.0	851m ($\nu_{\mathrm{P-N}}$)	N: 2.15 (2.63)	498 [M − Cl]$^+$	
			3.23 (s, 3H, OCH$_3$)	$^3J_{\mathrm{PNCH}}$ 7.0	2879 ($\nu_{\mathrm{C-H}}$)			
			1.17 (d, 3H, CH$_3$)	$^3J_{\mathrm{CHCH}}$ 7.0	2831 ($\nu_{\mathrm{C-H}}$)			
5b	61.6 (d)	158	7.88–7.34 (m, 10H, Ar H)		3276m ($\nu_{\mathrm{N-H}}$)	C: 53.93 (54.94)	633 [M]$^+$	+16.3
			4.48 (t, 1H, NH)	$^3J_{\mathrm{CHNH}}$ 12.0	1735vs ($\nu_{\mathrm{C=O}}$)	H: 5.90 (6.04)	598 [M − Cl]$^+$	(1.3)
			4.02 (q, 2H, OCH$_2$)	$^2J_{\mathrm{PNH}}$ 12.0	851m ($\nu_{\mathrm{P-N}}$)	N: 1.92 (2.21)		
			3.67 (q + m, 3H, OCH$_2$ + CH)	$^3J_{\mathrm{CHCH}}$ 7.1	2879 ($\nu_{\mathrm{C-H}}$)			
			2.29 (t, 2H, CHCH$_2$CH_2)		2831 ($\nu_{\mathrm{C-H}}$)			
			1.88 (m, 2H, CHCH_2CH$_2$)					
			1.17 (t, 3H, OCH$_2$CH_3)					
			1.00 (t, 3H, OCH$_2$CH_3)					
5c	60.5 (d)	158	7.92–7.39 (m, 10H, Ar H)		3265m ($\nu_{\mathrm{N-H}}$)	C: 56.61 (55.58)	584 [M + Na]$^+$	−21.6
			4.59 (t, 2H, NH)	$^3J_{\mathrm{CHNH}}$ 12.5	1732vs ($\nu_{\mathrm{C=O}}$)	H: 6.42 (6.10)	561 [M]$^+$	(1.0)
			3.21 (s, 2H, OCH$_3$)	$^2J_{\mathrm{PNH}}$ 12.5	868m ($\nu_{\mathrm{P-N}}$)	N: 2.50 (2.49)	526 [M − Cl]$^+$	
			3,37 (ddd, 1H, CH)	$^3J_{\mathrm{CHCH}}$ 5.2	2882 ($\nu_{\mathrm{C-H}}$)			
			0.852 (d, 2H, CH$_3$)	$^3J_{\mathrm{PNCH}}$ 7.7	2831 ($\nu_{\mathrm{C-H}}$)			
			0.847 (d, 2H, CH$_3$)	$^3J_{\mathrm{CHCH3}}$ 6.8				
5d	61.7 (d)	158	7.84–7.01 (m, 15H, Ar H)		3268m ($\nu_{\mathrm{N-H}}$)	C: 59.55 (59.08)	609 [M]$^+$	−14.9
			4.47 (t, 1H, NH)	$^3J_{\mathrm{CHNH}}$ 12.5	1742vs ($\nu_{\mathrm{C=O}}$)	H: 5.94 (5.62)	574 [M − Cl]$^+$	(3.7)
			3.71 (m, 1H, CH)	$^2J_{\mathrm{PNH}}$ 12.5	866m ($\nu_{\mathrm{P-N}}$)	N: 1.99 (2.30)		
			3.15 (s, 3H, OCH$_3$)	$^3J_{\mathrm{PNCH}}$ 6.5	2878 ($\nu_{\mathrm{C-H}}$)			
			2.66 (dd, 4H, CH_2Ph)	$^3J_{\mathrm{CHCH}}$ 6.5	2831 ($\nu_{\mathrm{C-H}}$)			
				$^2J_{\mathrm{CHH}}$ 13.5				
5e	61.3 (d)	158	7.85–7.36 (m, 10H, Ar H)		3277m ($\nu_{\mathrm{N-H}}$)	C: 51.22 (52.58)	594 [M]$^+$	+12.3
			4.49 (t, 2H, NH)	$^3J_{\mathrm{NHCH}}$ 12.5	1740s ($\nu_{\mathrm{C=O}}$)	H: 5.70 (5.77)	559 [M − Cl]$^+$	(1.3)
			3.67 (m, 1H, CH)	$^2J_{\mathrm{PNH}}$ 12.5	854m ($\nu_{\mathrm{P-N}}$)	N: 2.13 (2.36)		
			3.33 (s, 3H, OCH$_3$)	$^3J_{\mathrm{PNCH}}$ 6.8	2878 ($\nu_{\mathrm{C-H}}$)			
			2.43 (m, 2H, SCH$_2$)	$^3J_{\mathrm{CHCH}}$ 7.6	2831 ($\nu_{\mathrm{C-H}}$)			
			1.97 (s, 3H, SCH$_3$)					
			1.85 (m, 4H, CHCH_2CH$_2$)					

Table 4 Selected bond lengths (Å) and angles (°) in compound **6a**

Au(1)–P(1)	2.230(2)	Au(1)–Cl(1)	2.304(2)
P(1)–N(1)	1.660(8)	P(1)–C(5)	1.798(9)
P(1)–C(11)	1.820(10)	N(1)–C(1)	1.450(13)
H(1n)···Cl(1)	2.41		
C(1)–C(2)	1.49(2)	C(1)–C(4)	1.514(13)
C(2)–O(2)	1.179(14)	C(2)–O(3)	1.342(13)
P(1)–Au(1)–Cl(1)	178.90(9)	N(1)–P(1)–C(5)	110.0(4)
N(1)–P(1)–C(11)	101.1(4)	C(5)–P(1)–C(11)	104.6(4)
C(1)–N(1)–P(1)	124.0(6)	N(1)–P(1)–Au(1)	112.2(3)
C(5)–P(1)–Au(1)	112.9(3)	C(11)–P(1)–Au(1)	115.1(3)
N(1)–H(1n)···Cl(1)	155.87(11.77)		



(6)

8 M = Pd, **9** M = Pt

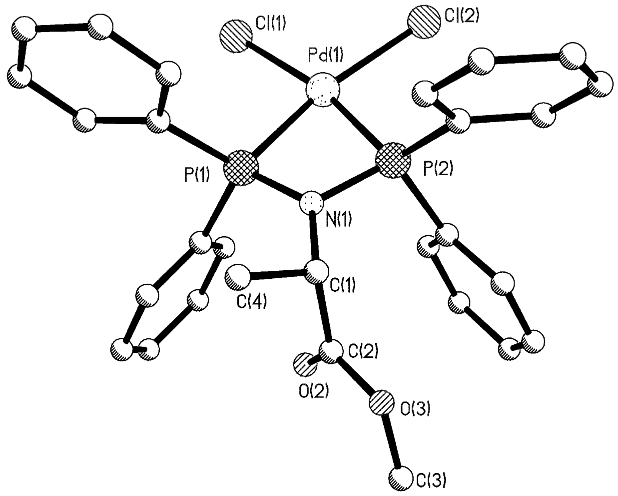


Fig. 2 The crystal structure of complex **8**.

shifted compared to the "free" ligand **7**. In the IR spectra **8** and **9** show strong $\nu_{(\mathrm{C=O})}$ at 1737 and 1730 cm^{-1} respectively. Their $\nu_{(\mathrm{M-Cl})}$ stretches at about 310 and 290 cm^{-1} as well as the large $^1J_{\mathrm{Pt-P}}$ coupling constant of **9** are in accordance with the *cis* geometry which has been confirmed by the crystal structures.

Figs. 2 and 3 reveal two closely similar structures of complexes **8** and **9**. In both cases the ligand is co-ordinated in a bidentate mode with the metal in a roughly square-planar geometry. The mean deviation of the Pd(1)–Cl(1)–Cl(2)–P(1)–P(2) mean plane for **8** is 0.02 Å (maximum deviation for P(2) 0.03 Å below the mean co-ordination plane). In compound **9** the maximum deviation for P(1) and P(2) from the mean co-ordination plane Pt(1)–P(1)–P(2)–Cl(1)–Cl(2) is 0.03 Å. The nitrogen atom lies 0.08 Å for **8** and 0.22 Å for **9** above the M(1)–P(1)–P(2) plane due to a folding along the P(1)···P(2) axis. The fold angle between the MP$_2$ and P$_2$N planes is 4° for **8** and 11° for **9**. As shown by Table 6, the corresponding bond lengths and angles are quite close except for the slight difference in the Cl(1)–M(1)–Cl(2), Cl(1)–M(1)–P(1) and Cl(2)–M(1)–P(2) angles between the two complexes. The P(1)–N(1)–P(2) bond angle [100.08(10)° for **8** and 99.9(2)° for **9**] is considerably less than the expected trigonal angle if the N atom were sp^2 hybridised. The chelate bite angles [72.32°(2) for **8** and 72.77°(6) for **9**] show large distortions from the idealised (90°) for a square-planar geometry. Small bite angles and P(1)–N(1)–P(2) angles were also observed in other four-membered-chelate ring complexes like *cis*-[PdCl$_2${*S*-(Ph$_2$P)$_2$NCH(CH$_3$)(Ph)-*P*,*P′*}],[22] [PtCl(PMe$_2$Ph)(Ph$_2$PNHPPh$_2$-*P*,*P′*)]Cl, and [PtCl(PBu$^n_3$)-(Ph$_2$PNHPPh$_2$-*P*,*P′*)]Cl, and [PtCl(Ph$_2$P(CH$_2$)$_2$PPh$_2$)(Ph$_2$-

Table 5 Spectroscopic data for *N*,*N*-bis(diphenylphosphino)alanine methyl ester and complexes

Compound	^{31}P-{^{1}H} NMR δ	^{31}P-{^{1}H} NMR J/Hz	^{1}H NMR δ	^{1}H NMR J/Hz	IR (cm^{-1})	Microanalysis (%) Found (Calculated)	FAB$^+$ (m/z)	$[\alpha]_D^{25}$ (c) in CHCl$_3$
7	55.0		7.35 (m, 20H, Ar H) 4.27 (m, 1H, CH) 3.52 (s, 3H, OCH$_3$) 1.44 (d, 3H, CCH$_3$)	 $^3J_{CHCH}$ 7.1 $^3J_{PNCH}$ 12.0	1733vs ($\nu_{C=O}$) 882m (ν_{P-N}) 840m (ν_{P-N})	C: 71.16 (71.33) H: 5.88 (5.77) N: 2.73 (2.97)	472 [M]$^+$	−58.6 (6.0)
8	35.0		8.14–7.27 (m, 20H, Ar H) 4.08 (m, 1H, CH) 3.03 (s, 3H, OCH$_3$) 0.96 (d, 3H, CCH$_3$)	 $^3J_{CHCH}$ 7.4 $^3J_{PNCH}$ 16.7	1737vs ($\nu_{C=O}$) 870m (ν_{P-N}) 852m (ν_{P-N}) 302m (ν_{Pd-Cl}) 288 (ν_{Pd-Cl})	C: 52.05 (51.92) H: 4.64 (4.20) N: 1.82 (2.16)	648 [M]$^+$ 614 [M − Cl]$^+$ 577 [M − 2Cl]$^+$	−14.5 (1.9)
9	20.5	$^1J_{Pt-P}$ 3308	8.10–7.529 (m, 20H, Ar H) 3.97 (m, 1H, CH) 2.98 (s, 3H, OCH$_3$) 0.94 (d, 3H, CCH$_3$)	 $^3J_{CHCH}$ 7.4 $^3J_{PNCH}$ 17.0	1730vs ($\nu_{C=O}$) 870m (ν_{P-N}) 849w (ν_{P-N}) 314m (ν_{Pt-Cl}) 293m (ν_{Pt-Cl})	C: 46.75 (45.60) H: 3.93 (3.69) N: 2.09 (1.90)	737 [M]$^+$ 702 [M − Cl]$^+$ 1438 [2M − Cl]$^+$	−10.9 (1.9)

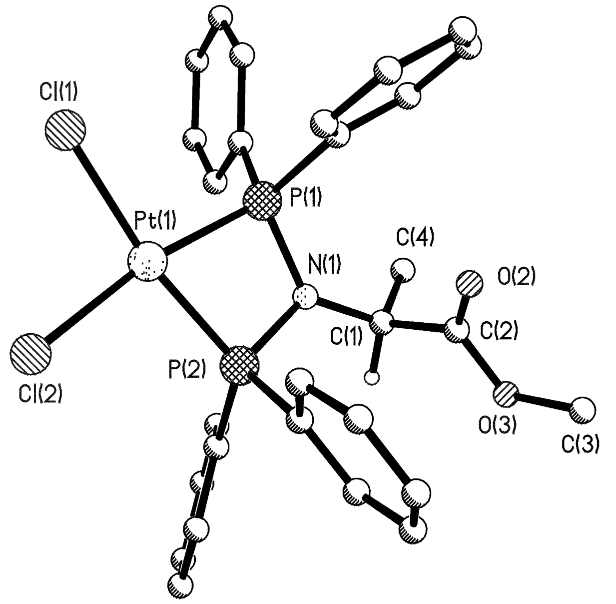


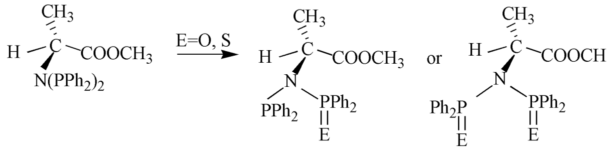
Fig. 3 The crystal structure of complex **9**.

Table 6 Selected bond lengths (Å) and angles (°) in complexes **8** and **9**

	8	**9**
M(1)–P(1)	2.2300(6)	2.218(2)
M(1)–P(2)	2.2128(6)	2.206(2)
M(1)–Cl(1)	2.3520(6)	2.351(2)
M(1)–Cl(2)	2.3560(7)	2.351(2)
P(1)–N(1)	1.710(2)	1.713(5)
N(1)–P(2)	1.710(2)	1.715(5)
N(1)–C(1)	1.472(3)	1.459(3)
C(1)–C(2)	1.517(4)	1.532(10)
C(1)–C(4)	1.526(4)	1.518(9)
C(2)–O(2)	1.182(3)	1.186(8)
C(2)–O(3)	1.328(3)	1.335(8)
P(2)–M(1)–P(1)	72.32(2)	72.77(6)
P(2)–M(1)–Cl(1)	168.93(3)	170.59(6)
P(1)–M(1)–Cl(1)	96.97(3)	97.90(6)
P(2)–M(1)–Cl(2)	94.93(3)	96.88(7)
P(1)–M(1)–Cl(2)	167.18(3)	169.48(7)
Cl(1)–M(1)–Cl(2)	96.02(3)	92.48(7)
N(1)–P(1)–M(1)	92.93(7)	92.9(2)
N(1)–P(2)–M(1)	93.53(7)	93.3(2)
P(2)–N(1)–P(1)	100.08(10)	99.9(2)
C(1)–N(1)–P(2)	135.0(2)	135.2(5)
C(1)–N(1)–P(2)	122.9(2)	123.3(4)

PNHPPh$_2$-*P*,*P*′)]Cl$_2$.[23] The mean M–P and M–Cl bond lengths in **8** and **9** are comparable to the corresponding parameters in related structures.[22–24] In spite of the strained geometry of the four-membered chelate ring, the planarity around the nitrogen atom is retained (maximum deviation for N(1) is 0.09 Å above the P(1)–P(2)–C(1) plane for both **8** and **9**). The geometry around the two phosphorus atoms is tetrahedral. It is remarkable that the P(1)–N(1)–C(1) bond angles [135.0(2)° for **8** and 135.2(5)° for **9**] are more open than P(2)–N(1)–C(1) [122.9(2)° for **8** and 123.3(4)° for **9**]. This may result from the absolute structure with the CH$_3$ group lying at the side of P(1), while H lies at the side of P(2). However, in *cis*-[PdCl$_2${*S*-(Ph$_2$P)$_2$-NCH(CH$_3$)(Ph)-*P*,*P*′}],[22] where one of the phenyl groups at P(1) and the one at C(1) are almost parallel, similar P(1)–N(1)–C(1) [131.6(6)°] and P(2)–N(1)–C(1) [130.2(6)°] bond angles are observed.

Oxidation of compound **7** with H$_2$O$_2$ (30%) or elemental sulfur S$_8$ in THF leads to mono- and di-oxidised species *N*-diphenylphosphino-*N*-diphenylphosphinoylalanine methyl ester (bdppalO) **10**, *N*-diphenylphosphino-*N*-diphenylthiophosphinoylalanine methyl ester (bdppalS) **11**, *N*,*N*-bis(diphenylphosphinoyl)alanine methyl ester (bdppalO$_2$) **12** and *N*-bis(diphenylthiophosphinoyl)alanine methyl ester (bdppalS$_2$) **13** (eqn. 7). Compound **10** is quite unstable in solution. In fact it can only be observed as an intermediate by the ^{31}P-{^{1}H} NMR spectrum (doublets at δ 45.8 and 33.2, $^3J_{PP}$ = 80 Hz, see Table 7)



(7)

10 E = O
11 E = S

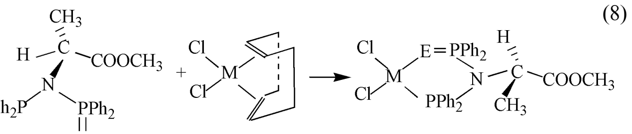
12 E = O
13 E = S

in the reaction mixture in the first 30 min, and always accompanied by either starting reactant **7** (δ_P 55.0) at lower molar ratio of H$_2$O$_2$ (**7**:H$_2$O$_2$ > 1 : 1), or the dioxidised product **12** (δ_P 32.8) in the case of excess of H$_2$O$_2$ (**7** : H$_2$O$_2$ < 1 : 1), or by both. Attempts to separate these compounds were unsuccessful. Longer reaction time (**7** : H$_2$O$_2$ = 1 : 1.5) only leads to **12**. **12** has no co-ordination activity to [MCl$_2$(cod)] (M = Pd or Pt). Therefore, we used a slight excess of H$_2$O$_2$ (**7**:H$_2$O$_2$ = 1 : 1.5) to oxidise **7** and monitor the reaction by ^{31}P-{^{1}H} NMR; once the phosphorus resonance of **7** at δ 55.0 vanished, usually in 20 min, about 1/3 to 1/2 equivalent of [PdCl$_2$(cod)] was added according to the integration result in the ^{31}P-{^{1}H} NMR spectrum of the reaction mixture. We successfully co-ordinated **10** to [PdCl$_2$(cod)] to give an orange complex *cis*-[PdCl$_2$-(bdppalO-*P*,*O*)] **14** (eqn. 8). Similar attempts to capture **10** by [PtCl$_2$(cod)] was unsuccessful.

By stirring compound **7** with two equivalents of elemental

Table 7 Spectroscopic data for *N*,*N*-bis(diphenylphosphino)alanine methyl ester derivatives

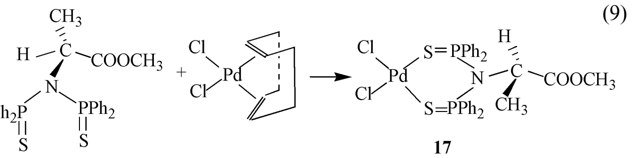
Com-pound	^{31}P-{^{1}H} NMR		^{1}H NMR					
	δ	$^{1}J_{P-P}$/Hz	δ	*J*/Hz	IR (cm^{-1})	Microanalysis (%) Found (Calculated)	FAB^{+} (*m*/*z*)	$[\alpha]_D^{25}$ (*c*) in CHCl$_3$
10	45.8 (d, P)	80						
	33.2 (d, P=O)							
11	68.8 (d, P=S)	79	8.20–7.26 (m, 20H, Ar H)		1737vs ($\nu_{C=O}$)	C: 66.43 (66.79)	504 [M]$^{+}$	−90.7
			4.34 (m, 1H, CH)	$^{3}J_{CHCH}$ 7.0	872m (ν_{P-N})	H: 5.65 (5.40)		(2.2)
	53.9 (d, P)		3.60 (s, 3H, OCH$_3$)	$^{3}J_{SPNCH}$ 27.0	845m (ν_{P-N})	N: 2.78 (2.78)		
			1.30 (d, 3H, CH$_3$)	$^{3}J_{PNCH}$ 2.8	641m ($\nu_{P=S}$)			
12	32.8 (P=O)		7.97–7.25 (m, 20H, Ar H)		1751s ($\nu_{C=O}$)	C: 66.80 (66.80)	504 [M]$^{+}$	−58.1
			4.05 (m, 1H, CH)	$^{3}J_{CHCH}$ 6.9	1209vs ($\nu_{P=O}$)	H: 5.64 (5.40)		(4.2)
			3.72 (s, 3H, OCH$_3$)	$^{3}J_{PNCH}$ 17.6	946m (ν_{P-N})	N: 2.72 (2.78)		
			1.35 (d, 3H, CCH$_3$)		913m (ν_{P-N})			
13	70.0 (P=S)		8.22–7.24 (m, 20H, Ar H)		1737vs ($\nu_{C=O}$)	C: 62.13 (62.79)	536 [M]$^{+}$	−63.6
			4.57 (m, 1H, CH)	$^{3}J_{CHCH}$ 7.4	884s (ν_{P-N})	H: 4.84 (5.08)		(1.0)
			3.53 (s, 3H, OCH$_3$)	$^{3}J_{PNCH}$ 20.0	834m (ν_{P-N})	N: 2.76 (2.62)		
			1.54 (d, 3H, CH$_3$)		645s ($\nu_{P=S}$)			



(8)

14 M = Pd, E = O
15 M = Pd, E = S
16 M = Pt, E = S

sulfur in THF at room temperature for 2 days we obtained the monosulfide **11** as a white solid in 40% yield. However to obtain the disulfide **13** the reaction mixture requires refluxing for one week. Reaction of **11** with [MCl$_2$(cod)] (M = Pd or Pt) in CH$_2$Cl$_2$ gives *cis*-[PdCl$_2$(bdppalS-*P*,*S*)] **15** as a light brown solid and *cis*-[PtCl$_2$(bdppalS-*P*,*S*)] **16** as a yellow-green solid, respectively. Compound **13** is much less reactive than **11**; it reacts with [PdCl$_2$(cod)] to give *cis*-[PdCl$_2$(bdppalS$_2$-*S*,*S*′)] **17** (eqn. 9) but stirring [PtCl$_2$(cod)] with **13** in CH$_2$Cl$_2$ or THF for several days led to nothing else except the starting material.



(9)

17

Compounds **11**–**13** (Table 7) gave satisfactory microanalysis and anticipated parent and fragment ions in the positive FAB mass spectra. In the ^{31}P-{^{1}H} NMR spectrum of **11** two doublets are observed. That at δ 68.8 is assigned to the P=S resonance, while the other at δ 53.9 corresponds to the phosphorus(III) resonance; the coupling constant [$^{2}J_{PP}$ = 79 Hz] is similar to that of **10** [80 Hz]. Compared with **7**, the P=S resonance was shifted to higher frequency by *ca.* 14 ppm, while the phosphorus(III) resonance is unaffected. **12** and **13** show singlets at δ 32.8 and 70.0 in their ^{31}P-{^{1}H} NMR spectra, shifted *ca.* 22 ppm to lower and 15 ppm to higher frequency respectively compared to that of **7**. ^{1}H NMR spectra of **12** and **13** are quite similar; both show the expected multiplets at δ 7.97–7.25 and 8.22–7.24 for phenyl protons, multiplets at δ 4.05 [$^{3}J_{CHCH}$ = 6.9, $^{2}J_{OPNCH}$ = 17.6 Hz] and 4.57 [$^{3}J_{CHCH}$ = 7.4, $^{3}J_{SPNCH}$ = 20.0 Hz] for CH, singlets at δ 3.72, 3.53 for OCH$_3$ and doublets at δ 1.35 and 1.54 for CCH$_3$, respectively. Obviously, $^{3}J_{PNCH}$ has increased after the oxidation. In their IR spectra compounds **11**–**13** show stretches at about 1740 cm^{-1} for $\nu_{(C=O)}$, at 880–840 cm^{-1} for $\nu_{(P-N)}$, similar to that of **7**, and $\nu_{(P=O)}$ at 1209 cm^{-1} for **12** and $\nu_{(P=S)}$ at 645 cm^{-1} for **13**.

The crystal structure of compound **11** (Fig. 4, Table 8) reveals that N(1) lies above the P(1)–P(2)–N(1)–C(1) mean plane by 0.11 Å. The geometry at P(1) is tetrahedral while P(2) adopts a pyramidal geometry. The P(1)–S(1) bond length [1.9441(11) Å] is comparable to that of related compounds,[18,25,26] while the P(1)–N(1) bond length [1.692(2) Å] is slightly shorter than P(2)–N(1) [1.737(2) Å] as a result of the conjugation effect or p–π electron delocalisation of S=P–N.

Table 8 Selected bond lengths (Å) and angles (°) in compound **11**

S(1)–P(1)	1.9441(11)	P(1)–N(1)	1.692(2)
N(1)–C(1)	1.488(3)	N(1)–P(2)	1.737(2)
C(1)–C(2)	1.511(4)	C(1)–C(4)	1.537(3)
C(2)–O(2)	1.197(3)	C(2)–O(3)	1.329(3)
N(1)–P(1)–C(5)	105.38(11)	N(1)–P(1)–C(11)	107.46(10)
C(5)–P(1)–C(11)	106.56(14)	N(1)–P(1)–S(1)	113.67(8)
C(5)–P(1)–S(1)	112.30(9)	C(11)–P(1)–S(1)	111.03(10)
C(1)–N(1)–P(1)	120.8(2)	C(1)–N(1)–P(2)	120.9(2)
P(1)–N(1)–P(2)	115.84(11)	N(1)–P(2)–C(23)	104.28(12)
N(1)–P(2)–C(17)	103.21(11)	C(23)–P(2)–C(17)	101.03(14)

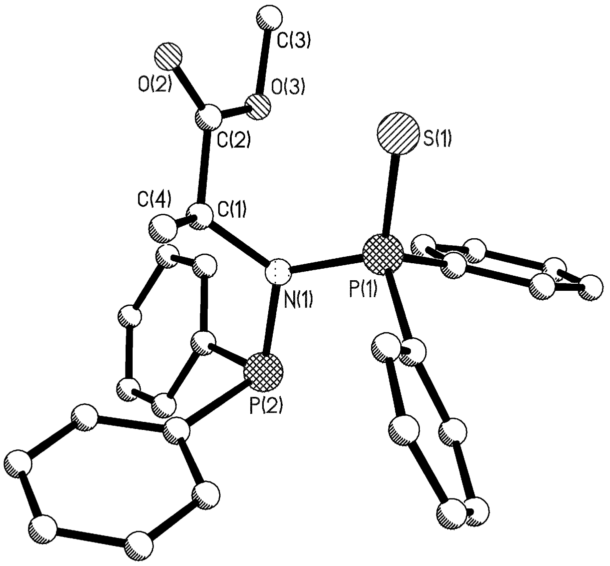


Fig. 4 The crystal structure of compound **11**.

The crystal structure of compound **12** (Fig. 5, Table 9) shows no deviation of N(1) from the P(1)–P(2)–N(1)–C(1) plane in contrast to the large deviation of N(1) for **11**. The geometry around the phosphorus atoms is tetrahedral with the two P=O bonds orienting in the *anti* positions. This structure displays a clear contrast with that of [Ph$_2$P(O)]$_2$NH which exists in the solid state as the tautomer with *syn*-P=O groups and symmetrical intramolecular hydrogen bonding in a H–O–P–N–P–O six-membered ring.[27] Owing to the delocalisation of the p–π electrons along the O(1)–P(1)–N(1)–P(2)–O(2) backbone and the absence of hydrogen bonding, the P=O bond lengths [1.4723(13) and 1.4568(14) Å] are shorter than those observed in $[Ph_2P(O)]_2NH$ [1.519(2) Å][27] and in $Ph_2P(S)NHP(O)Ph_2$ [1.54(3) Å].[28]

The microanalysis and positive FAB mass spectra of complexes **14**–**17** (Table 10) are satisfactory. In the ^{31}P-{^{1}H} NMR spectrum **14** shows two doublets at δ 78.6 and 61.7 [$^2J_{PP}$ = 34 Hz] corresponding to the phosphorus(III) and P=O resonances, respectively. The phosphorus resonances are shifted to higher frequency by *ca.* 30 ppm relative to that of the ligand **10** in solution, and the coupling constant between the two phosphorus atoms decreases from 80 to 34 Hz. The ^{31}P-{^{1}H} NMR spectrum of **15** contains two doublets at δ 99.8 and 78.7 for P=S and P^{III} [$^2J_{PP}$ = 50 Hz]. The spectrum of **16** is slightly complicated with two sets of satellites, δ 76.1 (d, P=S), 72.6 (d, P–N) [$^2J_{PP}$ = 47, $^2J_{PtP}$ = 95, $^1J_{PtP}$ = 3866 Hz]. The ^{1}H NMR spectra of **15**, **16** are quite similar to that of the "free" ligand **11**, but $^3J_{PNCH}$ has increased from 3 to *ca.*10 Hz, and $^3J_{SPNCH}$ decreased from 27 to *ca.* 25 Hz. **17** displays a singlet at δ 67.8 in the ^{31}P-{^{1}H} NMR spectrum; its ^{1}H NMR spectrum is similar to that of the "free" ligand. All these compounds show $\nu_{(C=O)}$ at about 1735 cm^{-1} and $\nu_{(M-Cl)}$ at *ca.* 325, 290 cm^{-1} are consistent with the *cis* geometry. However $\nu_{(P=O)}$ at 1124 cm^{-1} for **14** is at a lower wavenumber relative to $\nu_{(P=O)}$ of **12**, and $\nu_{(P=S)}$ of **15**–**17** are shifted to lower wavenumber by *ca.* 147, 150 and 36 cm^{-1}, respectively. It is presumed that co-ordination of the oxygen/sulfur atom with the metal weakens the P=O/P=S bond. The crystal structure of **14** (Fig. 6, Table 11) exhibits a square-planar geometry at the palladium with the oxygen deviating 0.04 Å below the Cl(1)–Cl(2)–Pd(1)–P(2)–O(1) mean plane. The five-membered-chelate Pd(1)–P(2)–N(1)–P(1)–O(1) ring adopts an envelope shape, with P(1) 0.043 Å above the ring plane. P(1)–P(2)–N(1)–C(1) are perfectly planar with N(1) displaying bond angles which closely approximate the expected 120°. The P(1)–O(1) bond length [1.524(7) Å] is longer than that in **12** because the co-ordination of palladium and oxygen weakens the P=O bond. The Pd–Cl bond lengths [2.346(3) and 2.273(3) Å] are slightly shorter than those in **8** [2.3520(6) and 2.3560(7) Å]. The bond angles in the chelate ring are comparable to those of related five-membered chelate complexes.[29,30]

The hybrid ligand complexes **14**–**16** may be of catalytic importance, because the soft phosphorus atom is strongly bound to the metal and is inert to substitution, while the oxygen/sulfur is substitutionally labile. Further studies of these compounds are in progress.

Table 9 Selected bond lengths (Å) and angles (°) in compound **12**

N(1)–P(1)	1.7112(14)	N(1)–P(2)	1.6893(14)
N(1)–C(1)	1.489(2)	P(1)–O(1)	1.4723(13)
P(2)–O(2)	1.4568(14)		
C(1)–C(2)	1.531(2)	C(1)–C(4)	1.512(3)
C(2)–O(2)	1.193(2)	C(2)–O(3)	1.322(2)
C(1)–N(1)–P(1)	117.21(11)	C(1)–N(1)–P(2)	117.66(11)
P(1)–N(1)–P(2)	125.13(9)	O(1)–P(1)–N(1)	110.26(8)
O(1)–P(1)–C(11)	112.01(8)	O(1)–P(1)–C(5)	111.40(9)
C(5)–P(1)–C(11)	108.00(10)	N(1)–P(1)–C(5)	105.74(7)
N(1)–P(1)–C(11)	109.20(9)	O(2)–P(2)–N(1)	111.52(7)
O(2)–P(2)–C(17)	112.59(9)	O(2)–P(2)–C(23)	111.35(8)
N(1)–P(2)–C(17)	106.37(8)	N(1)–P(2)–C(23)	107.62(8)
C(17)–P(2)–C(23)	107.09(8)		

Table 11 Selected bond lengths (Å) and angles (°) in compound **14**

Pd(1)–P(2)	2.214(3)	Pd(1)–O(1)	2.039(7)
Pd(1)–Cl(1)	2.273(3)	Pd(1)–Cl(2)	2.346(3)
O(1)–P(1)	1.524(7)	P(1)–N(1)	1.689(9)
N(1)–P(2)	1.716(9)	N(1)–C(1)	1.496(13)
P(1)–C(5)	1.788(12)	P(1)–C(11)	1.789(11)
P(2)–C(17)	1.819(10)	P(2)–C(23)	1.812(11)
C(1)–C(2)	1.48(2)	C(1)–C(4)	1.50(3)
C(2)–O(2)	1.212(14)	C(2)–O(3)	1.339(13)
P(2)–Pd(1)–O(1)	87.8(2)	P(2)–Pd(1)–Cl(1)	89.25(11)
O(1)–Pd(1)–Cl(1)	176.1(2)	P(2)–Pd(1)–Cl(2)	176.91(11)
O(1)–Pd(1)–Cl(2)	89.2(2)	Cl(1)–Pd(1)–Cl(2)	93.81(11)
P(1)–O(1)–Pd(1)	117.2(4)	O(1)–P(1)–N(1)	107.0(4)
P(1)–N(1)–P(2)	115.5(5)	C(1)–N(1)–P(1)	124.2(8)
C(1)–N(1)–P(2)	120.3(8)	N(1)–P(2)–Pd(1)	103.9(3)

Table 10 Spectroscopic data for complexes from oxidised *N*,*N*-bis(diphenylphosphine)alanine methyl ester

Compound	^{31}P-{^{1}H} NMR		^{1}H NMR					
	δ	*J*/Hz	δ	*J*/Hz	IR (cm^{-1})	Microanalysis (%) Found (Calculated)	FAB$^+$ (*m*/*z*)	$[\alpha]_D^{25}$ (*c*) in $CHCl_3$
14	78.6 (d, N–**P**)	$^2J_{P-P}$ 34	8.16–7.46 (m, 20H, Ar H)		1741vs ($\nu_{C=O}$)	C: 49.90 (50.66)	630 $[M - Cl]^+$	+204
	61.7 (d, P=**O**)		4.20 (m, 1H, CH_3)	$^3J_{CHCH}$ 7.4	1124vs ($\nu_{P=O}$)	H: 3.96 (4.10)	593 $[M - 2Cl]^+$	(2.0)
			3.17 (s, 3H, CH_3)	$^3J_{PNCH}$ 12.0	886m (ν_{P-N})	N: 1.91 (2.11)		
			0.95 (d, 3H, CCH_3)	$^3J_{OPNCH}$ 21.0	843m (ν_{P-N})			
					343m (ν_{Pd-Cl})			
					289m (ν_{Pd-Cl})			
15	99.8 (d, P=S)	$^2J_{P-P}$ 50	8.11–7.49 (m, 20H, Ar H)		1739vs ($\nu_{C=O}$)	C: 49.55 (49.47)	645 $[M - Cl]^+$	+70.5
	78.7 (d, P)		4.28 (m, 1H, CH)	$^3J_{CHCH}$ 7.4	881m (ν_{P-N})	H: 4.28 (4.00)	609 $[M - 2Cl]^+$	(2.0)
			3.24 (s, 3H, OCH_3)	$^3J_{PNCH}$ 10.0	840m (ν_{P-N})	N: 2.11 (2.06)		
			0.97 (d, 3H, CCH_3)	$^3J_{SPNCH}$ 24.0	491m ($\nu_{P=S}$)			
					314m (ν_{Pt-Cl})			
					289m (ν_{Pt-Cl})			
16	76.1 (d, P=**S**)	$^2J_{P-P}$ 47	8.11–7.45 (m, 20H, Ar H)		1738vs ($\nu_{C=O}$)	C: 44.32 (43.70)	769 $[M]^+$	+42.3
	72.6 (d, N**P**)	$^1J_{Pt-P}$ 3866	4.35 (m, 1H, CH)	$^3J_{CHCH}$ 7.4	881m (ν_{P-N})	H: 3.98 (3.54)	734 $[M - Cl]^+$	(1.9)
		$^2J_{Pt-S+P}$ 95	3.27 (s, 3H, OCH_3)	$^3J_{SPNCH}$ 24.5	839m (ν_{P-N})	N: 1.85 (1.82)	698 $[M - 2Cl]^+$	
			0.97 (d, 3H, CH_3)	$^3J_{PNCH}$ 10.7	494m ($\nu_{P=S}$)			
					325m (ν_{Pt-Cl})			
					297m (ν_{Pt-Cl})			
17	67.8		8.47–7.51 (m, 20H, Ar H)		1741s ($\nu_{C=O}$)	C: 46.36 (47.24)	676 $[M - Cl]^+$	−63.6
			4.31 (m, 1H, CH)	$^3J_{CHCH}$ 7.1	881m (ν_{P-N})	H: 3.90 (3.82)	642 $[M - 2Cl]^+$	(1.9)
			3.33 (s, 3H, OCH_3)	$^3J_{PNCH}$ 20.4	839m (ν_{P-N})	N: 1.84 (1.98)		
			1.14 (d, 3H, CCH_3)		599m ($\nu_{P=S}$)			

Table 12 Details of the X-ray data collections and refinements for compounds **6a**, **8**, **9**, **11**, **12** and **14**

	6a	**8**	**9**	**11**	**12**	**14**·0.5CHCl$_3$
Empirical formula	$C_{16}H_{18}AuClNO_2P$	$C_{28}H_{27}Cl_2NO_2P_2Pd$	$C_{28}H_{27}Cl_2NO_2P_2Pt$	$C_{28}H_{27}NO_2P_2S$	$C_{28}H_{27}NO_4P_2$	$C_{28.50}H_{27.50}Cl_{3.50}NO_3P_2Pd$
Crystal colour, habit	Clear, prism	Pale green, block	Clear, block	Clear, prism	Clear, block	Red, prism
Crystal system	Tetragonal	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P4_32_12$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$
a/Å	11.43660(10)	9.6722(2)	9.6790(2)	8.8209(6)	8.48440(10)	12.3753(2)
b/Å	11.43660(10)	15.4694(3)	15.4917(3)	11.8478(7)	14.1005(2)	16.1471(4)
c/Å	27.55910(10)	18.4553(10)	18.500	25.471(2)	21.19600(10)	17.45540(10)
β/°						108.8930(10)
U/Å^3	3604(1)	2761(1)	2.774(1)	2662(1)	2534(1)	3300(1)
Z	8	4	4	4	4	4
M	519.70	648.75	737.44	503.51	503.45	724.43
μ/mm^{-1}	8.404	1.008	5.393	0.267	1.319	0.971
Measured reflections	15937	17341	12326	11599	16024	14166
Independent reflections (R_{int})	2661(0.1386)	3968(0.0231)	3989(0.0846)	3830(0.0348)	6227(0.0952)	4743 (0.0450)
Final $R1$, $wR2[I > \sigma(I)]$	0.0346, 0.0655	0.0158, 0.0426	0.0248, 0.0511	0.0319, 0.0627	0.0351, 0.0743	0.0813, 0.2083

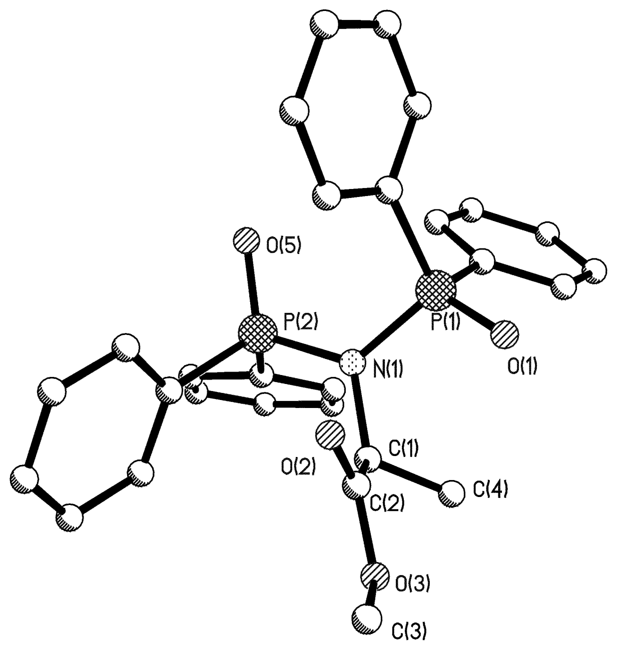


Fig. 5 The crystal structure of compound **12**.

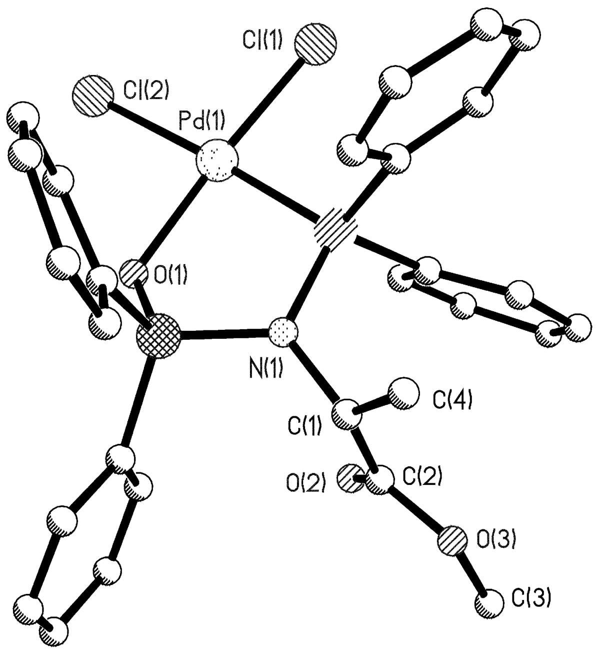


Fig. 6 The crystal structure of compound **14**.

Acknowledgements

We wish to thank JREI for equipment grants and Johnson Matthey plc for loan of precious metals. Qingzhi Zhang is indebted to St Andrews University and the Chinese Scholarship Council for financial support.

References

1 F. Agbossoll, J.-F. Carpentier, F. Hapiot, I. Suisse and A. Mortreux, *Coord. Chem. Rev.*, 1998, **221**, 1615.
2 L. R. Falvello, S. Fernandez, R. Navarro and A. Urriolabeitia, *New J. Chem.*, 1997, **21**, 909.
3 P. W. Lednor, W. Beck, H. G. Fick and H. Zippel, *Chem. Ber.*, 1978, **111**, 615.
4 P. W. Lednor, W. Beck and H. G. Fick, *J. Organomet. Chem.*, 1978, **113**, 19.
5 H. Trampisch and W. Beck, *Z. Naturforsch., Teil B*, 1983, **38**, 365.
6 N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 203.

7 N. C. Payne and D. W. Stephan, *J. Organomet. Chem.*, 1981, **221**, 223.

8 A. Badia, L. R. Falvello, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1998, **554**, 105.

9 A. Badia, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1998, **554**, 105.

10 O. I. Kolodiazhnyi, E. V. Grishkun, S. V. Galushko and O. R. Golovatyi, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1995, **103**, 183.

11 A. M. Z. Slawin, J. D. Woollins and Q. Zhang, *Inorg. Chem. Commun.*, 1999, **2**, 386.

12 A. Bader and E. Linder, *Coord. Chem. Rev.*, 1991, **108**, 27.

13 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1991, **28**, 346.

14 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1982, **19**, 218.

15 R. Uson, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85.

16 G. M. Sheldrick, SHELXTL, Bruker AXS, Madison, WI, 1999.

17 T. Q. Ly, A. M. Z. Slawin and J. D. Woollins, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2501.

18 T. Q. Ly, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 1161.

19 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Chem. Commun.*, 1996, 2095.

20 S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, *Phosphorus*, *Sulfur*, *Silicon Relat. Elem.*, 1997, **124** & **125**, 473.

21 E. Drent, P. Arnoldy and P. H. M. Budzelaar, *J. Organomet. Chem.*, 1993, **455**, 247.

22 R. P. K. Babu, S. S. Krishnamurthy and M. Nethaji, *Tetrahedron*: *Asymmetry*, 1995, **6**, 427.

23 P. Bhattacharyya, R. N. Sheppard, A. M. Z. Slawin, M. B. Smith, D. J. Williams and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2393.

24 P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, D. J. Williams and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3647.

25 D. Cupertino, R. Keyte, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Inorg. Chem.*, 1996, **35**, 2695.

26 D. Cupertino, R. Keyte, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1999, **18**, 311.

27 H. Nöth, *Z. Naturforsch.*, *Teil B*, 1982, **37**, 1491.

28 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3659.

29 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 4567.

30 M. B. Smith, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1996, **15**, 1579.