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Polyhedron 22 (2003) 1397–1405
POLYHEDRON
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Preparation and coordination chemistry of $Ph_2PNHNHpy$

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Received 6 January 2003; accepted 24 February 2003

Abstract

$Ph_2PNHNHpy$ (**1**) can be oxidised to form $Ph_2P(E)NHNHpy$ (E = O, S, Se, **2**–**4**) or reacted with appropriate metal complexes such as $[PtCl_2(cod)]$, $[PtMe_2(cod)]$, $[Pd(\mu Cl)(\eta^3\text{-}C_3H_5)]_2$, $[RhCl(cod)]_2$, $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$, $[RuCl_2(p\text{-}Cy)]_2$, $[IrCp^*Cl_2]_2$, and $[Cu(MeCN)_4][PF_6]$ to give a range of new monodentate complexes. All new compounds have been characterised by elemental analyses, NMR, IR and mass spec. The X-ray structures of $Ph_2PNHNHpy$, $Ph_2P(Se)NHNHpy$ $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(Ph_2PNHNHpy\text{-}P)]$ and $[IrCp^*Cl_2(Ph_2PNHNHpy\text{-}P)]$ are reported. Apart from monodentate P coordination all of the structures contain hydrazine based NH hydrogen bonding.

Keywords: Hydrazine; Hydrogen; Bonding; Structures

1. Introduction

Hemilabile phosphines are of interest in both homogenous catalysis and coordination chemistry [1]. Phosphorus–nitrogen containing ligands have particular use in catalysis where it is necessary for part of the ligand to dissociate to allow an organic fragment to coordinate and undergo transformation. The presence of P–N bidentate ligands enables many different and important catalytic processes to occur including asymmetric hydroboration [2], carbonylation of alkynes [3], Stille coupling [4] and asymmetric hydrogenation of highly substituted alkenes [5] to name a few. Some of these processes have had pyridyl phosphines such as 2-(diphenylphosphino)pyridine applied to them successfully [6]. Properties of this ligand have been extensively studied [1,6,7] together with related ligands containing organic spacer units which have been developed to increase the distance between the phosphorus and pyridyl nitrogen donor sites and these include $Ph_2PCH(R)py$ (where R = H [8–10], CH_2OEt [11,12], or PPh_2 [13–17]) and $Ph_2PCH_2CH_2py$ [18–26].

Relatively few examples of amino containing pyridylphosphine ligands are known despite the relative ease of formation of phosphorus–nitrogen bonds compared to phosphorus–carbon bonds. Examples include 2-(diphenylphosphinoamino)pyridine [27], 2-(phenylphosphino)-bisaminopyridine [27] and 2-(trisaminopyridyl)phosphine [27]. We have recently reported studies on 2-(diphenylphosphinoamino)pyridine [27] and demonstrated that it display three, possibly four different coordination modes. Katti et al. [28,29] reported the inclusion of phosphorus donors within the hydrazine ligand to develop new ligand systems. These ligands possess either N–N–P–N–N or P–N–N–P backbones.

In this work, we report the preparation of a new phosphine which has a hydrazine backbone and the potential to act as a hemilable ligand. Illustrative coordination complexes have been prepared.

2. Experimental

2.1. General

Unless otherwise stated, all reactions were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and thf were purified by reflux over sodium-benzophenone and dis-

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0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00115-3

tillation under nitrogen. Dichloromethane was heated to reflux over calcium hydride and distilled under nitrogen. Toluene and hexane were heated to reflux over sodium and distilled under nitrogen. The complexes $[MCl_2(cod)]$ (M = Pt or Pd; cod = cycloocta-1,5-diene), [PtMeX(cod)] (X = Cl or Me), $[Pd(\mu Cl)(\eta^3\text{-}C_3H_5)]_2$, $[RhCl(cod)]_2$, $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$, $[RuCl_2(p\text{-}Cy)]_2$, $[IrCp^*Cl_2]_2$, and $[Cu(MeCN)_4][PF_6]$ and $Ph_2PNHNHpy$ **1** were prepared as described previously [27,30]. Infrared spectra were recorded as KBr discs in the range 4000–200 cm^{-1} on a Perkin–Elmer 2000 FTIR/RAMAN spectrometer. NMR spectra were recorded on a Gemini 2000 spectrometer (operating at 121.4 MHz for ^{31}P and 300 MHz for ^{1}H). Microanalyses were performed by the St. Andrews University service and mass spectra by the Swansea Mass Spectrometer Service.

2.2. $Ph_2P(O)NHNHpy$ (**2**)

$Ph_2PNHNHpy$ (300 mg, 1 mmol) was dissolved in thf (20 cm^3). H_2O_2 (35 mg, 1 mmol) was added dropwise over 5 min to give a colourless solution. The reaction mixture was stirred at room temperature for 1 h before removing all the solvent on the vacuum line. The solid formed was dissolved in CH_2Cl_2 before reducing the volume to 0.5 cm^3 on the vacuum line. Diethyl ether (2 cm^3) was added to precipitate the product, which was isolated by filtration. Yield 203 mg, 64%. Microanalysis: Found (calculated for $C_{17}H_{16}N_3OP$) C 65.56 (66.01), H 5.42 (5.21), N 13.15 (13.59). δ_p ($CDCl_3$) 26.9 ppm. δ_H ($CDCl_3$) 8.1 (m, 5H, aromatic), 7.2–7.7 (m, 9H, aromatic), 6.7 (m, 1H, NH), 6.1 (d, 1H, $^1J\{^1H\text{–}^1H\}$ 21 Hz, NH). IR (KBr) cm^{-1} ν_{NH} 3344, ν_{NH} 3076, $\nu_{CN[py]}$ 1595, ν_{PO} 1312, ν_{PN} 997. Mass spec (EI^+): 309(M^+).

2.3. $Ph_2P(S)NHNHpy$ (**3**)

Elemental sulfur (219 mg, 0.7 mmol) and $Ph_2PNHNHpy$ (2 g, 0.7 mmol) were dissolved together under nitrogen in dry toluene (18 cm^3). The reaction mixture was sonicated to ensure that the entire solid was dissolved before heating with a heat gun. The reaction mixture was left to cool overnight with stirring, which precipitated out a solid that was isolated by filtration. Yield 1.9 g, 85%. Microanalysis: Found (calculated for $C_{17}H_{16}N_3PS$) C 62.91 (62.75), H 4.67 (4.96), N 13.12 (12.92). δ_p ($CDCl_3$) 63.8 ppm. δ_H ($CDCl_3$) 7.9–8.1 (m, 4H, aromatic), 7.4–7.55 (m, 8H, aromatic), 6.8 (d, 1H, aromatic), 6.65 (t, 1H, aromatic), 6.4 (br s, 1H, NH[py]), 5.0 (d, 1H, $^2J\{^{31}P\text{–}^1H\}$ 19 Hz, NH[P]). IR (KBr) cm^{-1} ν_{NH} 3276, ν_{NH} 3090, $\nu_{CN[py]}$ 1602, ν_{PN} 991, ν_{PS} 648. Mass spec (NOBA Marix): 348(M + Na), 325(M^+).

2.4. $Ph_2P(Se)NHNHpy$ (**4**)

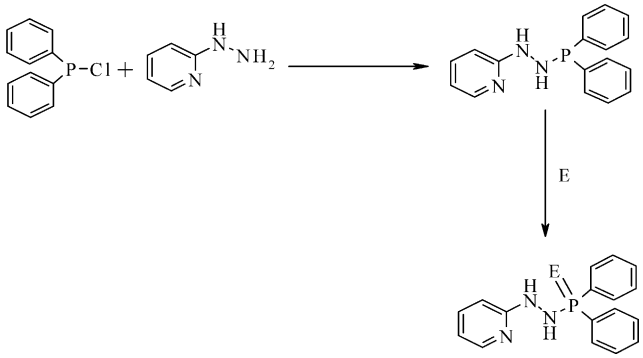
Elemental selenium (40 mg, 0.5 mmol) and $Ph_2PNHNHpy$ (150 mg, 0.5 mmol) were dissolved together under nitrogen in dry toluene (10 cm^3). The reaction mixture was heated for 4 h, and then most of the solvent was removed under reduced pressure. The remaining mixture was placed in the fridge overnight and a white powder precipitated from the solution, which was isolated by filtration. Yield 119 mg, 63%. Microanalysis: Found (calculated for $C_{17}H_{16}N_3PSe$) C 55.16 (54.85), H 4.18 (4.33), N 10.98 (11.29). δ_p ($CDCl_3$) 61 ppm $^1J\{^{31}P\text{–}^{77}Se\}$ 768 Hz. δ_H 7.9–8.1 (m, 4H, aromatic), 7.4–7.5 (m, 8H, aromatic), 6.8 (d, 1H, aromatic), 6.65 (t, 1H, aromatic), 6.5 (br s, 1H, NH[py]), 5.0 (d, 1H, $^2J\{^{31}P\text{–}^1H\}$ 19 Hz, NH[P]). IR (KBr) cm^{-1} ν_{NH} 3255, ν_{NH} 3076, $\nu_{CN[py]}$ 1601, ν_{PN} 992, ν_{PSe} 587. Mass spec (EI^+): 373(M^+) (Scheme 1).

2.5. $[PtCl_2(Ph_2PNHNHpy)_2\text{-}P]$ (**5**)

A CH_2Cl_2 (5 cm^3) solution of $[Pt(cod)Cl_2]$ (64 mg, 0.1 mmol) was added dropwise to a CH_2Cl_2 (5 cm^3) solution of $Ph_2PNHNHpy$ (100 mg, 0.3 mmol). The resulting solution was stirred for a few hours before, the white solid that formed on stirring, being isolated by filtration. Yield 104 mg, 72%. Microanalysis: Found (calculated for $C_{34}H_{32}N_6P_2Cl_2Pt$) C 48.30 (47.90), H 3.15 (3.78), N 9.88 (9.86). δ_p ($CDCl_3$) 44.0 ppm $^1J\{^{31}P\text{–}^{195}Pt\}$ 3855 Hz. δ_H ($CDCl_3$) 7.9–8.1 (m, 8H, aromatic), 7.4–7.55 (m, 16H, aromatic), 6.8 (d, 2H, aromatic), 6.65 (t, 2H, aromatic), 6.4 (br s, 2H, NH[py]), 5.0 (d, 2H, $^2J\{^{31}P\text{–}^1H\}$ 19 Hz, NH[P]). IR (KBr) cm^{-1} ν_{NH} 3143, $\nu_{CN[py]}$ 1600, ν_{PN} 997, ν_{PtCl} 307, ν_{PtCl} 288. Mass spec (NOBA Matrix): 817(M − Cl^-), 780(M − 2Cl^-).

2.6. $[PtMe_2(Ph_2PNHNHpy\text{-}P)_2\text{-}P]$ (**6**)

$Ph_2PNHNHpy$ (150 mg, 0.5 mmol) and $[PtMe_2(cod)]$ (85 mg, 0.5 mmol) were dissolved together in CH_2Cl_2 (7 cm^3) under nitrogen and stirred for 5 min. Excess



Scheme 1. Formation of $Ph_2PNHNHpy$ and $Ph_2P(E)NHNHpy$ ligands (E = O, S, Se).

hexane was added, then most of the solvent removed under reduced pressure. The solid formed was subsequently isolated by filtration. Yield 54 mg, 13%. Microanalysis: Found (calculated for $C_{36}H_{38}N_6P_2Pt$) C 53.66 (53.27), H 5.29 (4.72), N 9.90 (10.35). δ_p ($CDCl_3$) 71.2 ppm $^1J\{^{31}P-^{195}Pt\}$ 1984 Hz. IR (KBr) cm^{-1} ν_{NH} 3341, ν_{NH} 3051, $\nu_{CN[py]}$ 1598, ν_{PN} 985.

2.7. [PtMeCl (Ph$_2$PNHNHpy)$_2$-P] (7)

$Ph_2PNHNHpy$ (87 mg, 0.3 mmol) and [PtMeCl(cod)] (50 mg, 0.1 mmol) were dissolved under nitrogen in dry toluene (10 cm^3). The resulting solution was stirred vigorously for a few hours yielding a white precipitate that was isolated by filtration. Yield 98 mg, 40%. Microanalysis: Found (calculated for $C_{35}H_{35}N_6P_2ClPt$) C 51.61 (50.52), H 3.87 (4.24), N 10.17 (10.10). δ_p ($CDCl_3$) 60.4 ppm $^1J\{^{31}P-^{195}Pt\}$ 3183 Hz. δ_H ($CDCl_3$) 7.8–8.1 (m, 9H, aromatic), 7.2–7.6 (m, 16H, aromatic), 6.7 (m, 5H, NH and aromatic), 6.3 (s, 2H, NH), 0.0 (s, 3H, $^2J\{^{195}Pt-^1H\}$ 829 Hz, CH_3). IR (KBr) cm^{-1} ν_{NH} 3251, ν_{NH} 3224, $\nu_{CN[py]}$ 1600, ν_{PN} 997, ν_{PtCl} 266. Mass spec (NOBA Matrix): 796(M−Cl^-).

2.8. [PdCl(η^3-C$_3$H$_5$)(Ph$_2$PNHNHpy-P)] (8)

A CH_2Cl_2 (10 cm^3) solution of $Ph_2PNHNHpy$ (113 mg, 0.39 mmol, 2 equiv.) was added dropwise by use of a syringe pump to a CH_2Cl_2 (3 cm^3) solution of [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ (71 mg, 0.195 mmol) under nitrogen over 2.5 h with stirring. The solvent volume was removed under pressure before excess hexane was added to precipitate a beige solid after cooling overnight then isolated by filtration. Yield 92 mg, 50%. Microanalysis: Found (calculated for $C_{21}H_{21}ClN_3PPd$) C 50.28 (50.44), H 4.37 (4.44), N 8.28 (8.82). δ_p ($CDCl_3$) 66.4 ppm. δ_H ($CDCl_3$) 7.9 (m, 4H, aromatic), 7.7 (d, 1H, aromatic), 7.4 (m, 6H, aromatic), 7.1 (t, 1H, aromatic), 6.7 (d, 1H, aromatic), 6.5 (t, 1H, aromatic), 6.1 (s, 1H, NH[py]), 5.5 (d, 1H, $^2J\{^{31}P-^1H\}$ 8 Hz, NH[P]), 5.4 (t, 2H, $J\{^1H-^1H\}$ 22 Hz, CH_2), 4.7 (t, 1H, $J\{^1H-^1H\}$ 14 Hz, CH), 3.7 (t, 2H, $J\{^1H-^1H\}$ 24 Hz, CH_2). IR (KBr) cm^{-1} ν_{NH} 3202, ν_{NH} 3051, $\nu_{CN[py]}$ 1601, ν_{PN} 997, ν_{PdCl} 285. Mass spec (NOBA Matrix): 440(M−Cl^-).

2.9. [Rh(C$_8$H$_{12}$)Cl Ph$_2$PNHNHpy-P] (9)

A toluene (5 cm^3) solution of [Rh(cod)Cl]$_2$ (84 mg, 0.2 mmol) was added dropwise to a toluene solution of $Ph_2PNHNHpy$ (100 mg, 0.3 mmol) under nitrogen. The resulting solution was stirred for 10 min before the solvent volume was reduced and hexane added to precipitate a brown solid that was isolated by filtration. Yield 126 mg, 68%. Microanalysis: Found (calculated for $C_{25}H_{28}PClN_3Rh\cdot(CH_2Cl_2)_{0.5}$) C 52.51 (52.50), H 4.57 (5.02), N 7.90 (7.22). δ_p ($CDCl_3$) 71.0 ppm, d, $^1J\{^{31}P-^{103}Rh\}$ 156 Hz. δ_H ($CDCl_3$) 7.9 (d, 1H, pyC[6]H), 7.1–7.6 (m, 12H, aromatic), 6.7 (d, 1H, aromatic), 6.5 (t, 1H, aromatic), 6.1 (s, 1H, NH[py]), 4.5 (d, 1H, $^2J\{^{31}P-^1H\}$ 12 Hz, NH[P]), 4.0 (br s, 4H, C_8H_{12}), 2.3 (m, 4H, C_8H_{12}), 1.7 (m, 4H, C_8H_{12}). IR (KBr) cm^{-1} ν_{NH} 3206, $\nu_{CN[py]}$ 1597, ν_{PN} 996, ν_{RhCl} 250. Mass spec (NOBA Matrix): 540(M+H), 504 (M−Cl^-).

2.10. [RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)Ph$_2$PNHNHpy-P] (10)

$Ph_2PNHNHpy$ (50 mg, 0.1 mmol) and [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)]$_2$ (52 mg, 0.08 mmol) were dissolved under nitrogen in dry toluene (10 cm^3). The resulting solution was stirred for an hour before reducing the solvent volume to 2 cm^3. Diethyl ether was added to form a precipitate, which redissolved on the addition of excess ether. The solvent was reduced before hexane was added drop wise to form an orange/yellow precipitate that was then isolated by filtration. Yield 43 mg, 42%. Microanalysis: Found (calculated for $C_{27}H_{32}N_3PCl_2Ru$) C 54.51 (53.90), H 5.42 (5.37), N 6.98 (6.99). δ_p ($CDCl_3$) 69.5 ppm. δ_H ($CDCl_3$) 7.9–8.1 (m, 4H, aromatic), 7.4–7.55 (m, 8H, aromatic), 6.8 (d, 1H, aromatic), 6.65 (t, 1H, aromatic), 6.4 (br s, 1H, NH[py]), 5.0 (d, 1H, $^2J\{^{31}P-^1H\}$ 19 Hz, NH[P]), 5.2 (br m, 2H, CH_c), 4.3 (d, 2H, $J\{^1H-^{31}P\}$ 8.8 Hz, CH_a), 3.4 (m, 2H, CH_b), 3.2 (d, 2H, $J\{^1H-^{31}P\}$ 3.3 Hz, CH), 2.7 (m, 2H, CH_2), 2.2 (s, 6H, CH_3). IR (KBr) cm^{-1} ν_{NH} 3279, $\nu_{CN[py]}$ 1596, ν_{PN} 984, ν_{RuCl} 305, ν_{RuCl} 245. Mass spec (NOBA Matrix): 624(M+Na), 602(M+H).

2.11. [RuCl$_2$(p-Cy)Ph$_2$PNHNHpy-P] (11)

$Ph_2PNHNHpy$ (200 mg, 0.7 mmol) and [Ru(*p*-Cy)Cl_2]$_2$ were dissolved under nitrogen in dry CH_2Cl_2 (10 cm^3). The resulting red/orange solution was stirred for 15 min before the solvent was reduced to 2 cm^3. Hexane was added to precipitate an orange solid that was isolated by filtration. Yield 330 mg, 81%. Microanalysis: Found (calculated for $C_{27}H_{30}N_3PCl_2Ru$) C 54.17 (54.08), H 4.21 (5.05), N 6.96 (7.01). δ_p ($CDCl_3$) 72.7 ppm. δ_H ($CDCl_3$) 7.9 (m, 4H, aromatic), 7.7 (d, 1H, aromatic), 7.4 (m, 6H, aromatic), 7.1 (t, 1H, aromatic), 6.7 (d, 1H, aromatic), 6.5 (t, 1H, aromatic), 6.1 (s, 1H, NH[py]), 5.4 (d, 1H, $^2J\{^{31}P-^1H\}$ 12 Hz, NH[P]), 5.3 (d, 2H, $^1J\{^1H$-$^1H\}$ 2 Hz, cymene), 5.2 (d, 2H, $^1J\{^1H-^1H\}$ 6 Hz, cymene), 2.5 (m, 1H, ArCH), 1.9 (s, 3H, $ArCH_3$), 0.9 (d, 6H, $ArCH_3$). IR (KBr) cm^{-1} ν_{NH} 3332, ν_{NH} 3296, $\nu_{CN[py]}$ 1597, ν_{PN} 987, ν_{RuCl} 294. Mass spec (NOBA Matrix): 622(M+Na), 600(M+H), 564(M−Cl^-), 528(M−2Cl^-).

2.12. [IrCp*Cl$_2$(Ph$_2$PNHNHpy-P)] (12)

A CH_2Cl_2 (10 cm^3) solution of $Ph_2PNHNHpy$ (78 mg, 0.26 mmol) was added dropwise by a syringe pump

to a CH_2Cl_2 (3 cm^3) solution of $[Cp^*IrCl_2]_2$ (105 mg, 0.13 mmol) under nitrogen over 2 h with stirring. The solvent was reduced under pressure before excess hexane was added to precipitate an orange solid after cooling overnight that was isolated by filtration. Yield 157 mg, 86%. Microanalysis: Found (calculated for $C_{27}H_{33}Cl_2N_3Pir$) C 46.60 (46.75), H 4.45 (4.80), N 5.74 (6.06). δ_p ($CDCl_3$) 45.0 ppm. δ_H ($CDCl_3$) 7.9 (m, 4H, aromatic), 7.8 (d, 1H, aromatic), 7.4 (m, 6H, aromatic), 7.15 (t, 1H, aromatic), 6.6 (d, 1H, aromatic), 6.4 (t, 1H, aromatic), 6.05 (s, br, 1H, NH), 5.8 (d, 1H, $J\{^{31}P-^{1}H\}$ 33.1 Hz, NH[P]), 1.4 (d, 15H). IR (KBr) cm^{-1} ν_{NH} 3318, ν_{NH} 3057, $\nu_{CN[py]}$ 1598, ν_{PN} 987, ν_{IrCl} 285. Mass spec (NOBA Matrix): 692(M^+), 656($M-Cl^-$), 619($M-2Cl^-$).

2.13. [Cu (Ph2PNHNHpy-P,N)2][PF6] (13)

$Ph_2PNHNHpy$ (200 mg, 0.6 mmol) and $[Cu(MeCN)_4][PF_6]$ (127 mg, 0.3 mmol) were dissolved under nitrogen in dry CH_2Cl_2 (5 cm^3). The resulting solution was stirred for about 10 min before the solvent volume was reduced on the vacuum line to 2 cm^3. Dry diethyl ether (8 cm^3) was added to yield a creamy white precipitate, which was isolated by filtration and washed with excess ether then dried on the vacuum line. Yield 193 mg, 71%. Microanalysis: Found (calculated for $C_{34}H_{32}N_6P_3F_6Cu$) C 51.04 (51.36), H 4.05 (4.06), N 10.86 (10.57). IR (KBr) cm^{-1} ν_{NH} 3291, $\nu_{CN[py]}$ 1614, ν_{PN} 999. Mass spec (NOBA Matrix): 649($M-PF_6^-$).

2.14. [Rh(C8H12) Ph2P(S)NHNHpy-S,N][Cl] (14)

$Ph_2P(S)NHNHpy$ (200 mg, 0.6 mmol) was dissolved under nitrogen in dry toluene (8 cm^3). $[Rh(cod)Cl]_2$ (152 mg, 0.3 mmol) was dissolved in dry toluene (5 cm^3) under nitrogen. The rhodium complex solution was added drop wise over about 10 min with stirring. The reaction mixture was then stirred for 20 min at room temperature, to yield a yellow precipitate that was isolated by filtration, washed with ether and dried on the vacuum line. Yield 274 mg, 79%. Microanalysis: Found (calculated for $C_{25}H_{30}N_3PSRhCl$) C 53.08 (52.50), H 4.73 (4.93), N 7.28 (7.35). δ_p ($CDCl_3$) 64.3 ppm. δ_H ($CDCl_3$) 7.9–8.1 (m, 4H, aromatic), 7.4–7.55 (m, 8H, aromatic), 6.8 (d, 1H, aromatic), 6.65 (t, 1H, aromatic), 6.4 (br s, 1H, NH[py]), 5.0 (d, 1H, $^2J\{^{31}P-^{1}H\}$ 19 Hz, NH[P]), 4.0 (br s, 4H, C_8H_{12}), 2.3 (m, 4H, C_8H_{12}), 1.7 (m, 4H, C_8H_{12}). IR (KBr) cm^{-1} ν_{NH} 3163, $\nu_{CN[py]}$ 1611, ν_{PN} 998, ν_{PS} 640. Mass spec (NOBA Matrix): 536($M-Cl^-$).

2.15. [Ru (p-Cy)Ph2P(S)NHNHpy-S,N][Cl2] (15)

$Ph_2P(S)NHNHpy$ (200 mg, 0.6 mmol) and $[RuCl_2(p\text{-}Cy)]_2$ (188 mg, 0.3 mmol) were dissolved together under nitrogen in dry CH_2Cl_2 (10 cm^3). The resulting dark orange solution was stirred for 20 min before removing the solvent on the vacuum line. Dry hexane (2 cm^3) was added to precipitate a dark brown solid, which was isolated by filtration. Yield 310 mg, 80%. Microanalysis: Found (calculated for $C_{27}H_{30}N_3PSCl_2Ru$) C 50.88 (51.34), H 4.41 (4.79), N 6.46 (6.66). δ_p ($CDCl_3$) 81.1 ppm. IR (KBr) cm^{-1} ν_{NH} 3448, ν_{NH} 3178, $\nu_{CN[py]}$ 1611, ν_{PN} 995, ν_{PS} 635. Mass spec (NOBA Matrix): 559($M-Cl_2$).

2.16. [Cu (Ph2P(S)NHNHpy-S,N)2][PF6] (16)

$Ph_2P(S)NHNHpy$ (200 mg, 0.6 mmol) and $[Cu(MeCN)_4][PF_6]$ (115 mg, 0.3 mmol) were dissolved together under nitrogen in dry CH_2Cl_2 (20 cm^3). The resulting dark green solution was stirred for 2 h before the volume of solvent present was reduced to about 2 cm^3. Dry diethyl ether (15 cm^3) was added to yield a precipitate that was isolated by filtration to yield a green/blue solid. Yield 204 mg, 77%. Microanalysis: Found (calculated for $C_{34}H_{32}P_3N_6S_2F_6Cu$) C 47.30 (47.55), H 3.66 (3.76), N 9.70 (9.79). δ_p ($CDCl_3$) 65.9 ppm. δ_H (CD_2Cl_2) 7.9–8.1 (m, 8H, aromatic), 7.4–7.55 (m, 16H, aromatic), 6.8 (d, 2H, aromatic), 6.65 (t, 2H, aromatic), 5.0 (d, 2H, $^2J\{^{31}P-^{1}H\}$ 19 Hz, NH[P]). IR (KBr) cm^{-1} ν_{NH} 3262, $\nu_{CN[py]}$ 1611, ν_{PN} 997, ν_{PS} 622. Mass spec (NOBA Matrix): 713($M-PF_6^-$).

2.17. Crystallography

X-ray diffraction studies were performed at 293 K using a Rigaku AFC7S with Cu Kα radiation [compound **1**] or a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation. The structures were solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealised, the NH protons were located by a ΔF map. Structural refinements were by the full-matrix least-squares method on F [compound **1**, TeXsan [31]] or F^2 using SHELXTL [32]. Details of the data collections are summarised in Table 1.

3. Results and discussion

Reaction of 2-hydrazinopyridine with 1 equiv. of Ph_2PCl in the presence of NEt_3, proceeds in thf to give **1** which was isolated (50% yield) by filtration from the $Et_3NH^+Cl^-$ as a white crystalline solid upon recrystallisation from chloroform. The $^{31}P\{^{1}H\}$ NMR spectrum of **1** consists of a singlet at δ_p 49.6 ppm. In the IR spectrum two bands are observed at 3313 and 3200 cm^{-1} which are assigned to the two ν_{NH} vibrations whilst the $\nu_{CN[py]}$ and ν_{PN} vibrations are observed at

Table 1
Details of the X-ray data collections and refinements

	1	4	10	12
Empirical formula	$C_{17}H_{16}N_3P$	$C_{17}H_{16}N_3PSe$	$C_{28}H_{33}Cl_5N_3PRu$	$C_{27}H_{31}Cl_2IrN_3P$
M	293.31	372.26	720.86	691.62
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	5.592(4)	15.7931(19)	8.9712(2)	13.2992(3)
b (Å)	17.947(6)	11.8898(14)	13.5564(7)	14.4656(3)
c (Å)	15.139(3)	9.3268(11)	13.6359(7)	16.7774(4)
α (°)	90	90	106.947(2)	71.7020(10)
β (°)	97.81(3)	98.024(3)	103.608(2)	83.7060(10)
γ (°)	90	90	93.094(3)	64.4440(10)
U (Å^3)	1505.3(9)	1734.2(4)	1528.36(12)	2763.38(11)
Z	4	4	2	4
μ (mm^{-1})	1.579	2.257	1.026	5.103
Reflections measured	2605	7237	7628	13884
Independent reflections	2339	2439	4303	7819
Final R_1, $wR_2[I > 2\sigma(I)]$	0.070, 0.057	0.0553, 0.1283	0.0676, 0.1129	0.0269, 0.0460

1602 and 989 cm^{-1}, respectively. The FAB mass spectrum gave the expected parent ion and fragmentation pattern and microanalysis gave satisfactory results. In the solid state structure (Fig. 1) the N(14)–C(13)–N(2)–N(1) backbone of this ligand is almost planar, with the phosphorus being above this plane by 1.65 Å. **1** forms an infinite chain of hydrogen bonded dimer pairs in the solid state, via the interaction of the hydrazine N–H groups with the pyridyl N on adjacent molecules [N(14)···N(2A) separation 2.99 Å, the N(14)···H(2n) 1.89 Å, N(2)–H(2n)···N(14) 159.5°]. A second weaker hydrogen bond from the other N–H group links these dimers together to form infinite chains [N(14B)···N(1) 3.33 Å, N(14B)···H(1n) distance of 2.29 Å, N(1)–H(1n)···N(14B) of 153°].

The oxide (**2**) $Ph_2P(O)NHNHpy$ was easily prepared by the addition of excess aqueous hydrogen peroxide to **1** in thf whilst the sulfur (**3**) and seleno (**4**) analogues were prepared by the addition of elemental S or Se to the ligand in toluene. Satisfactory microanalyses were obtained for **3** and **4** though **2** proved difficult to purify completely [this may be due to overoxidation] and the EI$^+$ mass spectral data gave the expected parent ion and fragmentation patterns. $^{31}P\{^1H\}$ NMR show single resonances ($CDCl_3$) at δ_P 26.9 and 63.8 ppm for the oxide and the sulfide, respectively. The selenide analogue exhibits a single $^{31}P\{^1H\}$ NMR resonance ($CDCl_3$) at δ_P 61.0 ppm with selenium satellites $^1J(^{31}P-^{77}Se)$ 768 Hz which is typical for a P=Se group (Table 2). In the solid state the sulfur and selenide analogues are isomorphous; the Se compound **4** is reported since this behaved better crystallographically. The P–N bond in **4** is significantly shorter than that in **1**. The N(14)–C(13)–N(2)–N(1) backbone is planar, and the phosphorus is not as far out of plane in **4** [1.18 Å] as is the case in **1**. The hydrogen-bonding motif observed here is considerably different to that of **1**. There are two types of H bond N–N···N and N–H···Se to give an infinite chain. [N(1)···N(14A) 2.94, H(1n)···N(14) 1.99 Å, N(1)–H(1n)···N(14) 163°; N(2)···Se(1B) 3.75, H(2N)···Se(1B) 2.78 Å N(2)–H(2N)···Se(1B) 169°] (Fig. 2).

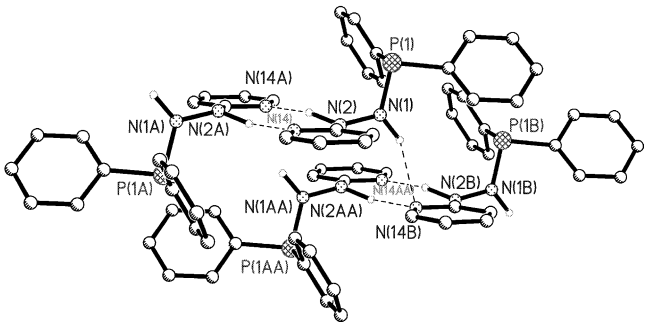


Fig. 1. The X-ray structure of $Ph_2PNHNHpy$ (**1**).

3.1. Coordination chemistry of $Ph_2PNHNHpy$

Reaction of $[PtCl_2(cod)]$ with $Ph_2PNHNHpy$ gives $[PtCl_2(Ph_2PNHNHpy)_2$-*P*] (**5**) in good yield (72%), however, there was no evidence of *P*,*N* chelate formation. The FAB mass spectrum of **5** contains the expected parent ion and fragmentation pattern and the complex displays a single resonance with platinum satellites in the $^{31}P\{^1H\}$ NMR spectrum (δ_p 44.0 ppm, $^1J\{^{31}P-^{195}Pt\}$ 3855 Hz), which indicates the presence of Cl^- *trans* to P. The IR spectrum has ν_{NH} at 3143 cm^{-1}, $\nu_{CN[py]}$ and ν_{PN} at 1600 and 997 cm^{-1}, respectively and two ν_{PtCl} bands at 307 and 288 cm^{-1} which support the *cis* geometry (Table 3).

Reaction of $[PtMe_2(cod)]$ with 2 equiv. of $Ph_2PNHNHpy$ gives $[PtMe_2(Ph_2PNHNHpy)_2$-*P*] (**6**) (δ_p 71 ppm, $^1J\{^{31}P-^{195}Pt\}$ 1985 Hz). IR spectral analysis showed that the pyridyl N is not bound in

Table 2
Characterisation data for $Ph_2PNHNHpy$ and its derivatives

Compound	$^{31}P\{^1H\}$ NMR	IR (cm^{-1})					Microanalysis/% Found (calc.)		
	δ_p (ppm)	ν_{PN}	ν_{NH}	ν_{NH}	$\nu_{CN[py]}$	ν_{MCl}	C	H	N
$Ph_2PNHNHpy$ (**1**)	49.6	989	3313	3200	1602	–	69.09 (69.60)	5.29 (5.50)	14.01 (14.33)
$Ph_2P(O)NHNHpy$ (**2**)	26.9	997	3344	3076	1595	1312	65.56 (66.01)	5.42 (5.21)	13.15 (13.59)
$Ph_2P(S)NHNHpy$ (**3**)	63.8	991	3276	3090	1602	648	62.91 (62.75)	4.67 (4.96)	13.12 (12.92)
$Ph_2P(Se)NHNHpy$ (**4**) [a]	61.0 [a]	992	3255	3076	1601	587	55.16 (54.85)	4.18 (4.33)	10.98 (11.29)
$[PtCl_2(Ph_2PNHNHpy\text{-}P)_2]$ (**5**)	44.0 [b]	997	–	3143	1600	307, 288	48.30 (47.90)	3.15 (3.78)	9.88 (9.86)
$[PtMe_2(Ph_2PnHNHpy\text{-}P)_2]$ (**6**)	71.2 [c]	985	3341	3051	1598	–	53.66 (53.27)	5.29 (4.72)	9.90 (10.35)
$[PtClMe(Ph_2PnHNHpy\text{-}P)_2]$ (**7**)	60.4 [d]	997	3251	3224	1600	266	51.61 (50.52)	3.87 (4.24)	10.17 (10.10)
$[PdCl(\eta^3\text{-}(C_3H_5)\ (Ph_2PNHNHpy\text{-}P)]$ (**8**)	66.4	997	3202	3051	1601	285	50.28 (50.44)	4.37 (4.44)	8.28 (8.82)
$[Rh(C_8H_{12})Cl(Ph_2PNHNHpy\text{-}P)]\cdot(CH_2Cl_2)_{0.5}$ (**9**)	71.0 [e]	996	3206	–	1597	250	52.51 (52.50)	4.57 (5.02)	7.90 (7.22)
$[RuCl_2(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\ (Ph_2PNHNHpy\text{-}P)]$ (**10**)	69.5	984	3279	–	1596	305, 245	54.51 (53.90)	5.42 (5.37)	6.98 (6.99)
$[RuCl_2(p\text{-Cy})\ (Ph_2PNHNHpy\text{-}P)]$ (**11**)	72.7	987	3332	3296	1597	294	54.17 (54.08)	4.21 (5.05)	6.96 (7.01)
$[IrCp^*Cl_2(Ph_2PnHNHpy\text{-}P)]$ (**12**)	45.0	987	3318	3057	1598	285	46.60 (46.75)	4.45 (4.80)	5.74 (6.06)
$[Cu(Ph_2PNHNHpy\text{-}P,N)_2][PF_6]$ (**13**)	–	999	3291	–	1614	–	51.04 (51.36)	4.05 (4.06)	10.86 (10.57)
$[Rh(cod)(Ph_2P(S)NhNHpy\text{-}S,N)][Cl]$ (**14**)	64.3	998	–	3168	1611	640	53.08 (52.50)	4.73 (4.93)	7.28 (7.35)
$[Ru(p\text{-Cy})(Ph_2P(S)NHNHpy\text{-}S,N][Cl_2]$ (**15**)	81.1	995	3448	3178	1611	635	50.88 (51.34)	4.41 (4.79)	6.46 (6.66)
$[Cu(Ph_2P(S)NhNHpy\text{-}S,N][PF_6]$ (**16**)	65.9	997	–	3262	1611	622	47.30 (47.55)	3.66 (3.76)	9.70 (9.79)

[a] $^1J\{^{31}P\text{–}^{77}Se\}$ 768 Hz.
[b] $^1J\{^{31}P\text{–}^{195}Pt\}$ 3855 Hz.
[c] $^1J\{^{31}P\text{–}^{195}Pt\}$ 1984 Hz.
[d] $^1J\{^{31}P\text{–}^{195}Pt\}$ 3183 Hz.
[e] $^1J\{^{31}P\text{–}^{103}Rh\}$ 156 Hz.

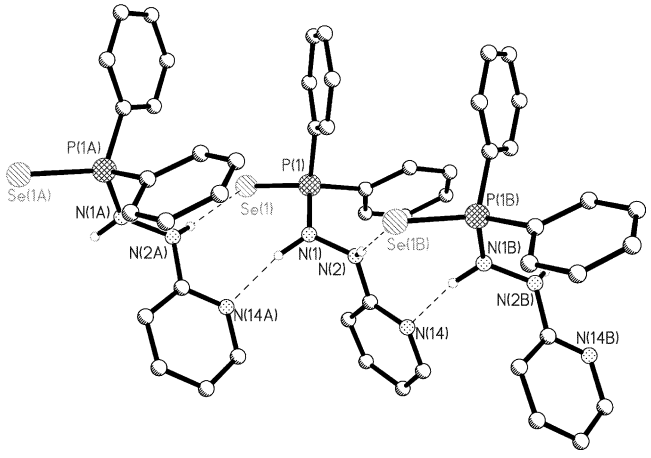
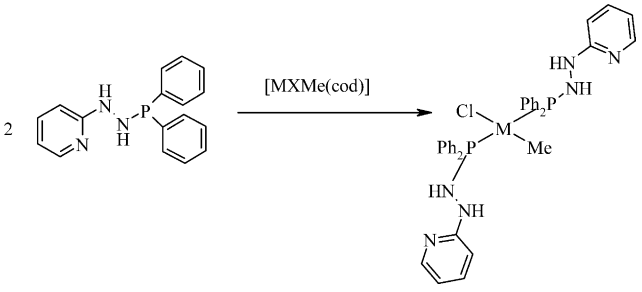


Fig. 2. The X-ray structure of $Ph_2P(Se)NHNHpy$ (**4**).

this complex as $\nu_{CN[py]}$ is observed at 1598 cm^{-1}. $[PtMeCl(Ph_2PNHNHpy)_2\text{-}P]$ (**7**) was prepared in a similar manner (Eq. 1). The complex was isolated by filtration in a yield of 40% and its microanalyses gave satisfactory results for the bis(phosphine) species formed. The FAB mass spectrum contains $M-Cl^-$ at 796 whilst $^{31}P\{^1H\}$ NMR spectroscopy revealed a single sharp resonance with platinum satellites, (δ_p 60.4 ppm, $^1J\{^{31}P\text{–}^{195}Pt\}$ 3183 Hz), indicating the two phosphorus atoms are *trans* to each other. The IR bands observed at 3251, 3224, 1600, 997 and 266 cm^{-1} represent ν_{NH}, ν_{NH}, $\nu_{CN[py]}$, ν_{PN} and ν_{PtCl}, respectively.

The reaction of $Ph_2PNHNHpy$ with $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ gave the expected product $[PdCl(\eta^3\text{-}C_3H_5)(Ph_2PNHNHpy)_2\text{-}P]$ (**8**). The ^{31}P NMR ($CDCl_3$) showed a single broad peak at 66.4 ppm, indicating that the complex is fluxional. The IR spectrum was again useful in determining the coordination of the ligand around the Pd centre. The peak observed at 1601 cm^{-1} indicating the pyridyl N is not bound to the metal centre and the Pd–Cl stretch was observed at 280 cm^{-1}.



(1)

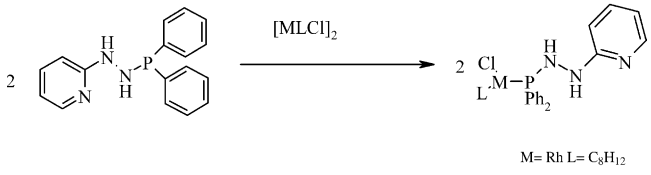
Upon slow addition of $[RhCl(cod)]_2$ to $Ph_2PNHNHpy$, $[Rh(cod)Cl(Ph_2PNHNHpy\text{-}P)]$ (**9**) was obtained in a yield of 68%. Microanalysis gave only fairly satisfactory results though the $^{31}P\{^1H\}$ NMR ($CDCl_3$) displayed the expected peak at δ_p 71.0 ppm with a coupling constant of $^1J\{^{31}P\text{–}^{103}Rh\}$ of 156 Hz. FAB mass spectral analysis gave the expected parent ion and fragmentation pattern and the IR spectrum showed bands at 3206, 996 and 250 cm^{-1} which are assigned as ν_{NH}, ν_{PN} and ν_{RhCl} vibrations, respectively. The presence of the $\nu_{CN[py]}$ at 1597 cm^{-1} was found is indicative of a non-chelated complex. However, upon further analysis of the NMR and IR spectra we believe that the complex formed was fluxionally chelated due to the

Table 3
Selected bond lengths (Å) and angles (°) for $Ph_2PNHNHpy$ and $Ph_2P(Se)NHNHpy$

Selected bond lengths (Å) and angles (°)	1	4
Bond lenghts		
P(1)–N(1)	1.709(7)	1.656(5)
Se(1)–P(1)	–	2.1145(15)
N(14)–C(13)	1.356(9)	1.332(7)
P(1)–C(7)	1.842(8)	1.797(5)
P(1)–C(1)	1.821(8)	1.814(6)
N(2)–C(13)	1.346(9)	1.390(7)
N(1)–N(2)	1.411(8)	1.410(6)
Bond angles		
N(1)–P(1)–C(1)	98.5(4)	106.5(3)
C(1)–P(1)–C(7)	100.1(4)	105.4(3)
N(1)–N(2)–C(13)	118.9(7)	118.0(5)
N(2)–C(13)–C(18)	125.1(8)	122.7(5)
N(1)–P(1)–C(7)	104.5(4)	108.7(3)
P(1)–N(1)–N(2)	117.8(5)	120.7(4)
N(2)–C(13)–N(14)	113.7(7)	114.2(5)
N(14)–C(13)–C(18)	121.2(8)	123.2(6)
C(7)–P(1)–Se(1)	–	112.45(18)
N(1)–P(1)–Se(1)	–	109.18(18)
C(1)–P(1)–Se(1)	–	114.2(2)

existence of broad peaks in the $^{31}P\{^1H\}$ spectrum. Also in the IR spectrum there appeared to be a shoulder at 1610 cm^{-1} which also indicated that this complex was fluxionally chelated.

Reaction of $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})]_2$ with $Ph_2PNHNHpy$ gives $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(Ph_2PNHNHpy\text{-}P)]$ (**10**) in 42% yield (Table 4). The IR spectrum showed



(2)

characteristic bands of ν_{NH}, $\nu_{CN[py]}$ and ν_{PN} at 3279, 1596 and 984 cm^{-1}, respectively with bands at 305 and 245 cm^{-1} corresponding to the presence of ν_{RuCl} vibrations. A single resonance was observed in the $^{31}P\{^1H\}$ NMR spectrum at δ_p 69.5 ppm. Microanalysis and FAB mass spectral data gave satisfactory results for the suggested structure. In the solid state the compound exhibits monodentate coordination, there is an intramolecular N–H···Cl H-bond [N(1)···Cl(1) 3.75, H(1N)···Cl(1) 2.99 Å N–H···Cl 135°] (Fig. 3).

Table 4
Selected bond length (Å) and angles (°) for $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(Ph_2PNHNHpy\text{-}P)]$ and $[IrCp^*Cl_2(Ph_2PNHNHpy\text{-}P)]$

Selected bond lengths (Å) and angles (°)	10	12
Bond lengths		
M(1)–Cl(1)	2.458(3)	2.4009(15)
M(1)–Cl(2)	2.422(3)	2.4284(14)
M(1)–P(1)	2.432(3)	2.2928(13)
Average M(1)–C(L)	2.25	2.19
P(1)–N(1)	1.698(8)	1.660(4)
N(14)–C(13)	1.352(13)	1.355(6)
N(2)–C(13)	1.379(14)	1.362(7)
N(1)–N(2)	1.406(11)	1.404(5)
Bond angles		
P(1)–M(1)–Cl(2)	80.71(10)	88.48(5)
Cl(1)–M(1)–Cl(2)	170.07(11)	88.43(5)
N(1)–P(1)–M(1)	108.3(4)	108.27(16)
N(2)–N(1)–P(1)	119.2(8)	122.4(3)
N(14)–C(13)–N(2)	113.3(11)	113.6(5)
C(13)–N(2)–N(1)	118.2(10)	118.9(5)
Cl(1)–M(1)–P(1)	82.40(8)	88.71(5)

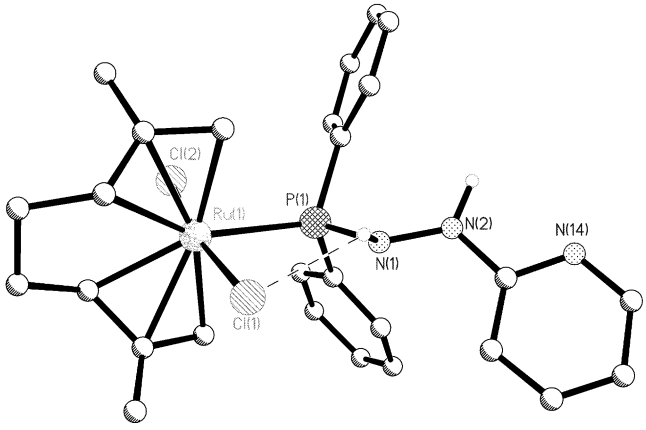
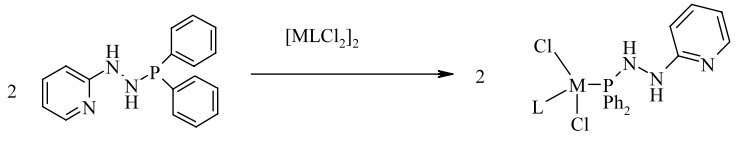


Fig. 3. The X-ray structure of $[RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})Ph_2PNHNHpy\text{-}P]$ (**10**).

We also prepared $[IrCp^*Cl_2(Ph_2PNHNHpy\text{-}P]$ (**12**). In the solid state the X-ray structure contains two independent molecules [the second molecule is numbered by addition of 30 to all atom labels]. The bond lengths and the hydrogen bonding is the same for each independent molecule. The both display a intramolecular H···Cl [N(1)···Cl(1) 3.15, H(1N)···Cl(1) 2.64 Å N–H···Cl 112°] and intermolecular NH···N to form dimer pairs [N(2)···N(14A) 3.09, H(2N)···N(14A) 2.11 Å N(2)–H(2N)···N(14A) 179°] (Fig. 4).



(3)

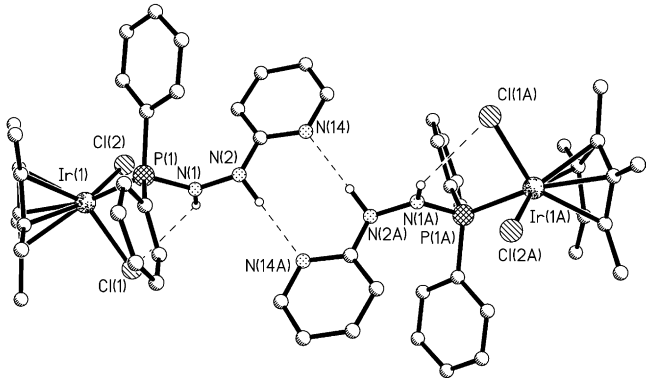
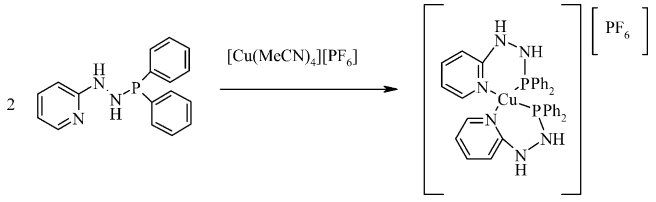


Fig. 4. The X-ray structure of [IrCp*Cl_2(Ph_2PNHNHpy *P*)] (**12**).

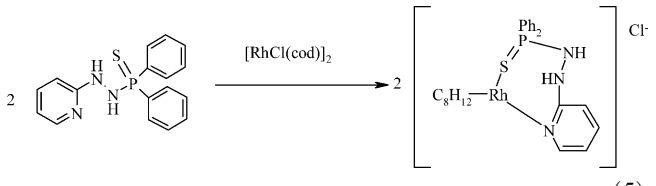
[Cu(MeCN)$_4$][PF_6] formed the bis-chelate complex [Cu(Ph_2PNHNHpy)$_2$][PF_6] (**13**) in good yield (71%), isolated as a cream coloured solid. No NMR data was observed for this complex since it is paramagnetic. Microanalysis and FAB mass spectral determination gave the expected results for the presence of the bis-chelate complex and this was subsequently confirmed by the existence of the $\nu_{CN[py]}$ vibration at 1614 cm^{-1} in the IR spectrum.



(4)

3.2. Coordination chemistry of $Ph_2P(S)NHNHpy$

Similar reactions to those described above can be performed using Ph_2P(S)NHNHpy. Reaction with [Rh(cod)Cl]$_2$ in toluene formed [Rh(cod)(Ph_2P(S)-NHNHpy-*S,N*)][Cl] in good yield (79%). Analysis by FAB mass spectrometry gave the parent ion at M − Cl^- = 536 and microanalysis gave satisfactory results. The presence of ν_{NH}, $\nu_{CN[py]}$, ν_{PN} and ν_{PS} vibrations in the IR spectrum were observed at 3163, 1611, 998 and 640 cm^{-1}, respectively. A single NMR resonance in $CDCl_3$ was observed in the $^{31}P\{^1H\}$ spectrum at δ_p 64.3 ppm. The existence of the $\nu_{CN[py]}$ vibration at 1611 cm^{-1} indicated that the complex formed is a chelate with the Cl acting as a counter ion.



(5)

The reaction of Ph_2P(S)NHNHpy with [$RuCl_2$(*p*-Cy)]$_2$ [Cy = cymene] proceeded in good yield (80%) to give the chelate complex [Ru(*p*-Cy)(Ph_2P(S)NHNHpy-*S,N*)][Cl_2]. FAB mass spectral analysis gave the expected fragmentation pattern and parent ion at M − Cl_2 = 559. Elemental analysis of this complex gave satisfactory results and the $^{31}P\{^1H\}$ NMR spectrum showed a single resonance at δ_p 81.1 ppm. Analysis by IR indicated the presence of vibrations at 3448, 3178, 1611, 995 and 635 cm^{-1} which correspond to ν_{NH}, ν_{NH}, $\nu_{CN[py]}$, ν_{PN} and ν_{PS}, respectively. The absence of any ν_{RuCl} vibrations in the IR spectrum indicated that the complex formed was a chelate and this was further confirmed by the presence of $\nu_{CN[py]}$ at 1611 cm^{-1}.

[Cu(MeCN)$_4$][PF_6] reacts with Ph_2P(S)NHNHpy similarly to Ph_2PNHNHpy to form the bis-chelate complex [Cu(Ph_2P(S)NHNHpy-*S,N*)][PF_6], in good yield (77%). Analysis by $^{31}P\{^1H\}$ NMR gave a single broad resonance at δ_p 65.9 ppm. Elemental analysis confirmed the suggested bis-chelate structure, as did FAB mass spectral analysis with the parent ion occurring at M − PF_6 = 713. The IR spectrum also confirmed the presence of the bischelate structure with existence of $\nu_{CN[py]}$ vibrations at 1611 cm^{-1}. Other vibrations present in the IR spectrum include ν_{NH}, ν_{PN} and ν_{PS} at 3262, 997 and 622 cm^{-1}, respectively.

4. Supplementary data

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. 199 732 and 199 735 at the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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