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P- versus P,O- coordination in complexes of *N*-(diphenylphosphino)arylamide ligands $ArC(O)NHPPh_2$ (Ar = 3-pyridyl, phenyl). X-ray crystal structures of $[RhCl_2(\eta^5\text{-}C_5Me_5)L^2]$ and $[NiCl(EtOH)L^2_2]\cdot Cl\cdot[NiCl_2L^2_2]$ ($L^2 = C_6H_5CONHPPh_2$)

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Abstract

The *N*-(diphenylphosphino)arylamide ligands $3\text{-}NC_5H_4CONHPPh_2$ (L^1) and $C_6H_5CONHPPh_2$ (L^2) function as monodentate p-donors in the complexes $[RhCl_2(\eta^5\text{-}C_5Me_5)L]$, $[RuCl_2(\eta^6\text{-}p\text{-cymene})L]$ and *cis*-$[PtCl_2L_2]$, as exemplified by the X-ray crystallographically determined structure of $[RhCl_2(\eta^5\text{-}C_5Me_5)L^2]$. For nickel(II), P,O- chelation by $L^{1,2}$ is exhibited in the bis(bidentate) complexes $[NiCl_2L_2]$, as demonstrated by the crystal structure of $[NiCl(EtOH)L^2_2]\cdot Cl\cdot[NiCl_2L^2_2]$; the five-membered Ni–O–C–N–P chelate rings are approximately planar with the phosphorus atoms in the dichloro complex being *trans* whereas their arrangement is *cis* in the cation. Comparison of this structure with $[RhCl_2(\eta^5\text{-}C_5Me_5)L^2]$ reveals slight elongation of the C=O and P–N lengths upon P,O-chelation of L^2. Solvatochromism for the Ni(II)-L^2 complex (green in ethanol or acetone, brown in chlorinated solvents) arises from solvent-dependent hemilability of the amide oxygen atom, although the L^1 complex of Ni(II) is exempt from this behaviour. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphinoamide; Heterobidentate; Solvatochromism; Complexes; X-ray

1. Introduction

In recent years the synthesis and coordination chemistry of phosphorus(III) ligands containing P–N linkages, generally derived by the condensation of chlorophosphines with primary amines in the presence of a tertiary amine base, has received widespread attention [1–7]. The importance of mono- and bidentate phosphorus(III) ligands in a multiplicity of homogeneous catalytic applications and the enormous diversity of amines available have fuelled interest in this burgeoning area, leading to the rapid establishment of an extensive library of ligands constructed by P–N bond formation.

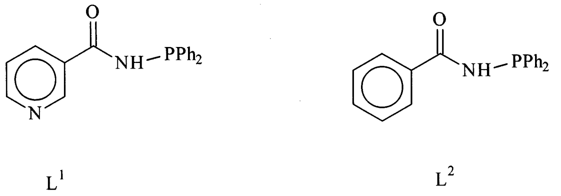

Fig. 1. Structures of $L^{1,2}$.

Despite this increasing interest in P–N bond formation as a ligand construction methodology, phosphorus(III) functionalised (i.e. containing a P–N linkage) amides and thioamides remain rare [8–12]. While P- or E- monodentate (E = O or S) and P,E- chelation modes are available for these compounds, the amide oxygen (or sulphur) atom is in general reluctant to bind to transition metal centres. The prominence of ambidentate P,O- donor ligands in catalysis, whose activity stems from partially labile metal–oxygen bonds [13–

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17], suggests that further exploration of phosphinoamide ligands is overdue.

We have reported previously that $Ph_2P(O)NHPPh_2$ is adept at P-monodentate and P,O- bidentate coordination modes in both its neutral form and as the monoanion $[Ph_2P(O)NPPh_2]^-$ at platinum(II), ruthenium(II) and iridium(III) [1,2,5]. This versatility has prompted us to investigate the related P,O-hybrids 3-NC_5H_4-$CONHPPh_2$ (L^1) and $C_6H_5CONHPPh_2$ (L^2) (Fig. 1) as a new class of heterobidentate ligands which exhibit both mono- and bidentate behaviour for selected transition metals.

2. Results and discussion

Cleavage of $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ or $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$ with 2 equiv. of $L^{1,2}$ in dichloromethane gives $[RhCl_2(\eta^5\text{-}C_5Me_5)L]$ ($L = L^1$ 1 or L^2 2) and $[RuCl_2(\eta^6\text{-}p\text{-cymene})L]$ ($L = L^1$ (**3**) or L^2 (**4**)), respectively, while the treatment of $[PtCl_2(MeCN)_2]$ with 2 equiv. of $L^{1,2}$ leads to bis(phosphine) complexes *cis*-$[PtCl_2L_2]$ ($L = L^1$ (**5**) or L^2 (**6**)). In the ruthenium(II), rhodium(III) and platinum(II) complexes $L^{1,2}$ are coordinated to the metal centre through the phosphorus(III) atom only, the non-coordination of the oxygen atom is analogous to $Ph_2P(O)NHPPh_2$ [1,2,5] and $Ph_2PCH_2C(O)R$ [15,18,19], which are P-monodentate at late transition metals. This assertion is further supported by the crystal structure of $[RhCl_2(\eta^5\text{-}C_5Me_5)L^2]$ (**2**) (vide infra) in which the carbonyl group of L^2 is pendant. The complexes **1**–**6** are air- and moisture- stable solids soluble in chlorinated solvents, acetone and THF.

Attempts to prepare nickel(II) complexes of $L^{1,2}$ in ethanol–dichloromethane are complicated by partial solvolysis of one geometric isomer of $[NiCl_2L_2]$. X-ray crystallographic analysis of the product from the $NiCl_2$-L^2 system (vide infra) shows it to be $[NiCl(EtOH)L^2_2]\cdot Cl\cdot[NiCl_2L^2_2]$ (**8**). A similar fate undoubtedly befalls the corresponding L^1 complex **7**. Notably **8** is solvatochromic, being green in ethanol and acetone whereas solutions in chlorinated solvents are brown; the green colour is restored upon removal of the solvent, suggesting a facile solvent-dependent interconversion between P,O-bidentate (green) and P-monodentate (brown) forms. However the sparingly soluble **7** retains its turquoise colour in all solvents, indicating that the donor properties of the carbonyl oxygen in $L^{1,2}$ are modulated to some extent by the aryl group.

The complexes **1**–**8** have been characterised using NMR, FAB^+ mass and IR spectroscopies and by elemental analyses, the most prominent peaks in their FAB^+ mass spectra corresponding to $[M^+ - Cl]$. In their IR spectra, the carbonyl bands for **1**–**6** (1674–1686 cm^{-1}) are raised by approximately 40 cm^{-1} from the free ligand values (1639, 1654 cm^{-1} for L^1, L^2) whereas for **7**, **8** there is a reduction by a similar amount (1618 and 1604 cm^{-1}); an analogous sensitivity in ν(CO) energies upon coordination of the carbonyl oxygen has been noted in platinum(II) and palladium(II) complexes of the N-donor iminophosphorane ligands $Ph_3P{=}NC(O)CH_2Cl$ and $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ [20]. The ν(NH) vibration in $L^{1,2}$ (3264 and 3262 cm^{-1}, respectively) moves 30–50 cm^{-1} to lower energy upon complexation to platinum(II) while conversely there is an increase by approximately 50 cm^{-1} in this band for $[RhCl_2(\eta^5\text{-}C_5Me_5)L]$ and $[RuCl_2(\eta^6\text{-}p\text{-cymene})L]$. The ν(NH) bands of **7**, **8** are obscured by the ν(OH) absorption from the coordinated ethanol molecule.

In the $^{31}P\{^1H\}$ NMR spectra of **5**, **6** the ^1J(Pt–P) coupling constants (3849, 3876 Hz) confirm the *cis* geometry of L ligands, their magnitude being substantially larger than for *cis*-$[PtCl_2(PPh_3)_2]$ (3677 Hz), suggesting a greater electronegativity for an *N*-arylamido group compared with C_6H_5. In **1**, **2** the ^1J(Rh–P) coupling constants (149 and 145 Hz, respectively) are comparable with the values of 145 and 147 Hz for $L = PPh_3$ and $Ph_2P(O)NHPPh_2$–P [2,21]. While no appreciable coordination shift is noted for the phosphorus atom in the platinum(II) complexes **5**, **6** the δ_P values for $L^{1,2}$ (26.0 and 25.0 ppm) move by 30 ppm to high frequency upon complexation to rhodium(III) and ruthenium(II). The nickel(II) complexes **7**, **8** are paramagnetic in all solvents, precluding NMR measurements. As found for $L^{1,2}$ there is little variation in δ_P with the *N*-aryl substituent in **1**–**6**. In the ^1H NMR spectra of **1**, **2** the $^4J(P\text{–}CH_3)$ coupling constant of ^{31}P to the C_5Me_5 ring protons is 4 Hz.

2.1. Single crystal X-ray diffraction studies

The molecular structure of $[RhCl_2(\eta^5\text{-}C_5Me_5)L^2]$ (**2**) (Fig. 2) displays a piano-stool geometry with an η^5-bound pentamethylcyclopentadienyl ring and two chloride ligands Cl(1) and Cl(2), with L^2 bound through P(1) completing the coordination sphere at Rh(1). The C(13)–O(13) vector is directed away from Rh(1) and is uninvolved in hydrogen-bonding interactions with adjacent molecules, however there are internal bifurcated hydrogen bonds between H(1N) and the chloride ligands [H(1N)···Cl(1) 2.52 Å, H(1N)···Cl(2) 2.90 Å; N(1)–H(1N)···Cl(1) 116°, N(1)–H(1N)···Cl(2) 113°]. The bond lengths within the metal coordination sphere are unexceptional [Rh(1)–P(1) 2.318(2) Å, Rh(1)–Cl(1) 2.404(1) Å, Rh(1)–Cl(2) 2.406(1) Å, Rh(1)···C_5Me_5 (centroid) 1.83 Å], the Rh–P distance comparing favourably with isostructural complexes [2.254(3)–2.332(3) Å] [21,22].

As outlined above, attempts to prepare $[NiCl_2L^2_2]$ in ethanol are accompanied by Ni–Cl hydrolysis, noted during the recrystallisation of $[NiCl_2L^2_2]$ from ethanol–

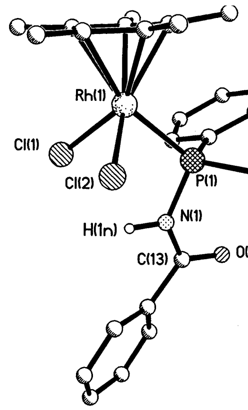

Fig. 2. Molecular structure of [$RhCl_2(\eta^5$-$C_5Me_5)L^2$] (**2**) (C–H atoms omitted for clarity). Selected bond lengths (Å) and angles (°); Rh(1)–P(1) 2.318(2), Rh(1)–Cl(1) 2.404(1), Rh(1)–Cl(2) 2.406(1), P(1)–N(1) 1.696(5), N(1)–C(13) 1.366(7), C(13)–O(13) 1.231(6); P(1)–Rh(1)–Cl(1) 87.39(5), P(1)–Rh(1)–Cl(2) 88.67(5), Cl(1)–Rh(1)–Cl(2) 89.31(6), N(1)–P(1)–Rh(1) 107.8(2), C(13)–N(1)–P(1) 129.1(4), O(13)–C(13)–N(1) 122.7(5).

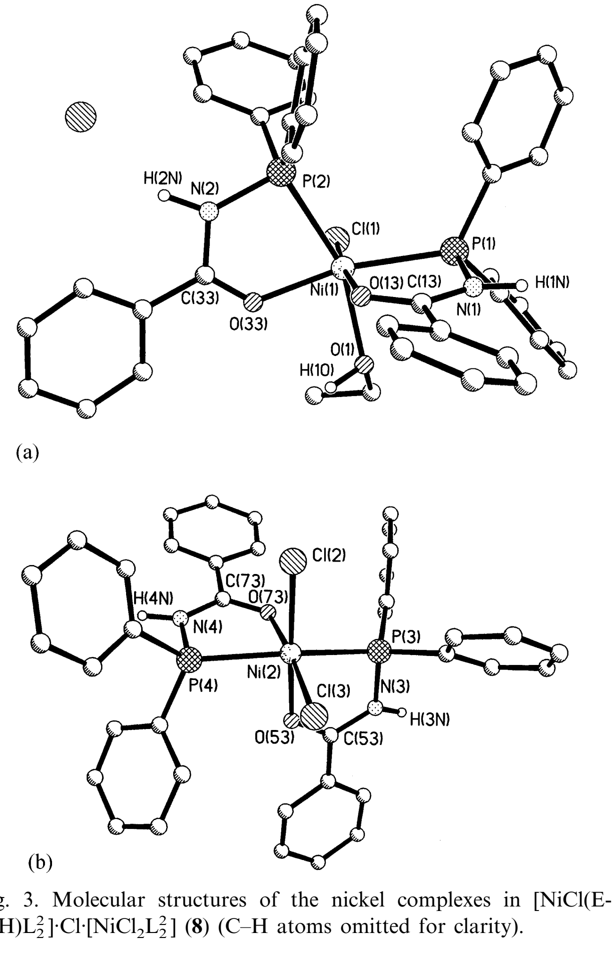

Fig. 3. Molecular structures of the nickel complexes in [NiCl(EtOH)L^2_2]·Cl·[$NiCl_2L^2_2$] (**8**) (C–H atoms omitted for clarity).

diethyl ether. The unit cell contains two distinct species [NiCl(EtOH)L^2_2]Cl and [$NiCl_2L^2_2$], hereafter **8a** and **8b**, respectively (Fig. 3, Table 1). The co-crystallisation of **8a**,**b** and the inclusion of ethanol and methanol solvate molecules contribute to the poor *R* factor of 9.8% for this structure. The complexation of L^2 to nickel(II) generates both *cis*,*trans*,*cis* and *cis*,*cis*,*cis* isomers of [$NiCl_2(L^2$-P,O$)_2$]; the formation of **8a** from **8b** can be attributed to the labilising influence of P(2) on the *trans* Ni–Cl bond in the *cis*,*cis*,*cis* isomer, promoting displacement of the chloro ligand by an ethanol molecule to give the cationic complex [NiCl(EtOH)L^2_2]Cl (**8a**).

Both **8a**,**b** show substantial distortion from regular octahedral geometry, the *cis* angles are between 77.6(2)–111.84(11)° and 77.6(2)–98.39(11)°, the $O_{carbonyl}$–Ni–P angles within the chelate rings being the smallest [O(13)–Ni(1)–P(1) 79.6(2)°, O(33)–Ni(1)–P(2) 77.6(2)° in **8a**; O(53)–Ni(2)–P(3) 77.6(2)°, O(73)–Ni(2)–P(4) 78.0(2)° in **8b**]. The unequal Ni–$O_{carbonyl}$ and Ni–P bond lengths in **8a** [Ni(1)–O(33) 2.026(7) Å,

Table 1
Selected bond lengths (Å) and angles (°) for [NiCl(EtOH)L^2_2]·Cl·[$NiCl_2L^2_2$] (**8**) (e.s.d.s in parentheses)

[NiCl(EtOH)$L^2{}_2$]·Cl (**8a**)			
Bond lengths			
Ni(1)–O(33)	2.026(7)	Ni(1)–O(13)	2.119(7)
Ni(1)–O(1)	2.142(7)	Ni(1)–Cl(1)	2.308(3)
Ni(1)–P(1)	2.376(3)	Ni(1)–P(2)	2.502(3)
P(1)–N(1)	1.733(9)	P(2)–N(2)	1.722(9)
C(13)–O(13)	1.256(12)	C(33)–O(33)	1.244(10)
Bond angles			
O(33)–Ni(1)–O(13)	89.3(3)	O(33)–Ni(1)–O(1)	82.4(3)
O(13)–Ni(1)–O(1)	82.0(3)	O(33)–Ni(1)–Cl(1)	96.5(2)
O(13)–Ni(1)–Cl(1)	173.9(2)	O(1)–Ni(1)–Cl(1)	96.8(2)
O(33)–Ni(1)–P(1)	165.3(2)	O(13)–Ni(1)–P(1)	79.6(2)
O(1)–Ni(1)–P(1)	86.5(2)	Cl(1)–Ni(1)–P(1)	94.37(12)
O(33)–Ni(1)–P(2)	77.6(2)	O(13)–Ni(1)–P(2)	90.7(2)
O(1)–Ni(1)–P(2)	158.8(2)	Cl(1)–Ni(1)–P(2)	92.37(11)
P(1)–Ni(1)–P(2)	111.84(11)	N(1)–P(1)–Ni(1)	98.1(4)
C(13)–N(1)–P(1)	117.7(9)	O(13)–C(13)–N(1)	123.3(13)
C(13)–O(13)–Ni(1)	119.7(8)	N(2)–P(2)–Ni(1)	95.9(3)
O(33)–C(33)–N(2)	120.2(10)	C(33)–O(33)–Ni(1)	126.7(7)
C(33)–N(2)–P(2)	118.3(8)		
[$NiCl_2L^2{}_2$] (**8b**)			
Bond lengths			
Ni(2)–O(73)	2.097(6)	Ni(2)–O(53)	2.112(7)
Ni(2)–Cl(2)	2.387(3)	Ni(2)–Cl(3)	2.359(3)
Ni(2)–P(3)	2.387(3)	Ni(2)–P(4)	2.418(3)
P(3)–N(3)	1.708(8)	P(4)–N(4)	1.742(8)
C(53)–O(53)	1.235(11)	C(73)–O(73)	1.248(9)
Bond angles			
O(73)–Ni(2)–O(53)	85.2(3)	O(73)–Ni(2)–Cl(3)	173.5(2)
O(53)–Ni(2)–Cl(3)	89.4(2)	O(73)–Ni(2)–P(3)	85.8(2)
O(53)–Ni(2)–P(3)	77.6(2)	Cl(3)–Ni(2)–P(3)	96.69(11)
O(73)–Ni(2)–Cl(2)	88.9(2)	O(53)–Ni(2)–Cl(2)	173.1(2)
Cl(3)–Ni(2)–Cl(2)	96.72(12)	P(3)–Ni(2)–Cl(2)	98.39(11)
O(73)–Ni(2)–P(4)	78.0(2)	O(53)–Ni(2)–P(4)	88.7(2)
Cl(3)–Ni(2)–P(4)	98.21(11)	P(3)–Ni(2)–P(4)	159.65(12)
Cl(2)–Ni(2)–P(4)	93.56(11)	N(3)–P(3)–Ni(2)	99.7(3)
C(53)–N(3)–P(3)	118.1(8)	O(53)–C(53)–N(3)	120.1(12)
C(53)–O(53)–Ni(2)	124.0(8)	N(4)–P(4)–Ni(2)	97.7(3)
C(73)–N(4)–P(4)	119.1(7)	O(73)–C(73)–N(4)	119.6(10)
C(73_–O(73)–Ni(2)	124.2(7)		

Table 2
Hydrogen–bonding distances (Å) and angles (°) for [NiCl(EtOH)L^2_2]·Cl·[NiCl$_2$$L^2_2$] (**8**) (e.s.d.s in parentheses) [a]

Bond lengths			
H(1N)···O(91)	1.86	H(1O)···O(93)	1.83
H(2N)···Cl(4)	2.48	H(1O)···O(33)	2.43
H(3N)···Cl(4)	2.49	H(91O)···Cl(2′)	2.24
H(4N)···Cl(4′)	2.36	H(93O)···Cl(3′)	2.19
Bond angles			
N(1)−H(1N)···O(91)	171	O(1)−H(1O)···O(93)	156
N(2)−H(2N)···Cl(4)	151	O(1)−H(1O)···O(33)	98
N(3)−H(3N)···Cl(4)	176	O(91)−H(91O)···Cl(2′)	162
N(4)−H(4N)···Cl(4′)	175	O(93)−H(93O)···Cl(3′)	166

[a] O(91), O(93) are oxygen atoms from ethanol solvate molecules, ′ refers to a symmetry-related atom.

Ni(1)–O(13) 2.113(7) Å; Ni(1)–P(1) 2.376(3) Å, Ni(1)–P(2) 2.502(3) Å] reflect differences in *trans* influences compared with **8b** [Ni(2)–O(53) 2.112(7) Å, Ni(2)–O(73) 2.097(6) Å; Ni(2)–P(3) 2.387(3) Å, Ni(2)–P(4) 2.418(3) Å]. The five-membered nickelacycles in **8a**,**b** are essentially planar [mean deviations of Ni(1)–P(1)–N(1)–C(13)–O(13) and Ni(1)–P(2)–N(2)–C(33)–O(33) planes of 0.07 and 0.06 Å, respectively, in **8a**, mean deviations of Ni(2)–P(3)–N(3)–C(53)–O(53) and Ni(2)–P(4)–N(4)–C(73)–O(73) planes of 0.03 and 0.05 Å, respectively, in **8b**]. There are only modest increases in C=O and P–N bond lengths upon O-coordination compared with **2** [P–N 1.696(5) Å, C=O 1.231(6) Å in **2**, cf. 1.708(8)−1.742(8) and 1.235(11)−1.256(12) Å, respectively, in **8a**,**b**]. There is an extensive array of hydrogen-bonding interactions involving the Cl(4) counterion, the amine protons H(1N)−H(4N), the co-ordinated ethanol molecule in **8a** and the ethanol solvate molecules (Table 2).

3. Conclusions

The *N*-(diphenylphosphino)arylamides 3-NC$_5$H$_4$CONHPPh$_2$ and C$_6$H$_5$CONHPPh$_2$ are P-monodentate in *cis*-[PtCl$_2$L$_2$] and [MCl$_2$(arene)L] (M = Rh, arene = η^5-C$_5$Me$_5$; M = Ru, arene = η^6-*p*-cymene) while nickel(II) is sufficiently hard to permit coordination by the amide oxygen in [NiCl$_2$L$_2$]. Variations in Ni–O bond lability for **7**, **8** suggests sensitivity of the carbonyl donor capacity to the aryl substituent. Further studies on the efficacy of L^{1,2} complexes in catalytic processes and the preparation of P,O-chelates at the second- and third-row d-block metals by halide abstraction using silver(I) salts are underway.

4. Experimental

Preparations of **1**–**8** were conducted under aerobic conditions. L^{1,2}, [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$], [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] and [PtCl$_2$(MeCN)$_2$] were prepared by literature methods [8,23–25], solvents were of reagent grade. ^{1}H and ^{31}P{^{1}H} NMR spectra (250.1 and 36.2 MHz, CHCl$_3$-d) were recorded on Bruker AM250 and JEOL FX90Q NMR spectrometers and referenced to external SiMe$_4$ (δ 0) and 85% H$_3$PO$_4$ (δ 0), respectively, using the high-frequency positive convention. IR spectra (KBr discs) were recorded on a Perkin–Elmer System 2000 NIR FT-Raman spectrometer, elemental analyses (PE 2400 CHN elemental analyser) were performed by the University of Loughborough Analytical Service, and FAB$^+$ mass spectra (3-NOBA matrix) by the EPSRC National Mass Spectrometry Service Centre, Swansea.

4.1. [RhCl$_2$(η^5-C$_5$Me$_5$)L]

A dichloromethane solution (1 cm^3) of L (0.1 mmol) was added to [{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$] (0.05 mmol) in dichloromethane (1 cm^3) and stirred for 24 h. Vapour diffusion of diethyl ether into this solution gave [RhCl$_2$(η^5-C$_5$Me$_5$)L] (L = L^1 (**1**) or L^2 (**2**)) as deep red crystals. Compound **1** Yield: 80%. *Anal.* Found: C, 54.7; H, 5.0; N, 4.2. Calc. for C$_{28}$H$_{30}$N$_2$OPRhCl$_2$: C, 54.0; H, 4.9; N, 4.5%. ^{31}P NMR: $\delta = 63.9$(d), (^1J(Rh–P) = 149 Hz). ^{1}H NMR: $\delta = 9.08$–7.53 (m, 14H, aromatic H), 1.44 (d, 15H, $^4J = 4$ Hz, C$_5$Me$_5$). IR (cm^{-1}): ν(NH) 3264; ν(CO) 1683. FAB$^+$ MS: 579, $M^+ - $Cl.

Compound **2** Yield 86%. *Anal.* Found: C, 55.4; H; 5.1; N, 2.3. Calc. for C$_{29}$H$_{31}$NOPRhCl$_2$): C, 56.7; H, 5.1; N, 2.1%. ^{31}P NMR: $\delta = 62.6$ (d), (^1J(Rh–P) = 145 Hz). ^{1}H NMR: $\delta = 8.38$–7.35 (m, 15H, C$_6$H$_5$), 1.44 (d, 15H, $^4J = 4$ Hz, C$_5$Me$_5$). IR (cm^{-1}): ν(NH) 3306; ν(CO) 1674. FAB$^+$ MS: 578, $M^+ - $Cl.

4.2. [RuCl$_2$(η^6-*p*-cymene)L]

A dichloromethane solution (1 cm^3) of L (0.1 mmol) was added to [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.05 mmol) in dichloromethane (1 cm^3) and stirred for 24 h. Vapour diffusion of diethyl ether into this solution gave [RuCl$_2$(η^6-*p*-cymene)L] (L = L^1 (**3**) or L^2 (**4**)) as brown crystals.

Compound **3** Yield 89%. *Anal.* Found: C, 54.3; H, 4.7; N, 4.1. Calc. for C$_{28}$H$_{29}$N$_2$OPRuCl$_2$: C, 54.9; H, 4.8; N, 4.5%. ^{31}P NMR: $\delta = 60.6$(s). ^{1}H NMR $\delta = 9.02$–7.27 (m, 14H, aromatic H), 5.37 (d, 2H, $^3J = 8$ Hz, C$_6$H$_4$), 5.24 (d, 2H, $^3J = 8$ Hz, C$_6$H$_4$), 2.55 (septet, 1H, $^3J = 9$ Hz, ^{i}Pr), 0.86 (d, 6H, $^3J = 9$ Hz, ^{i}Pr). IR (cm^{-1}): ν(NH) 3317; ν(CO) 1682. FAB$^+$ MS: 577, $M^+ - $Cl.

Compound **4** Yield 82%. *Anal.* Found: C, 56.1; H, 5.1; N, 2.2. Calc. for C$_{29}$H$_{30}$NOPRuCl$_2$: C, 56.9; H, 4.9; N, 2.3%. ^{31}P NMR: $\delta = 58.9$(s). ^{1}H NMR: $\delta = 8.12$–

7.32 (m, 15H, C_6H_5), 5.35 (d, 2H, $^3J = 6$ Hz, C_6H_4), 5.22 (d, 2H, $^3J = 6$ Hz, C_6H_4), 2.52 (septet, 1H, $^3J = 9$ Hz, $^iC_3H_7$), 0.85 (d, 6H, $^3J = 9$ Hz, $^iC_3H_7$). IR (cm^{-1}): ν(NH) 3324; ν(CO) 1675. FAB$^+$ MS: 576, $M^+ - \mathrm{Cl}$.

4.3. *cis*-$[PtCl_2L_2]$

A dichloromethane solution (1 cm^3) of L (0.1 mmol) was added to $[PtCl_2(MeCN)_2]$ (0.05 mmol) in dichloromethane (1 cm^3) and stirred for 24 h. Vapour diffusion of diethyl ether into this solution gave *cis*-$[PtCl_2L_2]$ (L = L^1 (**5**) or L^2 (**6**)) as colourless crystals.

Compound **5** Yield 53%. *Anal.* Found: C, 48.2; H, 3.6; N, 6.2. Calc. for $C_{36}H_{30}N_4O_2P_2PtCl_2$: C, 49.2; H, 3.4; N, 6.4%. ^{31}P NMR $\delta = 28.1$(s), (^1J(Pt–P) 3849 Hz). ^{1}H NMR: $\delta = 9.00$–7.43 (m, aromatic H). IR (cm^{-1}): ν(NH) 3213; ν(CO) 1684. FAB$^+$ MS: 843, $M^+ - \mathrm{Cl}$.

Compound **6** Yield 86%. *Anal.* Found: C, 51.9; H, 3.7; N, 3.0. Calc. for $C_{38}H_{32}N_2O_2P_2PtCl_2$: C, 52.1; H, 3.7; N, 3.2%. ^{31}P NMR: $\delta = 27.6$(s), (^1J(Pt–P) = 3876 Hz). ^{1}H NMR $\delta = 7.84$–7.18 (m, aromatic H). IR (cm^{-1}): ν(NH) 3242; ν(CO) 1686. FAB$^+$ MS: 841, $M^+ - \mathrm{Cl}$.

4.4. Reaction of $L^{1,2}$ with $NiCl_2 \cdot 6H_2O$

A solution of L (0.1 mmol) in dichloromethane (1 cm^3) was added to nickel chloride hexahydrate (0.05 mmol) in ethanol (1 cm^3), giving a turquoise solution which was stirred for 24 h. The solvent was removed in vacuo and the crude product extracted into ethanol (1 cm^3). Vapour diffusion of diethyl ether into this solution gave $[NiCl(EtOH)L_2]\cdot Cl\cdot[NiCl_2L_2]$ as turquoise (L^1 (**7**)) or green (L^2 (**8**)) solids.

Compound **7** Yield 75%. *Anal.* Found : C, 55.5; H, 4.4; N, 7.1. Calc for $C_{74}H_{66}N_8P_4O_5Ni_2Cl_4 \cdot 3H_2O$: C, 56.1; H, 4.6; N, 7.1%. IR (cm^{-1}): ν(CO) 1618. FAB$^+$ MS: 705, $[NiClL^1_2]^+$.

Compound **8** Yield 42%. *Anal.* Found: C, 60.9; H, 4.5; N, 3.4. Calc. for $C_{78}H_{70}N_4P_4O_5Ni_2Cl_4 \cdot CH_3OH \cdot 2C_2H_5OH$: C, 60.4; H, 5.2; N, 3.4%. IR (cm^{-1}): ν(CO) 1604. FAB$^+$ MS: 703, $[NiClL^2_2]^+$.

4.5. X-ray crystallography

X-ray diffraction studies on $[RhCl_2(\eta^5\text{-}C_5Me_5)L^2]$ (**2**) and $[NiCl(EtOH)L^2_2]\cdot Cl\cdot[NiCl_2L^2_2]\cdot 2EtOH\cdot MeOH$ (**8**), crystallised from dichloromethane–diethyl ether and ethanol–diethyl ether solutions, respectively, were performed at 293 K using a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to carbon were idealised and fixed (C–H 0.95 Å), amine NH and ethanol OH protons were located using a ΔF map and allowed to refine subject to a distance constraint. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL-PC [26].

$C_{29}H_{31}Cl_2NOPRh$, $M = 614.33$, orthorhombic, $a = 8.3541(1)$ Å, $b = 17.9890(4)$, $c = 18.0726(1)$ Å, $V = 2715.98(7)$ Å^3, $F(000) = 1256$, crystal size $0.1 \times 0.2 \times 0.3$ mm, space group $P2_12_12_1$, $Z = 4$, μ(Mo Kα) = 0.907 mm^{-1}. Of 12003 measured data, 3893 were unique (R_{int} 0.1138) to give $R_1[I > 2\sigma(I)] = 0.0344$ and $wR_2 = 0.0549$.

$C_{82.5}H_{84}Cl_4N_4Ni_2O_{7.5}P_4$, $M = 1634.64$, monoclinic, $a = 17.4983(8)$, $b = 23.7288(13)$, $c = 20.7976(11)$ Å, $V = 8155.2(7)$ Å^3, $F(000) = 3404$, crystal size = $0.12 \times 0.04 \times 0.04$ mm, space group $P2_1/n$, $Z = 4$, μ(Mo Kα) = 0.727 mm^{-1}. Of 47742 measured data, 18833 were unique (R_{int} 0.3319) to give $R_1[I > 2\sigma(I)] = 0.0977$ and $wR_2 = 0.1132$.

5. Supplementary materials

Crystallographic data for the structural analysis (**2**, **8**) has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 146548 and 146549. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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