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Synthesis and coordination of 2-diphenylphosphinothiophenocarboxamide and bis(2,5-diphenylphosphinepicolinamide)

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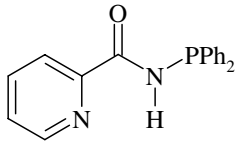
Abstract

2-Diphenylphosphinothiophenocarboxamide (dpptc) and bis(2,5-diphenylphosphinepicolinamide) (bdpppa) have been prepared and complexed with a variety of metals. Bdpptc behaves as a monodentate P donor ligand and can become bidentate by making use of the C=O site. Bdpppa behaves as a P donor bridging ligand. In many cases, the X-ray structures reveal that the ligand backbone geometry is strongly influenced by intramolecular H-bonding.

Keywords: Phosphine; Synthesis; Coordination; X-ray structure

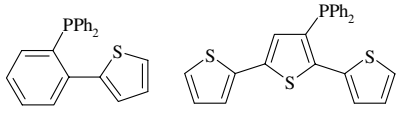
1. Introduction

Hemilabile phosphorus–nitrogen ligands are of great interest and we have recently described the synthesis and coordination of 2-diphenylphosphinopicolinamide (dpppa) and other P–N-based ligands [1,2].



dpppa

There are few known examples of phosphino-thiophenes, and even fewer that act as bidentate phosphino-thiophene ligands. Clot et al. described the major examples in 2000 [3]; 2-(2′-{diphenylphosphino}phenyl)thiophene (dpppth) (**A**) and 3′-diphenylphosphino-2,2′:5′,2″-terthiophene (dppterth) (**B**).



A **B**

These ligands were both shown to bind with a bidentate motif on reaction with $[RuCl_2(PPh_3)_3]$.

Early bridging diphosphines include 2,6-bis(diphenylphosphino)pyridine ($(Ph_2P)_2py$) (**C**), 2,6-(diphenylphosphinomethyl)pyridine (**D**) and *N*,*N*′-bis(diphenylphosphino)-2,6-diaminopyridine (**E**) [4]. These ligands are commonly found as bridging ligands and bidentate ligands with a variety of transition metals.

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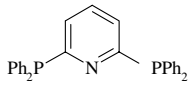
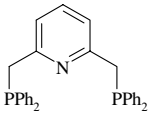


C



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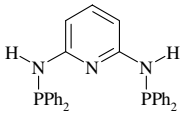
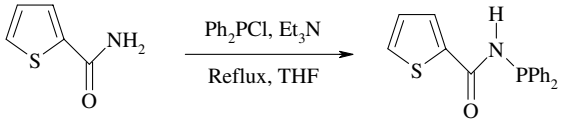


E

Here, we describe two new hemilabile ligands: 2-diphenylphosphinothiophenocarboxamide (dpptc) and bis(2,5-diphenylphosphinepicolinamide) (bdpppa). The coordination properties are compared with dpppa.

2. Results and discussion

The synthesis of dpptc (**1**) is analogous to that of dpppa (Eq. (1)).



(1)

1

The ligand is readily soluble in chlorinated solvents, acetone, tetrahydrofuran, somewhat less so in toluene, methanol and diethylether. A singlet is observed in the ^{31}P spectrum of dpptc at δ(P) 25.9 ppm; comparable with the value for dpppa. The ^{1}H NMR spectrum does not show the presence of an amide proton, as this resonance is obscured by the main body of the aromatic protons. The IR spectra shows the expected peaks, a weak ν(N–H) band is present at 3265 cm^{-1} together with bands attributable to ν(thCS) and ν(P–N) at 1096 and 996 cm^{-1} respectively, with ν(C–N) coming at 1522 cm^{-1}. The expected ν(C=O) signature is visible at 1624 cm^{-1}.

Only the sulfide of dpptc was synthesised (by reaction of dpptc with elemental sulfur in toluene, dpptc-S (**3**), δ(P) 57.2 ppm) as a representative example of the P(V) form. However, a crystal of the oxide derivative was obtained via air oxidation of the free ligand in a $CDCl_3$ solution (Fig. 1). In the solid state, the molecules adopt a chain line structure as a consequence of hydrogen bonding.

Dpptc reacts with [$PtCl_2$(cod)] in dichloromethane to give *cis*-[$PtCl_2$(dpptc-*P*)$_2$] (**4**), no *trans*-bis(dpptc) or mono-(dpptc) binding was observed. The ^{31}P NMR of **4** is a singlet at δ(P) 27.9 ppm with the expected platinum satellites, $^{1}J_{Pt-P}$ = 3870 Hz, consistent with phosphorus *trans* to chloride. The ^{1}H NMR spectrum

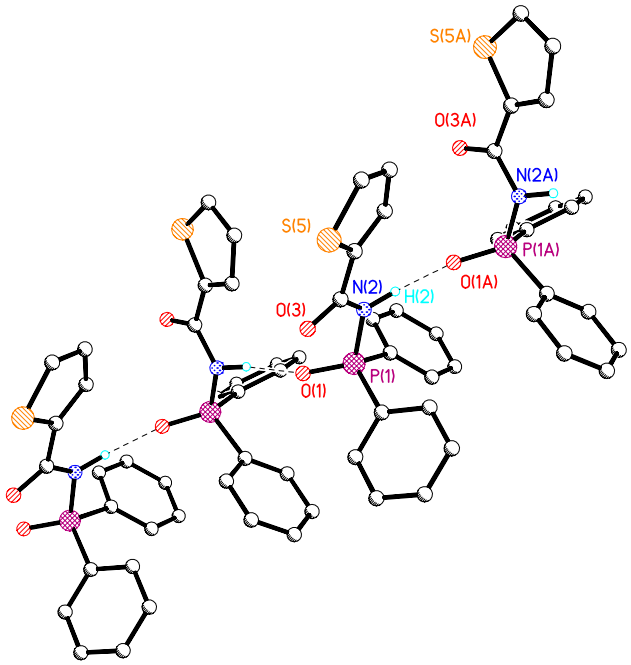


Fig. 1. Crystal structure of dpptc-*O*, **2**, selected bond lengths (Å) and angles (°): P(1)–O(1) 1.456(3), P(1)–N(2) 1.692(3), O(3)–C(3) 1.229(4), N(2)–C(3) 1.373(5), C(3)–C(4) 1.463(5), S(5)–C(4) 1.725(4), C(4)–C(8) 1.365(5), N(2)–O(1) 2.80, N(2)–P(1)–O(1) 115.10(16), C(17)–P(1)–O(1) 112.61(16), N(2)–H(2)···O(1) 171.

displays the anticipated changes from the free ligand. The amine proton is shifted to δ(H) 9.7 ppm, also the coupling constant has increased to $^{2}J_{P-H}$ = 11 Hz. The ν(N–H) vibration in the IR spectrum has shifted to a lower wave number (3214 cm^{-1}), suggesting the possibility of intermolecular hydrogen bonding interactions within the complex. The ν(C=O) also shifts considerably to 1672 cm^{-1} Two Pt-Cl stretches are visible in the spectrum (304 and 273 cm^{-1}), another indication of a *cis*-conformation in **4**.

Reaction of dpptc with [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] gives the expected monodentate dpptc complex [PdCl(η^3-C_3H_5)(dpptc-*P*)] (**5**), δ(P) 54.3 ppm. The X-ray structure of **5** (Fig. 2) confirms the *P* coordination and displays hydrogen bonding, [N(7)–H(7)···Cl(1) 3.166 Å, with a N(7)–H(7)···Cl(1) 131°], there is no evidence of sulfur coordination.

The mixed phosphine complex [$PtCl_2$($PPhMe_2$)-(dpptc-*P*)] (**6**) was synthesised from [{PtCl(μ-Cl)-($PPhMe_2$)}$_2$] and dpptc in dichloromethane. The ^{31}P NMR of **6** showed two doublets with the appropriate platinum satellites [δ(P) 29.7 ppm, $^{2}J_{P-P}$ = 18.8 Hz, $^{1}J_{Pt-P}$ = 3890 Hz, δ(P) −15.6 ppm, $^{2}J_{P-P}$ = 18.8 Hz, $^{1}J_{Pt-P}$ = 3500 Hz], which are consistent with two phosphorus *cis*- to each other and *trans*- to a chloride (see Fig. 3).

Further monodentate complexes were synthesised (Scheme 1) and these all exhibited the expected spectroscopic properties.

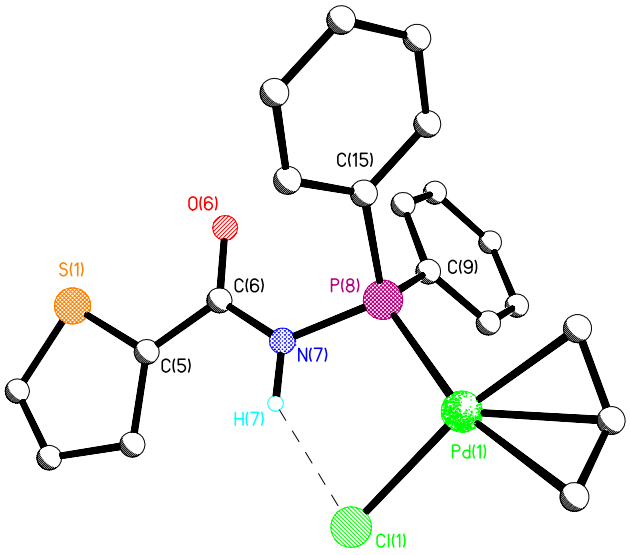


Fig. 2. Crystal structure of [PdCl(η^3-C_3H_5)(dpptc-P)] (**5**), selected bond lengths (Å) and angles (°): P(8)–Pd(1) 2.2937(14), Pd(1)–Cl(1) 2.3780(13), P(8)–N(7) 1.706(4), N(7)–C(6) 1.377(6), O(6)–C(6) 1.227(6) C(6)–C(5) 1.455(8), S(1)–C(5), 1.712(6), N(7)···Cl(1) 3.166(4), P(8)–Pd(1)–Cl(1) 97.18(4), C(15)–P(8)–Pd(1) 116.93(15), N(7)–P(8)–Pd(1) 106.26(14), C(9)–P(8)–Pd(1) 114.06(16), N(7)–H(7)···Cl(1) 131(4).

The X-ray structure of **8** is in space group $P2_12_12_1$ Flack parameter 0.01(3) but we have no evidence there is only one isomer in solution. In **8** there is an interaction between the amide proton and both chlorides attached to the metal and it is worthy of note that there is no interaction involving the oxygen or the sulfur heteroatom in the ring. This could be due to the fact that the sulfur is less likely to form a hydrogen bond, or that the geometry of the five-membered ring as opposed to that of the six-membered ring is less favourable for an N(2)–H(2)···S(5) interaction. These issues and the easy availability of the chlorides account for the chosen motif in this molecule. In the X-ray structure of **9** (Fig. 4), the two hydrogen bonds present are almost identical, showing the favourable motif that can be produced by *trans*-coordination. **10** also has (Fig. 5) H-bond interactions with a N(2)–H(2)···Cl(1) hydrogen bond controlling the ligands geometry, forming a pseudo five-membered ring, similar to the ones we have seen previously; again the sulfur has no part in the bonding motif.

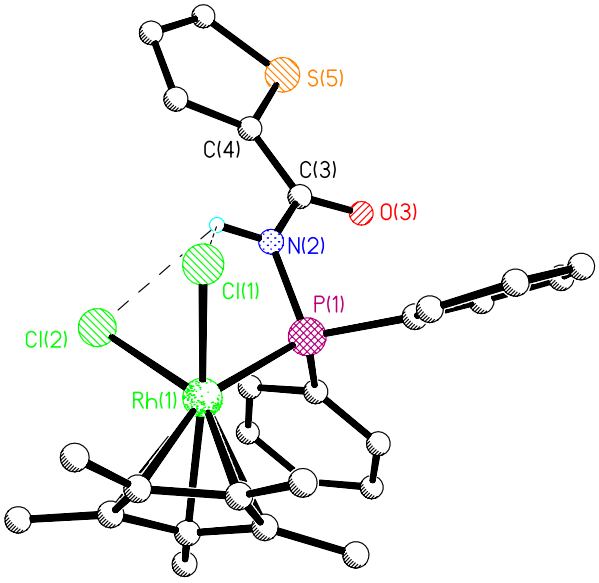
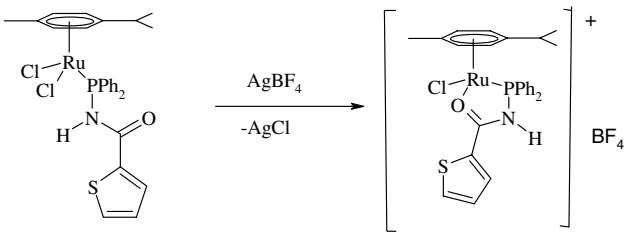


Fig. 3. Crystal structure of [$RhCl_2$(η^5-C_5Me_5)(dpptc-P)] (**8**), selected bond lengths (Å) and angles (°): P(1)–Rh(1) 2.3077(10), Rh(1)–Cl(1) 2.3998(9), Rh(1)–Cl(2) 2.4163(9), P(1)–N(2) 1.695(3), O(3)–C(3) 1.218(4) N(2)–C(3) 1.387(4), N(2)···Cl(1) 3.379(3), N(2)···Cl(2) 3.113(3), P(1)–Rh(1)–Cl(1) 89.44(3), P(1)–Rh(1)–Cl(2) 89.19(3), Rh(1)–P(1)–N(2) 106.88(10), Cl(1)–Rh(1)–Cl(2) 87.96(3), N(2)–H(2)···Cl(1) 112(3), N(2)–H(2)···Cl(2) 121(3).

Dpptc also exhibits bidentate chemistry, though there are significant differences between the chemistry of dpppa and dpptc. Reaction of a halide abstraction reagent with monodentate dpppa complexes gives the *P*,*N* bidentate species. In the case of dpptc, when the same reaction is undertaken one might expect the binding of the thiophene sulfur atom or chelation via the C=O group since thiophene is not an especially good ligand. The coordination mode can be investigated by IR spectroscopy, the frequency of the ν(C=O) vibration indicating chelation through the oxygen. The example investigated was reaction of [$RuCl_2$(*p*-cymene)(dpptc-*P*)] with $AgBF_4$ in CH_2Cl_2, the silver salt was removed by filtration and the product [RuCl(*p*-Cy)(dpptc-*P*,*O*)]BF_4 (**11**) precipitated with diethylether. The ^{31}P NMR displays the expected downfield shift in the spectrum, the peak moves from δ(P) 59.9–100.0 ppm, again the chelate ring effect is responsible for this. The proton spectrum shows some interesting aspects, as the amine proton moves from δ(H) 7.9 ppm in the monodentate complex to δ(H) 10.1 ppm in the bidentate complex and changes from a doublet to a broad singlet, this is typical of extensive hydrogen-bonding being present. The ν(NH) is unchanged in comparison with the monodentate complex at 3216 cm^{-1}. The important IR data is the ν(C=O) – chelation would cause a high frequency shift and this is observed with the band moving to 1561 cm^{-1}, a shift of 104 cm^{-1} from the monodentate complex, typical of C=O bound, bidentate ligand, as described by Braunstein [5]. We also observed the $[BF_4]^-$ counterion in the IR spectrum.



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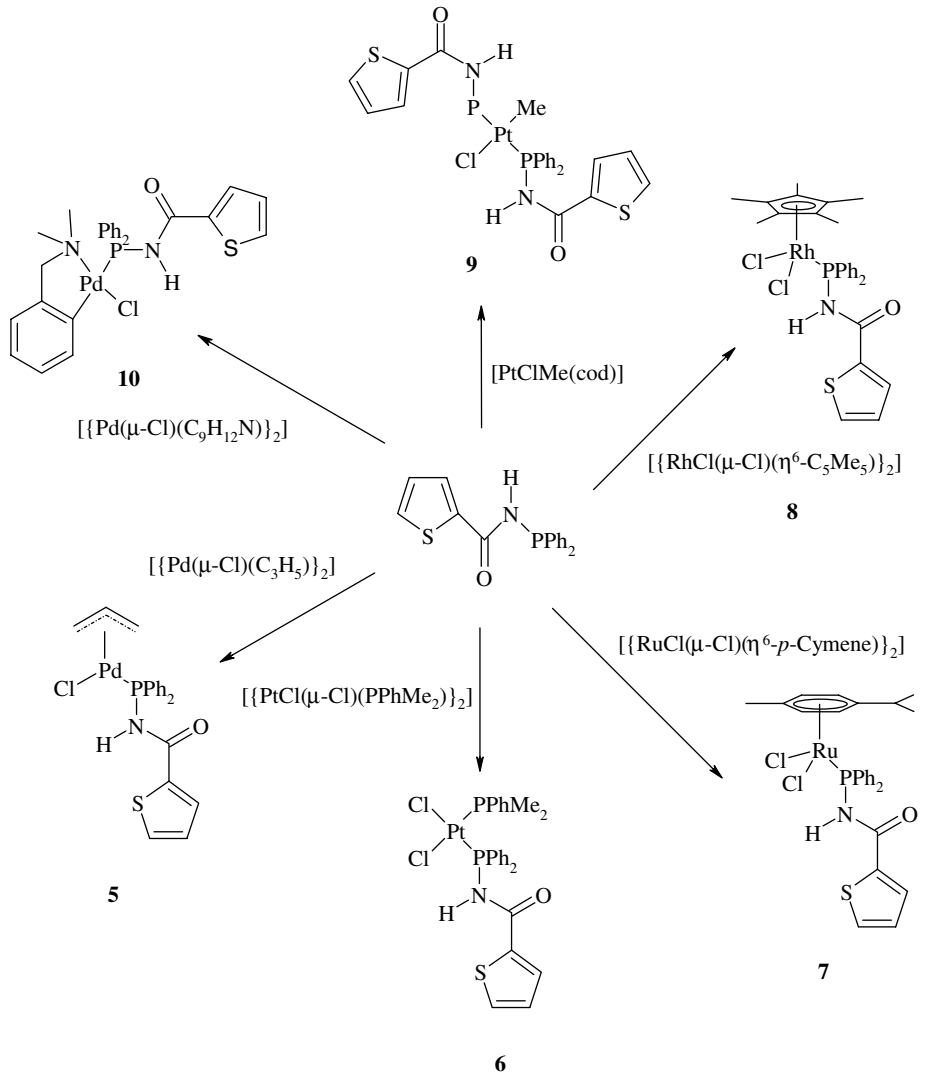
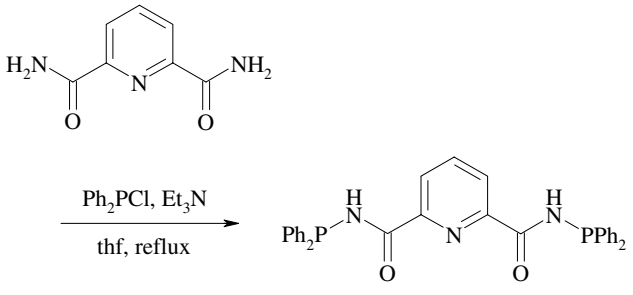


Scheme 1. Formation of monodentate complexes of dpptc.

The synthesis of bdpppa (**12**) is very similar to that of dpppa (Eq. (3)).



(3)

The expected singlet in the ^{31}P NMR is observed at δ(P) 21.9 ppm. This is extremely close to the value for dpppa (22.0 ppm). We see the same similarities in the proton spectra, the N–H peak appears again as a doublet with a more or less identical shift to dpppa at δ(H) 8.4 ppm, however the coupling constant is significantly larger for bdpppa, being 8 Hz as compared to 4 Hz for dpppa. When one examines the IR spectra for bdpppa we see some significant deviation in the characteristics of bdpppa compared to dpppa. In bdpppa ν(N–H) vibrations are visible at 3345 and 3262 cm^{-1}, this trend continues into the ν(C=O) vibrations – again two are visible at 1665 and 1646 cm^{-1}, the ν(C=N) stretches are also twinned at 1588 and 1571 cm^{-1}. However there is only one ν(P–N) vibration observed at 999 cm^{-1}; from this we could surmise that there is a slight difference in the to 'arms' of the molecule present in the solid state.

The presence of two P^{III} atoms in this molecule provides an opportunity for a variety of oxidation products to be synthesised. Bis(2,6-diphenylphosphino)picolinamide disulfide (**13**) and the diselenide (**14**) were prepared by refluxing bdpppa in toluene with a stoichiometric amount of sulfur or selenium for 1 h, the disulfide has

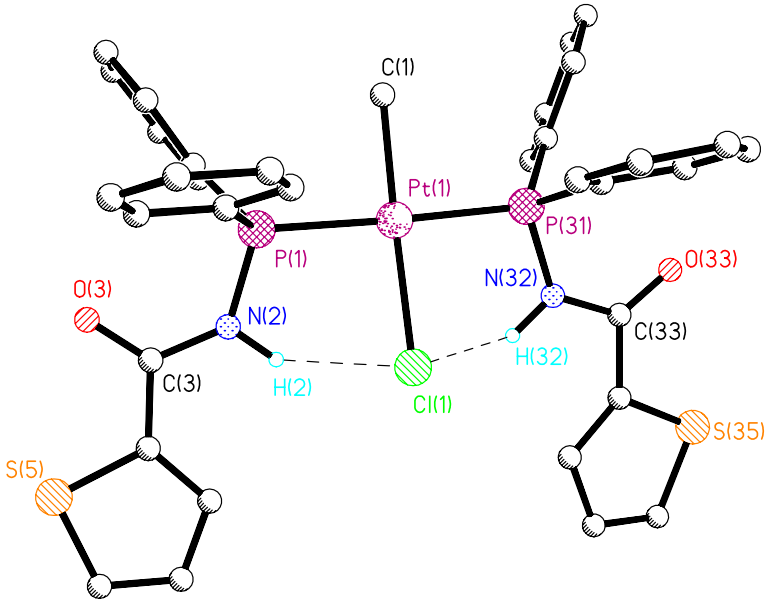


Fig. 4. Crystal structure of [PtMeCl(dpptc-P)$_2$] (**9**), selected bond lengths (Å) and angles (°): P(1)–Pt(1) 2.2902(15), P(31)–Pt(1) 2.2902(15), P(1)–N(2) 1.702(5), P(31)–N(32) 1.700(5), N(2)–C(3) 1.371(8), N(32)–C(33) 1.365(7), C(3)–O(3) 1.227(7), C(33)–O(33) 1.227(7), Pt(1)–Cl(1) 2.4343(16), Pt(1)–C(1) 2.074(6) N(2)···Cl(1) 3.085(6), N(32)···Cl(1) 3.045(5), P(1)–Pt(1)–Cl(1) 91.72(5), P(31)–Pt(1)–Cl(1) 90.34(5), P(1)–Pt(1)–C(1) 89.79(18), N(2)–P(1)–Pt(1) 106.14(18), N(32)–P(31)–Pt(1) 106.14(18), N(2)–H(2)···Cl(1) 139(4), N(32)–H(32)···Cl(1) 139(5).

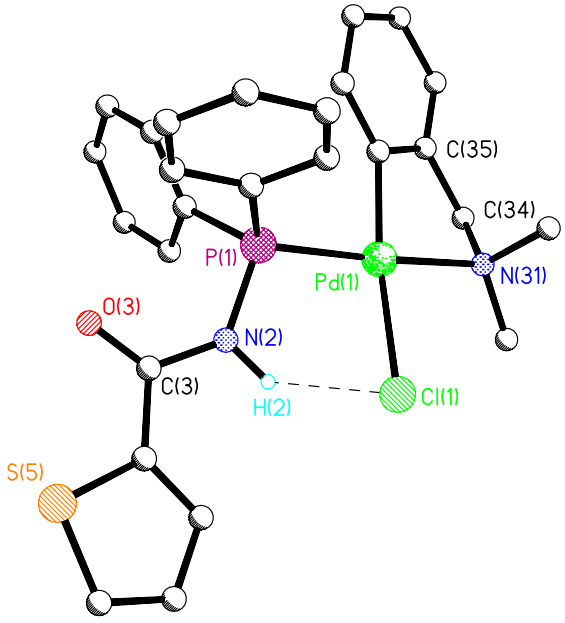


Fig. 5. Crystal structure of [PdCl($C_9H_{12}N$)(dpptc-P)] (**10**), Selected bond lengths (Å) and angles (°): P(1)–Pd(1) 2.2479(12), Pd(1)–N(31) 2.143(4), Pd(1)–Cl(1) 2.4249(12), C(3)–O(3) 1.219(5), N(2)–C(3) 1.382(5), C(4)–S(5) 1.713(4), N(2)···Cl(1) 3.027(4), P(1)–Pd(1)–Cl(1) 93.58(4), P(1)–Pd(1)–N(31) 173.10(10), Cl(1)–Pd(1)–N(31) 91.83(10), N(2)–H(2)···Cl(1) 141(4).

δ(P) 55.1 ppm and the diselenide δ(P) 49.7 ppm with $^1J_{P=Se}$ = 795 Hz. The amide protons in **13** and **14** are shifted to δ(H) 8.9 and 8.8 ppm, respectively, and are both doublets with $^2J_{P-H}$ = 9 Hz, these values are similar to the values observed for the unoxidized ligand. The IR data shows no real variation from the dpppa equivalents, for **13** the ν(N–H) is observed at 3360 cm^{-1} as a sharp peak, however the ν(C=O) is observed at 1697 cm^{-1} with significant line broadening, the ν(P–N) peak remains constant at 999 cm^{-1}. A similar pattern is observed for **14**, with ν(N–H), ν(C=O) and ν(P–N) coming at 3256, 1698 and 998 cm^{-1}, respectively, although the slightly lower value for the ν(N–H) may suggest more extensive hydrogen-bonding in **14** compared to both the disulfide and the free ligand. In the solid state (Fig. 6) **14** adopts a pseudo five-membered ring formed by an interaction of the amide hydrogen's with the pyridyl nitrogen (see Scheme 2).

By making use of the mild conditions involved in synthesis of the sulfur species one can isolate the mono-sulfur derivative of bdpppa, bdpppa-S (**15**). This generates a compound where only one sulfur is bound to phosphorus, leaving one free for further chemistry. The ^{31}P spectrum clearly shows this motif with two singlets being present at δ(P) 56.0 (P=S), and 21.7 ppm (P^{III}). The IR data shows the two now different arms of the molecule clearly, two ν(N–H) vibrations are observed, one at 3345 cm^{-1} which is consistent with bdpppa, and the other at 3262 cm^{-1}, similar to dpppa-S and bdpppa-diS. The same pattern is seen in the ν(C=O), a peak at 1697 cm^{-1} representing the sulfide arm, and a peak at 1665 cm^{-1} represents the P^{III} arm.

As we speculated the mono-oxidised form of bdpppa can use it is unoxidised phosphorus to react further, and reaction with one equivalent of selenium in toluene generates the unsymmetrical bdpppa-S,Se (**16**), δ(P) 55.0

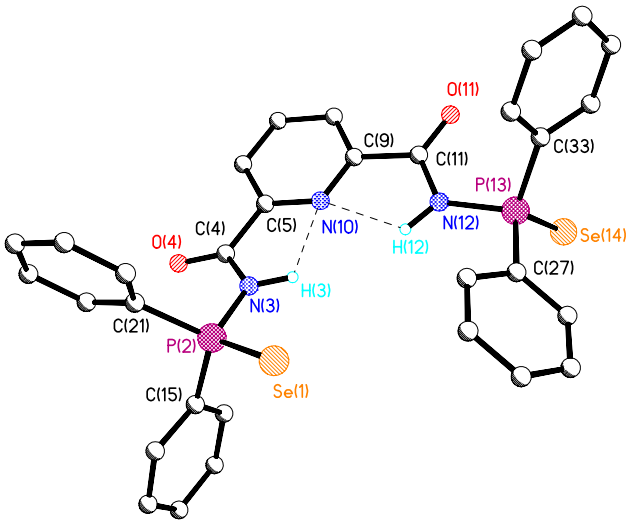
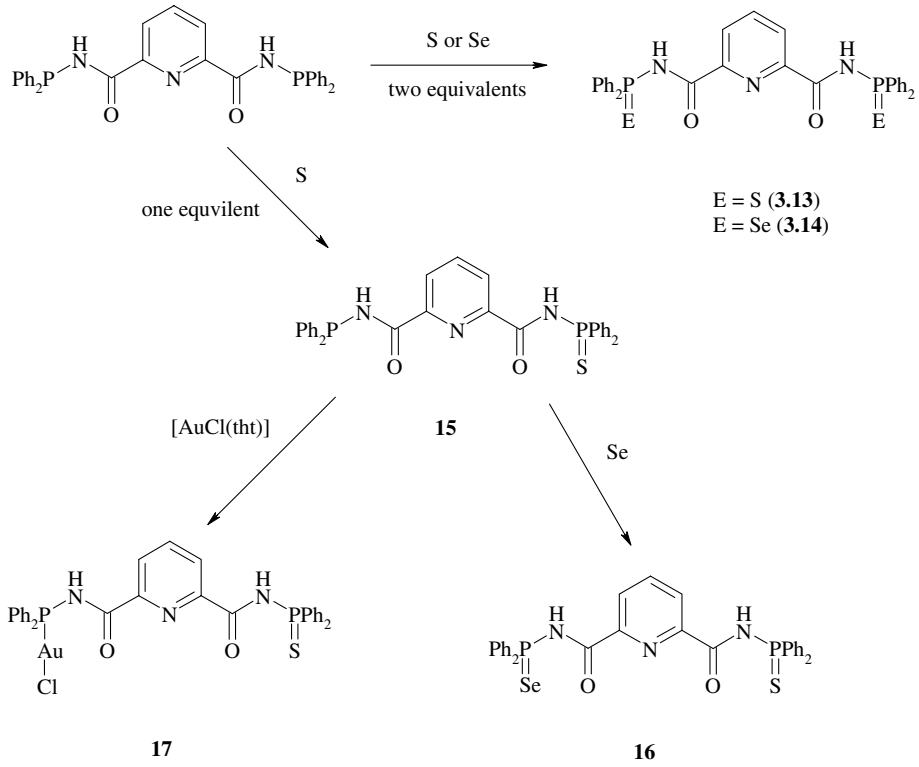


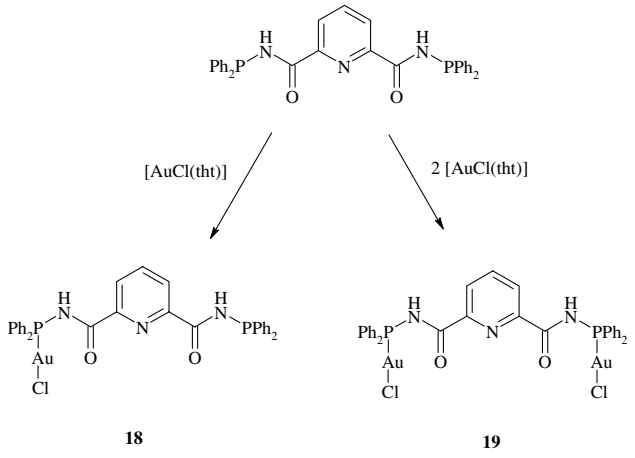
Fig. 6. Crystal structure of bdpppa-diSe (**14**), selected bond lengths (Å) and angles (°): P(2)–Se(1) 2.0974(14), P(13)–Se(14) 2.1014(15), P(2)–N(3) 1.687(4), P(13)–N(12) 1.698(4), N(3)–C(4) 1.374(6), N(12)–C(11) 1.373(6), C(4)–O(4) 1.209(6), C(11)–O(11) 1.207(6), C(4)–C(5) 1.513(6), C(11)–C(9) 1.510(7), C(5)–N(10) 1.334(6), C(9)–N(10) 1.334(16), N(3)···Cl(3) 3.050, N(12)···Cl(3) 3.368, N(3)···N(10) 2.684(5) N(12)···N(10) 2.721(5), Se(1)–P(2)–N(3) 107.68(16), Se(14)–P(13)–N(12) 114.97(16), P(2)–N(3)–H(3) 120(5), N(3)–H(3)···N(10) 113(5), N(12)–H(12)···N(10) 113(5).

ppm (consistent with P=S), δ(P) 49.7 ppm $^{1}J_{P=Se}$ of 795 Hz.. Compound **15** can also be reacted with one equivalent of [AuCl(tht)] in dichloromethane to generate [AuCl(bdpppa-S-*P*)] **17**, δ(P) 55.0 (P=S) and δ(P) 50.2 (P–Au). Reaction of bdpppa with [AuCl(tht)] in dichloromethane gives two products dependant on the stoichiometry of the reaction. One equivalent of [AuCl(tht)] generates the expected product with one phosphorus bound to gold and one remaining unbound (**18**). With two equivalents of [AuCl(tht)] both phosphorus atoms are coordinated (Scheme 3) to give (**19**). In the case of this digold complex, we see the expected singlet in the ^{31}P NMR at 50.0 ppm, this agrees well with the one previous gold complex of dpppa, and the peak seen in **17**. The proton spectrum also displays the characteristics of its dpppa analogue, the amide peak is clearly seen at δ(H) 10.3 ppm with a $^{2}J_{P-H}$ = 16 Hz and the aromatics are all found in the 8.2–7.2 region. The ν(N–H) stretch in the IR spectrum is a broad peak at 3261 cm^{-1}, also the ν(C=O) band is broad, located at 1698 cm^{-1}, both these values correlate well with [AuCl(dpppa-*P*)] (3288 and 1698 cm^{-1}, respectively).

However, when one considers the mono-gold complex it, unlike **15**, does not display two separate peaks in the ^{31}P NMR for P–Au and P^{III}, it displays a singlet at δ(P) 64.3 ppm, at significantly higher chemical shift than anything we have seen earlier, and does not correlate with the shift observed in the mono-sulfide/gold complex. Inspection of the IR data provides further evidence for a single phosphorus environment, with only single peaks being displayed for ν(N–H) and ν(C=O) (3054 and 1698 cm^{-1}, respectively). Also the ^{1}H NMR



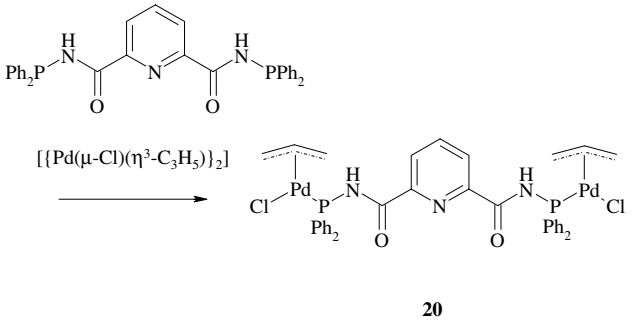
Scheme 2. Reactions of bdpppa and its mono-oxidized derivatives.



Scheme 3. Reaction of bdpppa with [AuCl(tht)].

data shows a single resonance for the amide proton, a broad singlet at δ(H) 11.0 ppm. The most plausible explanation for these data is for **18** to exist as a dimer, this is not a unique conformation as a similar system has been reported for dppap [13].

Reaction of bdpppa with a range of Pt and Pd dimers generates complexes where the bdpppa ligand bridges two metal atoms. Treatment of bdpppa with one equivalent of $[\{Pd(\mu\text{-}Cl)(\eta\text{-}C_3H_5)\}_2]$, generating $[Pd_2Cl_2(\eta\text{-}C_3H_5)_2$(bdpppa-*P*,*P*)] (**20**). The ^{31}P NMR shows a singlet at δ(P) 55.1 ppm, consistent with the complexes structure when compared to dpppa and dpptc.



(4)

The analogous reaction with $[\{Pt(\mu\text{-}Cl)(\eta\text{-}C_3H_5)\}_2]$ generated a similar product, $[Pt_2Cl_2(\eta\text{-}C_3H_5)_2$(bdpppa-*P*,*P*)] (**21**), δ(P) 51.7 ppm, $^1J_{Pt-P} = 4730$ Hz. A crystal of **21** was prepared for crystallographic analysis by vapour diffusion of diethylether into a concentrated solution of **21** in $CDCl_3$. Given our conclusions based on **20**, we could imagine the two compounds would be almost analogous in the solid state.

The X-rays structure of **21** (Fig. 7) shows it has an arrangement much like that of **14**, with the amide protons interacting with the pyridyl nitrogen, and if one considers the chlorides to be analogous to the selenium atoms, then we can see that again one is 'in' and one is 'out', of the hole in the centre of the complex. Similar

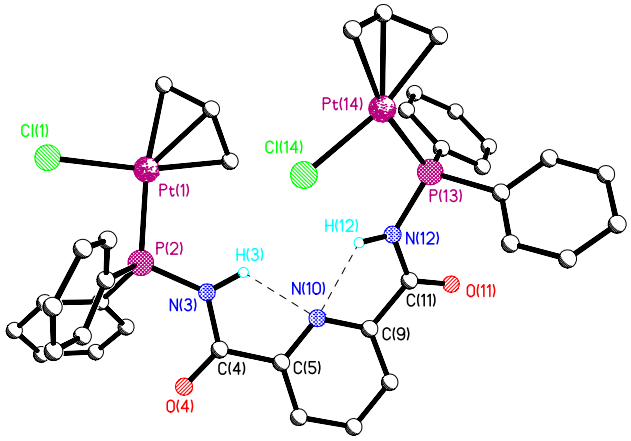


Fig. 7. Crystal structure of $[Pt_2Cl_2(\eta\text{-}C_3H_5)_2$(bdpppa-P,P)] (**21**), selected bond lengths (Å) and angles (°): P(2)–Pt(1) 2.249(2), P(13)–Pt(14) 2.250(2), P(2)–N(3) 1.699(7), P(13)–N(12) 1.720(7), N(3)···N(10) 2.689(10), N(12)···Cl(14) 3.167(7), N(12)···N(10) 2.674(9), Pt(1)–P(2)–N(3) 110.4(2), Pt(14)–P(13)–N(12) 109.9(3), N(3)–H(3)···N(10) 119(7), N(12)–H(12)···N(10) 110(6).

to **14** one can imagine in this scenario that there is probably too much steric bulk involved for both of the chlorides to occupy the 'in' slot as was the case with the selenium atoms.

3. Experimental

All manipulations were carried out in a atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropriate drying agent (thf, Et_2O, dcm) or obtained as anhydrous grade from Aldrich. ^{1}H and ^{31}P NMR spectra were recorded using a Jeol Delta FT (270 MHz) spectrometer. IR spectra were recorded as KBr discs (prepared in air) on a Perkin–Elmer 2000 FTIR/RAMAN spectrometer. All significant peaks (>800 cm^{-1}) are quoted to serve as a fingerprint. Silver salts, 2-thiophenecarboxamide, 2,6-pyridinedicarboxamide (Aldrich Chemical Co.) and BuLi (2.5 M, Lancaster) were purchased and used as received. Triethylamine and chlorodiphenylphosphine were distilled prior to use. Dimethylaminopyridine (DMAP) was sublimed before use. The various metal starting materials were made by the appropriate literature methods; [AuCl(tht)] [5], $[MCl_2(cod)]$ (M = Pt or Pd; cod = cycloocta-1,5-diene) [6,7], [PtMeCl(cod)] [8], $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ [9], $[\{MCl(\mu\text{-}Cl)(Cp^*)\}_2]$ (M = Rh or Ir) [10], $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)\}_2]$ [11], $[\{PdCl(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)\}_2]$ [12–14].

*3.1. 2-(Diphenylphosphino)thiophenecarboxamide (Dpptc) (**1**)*

Chlorodiphenylphosphine (3.53 ml, 20 mmol) was added to a solution of 2-thiophenecarboxamide (2.5 g,

20 mmol), triethylamine (2.88 ml, 20.6 mmol) and DMAP (240 mg, 2 mmol) in THF (100 cm^3) and refluxed overnight. The reaction mixture was filtered to remove a white solid (Et_3NHCl) and washed with THF (50 cm^3). The solvent was removed in vacuo leaving a pale yellow solid. This solid was recrystallised by cooling a concentrated methanol solution in a fridge overnight (yield: 3.28 g, 10.5 mmol, 54%). *Anal.* Calc. $C_{17}H_{14}NOSP$ requires: C, 65.5; H, 4.53; N, 4.50. Found: C, 63.8; H, 4.09; N, 4.70%. ν_{max}/cm^{-1}: 3265, 1624, 1522, 1442, 1270, 1096, 996. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 25.9. ^1H NMR (270 MHz, $CDCl_3$), 7.6 (2H, m, aromatic), 7.5–7.3 (10H, m, aromatic), 7.1 (2H, m, aromatic).

3.2. 2-(Diphenylphosphino)thiophenecarboxamide sulfide (**3**)

Sulfur (77 mg, 2.4 mmol) was added to a solution of 2-(diphenylphosphino)thiophenecarboxamide (750 mg, 2.4 mmol) in toluene (20 cm^3) and refluxed overnight. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystallised by cooling a concentrated toluene solution at 4 °C overnight (yield: 1.39 g, 93%). *Anal.* Calc. $C_{17}H_{14}NOPS_2$ requires: C, 59.5; H, 4.11; N, 4.08. Found: C, 59.2; H, 3.70; N, 4.48%. ν_{max}/cm^{-1}: 3167, 1624, 1436, 1000. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 57.2 ppm. ^1H NMR ($CDCl_3$), δ 8.0 (3H, m, aromatic), 7.7–7.3 (6H, m, aromatic), 7.3–7.1 (4H, m, aromatic), 7.0 (1H, d, N–H).

3.3. [$PtCl_2$(dpptc-P)$_2$] (**4**)

Dpptc (166 mg, 0.534 mmol) and [$PtCl_2$(cod)] (100 mg, 0.267 mmol) were weighed into a Schlenk type flask and DCM (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 170 mg, 72%). *Anal.* Calc. $C_{34.5}H_{29}N_2O_2P_2S_2Cl_3Pt$ requires: C, 44.5; H, 3.14; N, 3.01. Found: C, 44.0; H, 3.89; N, 2.95%. ν_{max}/cm^{-1}: 3214, 1672, 1424, 1398, 1042, 304, 273. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 27.9 ($J_{P–Pt}$ = 3870 Hz). ^1H NMR (270 MHZ, $CDCl_3$), 9.7 (2H, d, J = 11 Hz, N–H), 7.8–6.9 (26H, m, aromatic).

3.4. [PdCl(η^3-C_3H_6)(dpptc-P)] (**5**)

Dpptc (170 mg, 0.54 mmol) and [{Pd(μ -Cl)(η^3-C_3H_5)}$_2$] (100 mg, 0.27mmol) were weighed into a Shlenk type flask and DCM (5 ml) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 117 mg, 87%). *Anal.* Calc. $C_{20}H_{20}NOSPClPd$ requires: C, 48.5; H, 4.07; N, 2.83. Found: C, 48.3; H, 2.35; N, 2.82%. ν_{max}/cm^{-1}: 3208, 1671, 1435, 1394, 1010, 277. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 54.3. ^1H NMR (270 MHz, $CDCl_3$), 9.4 (1H, d, J = 19 Hz, N–H), 7.7 (1H, d, J = 1 Hz, thC[5**]H), 7.7–7.6 (4H, m, aromatic), 7.5–7.3 (7H, m, aromatic) 7.1 (1H, dd, J = 3, 6 Hz, thC[4**]) 5.5 (1H, m, allyl), 4.8 (1H, t, J = 6 Hz, allyl), 3.7 (1H, dd, J = 10, 13 Hz, allyl), 3.3 (1H, obscured, allyl), 2.6 (1H, d, J = 13 Hz, allyl).

3.5. [$PtCl_2$($PPhMe_2$)(dpptc-P)] (**6**)

Dpptc (58 mg, 0.18 mmol) and [{PtCl(μ-Cl)(Me_2PhP)}$_2$] (75 mg, 0.0927 mmol) were weighed into a Schlenk type flask and DCM (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A yellow solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 66 mg, 50%). *Anal.* Calc. $C_{25}H_{25}NOSP_2Cl_2Pt$ requires: C, 39.7; H, 4.20; N, 2.01. Found: C, 40.0; H, 3.31; N, 1.72%. ν_{max}/cm^{-1}: 3226, 1671, 1435, 948, 316, 281. ^{31}P NMR (109.3 MHz, $CDCl_3$) δ 29.7 (d, $J_{P–P}$ = 18.78 Hz, $J_{P–Pt}$ = 3890 Hz), -15.6 (d, $J_{P–P}$ = 18.78 Hz, $J_{P–Pt}$ = 3500 Hz). ^1H NMR (270 MHz, $CDCl_3$) δ 11.4 (1H, d, J = 16 Hz, N–H), 8.6 (1H, d, J = 7 Hz, pyC[6]H), 8.2 (4H, m, aromatic), 7.9–7.4 (9H, m, aromatic), 1.6–1.4 (9H, m, Me–H) 1.0–0.8 (6H, m, –CH_2–).

3.6. [$RuCl_2$(p-Cymene)(dpptc-P)] (**7**)

Dpptc (102 mg, 0.326 mmol) and [{RuCl(μ-Cl)(*p*-Cymene)}$_2$] (100 mg, 0.0163 mmol) were weighed into a Schlenk type flask and DCM (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A red solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 155 mg, 77%). *Anal.* Calc. $C_{27}H_{28}NOPCl_2Ru$ requires: C, 52.5; H, 4.57; N, 2.27. Found: C, 52.1; H, 3.48; N, 2.19%. ν_{max}/cm^{-1}: 3312, 1665, 1435, 1404, 1091, 288. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 59.9. ^1H NMR (270 MHZ, $CDCl_3$), 8.0 (5H, m, aromatic) 7.9 (1H, d, J = 14 Hz, N–H), 7.6 (1H, dd, J = 1, 4 Hz), 7.5–7.3 (10H, m, Aromatic), 5.3–5.2 (4H, m, *p*-Cy), 2.5 (1H, m, C–H), 1.9 (3H, s, Me–H), 0.8 (6H, d, J = 7Hz, ^{1}Pr–H).

3.7. [$RhCl_2$(η^5-C_5Me_5)(dpptc-P)] (**8**)

Dpptc (101 mg, 0.326 mmol) and [{RhCl(μ-Cl)(η^5-C_5Me_5)}$_2$] (100 mg,. 0161 mmol) were weighed into a Schlenk type flask and DCM (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A red solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 159 mg, 80%). $C_{27.5}H_{30}NSOPCl_3Rh$ requires: C, 49.8; H, 4.56; N, 2.11. Found: C, 50.7; H,

4.17; N, 2.27%. ν_{max}/cm^{-1}: 3299, 1669, 1435, 1097, 246, 231. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 63.5 ($^1J_{Rh-P}$ = 148 Hz).. ^1H NMR (270 MHZ, $CDCl_3$), 8.2 (1H, d, J = 14 Hz, N–H) 8.1–8.0 (4H, m, aromatic) 7.7 (1H, d, J = 4 Hz, N–H), 7.5–7.3 (7H, m, aromatic), 7.0 (1H, t, J = 8 Hz, aromatic), 1.4 (15H, d, Cp*Me–H).

3.8. [PtClMe(dpptc-P)$_2$] (**9**)

Dpptc (39 mg, 0.12 mmol) and [PtClMe(cod)] (22 mg, 0.06 mmol) were weighed into a Schlenk type flask and DCM (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A yellow solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 34 mg, 65%). *Anal.* Calc. $C_{35}H_{31}N_2S_2O_2P_2ClPt$ requires: C, 48.4; H, 3.60; N, 3.23. Found: C, 48.4; H, 3.40; N, 3.17%. ν_{max}/cm^{-1}: 3209, 1671, 1435, 1094. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 49.1 (J_{P-Pt} = 3220 Hz). ^1H NMR (270 MHZ, $CDCl_3$), 9.7 (2H, t, J_{Pt-H} = 19 Hz, N–H), 7.9 (10H, m, aromatic), 7.6–7.3 (14H, m, aromatic), 7.1 (2H, d, J = 3 Hz, thiophene), 1.5 (3H, s, Me).

3.9. [PdCl($C_9H_{12}N$)(dpptc-P)] (**10**)

Dpptc (79 mg, 0.25 mmol) and [Pd(μ-Cl)($C_9H_{12}N$)]$_2$ (70 mg, 0.13 mmol) were weighed into a Schlenk type flask and DCM (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A yellow solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 82 mg, 55%). *Anal.* Calc. $C_{26}H_{26}N_2SOPClPd$ requires: C, 53.0; H, 4.63; N, 4.76. Found: C, 52.3; H, 4.52; N, 4.53%. ν_{max}/cm^{-1}: 3171, 1672, 1438, 1259, 1101, 286. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 62.4ppm. ^1H NMR (270 MHZ, $CDCl_3$), 10.1 (1 H, bs, N–H) 8.2 (4 H, m, aromatic) 7.2–7.7 (10H, m, aromatic), 7.1 (1H, dd, J = 1, 4 Hz, aromatic) 7.0 (1H, d, J = 6 Hz, aromatic), 6.8 (1H, t, J = 15 Hz, aromatic) 6.4 (2H, m, aromatic) 2.9 (6H, s, N–Me).

3.10. [RuCl(p-Cy)(dpptc-P,O)]BF_4 (**11**)

$AgBF_4$ (22 mg, 0.11 mmol) was added under dark conditions to a solution of [$RuCl_2$(*p*-Cy)(dpptc-*P*)] (70 mg, 0.11 mmol) in DCM (5 cm^3). The solution was stirred overnight and filtered through a celite bed. The majority of the solvent was removed in vacuo. An orange solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 45 mg, 70%). *Anal.* Calc. $C_{27}H_{28}NRuClOSPBF_4$ requires: C, 48.48; H, 4.21; N, 2.09. Found: C, 48.0; H, 4.07; N, 2.02%. ν_{max}/cm^{-1}: 3216, 1561, 1460, 1433, 1084, 1060, 764. ^{31}P NMR (109.3 MHz, $CDCl_3$) δ 100.0. ^1H NMR (270 MHz, $CDCl_3$) δ 10.1 (1H, s, N–H), 8.3 (1H, d, J = 3Hz, thC[5]H), 8.0 (2H, m, aromatic), 7.7–7.1 (11H, m, aromatic), 5.9 (1H, dd, J = 7 Hz, *p*-Cy-H), 5.6 (1H, dd, J = 6 Hz, *p*-Cy-H), 5.3 (1H, m, *p*-Cy), 5.0 (1H, d, J = 6 Hz, *p*-Cy), 2.6 (1H, m, C–H), 2.1 (3H, s, Me–H), 1.3 (6H, m, Pr^i–H).

3.11. Bis(2,6-diphenylphosphino)picolinamide (bdpppa) (**12**)

Chlorodiphenylphosphine (5.44 cm^3, 30.3 mmol) was added to a solution of 2,6-pyridinedicarboxamide (2.5 g, 30.3 mmol), triethylamine (4.44 cm^3, 32 mmol) and DMAP (370 mg, 3.0 mmol) in thf (100 cm^3) and refluxed overnight. The reaction mixture was filtered to remove a white solid (Et_3NHCl) and washed with thf (50 cm^3). The solvent was removed in vacuo leaving a pale yellow solid. This solid was recrystallised by cooling a concentrated methanol solution at 4 °C overnight (yield: 4.89 g, 61%). *Anal.* Calc. $C_{31.5}H_{26}N_3O_2P_2Cl$ requires: C, 66.0; H, 4.50; N, 7.22. Found: C, 65.7; H, 4.41; N, 7.40%. ν_{max}/cm^{-1}: 3345, 3262, 1665, 1646,, 1588, 1571, 1408, 999. ^{31}P NMR ($CDCl_3$) 21.9. ^1H NMR ($CDCl_3$), 8.42 (2H, d, J = 8 Hz, N–H), 8.00 (3H, m, py), 7.5–7.1 (21H, m, aromatic).

3.12. Bis(2,6-diphenylphosphino)picolinamide disulfide (**13**)

Sulfur (120 mg, 3.7 mmol) was added to a solution of bis(2,6-diphenylphosphino)picolinamide (1 g, 3.7 mmol) in toluene (20 cm^3) and refluxed for 10 min. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystillised by cooling a concentrated toluene solution at 4 °C overnight (yield: 876 mg, 78%). *Anal.* Calc. $C_{31}H_{25}N_3O_2P_2S_2$ requires: C, 63.8; H, 4.32; N, 4.80. Found: C, 64.1; H, 4.46; N, 4.50%. ν_{max}/cm^{-1}: 3360, 1697, 1424, 999. ^{31}P NMR ($CDCl_3$) 55.1 ppm. ^1H NMR ($CDCl_3$), δ 8.9 (2H, d, J = 9 Hz, N–H), 8.3 (2H, d, J = 8 Hz, pyC[3,5]H), 8.1–7.9 (8H, m, aromatic), 7.6–7.4 (10H, m, aromatic), 7.1–7.3 (3H, m, aromatic).

3.13. 2,5-bis(Diphenylphosphino)picolinamide diselenide (**14**)

Selenium (74 mg, 0.9 mmol) was added to a solution of 2,5-bis(Diphenylphosphino)picolinamde (250 mg, 0.47 mmol) in toluene (20 cm^3) and refluxed for 10 min. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystillised by cooling a concentrated toluene solution in a fridge overnight (yield: 263 mg, 81%). *Anal.* Calc. $C_{31}H_{25}N_3O_2P_2Se_2$ requires: C, 53.9; H, 3.64; N, 6.08. Found: C, 53.7; H, 3.24; N, 6.17%. ν_{max}/cm^{-1}: 3256, 1698, 1421, 998. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 49.6 ($^1J_{P=Se}$ = 795 Hz). ^1H NMR (270 MHz, $CDCl_3$), δ 8.8 (2H, d, J = 9Hz, N–H), 8.3 (1H, d, J = 8Hz, pyC[6]H), 8.0 (8H, m, aromatic), 7.5 (13H, m, aromatic).

3.14. Bis(2,6-diphenylphosphino)picolinamide monosul-fide (**15**)

Sulfur (36 mg, 0.37 mmol) was added to a solution of bis(2,6-diphenylphosphino)picolinamide (600 mg, 0.37 mmol) in toluene (20 cm^3) and refluxed for 10 min. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystallised by cooling a concentrated toluene solution at 4 °C overnight (yield: 415 mg, 65%). *Anal.* Calc. $C_{31}H_{25}N_3O_2P_2S$ requires: C, 65.7; H, 4.46; N, 7.43. Found: C, 67.4; H, 4.47; N, 7.20%. ν_{max}/cm^{-1}: 3345, 3262, 1697, 1665, 1646, 1432, 999. ^{31}P NMR ($CDCl_3$) 56.0 (s, P═S), 21.7 (s, P^{III}). ^1H NMR ($CDCl_3$), δ 8.8 (2H, d, $J = 9$ Hz, N–H), 8.4 (4H, m aromatic), 7.8–8.1 (5H, m, aromatic), 7.0–7.6 (14H, m, aromatic).

3.15. Bis(2,6-diphenylphosphino)picolinamide monosulfide monoselenide (**16**)

Selenium (22 mg, 0.26 mmol) was added to a solution of bis(2,6-diphenylphosphino)picolinamide monosulfide (150 mg, 0.26 mmol) in toluene (10 cm^3) and refluxed for 10 min. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystillised by cooling a concentrated toluene solution at 4 °C overnight (yield: 120 mg, 71%). *Anal.* Calc. $C_{31}H_{25}N_3O_2P_2SSe$ requires: C, 57.7; H, 3.91; N, 6.52. Found: C, 58.8; H, 3.68; N, 6.30%. ν_{max}/cm^{-1}: 3449, 1697, 1421, 997. ^{31}P NMR ($CDCl_3$) 55.0 (s, P═S), 49.7 (s, P═Se, $^1J_{P-Se} = 789$ Hz). ^1H NMR ($CDCl_3$), δ 8.8 (2H, d, $J = 8$ Hz, N–H), 8.3 (2H, dd, $J = 8$, 1 Hz, pyC[3,5]H), 7.9-8.1 (7H, m, aromatic), 7.6–7.4 (14H, m, aromatic).

3.16. [{AuCl}(bdpppa-S)] (**17**)

[AuCl(tht)] (57 mg, 0.17 mmol) and Bis(2,6-diphenylphosphino)picolinamide (100 mg, 0.17 mmol) were added to a round bottomed flask and DCM (5 cm^3) added. The solvent volume was reduced to ~1 cm^3 and the product precipitated with *n*-hexane (20 cm^3). Yield 93 mg, 66%. *Anal.* Calc. $C_{32}H_{26}N_3O_2P_2SAuCl_3$ requires: C, 41.9; H, 2.80; N, 4.58. Found: C, 41.7; H, 2.74; N, 4.69%. ν_{max}/cm^{-1}: 3256, 1697, 1437, 999. ^{31}P NMR ($CDCl_3$) δ(P) 55.0 (s, P═S), 50.2 (s, P–Au). ^1H NMR ($CDCl_3$) δ (H) 10.2 (2H, bs, N–H), 7.0–8.0 (23H, m, aromatic).

3.17. [{AuCl} (bdpppa)] (**18**)

A solution of [AuCl(tht)] (120 mg, 0.37mmol) in DCM (10 cm^3) was dropped into a solution of bis(2,6-diphenylphosphino)picolinamide (200 mg, 0.37 mmol) in DCM (15 cm^3). The solvent volume was reduced to ~1cm^3 and the product precipitated with *n*-hexane (20cm^3). Yield 240 mg, 83%. *Anal.* Calc. $C_{31}H_{25}N_3O_2P_2AuCl$ requires: C, 48.6; H, 3.29; N, 5.49. Found: C, 48.2; H, 2.91; N, 5.48%. ν_{max}/cm^{-1}: 3054, 1698, 1436, 999. ^{31}P NMR ($CDCl_3$) δ(P) 64.3. ^1H NMR ($CDCl_3$) δ(H) 11.0 (2H, bs, N–H), 9.0 (2H, m, aromatic), 7.1–8.1 (21H, m, aromatic).

3.18. [{AuCl}$_2$(bdpppa)] (**19**)

[AuCl(tht)] (84 mg, 0.26 mmol) and bis(2,6-diphenylphosphino)picolinamide (70 mg, 0.13 mmol) were added to a round bottomed flask and DCM (5 cm^3) added. The solvent volume was reduced to ~1 cm^3 and the product precipitated with *n*-hexane (20 cm^3). Yield 125 mg, 95%. *Anal.* Calc. $C_{31}H_{25}N_3O_2P_2Au_2Cl_2$ requires: C, 37.3; H, 2.52; N, 4.21. Found: C, 37.16; H, 2.37; N, 4.12%. ν_{max}/cm^{-1}: 3261, 1697, 1436, 999. ^{31}P NMR ($CDCl_3$) δ(P) 50.0. ^1H NMR ($CDCl_3$) δ(H) 10.2 (2H, d, $J_{H-H} = 16$ Hz, N–H), 8.1 (2H, m, aromatic), 7.9–7.6 (8H, m, aromatic), 7.6–7.1 (13H, m, aromatic).

3.19. [Pd$_2$Cl$_2$(allyl)$_2$(bdpppa-P,P)] (**20**)

Bdpppa (397 mg, 0.7.45 mmol) and [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] (272 mg, 0.373 mmol) were weighed into a Schlenk type flask and DCM (10 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 671 mg, 91%). *Anal.* Calc. $C_{37}H_{37}N_3O_2P_2Cl_2Pd_2$ requires: C, 49.3; H, 4.13; N, 4.66. Found: C, 49.23; H, 3.68; N, 4.57%. ν_{max}/cm^{-1}: 3351, 3209, 1698, 1434, 1385, 999. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 55.1. ^1H NMR (270 MHZ, $CDCl_3$), 10.2 (2H, d, $J = 18$ Hz, N–H), 8.2 (2H, d, $J = 8$ Hz, –pyC[6]H), 8.0–7.8 (10H, m, aromatic), 7.6–7.4 (10H, m, aromatic), 5.5 (4H, quin, $J = 10$ Hz, allyl), 4.7 (4H, t, $J = 7$Hz, allyl), 3.7 (2H, t, $J = 10$ Hz, allyl).

3.20. [Pt$_2$Cl$_2$(allyl)$_2$(bdpppa-P,P)] (**21**)

Bdpppa (59 mg, 0.092 mmol) and [{Pt(μ-Cl)(η^3-C_3H_5)}$_2$] (60 mg, 0.046 mmol) were weighed into a Schlenk type flask and THF (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was isolated after addition of Et_2O then filtered and washed with further ether (yield: 43 mg, 43%). *Anal.* Calc. $C_{37}H_{37}N_3O_2P_2Cl_2Pt_2$ requires: C, 41.1; H, 3.46; N, 3.90. Found: C, 40.3; H, 3.59; N, 3.86%. ν_{max}/cm^{-1}: 3360, 3231, 1700, 1434, 1000. ^{31}P NMR (109.3 MHz, $CDCl_3$), δ 51.7 ($^1J_{Pt-P} = 4730$Hz). ^1H NMR (270 MHz, $CDCl_3$), 10.2 (2H, d, $J = 10$ Hz, N–H), 8.2 (2H, d, $J = 8$Hz, pyC[**6]H), 8.0–7.8 (10H, m, aromatic), 7.7–7.3 (12H, m, aromatic), 5.3 (2H, m, allyl), 5.0 (2H, m, allyl), 4.3 (2H, m, allyl), 3.2 (2H, m, allyl), 3.0 (2H, m, allyl), 2.2 (2H, m, allyl).

Table 1
Crystallographic data

	2	5	8	9 · $CHCl_3$	10	14 · $CHCl_3$	21
Formula	$C_{17}H_{14}NO_2PS$	$C_{20}H_{19}NOPSClPd$	$C_{27}H_{29}NOPSCl_2Rh$	$C_{36}H_{32}N_2OP_2S_2ClPt$	$C_{26}H_{26}N_2OPPSClPd$	$C_{32}H_{26}N_3O_2P_2Cl_3Se_2$	$C_{37}H_{35}N_2O_2P_2Cl_2Pt_2$
M	327.32	498.24	620.35	987.59	587.37	810.77	1076.7
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.617(2)	9.2350(18)	13.616(2)	12.256(1)	10.043(2)	9.617(2)	15.9450(9)
b (Å)	16.571(3)	12.097(2)	11.8190(17)	12.286(1)	10.325(2)	11.620(2)	9.0240(5)
c (Å)	9.877(2)	18.302(4)	16.918(2)	13.613(1)	13.541(3)	15.679(3)	26.5195(19)
α (°)				68.135(1)	87.629(4)	87.463(3)	
β (°)	94.111(4)	100.309(4)		77.150(1)	69.956(3)	74.728(3)	98.818(1)
γ (°)				82.407(1)	70.801(3)	82.062(4	
U (Å^3)	1570.0(6))	2011.5(7)	2722.7(7)	1851.9(3)	1241.7(4)	1673.9(6)	3770.7(4)
Z	4	4	4	2	2	2	4
ρ_{calcd} (g/cm^3)	1.385	1.632	1.513	1.771	1.571	1.609	1.897
μ (mm^{-1})	0.314	1.248	0.980	4.313	1.026	2.579	7.675
Reflections measured	7598	8199	11848	9348	6239	8493	18435
Independent reflections	2219	2780	3864	5256	3522	4727	5409
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0472, 0.1120	0.0449, 0.1114	0.0235, 0.0557	0.0309, 0.0714	0.0382, 0.0961	0.0393, 0.1223	0.0359, 0.0750

4. Crystallography

Details of the structure determination are given in Table 1. X-ray diffraction measurements were made with graphite-monochromated Mo Kα X-radiation using a Bruker SMART diffractometer. Intensity data were collected using ω/ϕ steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL). Hydrogen atoms were assigned isotropic displacement parameters and were constrained to idealised geometries. **8** gave a Flack parameter of 0.01(3). Refinements converged to residuals given in Table 1. All calculations were made with SHELXTL [15].

5. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC Nos. 243091–243097). Any request to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk) for this material should quote the full literature citation and the reference number.

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