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Investigating the effects of steric hindrance on the coordination of 2-aminothiazoyl based ligands

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Dedicated to Prof. F.G.A. Stone in recognition of his outstanding contributions to inorganic chemistry

Abstract

The ligands 2-(diphenylphosphino)aminothiazole (dppat) 2-(diphenylphosphino)amino-4-methylthiazole (Medppat) and 2-(diphenylphosphino)amino-4-*tert*-butylthiazole (Budppat) have been prepared. Reaction of these ligands with MCl_2 (COD) gives [MCl(dppat-P,N)(dppat-P)][Cl], [MCl(Medppat-P,N)(Medppat-P)][Cl], and [$PtCl_2$ (^{t}Bu-dppat-P_2], respectively. The increased bulk at the 4-position limits the formation of a P, N system in Budppat. The X-ray structure of [PtCl(Medppat-P,N)(Medppat-P)][Cl] reveals that the monodentate ligand has undergone a tautomerism upon coordination.

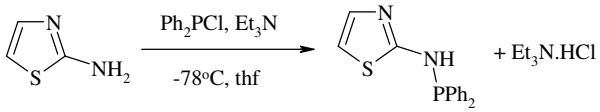
Keywords: Phosphorus; Hemilabile; Coordination; X -ray structure

1. Introduction

The study of hemilabile ligand is of continuing importance both because of the intrinsic academic interest and their potential in catalysis [1–8]. We have an ongoing interest in phosphines which are obtained by P–N bond forming reactions [9–14]. Here, we report on the synthesis and coordination of three new phosphines 2-(diphenylphosphino)aminothiazole (dppat) 2-(diphenylphosphino)amino-4-methylthiazole (Medppat)and 2-(diphenylphosphino)amino-4-*tert*-butylthiazole (Budppat). Preliminary complexation reactions indicate that whilst the parent compound and its methyl substituted congener behave as monodentate, P, and bidentate, PN, ligands when the substitutionally bulk is increased to a *tert*-butyl group bidentate coordination is blocked.

2. Results and discussion

The synthesis of dppat proceeds as we have seen for the previous phosphorus–nitrogen bond forming reactions, although the reaction was performed at −78 °C since this gave a purer product.



1 (1)

Dppat is colourless air tolerant solid which is readily soluble in chlorinated solvents, but less so in solvents such as toluene, acetone and methanol, and not at all

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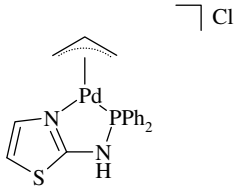
soluble in diethyl ether and hexane. The ^{31}P NMR ($CDCl_3$) of dppat displays a singlet at δ(P) 41.3 ppm whilst the ^{1}H spectrum clearly shows the presence of an amine proton at δ(H) 7.9 ppm as a broad peak, indicative of extensive hydrogen-bonding and the thiazoyl ring protons appear at δ(H) 6.7 and 6.5 ppm (doublets J_{H-H} = 4 Hz). The IR spectrum clearly shows the ν(N–H) band at 3076 cm $^{-1}$, and the expected ν(C–N) and ν(C–S) stretches at 1541 and 1150 cm^{-1}, respectively.

Reaction of dppat with elemental sulfur in toluene generated the expected sulfide of dppat; dppatS (**2**), which was recrystallised from warm toluene to give the desired product as a air stable colourless solid. The ^{31}P NMR shows a singlet at δ(P) 50.2 ppm whilst in the ^{1}H NMR of **2** the thiazoyl protons are clearly visible at δ(H) 6.4 and 6.2 ppm We reacted dppat with [$PtCl_2$(cod)] in dichloromethane to give [PtCl(dppat-P,N)(dppat-P)][Cl] (**3**). The structure was assigned from spectroscopic studies; in the ^{31}P NMR a pair of doublets is observed at δ(P) 65 ppm ($^1J_{Pt-P}$ = 4058 Hz), 23 ppm ($^1J_{Pt-P}$ = 3646 Hz), ($^2J_{P-P}$ = 11.74 Hz). The ^{1}H NMR of **3** shows a significant change in the chemical shift of the amine protons, at δ(H) 11.0 and 10.4 ppm and clearly displays the thiazoyl protons from both ligands at δ(H) 6.5, 6.0, 5.5 and 5.0 ppm. The IR spectrum of **3** has bands attributable to ν(N–H) in the 3100–2900 cm^{-1} region, whilst two peaks for ν(C–N) are found at 1577 and 1551 cm^{-1}, and the ν(C–S) bands from the thiazoyl ring are seen at 1159 and 1103 cm^{-1}. The 26 cm^{-1} difference in the ν(C–N) peaks is consistent for the chelated and non-chelated forms of the ligand. Dppat was also reacted with [$PdCl_2$(cod)] and [$PdBr_2$(cod)] to give the analogous compound [PdCl(dppat-P,N)(dppat-P)][Cl] (**4**) and [$PdBr_2$ (dppat-P,N)(dppat-P)][Br] (**5**)which displayed similar spectroscopic properties to (**3**) (see Fig. 1).

Reaction of dppat with [{Pd(μ-Cl)(η^3–C_3H_6)}$_2$] in acetonitrile could generate a mono- or a bi-dentate complex depending on the ligand's behaviour. The reaction generated a yellow solid which displays a singlet at δ(P) 84.4 ppm in the ^{31}P NMR, very close to the value seen for the chelated ligand in **5** and this together with the IR data suggests that the product of the reaction is indeed chelated being [Pd(η^3–C_3H_6)(dppat-P,N)][Cl] (**6**).



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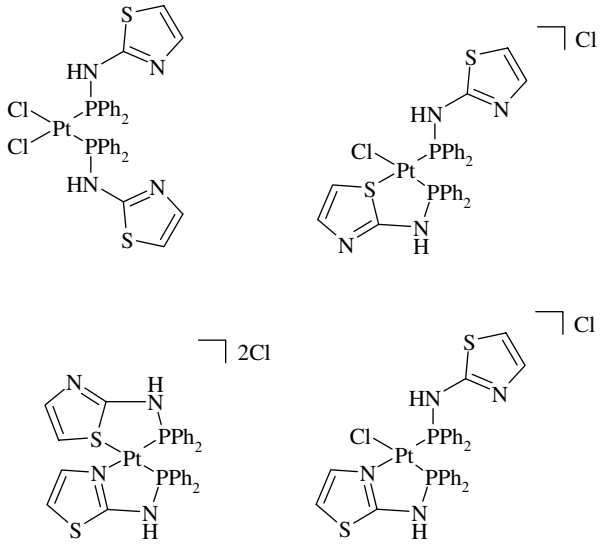
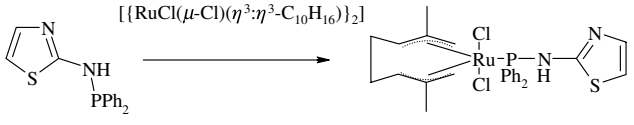


Fig. 1. The four possible isomers of [PtCl(dppat)(dppat-*P*)][Cl].

Reaction of dppat with [{RhCl(μ-Cl)(η^6–C_5H_5)}$_2$] in acetonitrile generated another chelated complex; [RhCl(η^6–C_5H_5)(dppat-P,N)][Cl] (**7**). The ^{31}P NMR shows a doublet at δ(P) 94.2 ppm ($^1J_{Rh-P}$ = 141 Hz), as was noted in the case of **6** this high shift is a first indication of dppat binding in a bidentate fashion. The ^{1}H NMR is consistent with the patterns seen in **6** with the amine proton disappearing from the spectra and the thiazoyl protons clearly visible at δ(H) 7.0 and 6.8 ppm. The IR spectrum shows the ν(C–N) at 1572 cm^{-1}, this is comparable with the data for **3**, **4** and **5** and strongly suggests a metal bound nitrogen. We also reacted dppat with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] in acetonitrile to generate the [RuCl(η^6-*p*-cymene)-(dppat-P,N)][Cl] (**8**), which spectroscopically compares well **7**.

In many previous literature examples complexes of [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(**L**)] (where **L** is a phosphorus–nitrogen ligand) generates a monodentate bound phosphorus bound ligand, due to the steric concerns based around the allyl ligand on the metal. The reaction of [RuCl(μ-Cl)($C_{10}H_{16}$)] with dppat in acetonitrile generated [$RuCl_2$ ($C_{10}H_{16}$)(dppat-P)] (**9**) as a brown solid in good yield. The ^{31}P NMR spectrum shows the expected singlet at (P) 42.5 ppm. The ^{1}H NMR clearly shows the amine proton at δ(H) 8.6 ppm as a doublet with $^2J_{P-H}$ = 15 Hz, which is similar to the values seen for monodentate behaviour in dpppa and it's derivatives.



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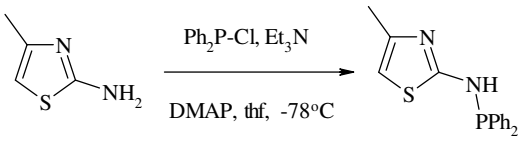
(2)

The IR spectrum shows close similarities with the monodentate complexes previously described. The ν(N–H) band is seen as a sharp peak once more at 3173 cm^{-1}, the allyl ν(C–H) stretches are seen in the range 2845–2956 cm^{-1}. The ν(C–N) and ν(C–S) stretches are clearly visible at 1519 and 1134 cm^{-1}, respectively. The X-ray structure of **9** (Fig. 2) confirms the monodentate coordination of the ligand, the bond lengths and angles are normal, though the P–N bond length is relatively short for P–N phosphines. There is an intramolecular hydrogen bond between the N–H group and one of the chloride ligands [N(2)···Cl(1) 3.02, H(2)···Cl(1) 2.20 Å, Cl(1)···H(2)–N(2) 139.9°].

The synthesis of the methyl derivative of dppat; Medppat (**10**) proceeds in a similar fashion to that of dppat itself. The major difference is that as a consequence of the extra methyl group the solubility of Medppat is greatly increased compared to dppat.



(3)

Medppat has δ(P) 40.2 ppm in the ^{31}P NMR and the ^{1}H nmr values which are as expected. MedppatS (**11**) was synthesised in toluene by addition of elemental sulfur to Medppat and recrystallisation from toluene generates a pure sample as a colourless solid.

To compare the coordination chemistry of Me-dppat to that of dppat, a series of complexes were synthesised. The reaction of Medppat with [$PtCl_2$(cod)] shows that Medppat does coordinate in much the same way as dppat, generating [PtCl(Me-dppat-P,N)(Me-dppat-P)][Cl] (**12**) with δ(P) 62.1 ppm ($^{1}J_{Pt-P}$ = 4089 Hz) and δ(P) 20.9 ppm ($^{1}J_{Pt-P}$ = 3700, $^{2}J_{P-P}$ = 9 Hz,). The IR data shows that there is no considerable difference in one of the ν(N–H) shift compared to the free ligand (3093 cm^{-1}), however a second ν(N–H) stretch located at 2790 cm^{-1} indicates either increased hydrogen-bonding in the complex, or a more dramatic shift in the amine proton, the phenomenon is more clearly understood on examination of the crystal data. The trend of two distinct ligands is continued by the shifts seen for the ν(C–N) and ν(C–S) stretches, this are seen at 1576, 1555, 1147 and 1105 cm^{-1}. The X-ray structure of **12** reveals (Fig. 3) that the amine proton on the monodentate bound ligand has shifted from the N–H spacer group to the nitrogen found in the thiazoyl ring. This effect does explain the frequencies of the ν(N–H) vibrations and the broadening seen in the ^{1}H NMR of the complexes and suggests fluxional behaviour.

We can see from Fig. 3 that the platinum is square planar. There are some significant differences between the two ligands in the complex not least because the monodentate bound ligand is deprotonated at N(7). Thus the P(1)–N(2) bond is much shorter in the mondentate ligand than for bidentate partner P(21)–N(22) similarly the C(3)–N(2) bond length is also reduced in the deprotonated ligand and there is a slight increase in the C(23)–N(27) bond length compared with C(3)–N(7).

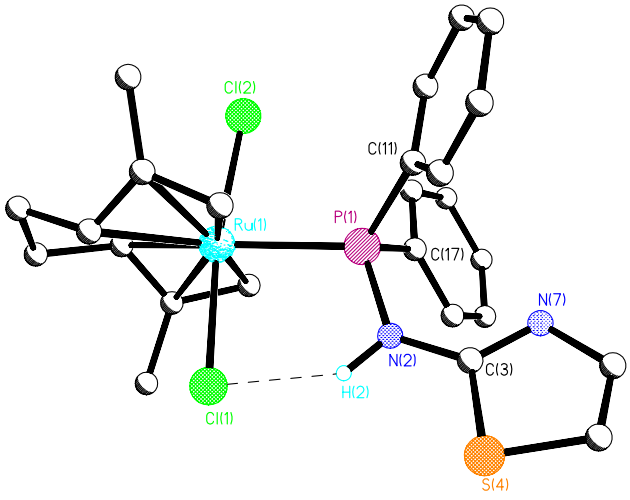


Fig. 2. Crystal Structure of [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(dppat-*P*)] (**9**), Selected bond lengths (Å) and angles (°): Ru(1)–Cl(2) 2.4117(13), Ru(1)–P(1) 2.4155(12), Ru(1)–Cl(1) 2.4450(14), P(1)–N(2) 1.684(4), N(2)–C(3) 1.379(6), Cl(2)–Ru(1)–Cl(1) 172.23(4), P(1)–Ru(1)–Cl(1) 89.19(4).

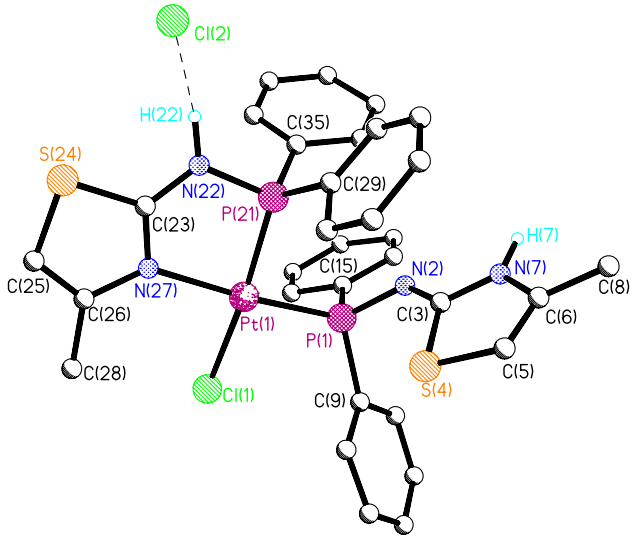
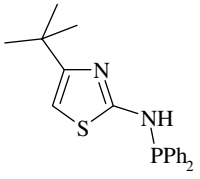


Fig. 3. Crystal Structure of [PtCl(Me-dppat-P,N)(Me-dppat-P)][Cl] (**12**). Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.256(3), Pt(1)–P(21) 2.214(3), Pt(1)–Cl(1) 2.332(3), Pt(1)–N(27) 2.141(8), P(1)–N(2), 1.616(9), P(21)–N(22), 1.674(10), N(2)–C(3), 1.292(12), N(22)–C(23), 1.333(13), P(1)–Pt(1)–P(21) 93.57(9), P(1)–Pt(1)–Cl(1) 88.26(10), P(1)–Pt(1)–N(27) 175.8(3), P(21)–Pt(1)–N(27) 85.5(3), N(27)–Pt(1)–Cl(1), 95.4(3) P(21)–Pt(1)–Cl(1) 171.50(12), Pt(1)–P(1)–N(2) 116.8(3), Pt(1)–P(21)–N(22) 101.3(4).

As with dppat, Medppat was also reacted with [$PdCl_2$(cod)] to give [PdCl(Me-dppat-P,N)(Me-dppat-P)][Cl] (**13**) as a yellow solidand with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] to give [RuCl(η^6-*p*-cymene)(Me-dppat-P,N)][Cl] (**14**) which have the expected spectroscopic properties.

To further investigate steric influence on the properties of these thiazoyl ligands we synthesised 2-diphenylphosphinoamino-5-*tert*-butylthiazoyl (Budppat) (**15**) by the same method as for dppat and Medppat. The increased solubility of Budppat made it difficult to obtain a pure sample, as recrystallisation was very difficult. Budppat gave the expected singlet δ(P) 39.7 ppm which correlates well with the values for dppat and Medppat (41.3 and 40.2 ppm, respectively).



Budppat.

The amine peak is seen as a doublet ($^2J_{P-H}$ = 7 Hz) at δ(H) 8.2 in the ^{1}H NMR spectrum of **15**, the thaizoyl proton is visible as a sharp singlet at δ(H) 6.2 ppm, and the ^{t}Bu protons are seen at δ(H) 1.2 ppm again as a sharp singlet. The IR data gave the expected resonances with bands at 3343 cm^{-1} for ν(N–H), 1524 for ν(C–N), 1098 for ν(C–S) and 996 for ν(P–N).

Reaction of Budppat with [$PtCl_2$(cod)] gave a very soluble white solid (**16**) which could only be isolated by cooling a saturated diethyl ether solution of **16** which has δ(P) 53.5 ppm [$^1J_{Pt-P}$ = 4040 Hz]. Based on the simplicity of the ^{31}P data **16** is formulated as [$PtCl_2$(^{t}Bu-dppat-P_2]. In the 1H nmr the ligand amine proton is observed as a broad singlet at δ(H) 11.2 ppm, the one remaining thiazoyl proton is also easily observed at δ(H) 5.9 as a sharp singlet which supports the proposed structure. It appears that the extra bulk provided by the ^{t}Bu group is sufficient to prevent binding by the nitrogen of the thiazoyl ring.

Further complexes of Budppat were synthesised to investigate the change in ligand behaviour. Reaction with [Pd(μ-Cl)(η^3-C_3H_6)]$_2$] generated the now expected monodentate complex [PdCl(η^3-C_3H_6)(b-dppat-P)] (**17**) with the ligand bound by the phosphorus; δ(P) 58.3 ppm and ν(C–N) 1527 cm^{-1}, which is only 2 cm^{-1} from the value seen for the free ligand, indicating monodentate coordination.

Reaction with [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] gave [$RuCl_2$ (η^6-*p*-cymene)(b-dppat-P)] (**18**), again it is a complex with the ligand mondentate bound via the phosphorus; δ(P) 62.3 ppm, ν(C–N) 1531 cm^{-1}.

The coordination chemistry of dppat and its derivatives correlates quite well. It is clear that the addition of a methyl group in the 4-position is not sufficient to prevent the chelation of the thiazoyl nitrogen. The addition of a ^{t}Bu group in the 4-position however does have an effect. In square planar complexes it is apparent that the butyl group blocks the bidentate P,N mode of coordination.

3. Experimental

All manipulations were carried out in an 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-aminothiazole, 2-amino-4-methylthiazole, 2-amino-4-*tert*-butylthiazole (Aldrich Chemical Co.) and BuLi (2.5M, 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; [MCl_2(cod)] (M = Pt or Pd; cod = cycloocta-1,5-diene) [15,16], [{MCl(μ-Cl)(Cp^*)}$_2$] (M = Rh or Ir) [17], [{Rh(μ-Cl)(cod)}$_2$] [18], [{RuCl(μ-Cl)(η^6*p*-$MeC_6H_4{}^iPr$)}$_2$] [19], [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] [20], [{PdCl(μ-Cl)(η^3-C_3H_5)}$_2$] [21].

3.1. 2-(diphenylphosphino)aminothiazole(dppat) (*1*)

Chlorodiphenylphosphine (4.23 cm^3, 24 mmol) in 30 cm^3 of thf was added dropwise to a mixture of 2-aminothiazole (2.36 g, 24 mmol) and triethylamine (3.44 cm^3, 25 mmol) in 100 cm^3 of thf at −78 °C. After addition was complete the mixture was allowed to warm to room temperature overnight. The resultant white precipitate was filtered and the filtrate reduced to dryness in vacuo. The crude product was recrystallised by cooling a concentrated chloroform solution at 4 °C overnight giving a white solid (yield: 2.5 g, 37%). $C_{15}H_{13}N_2$ SP requires: C, 63.2; H, 4.51; N, 9.86. Found: C, 62.2; H, 3.68; N, 9.32%. ν_{max}/cm^{-1}: 3076, 1541, 1492, 1432, 1150, 999. ^{31}P NMR ($CDCl_3$) δ 41.3 ppm. ^{1}H NMR ($CDCl_3$); 7.9 (1H, bs, N–H), 7.5–7.2 (10H, m, aromatic), 6.7 (1H, dd, J = 1; 4 Hz, thiazoyl), 6.5 (1H, d, J = 4 Hz, thiazoyl).

3.2. 2-(diphenylphosphino)aminothiazole sulfide (**2**)

Sulfur (23 mg, 0.7 mmol) was added to 2-(diphenylphosphino)aminothiazole (200 mg, 0.7 mmol) and the mixture refluxed in toluene (10 cm^3) for 30 min. The resulting solution was stored at 4 °C overnight generating a white solid. The product was filtered and isolated as a white solid (yield: 184 mg, 83%). $C_{15}H_{13}N_2S_2P$ requires: C, 56.9; H, 4.14; N, 8.85. Found: C, 56.8; H, 4.15; N, 8.88%. ν_{max}/cm^{-1}: 3141, 3097, 3050, 1576, 1432, 1412, 947. ^{31}P NMR ($CDCl_3$) δ 50.2 ppm. ^1H NMR ($CDCl_3$); δ 8.1–7.9 (4H, m, aromatic), 7.3–7.5 (6H, m, aromatic), 6.35 (1H, d, $J = 4$ Hz, thiazoyl), 6.2 (1H, dd, $J = 2$, 4 Hz, thiazoyl).

3.3. [PtCl(dppat-P)(dppat-P,N)][Cl] (**3**)

Dppat (301 mg, 1 mmol) and [$PtCl_2$(cod)] (200 mg, 1 mmol) were weighed into a round bottomed flask and acetonitrile (10 cm^3) added. This mixture was stirred for 2 h, and a colourless precipitate was generated. The solid was filtered and isolated as a colourless solid (yield: 333 mg, 80%). $C_{30}H_{26}N_4S_2P_2Cl_2Pt$ requires: C, 43.2; H, 3.15; N, 6.72. Found: C, 42.3; H, 2.80; N, 6.49%. ν_{max}/cm^{-1}: 3054, 2786, 1577, 1551, 1481, 1435, 1159, 1103, 998, 249. ^{31}P NMR ($CDCl_3$); δ 65.1 ($^2J_{P-P} = 14$ Hz, $^1J_{Pt-P} = 4060$ Hz), 23.9 ($^2J_{P-P} = 14$ Hz, $^1J_{Pt-P} = 3650$ Hz). ^1H NMR ($CDCl_3$) δ 11.1 (1H, bs, N–H), 10.4 (1H, s, N–H), 7.6–7.4 (4H, m, aromatic), 7.3–6.9 (16H, m, aromatic), 6.5 (1H, d, $J = 1$ Hz, thiazoyl), 6.0 (1H, d, $J = 1$ Hz, thiazoyl), 5.5 (1H, d, $J = 1$ Hz, thiazoyl), 5.0 (1H, s, thiazoyl).

3.4. [PdCl(dppat-P)(dppat-P,N)][Cl] (**4**)

Dppat (100 mg, 0.34 mmol) and [$PdCl_2$(cod)] (50 mg, 0.17 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the entire solid was dissolved, this mixture was then allowed to return to room temperature. An orange precipitate was formed during cooling and this was filtered isolating the product as an orange solid (yield: 94 mg, 74%). $C_{30}H_{26}N_4S_2P_2Cl_2Pd$ requires: C, 48.3; H, 3.52; N, 7.53. Found: C, 47.8; H, 3.05; N, 7.31%. ν_{max}/cm^{-1}: 2923, 2719, 1542, 1482, 1434, 1158, 1103, 996, 279. ^{31}P NMR ($CDCl_3$); δ 83.0 ($^2J_{P-P} = 14.1$ Hz), 50.0 ($^2J_{P-P} = 14.1$ Hz). ^1H NMR ($CDCl_3$); δ 10.3 (1H, s, N–H), 10.1 (1H, bs, N–H) 7.0–6.4 (21H, m, aromatic), 6.2 (1H, d, $J = 4$ Hz, thiazoyl), 5.7 (1H, d, $J = 4$ Hz, thiazoyl), 5.3 (1H, d, $J = 5$ Hz, thiazoyl).

3.5. [PdBr(dppat-P)(dppat-P,N)][Br] (**5**)

Dppat (76 mg, 0.27 mmol) and [$PdBr_2$(cod)] (50 mg, 0.135 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the solid was dissolved, this mixture was then allowed to return to room temperature. An orange precipitate was formed during cooling and this was filtered isolating the product as an orange solid, (yield: 73 mg, 33%). $C_{30}H_{26}N_4S_2P_2Br_2Pd$ requires: C, 43.2; H, 3.14; N, 6.71. Found: C, 43.4; H, 2.78; N, 6.72%. ν_{max}/cm^{-1}: 2938, 2799, 1570, 1542, 1483, 1433, 1156, 998, 381. ^{31}P NMR ($CDCl_3$); δ 82.0 ppm($^2J_{P-P} = 18.78$ Hz), 51.5 ppm ($^2J_{P-P} = 18.78$ Hz). ^1H NMR ($CDCl_3$); δ 10.5 (1H, s, N–H), 10.4 (1H, bs, N–H) 7.8-6.9 (21H, m, aromatic), 6.4 (1H, d, $J = 5$ Hz, thiazoyl), 6.2 (1H, d, $J = 5$ Hz, thiazoyl), 5.7 (1H, d, $J = 5$ Hz, thiazoyl).

3.6. [Pd(η^3-C_3H_6)(dppat-P,N)][Cl] (**6**)

Dppat (78 mg, 0.28 mmol) and [{Pd(μ-Cl)(η^3-C_3H_6)}$_2$] (50 mg, 0.14 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the entire solid was dissolved, this mixture was then allowed to return to room temperature. A yellow precipitate was formed during cooling and this was filtered isolating the product as a yellow solid (yield: 60 mg, 46%). $C_{18}H_{19}N_2$ SPClPd requires: C, 46.2; H, 4.10; N, 6.00. Found: C, 45.3; H, 3.27; N, 6.08%. ν_{max}/cm^{-1}: 2928, 2589, 1474, 1433, 1164, 1104, 997, 252. ^{31}P NMR ($CDCl_3$); δ 84.4 ppm. ^1H NMR ($CDCl_3$) 7.9–7.7 (4H, m, aromatic), 7.5–7.3 (6H, m, aromatic), 7.15 (1H, d, $J = 4$ Hz, thiazoyl), 6.6 (1H, dd, $J = 2$, 4 Hz, thiazoyl), 5.7 (1H, m, allyl), 4.9 (1H, bs, allyl), 3.8 (1H, bs, allyl), 3.5 (2H, bs, allyl).

3.7. [RhCl(dppat-P,N)(η-C_5Me_5)][Cl] (**7**)

Dppat (49 mg, 0.17 mmol) and [{RhCl(μ-Cl)(η-C_5Me_5)}$_2$] (53 mg, 0.17 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the entire solid was dissolved, this mixture was then allowed to return to room temperature. A red precipitate was formed during cooling and this was filtered isolating the product as a red solid (yield: 94 mg, 94%). $C_{25}H_{28}N_2SPCl_2$ Rh requires: C, 50.7; H, 4.77; N, 4.73. Found: C, 50.4; H, 4.62; N, 4.81%. ν_{max}/cm^{-1}: 3052, 2432, 1487, 1434, 1146, 1101, 998, 234. ^{31}P NMR ($CDCl_3$); δ 94.2 ($^1J_{Rh-P} = 141$ Hz). ^1H NMR ($CDCl_3$); δ 7.9 (2H, m, aromatic), 7.6–7.4 (6H, m, aromatic), 7.3–7.2 (2H, m, aromatic), 7.0 (1H, d, $J = 4$ Hz, thiazoyl), 6.8 (1H, dd, $J = 2.2$ Hz, thiazoyl), 1.55 (15H, d, $J = 3.7$ Hz, C_5Me_5).

3.8. [RuCl(p-Cymene)(dppat-P,N)][Cl] (**8**)

Dppat (56 mg, 0.19 mmol) and [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (61 mg, 0.95 mmol) were weighed into a round bottomed flask and dcm (10 cm^3) added. This mixture was stirred for 2 h, and a red precipitate was generated. The solid was filtered and isolated as a red

solid (yield: 86 mg, 77%). $C_{25}H_{27}N_2SPCl_2$ Ru requires: C, 50.8; H, 4.61; N, 4.75. Found: C, 49.8; H, 3.92; N, 4.60%. ν_{max}/cm^{-1}: 3043, 2957, 1523, 1474, 1434, 1130, 1000. ^{31}P NMR ($CDCl_3$); δ 62.7 ppm. ^1H NMR ($CDCl_3$); 8.0 (4H, m, aromatic), 7.5–7.2 (6H, m, aromatic), 6.8 (1H, bs, thiazoyl), 6.4 (1H, bs, thiazoyl), 5.3–5.1 (4H, m, *p*-Cy (aromatic)) 2.5 (1H, m, $-CMe_2$-*H*) 1.6 (3H, s, Me–H) 1.0–0.8 (6H, bs, Me–H).

*3.9. [$RuCl_2(\eta^3:\eta^3$-$C_{10}H_{16})$(dppat-P)] (**9**)*

Dppat (46 mg, 0.17 mmol) and [{RuCl(μ-Cl)($\eta^3:\eta^3$-$C_{10}H_{16}$)}$_2$] (50 mg, 0.085 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the entire solid was dissolved, this mixture was then allowed to return to room temperature. A brown precipitate was formed during cooling and this was filtered isolating the product as a brown solid (yield: 36 mg, 36 %). $C_{25}H_{29}N_2SPCl_2$ Ru requires: C, 50.4; H, 5.58; N, 4.70. Found: C, 51.2; H, 4.49; N, 4.70%. ν_{max}/cm^{-1}: 3173, 1519, 1474, 1438, 1420, 1134, 996. ^{31}P NMR ($CDCl_3$); δ 42.5 ppm. ^1H NMR ($CDCl_3$); δ 8.5 (1H, d, J = 15 Hz, N–H), 8.1–7.9 (4H, m, aromatic), 7.5–7.3 (6H, m, aromatic), 7.1 (1H, d, J = 4 Hz, thiazoyl), 6.5 (1H, d, J = 4 Hz, thiazoyl), 5.0 (2H, m, allyl), 3.7 (2H, d, J = 9 Hz, allyl), 3.4 (2H, m, allyl), 3.00 (2H, d, J = 4 Hz, allyl), 2.6 (2H, m, allyl), 2.0, (6H, s, allyl-Me).

*3.10. 2-(diphenylphosphino)amino-4-methylthiazole(Medppat) (**10**)*

Chlorodiphenylphosphine (3.93 cm^3, 22 mmol) in 40 cm^3 of thf was added dropwise to a mixture of 2-amino-4-methylthiazole (2.5 g, 22 mmol), DMAP (268 mg, 2.2 mmol) and triethylamine (3.36 cm^3, 24 mmol) in 80 cm^3 of thf at −78 °C. After addition was complete the mixture was allowed to warm to room temperature overnight. The resultant white precipitate was filtered and the filtrate reduced to dryness in vacuo over the course of five days to give the desired product (yield: 4.3 g, 69%). $C_{15}H_{13}N_2SP$ requires: C, 64.3; H, 5.07; N, 9.39. Found: C, 62.9; H, 5.31; N, 9.18%. ν_{max}/cm^{-1}: 3068, 1524, 1480, 1432, 1135, 986. ^{31}P NMR ($CDCl_3$); δ 40.2 ppm. ^1H NMR ($CDCl_3$); δ 7.5–7.2 (10H, m, aromatic), 6.1 (1H, d, J = 1 Hz, thiazoyl), 2.0 (3H, s, Me).

*3.11. 2-(diphenylphosphino)amino-4-methylthiazole sulfide (**11**)*

Sulfur (21 mg, 0.67 mmol) was added to 2-amino-4-methylthiazole (200 mg, 0.7 mmol) and the mixture refluxed in toluene (10 cm^3) for 30 min. The resulting solution was stored at 4 °C overnight generating a white solid. The product was filtered and isolated as a white solid (yield: 175 mg, 79%). $C_{16}H_{15}N_2S_2P$ requires: C, 58.2; H, 4.58; N, 8.48. Found: C, 56.8; H, 4.45; N, 8.14%. ν_{max}/cm^{-1}: 3098, 1577, 1554, 1433, 1401, 1112, 1018. ^{31}P NMR ($CDCl_3$); δ 48.2 ppm. ^1H NMR ($CDCl_3$); δ 8.1–7.9 (4H, m, aromatic), 7.5–7.2 (6H, m, aromatic), 5.7 (1H, d, J = 3 Hz, thiazoyl) 2.0 (3H, s, Me).

*3.12. [PtCl(Medppat-P)(Medppat-P,N)][Cl] (**12**)*

Me-dppat (80 mg, 0.27 mmol) and [$PtCl_2$(cod)] (50 mg, 0.135 mmol) were weighed into a round bottomed flask and acetonitrile (5 cm^3) added. This mixture was stirred for 2 h, and a colourless precipitate was generated. The solid was filtered and isolated as a colourless solid, (yield: 71 mg, 62%). $C_{32}H_{30}N_4S_2P_2Cl_2Pt$ requires: C, 44.5; H, 3.51; N, 6.49. Found: C, 44.0; H, 3.42; N, 6.42%. ν_{max}/cm^{-1}: 3093, 2790, 2551, 1576, 1555, 1480, 1437, 1147, 1105, 999. ^{31}P NMR ($CDCl_3$); δ 62.0 ($^2J_{P-P}$ = 9 Hz; $^1J_{Pt-P}$ = 4090 Hz), 20.9 ($^2J_{P-P}$ = 9 Hz; $^1J_{Pt-P}$ = 3805 Hz). ^1H NMR ($CDCl_3$); δ 7.8–7.2 (22H, m, aromatic), 6.9 (1H, bs, thiazoyl), 5.6 (1H, bs, thiazoyl), 1.6 (3H, bs, Me), 1.2 (3H, bs, Me).

*3.13. [PdCl(Medppat-P)(Mdppat-P,N)][Cl] (**13**)*

Me-dppat (104 mg, 0.35 mmol) and [$PdCl_2$(cod)] (50 mg, 0.175 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the solid was dissolved, this mixture was then allowed to return to room temperature. An orange precipitate was formed during cooling and this was filtered isolating the product as an orange solid (yield: 86 mg, 63%). $C_{32}H_{30}N_4S_2P_2Cl_2$ Pd requires: C, 49.6; H, 3.91; N, 7.24. Found: C, 48.8; H, 3.71; N, 7.07%. ν_{max}/cm^{-1}: 3085, 2914, 2570, 1574, 1551, 1477, 1434, 1101, 998. ^{31}P NMR ($CDCl_3$); δ 80.1 ($^2J_{P-P}$ = 23 Hz), 50.6 ($^2J_{P-P}$ = 23 Hz). ^1H NMR ($CDCl_3$); δ 10.5 (2H, s, N–H), 7.7-6.6 (20H, m, aromatic), 5.8 (1H, s, aromatic), 5.1 (1H, s, aromatic), 2.2 (3H, s, Me), 1.6 (3H, s, Me).

*3.14. [RuCl(p-Cymene)(Medppat-P,N)][Cl] (**14**)*

Me-dppat (68 mg, 0.23 mmol) and [{RuCl(μ-Cl)(*p*-cymene)}$_2$] (70 mg, 0.115 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the solid was dissolved, this mixture was then allowed to return to room temperature. A red precipitate was formed during cooling and this was filtered isolating the product as a red solid (yield: 97 mg, 70%). $C_{26}H_{29}N_2$ $SPCl_2$ Ru requires: C, 51.6; H, 4.84; N, 4.63. Found: C, 51.1; H, 5.21; N, 4.78%. ν_{max}/cm^{-1}: 3046, 2961, 1578, 1561, 1482, 1435, 1101, 994. ^{31}P NMR ($CDCl_3$);δ 99.9 ppm. ^1H NMR ($CDCl_3$);δ 10.2 (1H, s, N–H), 8.1–7.9 (4H, m, aromatic (ligand)), 7.6–7.1 (6H, m, aromatic (ligand)), 6.4 (1H, s, thiazoyl), 5.3–5.1 (2H, m, aromatic (*p*-cymene)), 2.3

(1H, m, –CMe_2-*H*), 1.9 (3H, s, Ar–Me), 1.0–0.7 (15H, m, Me and ^{t}Bu–H).

3.15. 2-(diphenylphosphino)amino-4-tert-butylthiazole (Budppat) (**15**)

Chlorodiphenylphosphine (2.80 cm^3, 16 mmol) in 40 cm^3 of thf was added dropwise to a mixture of 2-amino-4-*tert*-butylthiazole (2.5 g, 16 mmol), DMAP (191 mg, 1.6 mmol) and triethylamine (2.34 cm^3, 17 mmol) in 100 cm^3 of thf at −78 °C. After addition was complete the mixture was allowed to warm to room temperature overnight. The resultant white precipitate was filtered and the filtrate reduced to dryness in vacuo over the course of five days to give the desired product (yield: 3.4 g, 63%). $C_{19}H_{21}N_2SP$. ν_{max}/cm^{-1}: 3343, 2959, 1525, 1479, 1432, 1241, 1202, 1098, 996. ^{31}P NMR ($CDCl_3$); 39.7 ppm. ^{1}H NMR ($CDCl_3$); 8.2 (1H, d, $J = 7$ Hz, N–H), 7.5–7.2 (10H, m, aromatic), 6.1 (1H, s, thiazoyl), 1.2 (9H, s, ^{t}Bu–H).

3.16. [$PtCl_2$ (^{t}Budppat-P)$_2$] (**16**)

^{t}Budppat (99 mg, 0.29 mmol) and [$PtCl_2$(cod)] (54 mg, 0.145 mmol) were weighed into a round bottomed flask. Acetonitrile (5 cm^3) was added and the mixture heated until the solid was dissolved, this mixture was then allowed to return to room temperature. The solvent was removed in vacuo and diethyl ether (5 cm^3) added and the resultant solution cooled to −4 °C to generate a solid, this solid was subsequently filtered to isolate a expected colourless solid (yield: 72 mg, 53%). $C_{38}H_{42}N_4S_2P_2Cl_2Pt$ requires: C, 48.2; H, 4.46; N, 5.91. Found: C, 46.9; H, 4.55; N, 5.24%. ν_{max}/cm^{-1}: 3055, 2964, 1623, 1592, 1561, 1479, 1435, 1104, 1017, 997. ^{31}P NMR ($CDCl_3$); δ 53.9 ppm ($^1J_{Pt-P} = 4040$ Hz). ^{1}H NMR ($CDCl_3$); δ 11.2 (2H, bs, N–H), 8.0–7.1 (20H, m, aromatic), 5.9 (2H, s, thiazoyl), 1.3 (9H, s, ^{t}Bu–H).

3.17. [Pd(η-C_3H_6)(Budppat-P,N)][Cl] (**17**)

Budppat (93 mg, 0.27 mmol) and [{Pd(μ-Cl)(η-C_3H_6)}$_2$] (50 mg, 0.135 mmol) were weighed into a round bottomed flask. DCM (5 cm^3) was added and the mixture stirred for 1 h. The solvent was reduced in vacuo to approx. 1 cm^3 and the product precipitated with petroleum ether (15 cm^3), this solid was subsequently filtered to isolate a pale yellow solid (yield: 34 mg, 24%). $C_{22}H_{27}N_2$ SPClPd requires: C, 50.4; H, 5.19; N, 5.34. Found: C, 50.4; H, 5.05; N, 5.31%. ν_{max}/cm^{-1}: 3203, 2963, 1527, 1436, 1097, 955. ^{31}P NMR ($CDCl_3$); δ 58.3 ppm. ^{1}H NMR ($CDCl_3$), 7.9–7.7 (5H, m, aromatic), 7.5–7.2 (6H, m, aromatic), 6.1 (1H, s, thiazoyl), 5.5 (1H, m, allyl), 4.8 (1H, m, allyl), 3.6 (1H, m, allyl), 3.4 (1H, m, allyl), 3.0 (1H, m, allyl) 2.6 (1H, m, allyl), 1.0 (9H, s, ^{t}Bu–H).

3.18. [$RuCl_2$ (p-Cymene)(Budppat-P)] (**18**)

Budppat (78 mg, 0.23 mmol) and [{RuCl(μ-Cl)(*p*-cymene)}$_2$] (70 mg, 0.115 mmol) were weighed into a round bottomed flask. DCM (5 cm^3) was added and the mixture stirred for 1 hour. The solvent was reduced in vacuo to approx. 1 cm^3 and the product precipitated with petroleum ether (15 cm^3), this solid was subsequently filtered to isolate a red solid (yield: 83 mg, 78%). $C_{30}H_{35}N_2SPCl_2Ru$ requires: C, 54.6; H, 5.36; N, 4.25. Found: C, 53.6; H, 5.29; N, 4.28%. ν_{max}/cm^{-1}: 2690, 1532, 1435, 1100. ^{31}P NMR ($CDCl_3$); δ 62.3 ppm. ^{1}H NMR ($CDCl_3$); 8.1–8.0 (4H, m, aromatic (ligand)), 7.5–7.2 (6H, m, aromatic (ligand)), 5.9 (1H, s, thiazoyl), 5.3 (2H, m, aromatic (*p*-cymene)), 5.2 (2H, m, aromatic (*p*-cymene)), 2.5 (1H, m, –CMe_2-*H*), 1.9 (3H, s, Ar–Me), 1.0–0.7 (15H, m, Me and ^{t}Bu–H).

3.19. Crystallography

SMART diffractometer Mo Kα radiation, 293 K. Hemisphere of data. All data corrected for Lorentz, polarisation and absorption. Solution and refinement using SHELXTL [22], all non hydrogen atoms refined ansiotropically. **9** $C_{25}H_{29}Cl_2N_2PSRu$, $M = 592.50$, Triclinic $P\bar{1}$, $a = 9.2030(8)$, $b = 10.2156(8)$, $c = 17.6444(15)$ Å, $\alpha = 96.892(2)$, $\beta = 101.409(2)$, $\gamma = 114.1880(10)°$, $V = 1445.3(2)$ Å^3, $D_c = 1.361$ Mg/m^3, $\mu = 0.869$ mm^{-1}, 5182 independent reflections [$R_{int} = 0.0177$], $R1[I > 2\sigma(I)] = 0.0493$, $wR2 = 0.1298$. **12** $C_{32}H_{30}Cl_2N_4P_2PtS_2$, $M = 862.65$, orthorhombic, Pbcn, $a = 15.1534(10)$, $b = 15.1619(10)$, $c = 30.1776(19)$ Å, $V = 6933.4(8)$ Å^3, $D_c = 1.653$ Mg/m^3, $\mu = 4.443$ mm^{-1}, 6273 independent reflections 5182 [$R_{int} = 0.163$], $R1[I > 2\sigma(I)] = 0.0492$, $wR_2 = 0.0749$. Full lists of structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen atom parameters have been deposited as supplementary material, CCDC Nos. 239471, 239472 at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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