Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 23 (2004) 2569–2574

POLYHEDRON

www.elsevier.com/locate/poly

Preparation and coordination chemistry of *p*-(xylylenediaminodiphenyl) phosphine

Alexandra M.Z. Slawin, Joanne Wheatley, J. Derek Woollins *

School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

Received 17 June 2004; revised 10 September 2004; accepted 20 September 2004

Abstract

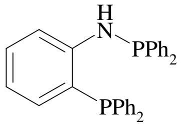
Reaction of *p*-xylene diamine with two equivalents of Ph_2PCl in the presence of NEt_3, proceeds in thf to give *p*-(xylylenediaminodiphenyl) phosphine **1** in good yield. **1** was derivatised as the dichalcogenides $Ph_2P(O)NHCH_2(C_6H_4)CH_2NHP(O)Ph_2$, $Ph_2P(S)NHCH_2(C_6H_4)CH_2NHP(S)Ph_2$ and $Ph_2P(Se)NHCH_2(C_6H_4)CH_2NHP(Se)Ph_2$ and the structures of the latter two compounds determined crystallographically. The binuclear compounds $[\{(PEt_3)PtCl_2(Ph_2PNHCH_2)\}_2C_6H_4]$ (**5**), $[\{(PPhMe_2)PtCl_2(Ph_2PNHCH_2)\}_2C_6H_4]$ (**6**), $[\{IrCl_2(\eta^5\text{-}C_5Me_5)(Ph_2PNHCH_2)\}_2C_6H_4]$ (**7**) $[\{RhCl_2(\eta^5\text{-}C_5Me_5)(Ph_2PNHCH_2)\}_2C_6H_4]$ (**8**), $[\{RuCl_2(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)(Ph_2PNHCH_2)\}_2C_6H_4]$ (**9**), $[\{Pd(\eta^3\text{-}C_3H_5)Cl(Ph_2PNHCH_2)\}_2C_6H_4]$ (**10**), $[\{RhCl(C_8H_{12})(Ph_2PNHCH_2)\}_2C_6H_4]$ (**11**), $[\{AuCl(Ph_2PNHCH_2)\}_2C_4H_6]$ (**12**) have been prepared and characterised spectroscopically.

Keywords: Ligand; Bidentate; Bridging; X-ray; Phosphine

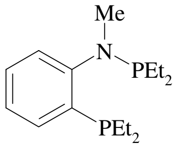
---

1. Introduction

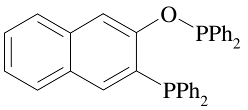
Bridging ligands are of interest as they can form a number of bi-, tri- and tetra-nuclear species. There are a variety of different ligands that can have bridging properties and these include *o*-, *m*- and *p*-derivatives of benzene or pyridine. For example, $Ph_2PNHC_6H_4PPh_2$ [1,2], (**A**), $(Et_2PN(Me)C_6H_4PEt_2)$ [3], (**B**), and 1-(diphenylphosphany)naphtha-2-oxydiphenylphosphane [4], (**C**)



A



B



C

whilst 2,6-bis(diphenylphosphino)pyridine, ($\{Ph_2P\}_2py$), an *o*-bidentate pyridine, has the potential to act as a tridentate PNP ligand [5,6] and was shown to react with a variety of platinum and palladium starting materials to give four different complexes. Gaw et al. [7] recently reported the preparation of the tetradentate (phosphine)amine $1,4\text{-}\{(Ph_2P)_2NCH_2\}_2C_6H_4$. They used this

---

* Corresponding author. Tel.: +441 334 463 869; fax: +441 334 463 384.

E-mail address: jdw3@st-and.ac.uk (J.D. Woollins).

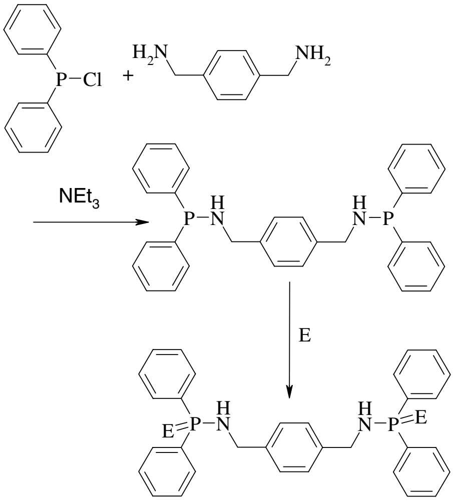
0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.09.012

ligand to form a binuclear complex containing two *cis*-[Mo(CO)$_4$] metal fragments.

Here, we report the preparation of a new phosphine *p*-(xylylenediamonodiphenyl)phosphine which has the potential to act as a bidentate bridging ligand. Illustrative coordination complexes have been prepared.

2. Results and discussion

Reaction of *p*-xylene diamine with two equivalents of Ph_2PCl in the presence of NEt_3, proceeds in thf to give **1** (Eq. (1)) in very good yield (89%) with δ_P 43.3 ppm. The IR spectrum has bands at 3303, 1432 and 997 cm^{-1} that are assigned to ν_{NH}, ν_{PPh} and ν_{PN}, respectively, (ν_{PPh} represents the ν_{CC} of the phosphine aromatic rings). The mass spectrum gave the expected parent ion and fragmentation pattern and microanalysis gave good results.



(1)

The oxide (**2**) $Ph_2P(O)NHCH_2(C_6H_4)CH_2NH$-$P(O)Ph_2$ was easily prepared by addition of excess aqueous hydrogen peroxide to **1** in thf whilst the sulfur (**3**) and selenide (**4**) analogues were prepared by the addition of elemental S or Se to **1** in toluene. The EI$^+$ mass spectral data obtained for these chalcogenides gave the expected parent ions and fragmentation patterns. $^{31}P\{^1H\}$ NMR showed single resonances ($CDCl_3$) at δ_P 24.5 and 60.5 ppm for the oxide and sulfide and at δ_P 58.6 ppm with selenium satellites $^1J(^{31}P–^{77}Se)$ 756 Hz for **4** which is typical for a P=Se group [8].

In the solid state the sulfur and selenide analogues, although not isomorphous, are isostructural, (Fig. 1, Table 1) both have a centre of symmetry; in **3** P(1)–S(1) = 1.9523(11) and P(1)–N(2) = 1.654(3) Å and in **4** P(1)–N(2) = 1.654(5) Å and the P(1)–Se(1) = 2.1198(10) Å which are in the range for previously reported bond lengths [8].

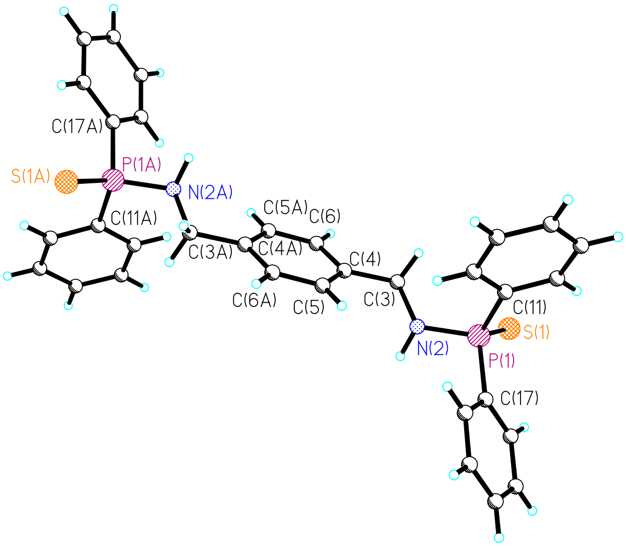


Fig. 1. X-ray structure of *p*-$Ph_2P(S)NHCH_2(C_6H_4)CH_2NHP(S)Ph_2$ (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for *p*-$Ph_2P(S)NHCH_2(C_6H_4)$-$CH_2NHP(S)Ph_2$ (**3**) and *p*-$Ph_2P(Se)NHCH_2(C_6H_4)CH_2NHP(Se)Ph_2$ (**4**). The values in square brackets are for the second independent molecule in **3**

	(3)	(4)
Bond lengths		
P(1)–N(2)	1.654(3)[1.661(2)]	1.654(5)
E(1)–P(1)	1.9523(11) [1.9568(11)]	2.1198(10)
N(2)–C(3)	1.471(4)[1.472(4)]	1.485(7)
P(1)–C(11)	1.811(3)[1.811(3)]	1.797(6)
P(1)–C(17)	1.812(3)[1.812(3)]	1.817(6)
Bond angles		
N(2)–P(1)–C(11)	103.43(13)[103.53(13)]	104.8(3)
N(2)–P(1)–C(17)	101.72(13)[103.36(13)]	104.0(3)
C(11)–P(1)–C(17)	106.39(14)[109.18(14)]	104.5(3)
N(2)–P(1)–E(1)	117.60(10)[116.27(10)]	116.79(19)
C(11)–P(1)–E(1)	112.64(11)[111.87(11)]	113.7(2)
C(17)–P(1)–E(1)	113.74(10)	111.8(2)
P(1)–N(2)–H(2)	109.1(18)[111.3(19)]	110(3)

A range of binuclear compounds were synthesised (Eq. (2)); thus reaction of $[\{PtCl(\mu\text{-}Cl)(PEt_3)\}_2]$ with **1** gives $[\{(PEt_3)PtCl_2(Ph_2PNHCH_2)\}_2C_6H_4]$ (**5**). The EI$^+$ mass spectrum of (**5**) contains the expected parent ion and fragmentation pattern and the complex displays resonances with platinum satellites in the $^{31}P\{^1H\}$ NMR spectrum (δ_{PA} 34.0 ppm, $^1J\{^{31}P_A–^{195}Pt\}$ 1984 Hz, δ_{PX} 7.5 ppm, $^1J\{^{31}P_X–^{195}Pt\}$ 1715 Hz $^2J\{^{31}P_A–^{31}P_X\}$ 18 Hz). The IR spectrum has ν_{NH} at 3289 cm^{-1}, ν_{PPh} and ν_{PN} at 1435 and 997 cm^{-1}, respectively, and two ν_{PtCl} (symmetric and antisymmetric) bands at 340 and 310 cm^{-1} suggesting a *cis* geometry at the metal. (**6**–**9**) were prepared in a similar way and have comparable spectroscopic properties to **5** (Table 2) see Fig. 2.

Table 2
Characterisation data for $Ph_2PNHCH_2C_6H_4CH_2NHPPh_2$ and its derivatives

	^{31}P-$\{^1H\}$ NMR	IR (cm^{-1})					Microanalysis % F_{calc}		
	δ_p (ppm)	ν_{PN}	ν_{NH}	ν_{PPh}	$\nu_{P=E}$	ν_{MCl}	C	H	N
$Ph_2PNHCH_2C_6H_4CH_2NHPPh_2 \cdot H_2O$ (**1**)	43.3	997	3303	1432	–	–	73.43 (73.55)	6.39 (6.17)	5.64 (5.36)
$Ph_2P(O)NHCH_2C_6H_4CH_2NHP(O)Ph_2$ (**2**)	24.5	998	3097	1437	1357	–	69.37 (69.31)	5.93 (5.82)	5.38 (5.05)
$Ph_2P(S)NHCH_2C_6H_4CH_2NHP(S)Ph_2$ (**3**)	60.5	997	3180	1437	625	–	65.27 (67.59)	5.35 (5.32)	5.11 (4.93)
$Ph_2P(Se)NHCH_2C_6H_4CH_2NHP(Se)Ph_2$ (**4**)[a]	58.6[a]	996	3177	1435	551	–	57.53 (58.02)	5.14 (4.56)	4.24 (4.23)
$[\{(PEt_3)PtCl(Ph_2PNHCH_2)\}_2C_6H_4]$ (**5**)	34.0, 7.5[b]	997	3289	1435	–	340, 310	41.36 (41.52)	5.12 (4.75)	2.36 (2.20)
$[\{(PPhMe_2)PtCl(Ph_2PNHCH_2)\}_2C_6H_4]$ (**6**)	35.1, −14.2[c]	998	3300	1435	–	334, 311	44.05 (43.92)	4.17 (3.99)	2.61 (2.13)
$[\{IrCl_2(\eta^5\text{-}C_5Me_5)(Ph_2PNHCH_2)\}_2C_6H_4]$ (**7**)	34.4	997	3309	1434	–	289, 268	47.64 (48.00)	4.64 (4.65)	2.35 (2.15)
$[\{RhCl_2(\eta^5\text{-}C_5Me_5)(Ph_2PNHCH_2)\}_2C_6H_4] \cdot 0.25CH_2Cl_2$ (**8**)	66.4[d]	996	3300	1434	–	282, 267	54.76 (54.86)	5.31 (5.33)	2.41 (2.45)
$[\{RuCl_2(\eta^6 p\text{-}MeC_6H_4{}^iPr)(Ph_2\ PNHCH_2)\}_2C_6H_4]$ (**9**)	61.1	996	3367	1434	–	291, 281	55.53 (55.92)	4.73 (5.23)	2.46 (2.51)
$[\{Pd(\eta^3\text{-}C_3H_5)Cl(Ph_2PNHCH_2)\}_2C_6H_4]$ (**10**)	58.1	998	3246	1433	–	276	52.34 (52.44)	4.78 (4.63)	3.45 (3.22)
$[\{RhCl(C_8H_{12})(Ph_2PNHCH_2)\}_2\ C_6H_4] \cdot CH_2\ Cl_2$ (**11**)	62.3[e]	995	3289	1434	–	279	54.66 (54.37)	5.32 (5.21)	2.89 (2.59)
$[\{AuCl(Ph_2PNHCH_2)\}_2C_4H_6]$ (**12**)	61.1	997	3279	1435	–	323	39.98 (39.65)	3.28 (3.12)	2.94 (2.89)

[a] $^1J\{^{31}P–^{77}Se\}$ 756 Hz.

[b] $^1J\{^{31}P_A–^{195}Pt\}$ 1984 Hz, $^1J\{^{31}P_X–^{195}Pt\}$ 1715 Hz, $^2J\{^{31}P_A–^{31}P_X\}$ 18 Hz.

[c] $^1J\{^{31}P_A–^{195}Pt\}$ 1956 Hz, $^1J\{^{31}P_X–^{195}Pt\}$ 1820 Hz, $^2J\{^{31}P_A–^{31}P_X\}$ 19 Hz.

[d] $^1J\{^{31}P–^{103}Rh\}$ 148 Hz.

[e] $^1J\{^{31}P–^{103}Rh\}$ 157 Hz.

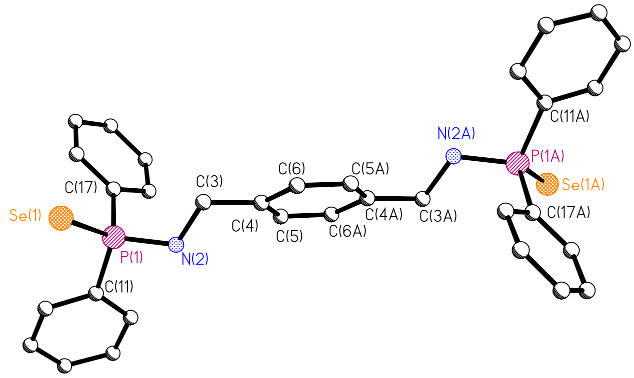
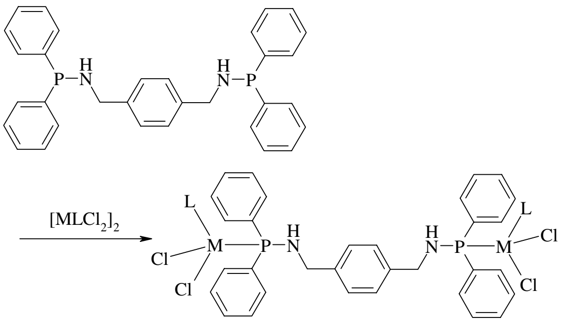


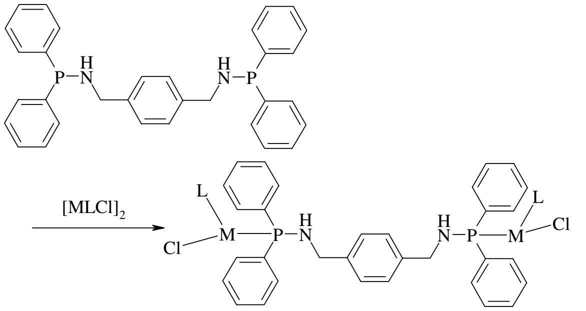
Fig. 2. The X-ray structure of p-$Ph_2P(Se)NHCH_2(C_6H_4)CH_2NHP(Se)Ph_2$ (**4**).



(2)

M= Pt L = PEt_3 **5**, L = PMe_2Ph **6**
M= Ir L= Cp* **7**, M = Rh L= Cp* **8**
M= Ru L= p-cymene **9**

$[(Pd(\eta^3\text{-}C_3H_5)Cl(Ph_2PNHCH_2))_2C_6H_4]$ (**10**) was prepared (68%) from $[\{Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)\}_2]$ and **1** in dichloromethane. The microanalysis obtained was satisfactory for the suggested structure and EI^+ mass spectral data gave the expected parent ion and fragmentation pattern. The IR spectrum has bands at 3246, 1433, 998, 276 cm^{-1} that correspond to the ν_{NH}, ν_{PPh}, ν_{PN} and ν_{PdCl} vibrations. The ^{31}P NMR ($CDCl_3$) is a single peak at δ_P 58.1 ppm. Similarly, complex (**11**) was prepared by reaction of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ and **1** (Eq. (3)).



(3)

M=Pd L=allyl **10**, L=Rh L = cod (cyclooctadiene) **11**

Table 3
Details of the X-ray data collections and refinements

	3	**4**
Empirical formula	$C_{32}H_3N_2P_2S_2$	$C_{32}H_3N_2P_2Se_2$
M	568.64	664.46
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions		
a (Å)	9.2393(13)	10.950(5)
b (Å)	10.6234(17)	10.964(5)
c (Å)	16.444(3)	12.459(6)
α (°)	92.828(3)	90
β (°)	100.309(3)	96.528(10)
γ (°)	112.799(3)	90
U (Å^3)	1451.3(4)	1468.1(12)
Z	2	2
μ (mm^{-1})	0.318	2.620
Reflections measured	7413	6267
Independent reflections	4150	2100
Final R_1, ωR_2 [$I > 2\sigma(I)$]	0.0402, 0.1035	0.0401, 0.0651

We also prepared a simple bimetallic gold complex **12**. It is clear from the above observations that **1** is readily prepared and able to function as a bridging ligand, but there is no evidence for **1** behaving as a bidentate *trans* ligand (see Table 3).

3. Experimental

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 distillation 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 [AuCl(tht)] (tht = tetrahydrothiophene)[9], [MCl_2(cod)] (M = Pt or Pd; cod = cycloocta-1,5-diene)[10,11], [{RuCl(μ-Cl)(η^6-*p*-MeC$_6$H$_4$^{i}Pr)}$_2$][12], [{Rh(μ-Cl)(cod)}$_2$][13], [{Pd(μ-Cl)(η^3-C$_3$H$_5$)}$_2$] [{MCl (μ-Cl)(η^5-C$_5$Me$_5$)}$_2$] (M = Rh or Ir) [14] [{PtCl (μ-Cl)(PMe$_2$Ph)}$_2$][15] and [{PtCl(μ-Cl)(PEt$_3$)}$_2$] [16] were prepared using the literature procedures. Chlorodiphenylphopshine was distilled prior to use. NEt_3 (99% purity), ^{t}BuOK (95% purity), H_2O_2 (30 wt% in H_2O), *p*-xylylene diamine and reagent grade KBr were used without further purification. Infra-red spectra were recorded as KBr discs in the range 4000–200 cm^{-1} on a Perkin–Elmer 2000 FTIR/RAMAN spectrometer. ^{31}P and ^{1}H NMR spectra were recorded on a Gemini 2000 spectrometer (operating at 121.4 MHz for ^{31}P and 300 MHz for ^{1}H) or a JEOL DELTA 270 and are referenced to 85% H_3PO_4 and tetramethylsilane, respectively. Microanalyses were performed by the St. Andrews University service and mass spectra by the Swansea Mass Spectrometer Service.

3.1. $Ph_2PNHCH_2C_6H_4CH_2NHPPh_2$ (**1**)

To a stirring solution of triethylamine (2.26 g, 22.29 mmol) in thf (100 cm^3) at room temperature was added a thf (50 cm^3) solution of chlorodiphenylphosphine (4.92 g, 22.29 mmol) over 2 h and simultaneously a thf solution of *p*-xylylene diamine (1.52 g, 11.14 mmol) over 2 h. The stirring was continued for a further hour before removing the colourless precipitate that had formed by filtration and the solvent removed to yield a colourless solid which was recrystallised from dichloromethane and hexane to give the desired product as a fine colourless solid that was collected by suction filtration and dried in vacuo. Yield 4.99 g, 89%. ^{1}H ($CDCl_3$) δ 1.4 (m, 4H, CH_2), 4.1 (br s, 2H, NH), 7.3–7.9 (m, 24H, aromatics). MS: *m*/*z* 504 [M]$^+$.

3.2. $Ph_2P(O)NHCH_2C_6H_4CH_2NHP(O)Ph_2$ (**2**)

AqueousHydrogen peroxide (30% w/w, 0.1 cm^3, 0.9 mmol) was added drop wise to a suspension of $Ph_2PNHCH_2C_6H_4CH_2NHPPh_2$ (223 mg, 0.4 mmol) in thf (10 cm^3) and the mixture was stirred for 30 min. The solution was filtered through Celite to remove a small amount of insoluble material and the solvent was removed in vacuo to give viscous oil, which was dissolved in dichloromethane (0.5 cm^3) before precipitating a colourless solid upon addition of diethyl ether (6 cm^3). The product was collected by suction filtration and dried in vacuo. Yield 188 mg, 79%. ^{1}H NMR ($CDCl_3$): δ 1.4 (m, 4H, CH_2), 4.1 (br s, 2H, NH), 7.3–7.9 (m, 24H, aromatics) ppm. MS: *m*/*z* 559 [M + Na]$^+$.

3.3. $Ph_2P(S)NHCH_2C_6H_4CH_2NHP(S)Ph_2$ (**3**)

$Ph_2PNHCH_2C_6H_4CH_2NHPPh_2$ (214 mg, 0.4 mmol) and sulfur (27 mg, 0.8 mmol) were heated to reflux in toluene (15 cm^3) for 4 h. The reaction mixture was filtered through Celite to remove any insoluble material remaining befpre reducing the solvent to yield an off-white solid that was washed with $CHCl_3$ (5 cm^3) and dried in vacuo. Yield 106 mg, 44%. ^{1}H NMR ($CDCl_3$): δ 1.4 (m, 4H, CH_2), 4.1 (d, 2H, ^2J (^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 24H, aromatics) ppm. MS: *m*/*z* 591 [M + Na]$^+$.

3.4. $Ph_2P(Se)NHCH_2C_6H_4CH_2NHP(Se)Ph_2$ (**4**)

$Ph_2PNHCH_2C_6H_4CH_2NHPPh_2$ (198 mg, 0.4 mmol) and grey selenium (62 mg, 0.8 mmol) were heated to reflux in toluene (10 cm^3) for 5 h. The solvent was removed in vacuo and the crude product was taken up in CH_2Cl_2 (5 cm^3) and filtered through Celite to remove a trace of unreacted selenium. The filtrate was evaporated to dryness to yield an off-white solid, which was dried in vacuo overnight. Yield 189 mg, 73%. ^{1}H NMR ($CDCl_3$): δ 1.4 (m, 4H, CH_2), 4.1 (d, 2H, ^2J (^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 24H, aromatics) ppm. MS: *m*/*z* 681 [M + Na]$^+$.

3.5. [{(PEt_3)$PtCl_2$(Ph_2PNHCH_2)}$_2$$C_6H_4$] (**5**)

[{PtCl(μ-Cl)(PEt$_3$)}$_2$](39 mg, 0.05 mmol) and ligand (26 mg, 0.05 mmol) were dissolved in dichloromethane (5 cm^3) and stirred overnight. The reaction mixture was filtered through Celite to remove any insoluble material and then reduced to 0.5 cm^3 before addition of diethyl ether (10 cm^3) to precipitate a colourless solid that was isolated by filtration and dried in vacuo. Yield 45 mg, 69%. ^{1}H ($CDCl_3$) δ 1.0 (m, 18H, CH_3), 1.2 (m, 12H, CH_2), 1.4 (m, 4H, CH_2N), 4.1 (d, 2H, ^2J(^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 24H, aromatics) ppm. MS: *m*/*z* 1293 [M + Na]$^+$, 1235 [M – Cl]$^+$, 1200 [M – 2Cl]$^+$.

3.6. *[{(PPhMe$_2$)PtCl$_2$(Ph$_2$PNHCH$_2$)}$_2$C$_6$H$_4$]* (**6**)

[{PtCl(μ-Cl)(PMe$_2$Ph)}$_2$](41 mg, 0.05 mmol) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (26 mg, 0.05 mmol) were dissolved in dry CH$_2$Cl$_2$ (5 cm^3) and stirred overnight. The pale yellow solution formed was filtered through Celite to remove any inorganic impurities before reducing the solvent volume to 0.5 cm^3 and addition of diethyl ether (10 cm^3) to precipitate a colourless solid that was isolated by suction filtration and dried in vacuo. Yield 40 mg, 60%. ^{1}H (CDCl$_3$) δ 1.2 (m, 12H, CH$_3$), 1.4 (m, 4H, CH$_2$N), 4.1 (d, 2H, ^2J(^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 34H, aromatics) ppm. MS: *m*/*z* 1333 [M + Na]$^+$, 1275 [M − Cl]$^+$, 1239 [M − 2Cl]$^+$.

3.7. *[{(IrCl$_2\eta^5$-C$_5$Me$_5$)(Ph$_2$PNHCH$_2$)}$_2$C$_6$H$_4$]* (7)

[{IrCl(μ-Cl)(^{5}-ηC$_5$Me$_5$)}$_2$](50 mg, 0.06 mmol) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (32 mg, 0.06 mmol) were dissolved in dry CH$_2$Cl$_2$ (5 cm^3) and stirred for 2 h. The orange solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 0.5 cm^3 and addition of diethyl ether (20 cm^3) to precipitate an orange solid that was isolated by filtration and dried in vacuo. Yield 60 mg, 73%. ^{1}H (CDCl$_3$) δ 1.3 (s, 30H, CH$_3$), 1.5 (m, 4H, CH$_2$N), 4.1 (d, 2H, ^2J (^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 24 H, aromatics) ppm MS: *m*/*z* 1323 [M + Na]$^+$, 1158 [M − 4Cl]$^+$.

3.8. *[{RhCl$_2$(η^5-C$_5$Me$_5$)(Ph$_2$PNHCH$_2$)}$_2$C$_6$H$_4$]* (**8**)

[{RhCl(μ-Cl)(η^5-C$_5$Me$_5$)}$_2$](48 mg, 0.08 mmol) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (39 mg, 0.08 mmol) were dissolved in dry CH$_2$Cl$_2$ (5 cm^3) and stirred for 2 h. The orange solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 0.5 cm^3 and addition of diethyl ether (10 cm^3) to precipitate an orange solid that was isolated by filtration and dried in vacuo. Yield 68 mg, 78%. ^{1}H (CDCl$_3$) δ 1.3 (s, 30H, CH$_3$), 1.5 (m, 4H, CH$_2$N), 4.1 (d, 2H, ^2J(^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 24 H, aromatics) ppm. MS: *m*/*z* 1145 [M + Na]$^+$, 1087 [M − Cl]$^+$, 1049 [M − 2Cl]$^+$.

3.9. *[{RuCl$_2$(η^6-p-MeC$_6$H$_4{}^i$Pr)(Ph$_2$PNHCH$_2$)}$_2$C$_6$H$_4$]* (**9**)

[{RuCl(μ-Cl)(η^6-*p*-MeC$_6$H$_4{}^i$Pr)}$_2$] (47 mg, 0.08 mmol) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (39 mg, 0.08 mmol) were dissolved in dry CH$_2$Cl$_2$ (5 cm^3) and stirred for 1 h. The orange solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 0.5 cm^3 and addition of diethyl ether (10 cm^3) to precipitate an orange solid that was isolated by filtration and dried in vacuo. Yield 62 mg, 72%. ^{1}H (CDCl$_3$) δ 0.8 (m, 12H, CH$_3$), 1.2 (6H, CH$_3$), 1.9 (m, 4H, CH$_2$N), 2.5 (m, 2H, CH), 4.1 (d, 2H, ^2J (^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 28H, aromatics) ppm. MS: *m*/*z* 1139 [M + Na]$^+$.

3.10. *[{Pd(η^3-C$_3$H$_5$)Cl(Ph$_2$PNHCH$_2$)}$_2$C$_6$H$_4$].* (**10**)

[{Pd(μ-Cl)(η^3-C$_3$H$_5$)}$_2$](61 mg, 0.2 mmol) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (84 mg, 0.2 mmol) were dissolved in dry CH$_2$Cl$_2$ (5 cm^3) and stirred overnight. The reaction mixture was filtered through Celite to remove any insoluble inorganic material before reducing the solvent to 0.5 cm^3 and addition of diethyl ether (10 cm^3) to precipitate a yellow microcrystalline solid that was isolated by suction filtration. Yield 98 mg, 68%. ^{1}H (CDCl$_3$) δ 1.3 (m, 8H, CH$_2$), 1.9 (m, 4H, CH$_2$N), 2.5 (m, 2H, CH), 4.1 (d, 2H, ^2J (^{31}P–^{1}H) 8 Hz, NH), 7.2–8.0 (m, 24H, aromatics) ppm. MS: *m*/*z* 835 [M − Cl]$^+$.

3.11. *[{RhCl(C$_8$H$_{12}$)(Ph$_2$PNHCH$_2$)}$_2$C$_6$H$_4$]* (**11**)

[{Rh(cod)Cl}$_2$](49 mg, 0.1 mmol) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (50 mg, 0.1 mmol) were dissolved in dry toluene (5 cm^3) and stirred for 2 h. The solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 0.5 cm^3 and addition of hexane (20 cm^3) to precipitate a yellow solid that was isolated by filtration and dried in vacuo. Recryst from CH$_2$Cl$_2$/hexane. Yield 56 mg, 57%. ^{1}H (CDCl$_3$) δ 1.8 (m, 24H, C$_8$H$_{12}$), 1.9 (m, 4H, CH$_2$N), 4.1 (d, 2H, ^2J(^{31}P–^{1}H) 8dz, NH), 7.2–8.0 (m, 24H, aromatics) ppm MS: *m*/*z* 961 [M − Cl]$^+$.

3.12. *[{AuCl(Ph$_2$PNHCH$_2$)}$_2$C$_4$H$_6$]* (**12**)

[AuCl(tht)] (116 mg, 0.4 mmol) was dissolved in dry CH$_2$Cl$_2$ (5 cm^3) and Ph$_2$PNHCH$_2$C$_6$H$_4$CH$_2$NHPPh$_2$ (91 mg, 0.2 mmol) was added in one portion before stirring for 30 min. The colourless solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 2 cm^3 precipitate a colourless solid that was isolated by suction filtration and dried in vacuo. Yield 88 mg, 43%. ^{1}H (CDCl$_3$) δ 1.6 (s, 4H, CH$_2$N), 4.2 (d, 2H, ^2J(^{31}P–^{1}H) 10 Hz, NH), 7.2–8.0 (m, 24H, aromatics) ppm MS: *m*/*z* 991 [M + Na]$^+$, 933 [M − Cl]$^+$.

4. Crystallography

X-ray diffraction studies were performed at 125 K using 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^2 using SHELXTL [17].

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. 239833 and 239834 at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk].

References

[1] S.M. Aucott, Coordination Chemistry of Aminophosphine Ligands, Ph.D. Thesis, University of Loughborough, 1999.
[2] M.K. Copper, J.M. Downes, P.A. Duckworth, E.R.T. Tiekink, Aust. J. Chem. 45 (1992) 595.
[3] J. Heinicke, A. Tzschach, J. Pract. Chem. 325 (1983) 232.
[4] J. Heinicke, R. Kadryov, M.K. Kindermann, M. Kloss, A. Fischer, P.G. Jones, Chem. Ber. 129 (1996) 1061.
[5] F.E. Wood, M.M. Olmstead, A.L. Balch, J. Am. Chem. Soc. 105 (1983) 6332.
[6] F.E. Wood, J. Hvoslef, H. Hope, A.L. Balch, Inorg. Chem. 23 (1984) 4309.
[7] K.G. Gaw, M.B. Smith, J.W. Steed, J. Organomet. Chem. 664 (2002) 294.
[8] A.M.Z. Slawin, J. Wheatley, M.V. Wheatley, J.D. Woollins, Polyhedron 22 (2003) 1397.
[9] R. Uson, A. Laguna, M. Laguna, Inorg. Synth. 28 (1991) 346.
[10] D. Drew, J.R. Doyle, Inorg. Synth. 28 (1991) 346.
[11] J.X. McDermott, J.F. White, G.M. Whiteside, J. Am. Chem. Soc. 60 (1976) 6521.
[12] M.A. Bennett, T.N. Huang, T.W. Matheson, Inorg. Synth. 21 (1982) 74.
[13] G. Giordano, R.H. Crabtree, Inorg. Synth. 19 (1979) 218.
[14] C. White, A. Yates, P.M. Maitlis, Inorg. Synth. 29 (1992) 228.
[15] W. Baratta, P.S. Pregosin, Inorg. Chim. Acta 209 (1993) 85.
[16] J. Chatt, R.G. Wilkins, J. Chem. Soc. (1952) 273.
[17] SHELXTL, Bruker AXS, Madison, WI, 2001.