

Synthesis and Coordination Chemistry of the New Unsymmetrical Ligand $\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2$

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Condensation of $\text{Ph}_2\text{PCH}_2\text{OH}$ with 2-(diphenylphosphanyl)-aniline in toluene gave the new unsymmetrical ligand $\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2$ (**1**) in good yield. Oxidation of **1** with H_2O_2 or elemental sulfur led to the oxidised products $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{NHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$ (**2**) and $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{NHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2$ (**3**). The new ligand **1** demonstrates three distinct modes of coordination. Reaction of compound **1** with $[\text{MX}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{Cl}, \text{Br}, \text{Me}$) or $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ gave the chelate complexes $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**4**), $[\text{PdBr}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**5**), $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**6**), $[\text{PtMe}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**7**) and $[\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**8**). Coordination of **1** with $[\{\text{RuCl}(\mu\text{-Cl})(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})\}_2]$ or $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ gave the monodentate complexes $[\text{RuCl}_2(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X})]$ (**9**) and $[\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X})]$ (**10**). Reaction of **1** with $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ led to a mixture from which the monodentate com-

plex $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X})]$ (**11**) and the chelate cationic complex $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})][\text{Cl}]$ (**12**) were separated. Abstraction of the chloride ligands from complexes **9** and **10** with AgClO_4 gave the cationic chelate complexes $[\text{RuCl}(\eta^3:\eta^3\text{-C}_{10}\text{H}_{16})(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})][\text{ClO}_4]$ (**13**) and $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})][\text{ClO}_4]$ (**14**). Compound **1** also functions as a bridging ligand when reacted with two molar equivalents of $[\text{AuCl}(\text{tht})]$ or one molar equivalent of $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ to give the bimetallic complexes $[\text{Ph}_2\text{P}\{\text{AuCl}\}\text{CH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\{\text{AuCl}\}]$ (**15**) and $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2)]$ (**16**). The dioxidised compounds **2** and **3** and several typical complexes **8**, **9**, **11** and **14** were structurally characterised by X-ray diffraction.

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Introduction

Chemically symmetrical bisphosphane ligands have been intensively investigated in all aspects of inorganic and organometallic chemistry, and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ [bis(diphenylphosphanyl)methane (dppm)], $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ [bis(diphenylphosphanyl)ethane (dppe)], and its $-(\text{CH}_2)_n-$ backboned homologues, the aromatic $\text{Ph}_2\text{PC}_6\text{H}_4\text{PPh}_2$ [1,2-phenylenebis(diphenylphosphane)] and the ferrocene backboned 1,1'-bis(diphenylphosphanyl)ferrocene are all well-known examples of this class of ligand.^[1–9] Unsymmetric bisphosphanes, with the notable exception of chiral aminophosphane-phosphinites,^[10] have received relatively little attention (for recent examples see refs.^[11–15]). We recently described the synthesis of $\text{Ph}_2\text{PC}_6\text{H}_4\text{NHPPH}_2$ an unsymmetrical diphosphane derived from 2-(diphenylphosphanyl)-aniline^[16] in which the two phosphorus atoms demonstrated different coordination activities.^[17,18] Herein we report another unsymmetrical diphosphane $\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2$ which has an additional methylene spacer group

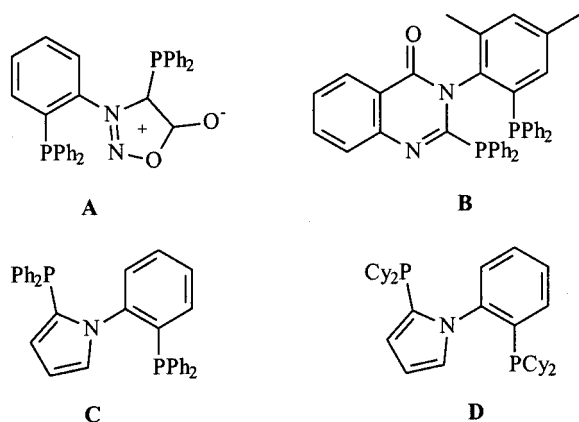
between the NH and the PPh_2 moieties giving the ligand a flexible PCNC_2P spine. Other rare literature examples of PCNC_2P backboned ligand systems include diphenyl[3-(2-diphenylphosphanylphenylsydonyl)-phosphane]^[19] **A**, the substituted quinazolinone ligand **B**^[20] and the bis(diphenylphosphanyl)- and bis(dicyclohexylphosphanyl)pyrrole-derived diphosphanes **C** and **D**^[21] (Scheme 1). The synthesis of $\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2$ and its reactivity towards a variety of late transition metals are described. The products from these reactions have been characterised principally by multi-element NMR spectroscopy and X-ray crystallography.

Results and Discussion

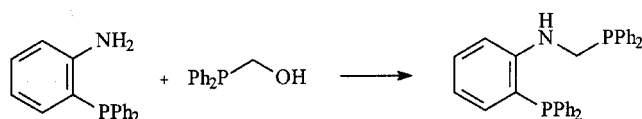
Preparation and Characterisation of the Ligand

The condensation of equimolar quantities of diphenylphosphanylmethanol and 2-(diphenylphosphanyl)aniline in toluene at 90–95 °C gave the unsymmetrical bisphosphane $\text{Ph}_2\text{PC}_6\text{H}_4\text{NHCH}_2\text{PPh}_2$ (**1**) in excellent yield (84.4%) (Scheme 2). The white solid product was stable to moisture and air. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 shows two distinct singlets at $\delta_\text{P} = -18.77$ and $\delta_\text{P} = -22.30$. Although it is not easy to assign the signals in reference to

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Scheme 1. Examples of PCNC₂P backboned ligands

the starting reactant 2-(diphenylphosphanyl)aniline^[16] (**17**) or the previously reported Ph₂PNHC₆H₄PPh₂^[17] (**18**) (Scheme 2, Table 1), the resonance at $\delta_P = -18.77$ was assigned to the phosphorus (P_X) of the NHCH₂PPh₂ group and the other signal at $\delta_P = -22.30$ to the triarylphosphane moiety (P_A) by comparing the ³¹P{¹H} NMR spectra of its monodentate complexes **9–11**, which will be discussed below. These assignments are also in accordance with those in other reported molecules (**19–22**)^[22–25] shown below (Scheme 3, Table 1).

Scheme 2. Preparation of ligand **11**Table 1. ³¹P{¹H} NMR chemical shifts of **1**, and related compounds **17–22**

Compound	Chemical shifts		Compound	Chemical shifts	
	$\delta(P_X)^{[a]}$	$\delta(P_A)^{[a]}$		$\delta(P_X)^{[a]}$	$\delta(P_A)^{[a]}$
1	-18.77	-22.30	20 ^[b]	-16.8	—
17 ^[b]	—	-19.75	21 ^[b]	-17.9	—
18 ^[b]	29.6	-19.5	22 ^[b]	—	-21.5
19 ^[b]	-18.16	—			

^[a] P_X is the phosphorus of either NHCH₂PPh₂ or NHPPH₂ groups and P_A is the phosphorus of triarylphosphane. ^[b] Literature compounds.

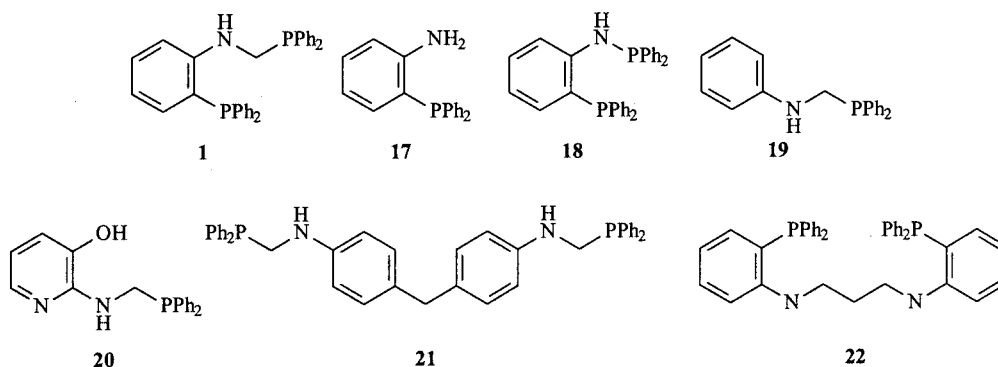
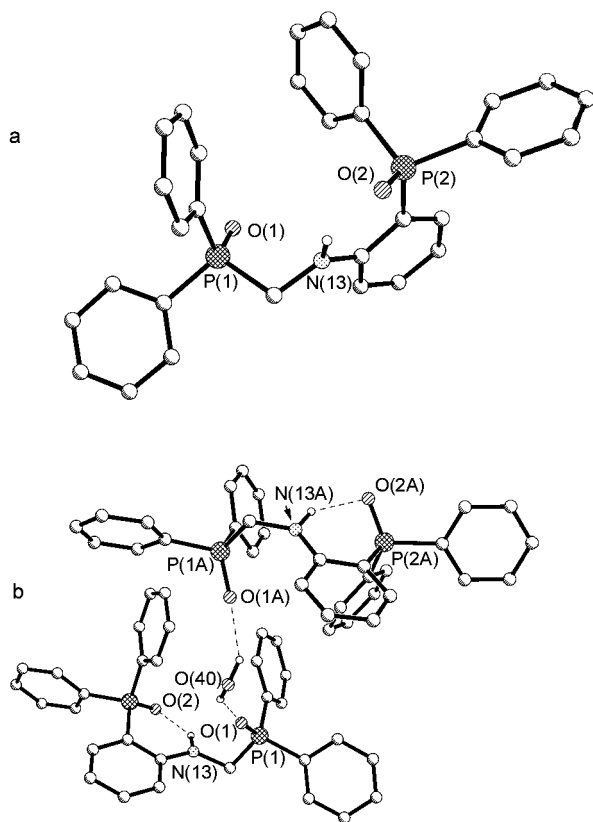
In the ¹H NMR spectrum, the resonances of the aromatic protons are found between $\delta_H = 7.40$ and 6.64. The NH proton appears as a broad singlet at $\delta_H = 4.97$. The triplet at $\delta_H = 3.83$ was assigned to the methylene group, with equal couplings (³J_{P,CH} = ³J_{CH,NH} = 5 Hz). The infrared spectrum of **1** shows ν_{NH} at 3345 cm⁻¹. Attempts to grow crystals of **1** suitable for X-ray analysis were not successful. However, the structures of its oxidised counterparts **2** (Figure 1, Table 2) and **3** (Figure 2, Table 2) were obtained.

Compound **2** was prepared by the oxidation of **1** with H₂O₂ and compound **3** by oxidation of **1** with elemental sulfur.

Compounds **2** and **3**, like their parent compound **1**, gave good microanalysis and the expected FAB-MS spectral patterns. The ³¹P{¹H} NMR spectrum of **2** (in CD₂Cl₂) exhibits two singlets at higher frequency than those of **1**. The singlet at $\delta_P = 36.38$ was assigned to the triarylphosphane (P_A) and that at $\delta_P = 28.58$ to the phosphorus (P_X) of the NHCH₂PPh₂ moiety by comparison with the signals of compounds **23** and **24** (Scheme 4, Table 3). The two singlets of compound **3** at $\delta_P = 39.35$ and 38.46 in CD₂Cl₂ were too close to be assigned unambiguously, but we have assigned the singlet at $\delta_P = 39.35$ to the triarylthiophosphinoyl (P_A) and that at $\delta_P = 38.46$ to the NHCH₂P(S)Ph₂ moiety (P_X) by comparing the signals with those of compounds **25** and **26** (Scheme 4, Table 3). The synthesis and complex formation of compounds **23–26** in Scheme 4 will be reported elsewhere.

The ¹H NMR spectra of **2** and **3** show similar aromatic proton signals to that of **1**. However, the NH resonance in **2** was obscured by the aromatic proton resonances; the ¹H-¹H COSY spectrum reveals that the NH signal lies at ca. $\delta_H = 7.30$. In compound **3** the NH signal was confirmed by an H/D exchange reaction. In both cases, the NH resonances are shifted to higher frequency by ca. 2 ppm relative to **1**. In the IR spectra, the ν_{NH} absorption was also shifted to lower frequency by 30 cm⁻¹ for **2** and 138 cm⁻¹ for **3**. This is attributed to the intramolecular hydrogen bonding interactions that occur in compounds **2** and **3**, as seen in the crystal structures.

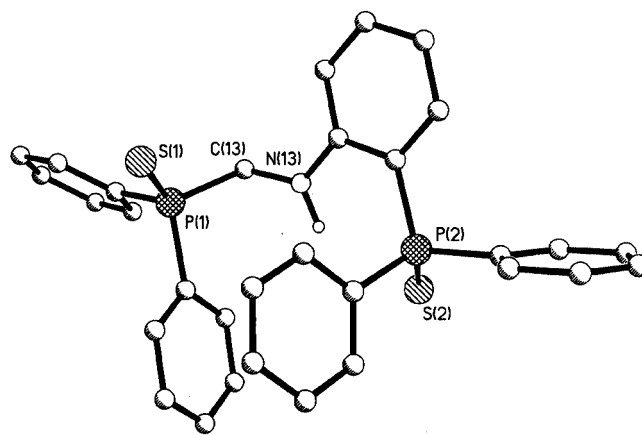
In the solid state, **2** and **3** (Figure 1a and 2, respectively) both form an envelope-like pseudo six-membered ring via intramolecular hydrogen bonding interactions between the H(13n) and the O(2) or S(2) at P(2). The O(2) atom in compound **2** is 0.60 Å out of the P(2)–C(15)–C(14)–H(13n)–N(13) mean plane (mean deviation of 0.07 Å) with a fold angle of 32°. In compound **3**, the deviation of S(2) from the P(2)–C(15)–C(14)–H(13n)–N(13) mean plane (mean deviation from each other 0.05 Å) of -1.27 Å is bigger than that in compound **2** due to the different bond lengths of P=O and P=S (Table 2), as well as the strength of the H bonding [H(13n)⋯O(2): 1.98 Å; O(2)⋯H(13n)–N(13): 144°; H(13n)⋯S(2): 2.47 Å; S(2)⋯H(13n)–N(13): 144°]. The hinge angle between the S(2)–P(2)–H(13) plane and the P(2)–C(15)–C(14)–H(13n)–N(13) mean plane along the P(2)–H(13n) axis is 46°. In addition to the intramolecular hydrogen bonding, compounds **2** and **3** share other common features: the two P=E (E = O, S) groups lie in an *anti*-position; the geometry around each phosphorus atom is approximately tetrahedral; the main skeleton of molecules **2** and **3** — P(2)–C(15)–C(14)–N(13)–C(13) — lies in a mean plane with a mean deviation of 0.04 Å and 0.02 Å, respectively. The planar skeleton can be explained from the sp² hybrid state of C(15) and C(14) as well as the conjugation of N(13) with the aromatic ring. The C(14)–N(13)–C(13) bond angle is 124.5(4)° and 126.0(2)° in **2** and **3**, respectively. There is one additional feature in

Scheme 3. Compound **1** and other related moleculesFigure 1. (a) Crystal structure of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{NHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$ (**2**): a single molecule; (b) crystal structure of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{NHC}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2$ (**2**) showing the hydrogen bonded dimer pairs

compound **2** (Figure 1b) that is not observed in compound **3**: each molecule of **2** crystallises with 0.5 molecules of water. The water links two molecules of **2** through weak intermolecular hydrogen bonding interactions with the oxygen atom of the $\text{NCH}_2\text{P}(\text{O})\text{Ph}_2$ moiety and O(1) and O(1A) [$\text{O}(1)\cdots\text{H}(40\text{o})$: 2.49 Å; $\text{O}(1)\cdots\text{H}(40\text{o})-\text{O}(40)$: 102°]. Therefore, it is not surprising to see that there is little difference between the two $\text{P}=\text{O}$ bond lengths [$\text{P}(1)-\text{O}(1)$: 1.487(3) Å; $\text{P}(2)-\text{O}(2)$: 1.483(4) Å] in compound **2**, while, in contrast, $\text{P}(2)-\text{S}(2)$ [1.9719(11) Å] is longer than $\text{P}(1)-\text{S}(1)$ [1.9443(12) Å] in **3**.

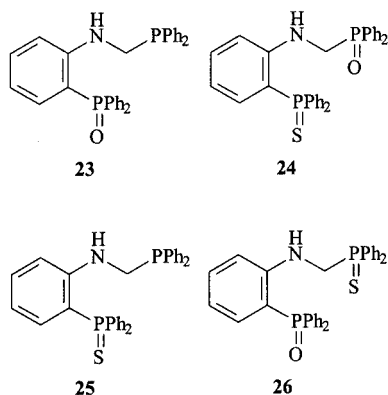
Table 2. A comparison of the bond lengths (Å) and angles ($^\circ$) in compounds **2** and **3**

	2	3
$\text{P}(1)-\text{E}(1)$	1.483(4)	1.9443(12)
$\text{P}(1)-\text{C}(13)$	1.812(5)	1.833(3)
$\text{N}(13)-\text{C}(13)$	1.450(6)	1.447(3)
$\text{N}(13)-\text{C}(14)$	1.383(6)	1.378(4)
$\text{C}(14)-\text{C}(15)$	1.414(6)	1.428(4)
$\text{C}(15)-\text{P}(2)$	1.808(5)	1.818(3)
$\text{P}(2)-\text{E}(2)$	1.487(3)	1.9717(11)
$\text{E}(1)-\text{P}(1)-\text{C}(13)$	112.6(2)	113.95(11)
$\text{N}(13)-\text{C}(13)-\text{P}(1)$	110.5(3)	112.0(2)
$\text{C}(14)-\text{N}(13)-\text{C}(13)$	124.5(4)	126.0(2)
$\text{N}(13)-\text{C}(14)-\text{C}(15)$	119.0(4)	119.7(2)
$\text{C}(14)-\text{C}(15)-\text{P}(2)$	120.5(4)	121.1(2)
$\text{E}(2)-\text{P}(2)-\text{C}(15)$	112.4(2)	114.34(10)

Figure 2. Crystal structure of $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{NHC}_6\text{H}_4\text{P}(\text{S})\text{Ph}_2$ (**3**)

Coordination Chemistry of Compound **1**

Both of the phosphorus atoms of **1** can coordinate with late transition metals. When reacted with Pd^{II} , Pt^{II} or Mo^0 , **1** functions as a bidentate ligand to give the seven-membered chelate complexes **4–8** (Scheme 5). However, due to their different chemical environments the reactivity of the two phosphorus atoms is different. The less bulky and less

Scheme 4. Compounds related to **2** and **3**Table 3. $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts of **2**, **3** and related compounds

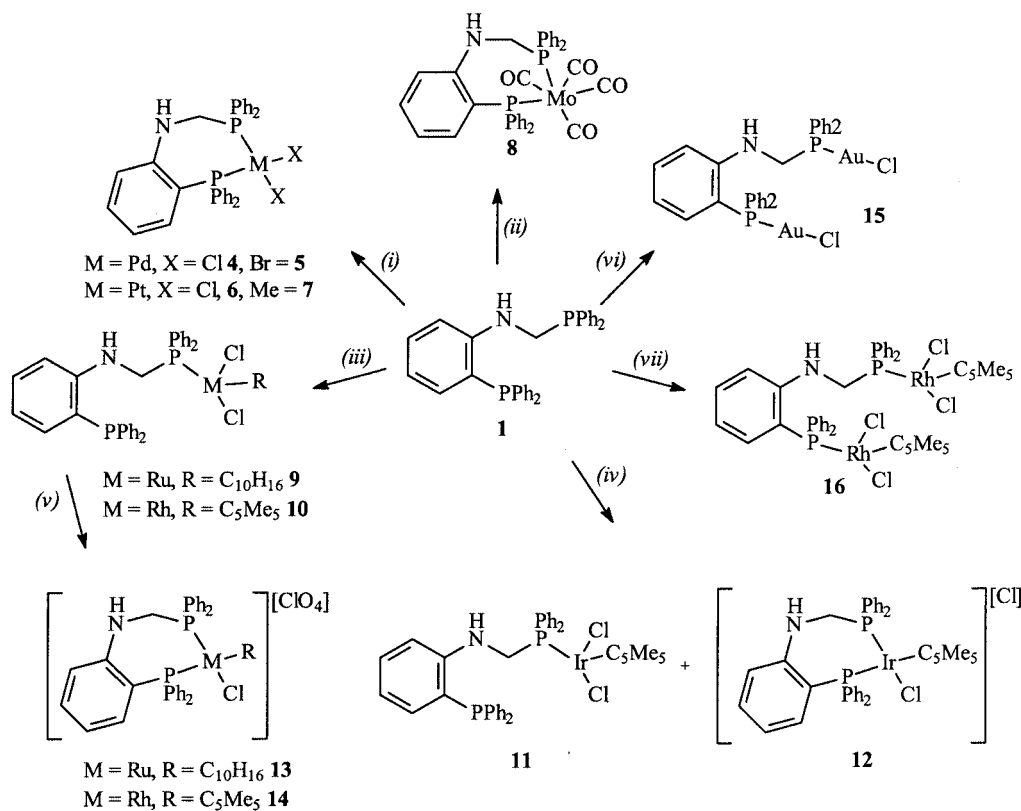
Compound	Chemical shifts		Compound	Chemical shifts	
	$\delta(\text{P}_\text{X})^{[\text{a}]}$	$\delta(\text{P}_\text{A})^{[\text{a}]}$		$\delta(\text{P}_\text{X})^{[\text{a}]}$	$\delta(\text{P}_\text{A})^{[\text{a}]}$
2	28.58	36.38	24 ^[a]	27.82	39.98
3	38.46	39.35	25 ^[a]	−20.46	39.67
23 ^[a]	−19.90	36.59	26 ^[a]	38.32	36.60

^[a] P_X is the phosphorus of $\text{NHCH}_2\text{PPh}_2$ groups and P_A is the phosphorus of triarylphosphane.

electron-delocalized phosphorus (P_X) of the $\text{NHCH}_2\text{PPh}_2$ group is more reactive than triarylphosphane (P_A). When **1** reacts with $\text{Rh}^{\text{III}}/\text{Ru}^{\text{IV}}$ chloride-bridged dimers in a 2:1 molar ratio, the “dangling” monodentate complexes **9** and **10** were obtained (Scheme 5). However, reaction of **1** with $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ in a 2:1 molar ratio led to the cationic chelate complex **12** together with monodentate **11**. Abstraction of chloride from **9** and **10** with silver perchlorate gave the cationic chelate complexes **13** and **14**. When $[\text{AuCl}(\text{tht})]$ was employed, both (P_X) and (P_A) in **1** coordinate to the gold centre. We believe that steric effects control the reaction. Changing the reactants molar ratio also change the products: when two molar equivalents of $[\text{AuCl}(\text{tht})]$ or one molar equivalent of $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ was reacted with ligand **1**, the bidentate bridging complexes **15** and **16** were obtained (Scheme 5).

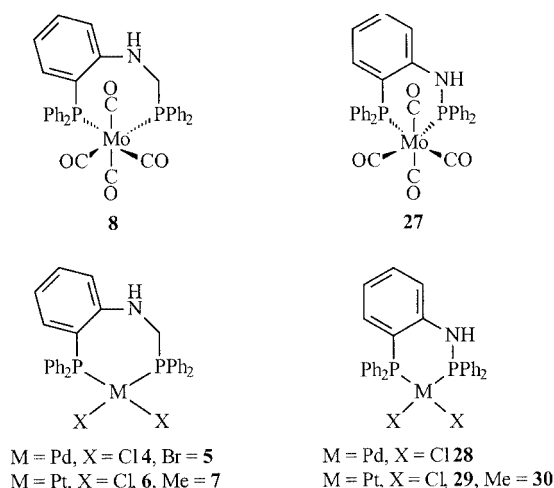
Bidentate Chelate Complexes

Reactions of equimolar quantities of ligand **1** and $[\text{PdCl}_2(\text{cod})]$, $[\text{PdBr}_2(\text{cod})]$, $[\text{PtCl}_2(\text{cod})]$, $[\text{PtMe}_2(\text{cod})]$ or $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ gave the corresponding seven-membered ring chelate complexes $[\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**4**), $[\text{PdBr}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**5**), $[\text{PtCl}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**6**), $[\text{PdMe}_2(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**7**) and $[\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**8**), respectively. All of the



Scheme 5. (i) $[\text{MX}_2(\text{cod})]$ ($\text{M} = \text{Pd}$, $\text{X} = \text{Cl}$ or Br ; $\text{M} = \text{Pt}$, $\text{X} = \text{Cl}$ or Me); (ii) $[\text{Mo}(\text{CO})_4(\text{pip})_2]$; (iii) 0.5 equiv. of $[\{\text{RuCl}(\mu\text{-Cl})(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})_2\}]$ or $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)_2\}]$; (iv) 0.5 equiv. of $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)_2\}]$; (v) AgClO_4 ; (vi) 2 equiv. of $[\text{AuCl}(\text{tht})]$; (vii) $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)_2\}]$

complexes gave satisfactory microanalysis and the expected fragmentation patterns in their positive ion FAB mass spectra. In the ³¹P{¹H} NMR spectra of **4** and **5** no ³¹P-³¹P coupling was observed, both compounds displayed two singlets at around δ_P = 42 and δ_P = 21. The ³¹P{¹H} NMR spectra of the platinum complex **6** exhibited a two-bond ³¹P-³¹P coupling and the expected platinum satellites at δ_P = 20.25 (d, ¹J_{Pt,P} = 3647 Hz, ²J_{P,P} = 18 Hz) and δ_P = 1.80 (d, ¹J_{Pt,P} = 3573, ²J_{P,P} = 18 Hz). The large one-bond ³¹P-¹⁹⁵Pt coupling constants are in agreement with the proposed *cis*-geometry of **6**. In compound **7**, two doublets at δ_P = 30.73 and 11.91 (²J_{P,P} = 12 Hz) with platinum satellites are observed. The coupling constants ¹J_{Pt,P} = 1853 Hz and ¹J_{Pt,P} = 1720 Hz are in agreement with those coupling constants found in compounds in which phosphane ligands are *trans* to methyl groups. The molybdenum complex **8** also displays coupling of the two phosphorus atoms at δ_P = 41.43 and δ_P = 28.31 (²J_{P,P} = 25 Hz) in the ³¹P{¹H} NMR spectrum. The assignment of the phosphorus resonances in the above chelate complexes is not straightforward. However, by comparing them with the corresponding complexes of PPh₂C₆H₄NHPPH₂ [18] (Scheme 6, Table 4), we assigned the signal at higher frequency in the ³¹P{¹H} NMR spectra of each chelate complex to the phosphorus of the NHCH₂PPh₂ group (P_X) and the lower frequency resonance to the triarylphosphane (P_A). The ¹H NMR spectra of **4–8** show similar patterns for the aromatic proton resonances, although the NH and CH₂ signals are slightly different depending upon the nature of the solvent and the complexes. The NH resonances of **4** and **5** appear as broad doublets of triplets in [D₆]DMSO at δ_H = 5.53 (³J_{PN,CH} = 10, ³J_{NH,CH} = 3 Hz) and δ_H = 5.44 (³J_{PN,CH} = 25, ³J_{NH,CH} = 3 Hz), respectively. Their CH₂ signals were found at ca. δ_H = 3.9 as a triplet (²J_{P,CH} = ³J_{NH,CH} = 3 Hz).

Scheme 6. Chelate complexes of **1** and Ph₂NHC₆H₄PPh₂

In the ¹H NMR spectrum of **6**, the doublet of triplets signal of NH was observed at δ_H = 3.55 (³J_{NH,CP} = 16 Hz). The doublet of doublets with two platinum satellites (³J_{Pt,CH} = 36 Hz) at δ_H = 3.96 was assigned to CH₂. The

Table 4. Chemical shifts of complexes **4–8** and those from Ph₂NHC₆H₄PPh₂

Complex	Chemical shifts		Complex	Chemical shifts	
	δ(P _X) ^[a]	δ(P _A) ^[a]		δ(P _X) ^[a]	δ(P _A) ^[a]
8	41.43	28.31	27 ^[b]	91.7	33.6
4	42.72	22.98	28 ^[b]	77.8	18.1
5	41.93	20.55			
6	20.25	1.80	29 ^[b]	53.8	−0.4
7	30.73	11.91	30 ^[b]	70.6	10.7

^[a] P_X is the phosphorus of either NHCH₂PPh₂ or NHPPH₂ groups and P_A is the phosphorus of triarylphosphane. ^[b] Literature complexes.^[8]

coupling constants ²J_{P,CH} = 3 Hz and ³J_{NH,CH} = 6 Hz were determined by an exchange reaction with D₂O.

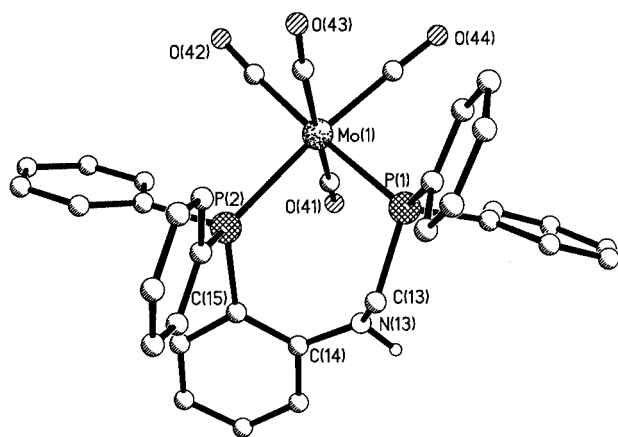
In the ¹H NMR spectrum of complex **7**, the NH and CH₂ resonances overlap at δ_H = 3.99. Addition of D₂O to the CDCl₃ solution of **7** gives a ²J_{P,CH} coupling constant of 9 Hz. Other information obtained from this compound is the two doublets of doublets at δ_H = 0.60 and 0.34 with platinum satellites for two CH₃ groups. Although the coupling constants are available (³J_{P,CH} = 7, ³J_{P',CH} = 9, ²J_{Pt,CH} = 70, ²J_{Pt,CH'} = 69 Hz) the accurate assignment of the two doublets is impossible. The resonance for the NH proton in complex **8** was obscured by aromatic multiplets. The CH₂ group in **8** appears as a broad singlet at δ_H = 4.04.

In the infrared spectra, compounds **4**, **5** and **6** show the ν_{NH} absorption at around 3250 cm^{−1}, shifted to lower frequency relative to **1**. Metal-halide stretches at ca. 320 cm^{−1} and 290 cm^{−1} are in agreement with the *cis*-geometry of the complexes. However, the ν_{NH} absorption at 3337 cm^{−1} in compound **7** and 3389 cm^{−1} in **8** occurs at a significantly higher frequency than in **4–6**. Obviously there is less opportunity for hydrogen bonding between the NH proton of the ligand and the methyl or carbonyl groups of **7** and **8**, respectively, than between the metal-bound chlorides and the amine protons of complexes **4–6**. The infrared spectrum of compound **8** also displayed ν_{C=O} absorption bands at 2013 cm^{−1}, 1914 cm^{−1}, 1892 cm^{−1} and 1878 cm^{−1}.

Pale yellow crystals of **8** suitable for X-ray analysis (Figure 3, Table 5) were obtained by layering methanol onto a dichloromethane solution of **8** for four days. As shown in Figure 3, the coordination geometry around Mo(1) is approximately octahedral, with P(1) and P(2) occupying the *cis* positions. The bite angle of the ligand is 87.47(2)°, slightly less than the expected 90° for a regular octahedron. The *cis* bond angles at Mo(1) are 84.29(2)–91.51(11)°, while the *trans* angle are in the range 172.59(10)–176.66(8)°. The seven-membered chelate ring is twisted, with N(13)–C(14)–C(15)–P(1)–P(2) coplanar (mean deviation 0.01 Å) and C(13) lying 0.96 Å above, and Mo(1) 1.49 Å below, the mean plane. The fold angles between the N(13)–C(14)–C(15)–P(1)–P(2) mean plane and the N(13)–C(13)–P(1) and P(2)–Mo(1)–P(1) planes are 54° and 88° respectively. The N(13)–C(14)–C(15) [124.7(2)°] and C(14)–C(15)–P(2) [124.6(2)°] bond angles are slightly more open than those in compounds **2** and **3**.

Table 5. Selected bond lengths (Å) and angles (°) for compound **8**

Mo(1)–C(41)	2.041(3)	Mo(1)–C(42)	1.992(3)
Mo(1)–C(43)	2.021(3)	Mo(1)–C(44)	1.985(3)
Mo(1)–P(1)	2.5048(6)	Mo(1)–P(2)	2.5884(6)
P(1)–C(13)	1.847(2)	N(13)–C(13)	1.460(3)
N(13)–C(14)	1.401(3)	C(14)–C(15)	1.414(3)
C(15)–P(2)	1.856(2)		
C(41)–Mo(1)–C(42)	87.97(10)	C(41)–Mo(1)–C(43)	172.59(10)
C(41)–Mo(1)–C(44)	91.51(11)	C(42)–Mo(1)–C(43)	85.99(11)
C(42)–Mo(1)–C(44)	90.79(11)	C(43)–Mo(1)–C(44)	84.29(11)
C(41)–Mo(1)–P(1)	94.78(7)	C(42)–Mo(1)–P(1)	176.66(8)
C(43)–Mo(1)–P(1)	91.12(7)	C(44)–Mo(1)–P(1)	87.25(7)
C(41)–Mo(1)–P(2)	87.00(8)	C(42)–Mo(1)–P(2)	94.58(8)
C(43)–Mo(1)–P(2)	97.74(8)	C(44)–Mo(1)–P(2)	174.38(8)
P(1)–Mo(1)–P(2)	87.47(2)	C(13)–P(1)–Mo(1)	112.36(7)
N(13)–C(13)–P(1)	107.9(2)	C(14)–N(13)–C(13)	122.6(2)
N(13)–C(14)–C(15)	124.7(2)	C(14)–C(15)–P(2)	124.6(2)
C(15)–P(2)–Mo(1)	119.01(7)		

Figure 3. Crystal structure of $[\text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**8**)

Monodentate Complexes

Monitoring of the reaction between **1** and either $[\{\text{RuCl}(\mu\text{-Cl})(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\}_2]$ or $[\{\text{RhCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{-Me}_5)\}_2]$ by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed that the monodentate complexes $[\text{RuCl}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X})]$ (**9**) and $[\text{RhCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X})]$ (**10**) are readily formed. The reaction of $[\{\text{IrCl}(\mu\text{-Cl})(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ and **1**, however, is not so straightforward. Several singlets between $\delta_\text{P} = 0.0$ and $\delta_\text{P} = -22$ appear in the crude reaction mixtures. Longer reaction times do not affect the product distribution. After several attempts to separate this mixture a monodentate complex $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X})]$ (**11**) was isolated as well-formed crystals from dichloromethane/acetone in low yield. Also obtained was the chelate cationic complex $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{Ph}_2\text{PCH}_2\text{NHC}_6\text{H}_4\text{PPh}_2\text{-P}_\text{X}, \text{P}_\text{A})]$ (**12**), although in much lower purity.

All of the monodentate complexes gave satisfactory microanalysis and the expected fragmentation patterns and molecular ions in the positive ion FAB mass spectra. Compound **9–11** have similar $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, with the

coordinated phosphorus resonance shifted to higher frequency and that of the dangling phosphorus at ca. $\delta_\text{P} = -22.5$ unshifted. For the rhodium complex **10**, a typical $^1J_{\text{Rh-P}}$ coupling constant of 141 Hz was observed at $\delta_\text{P} = 32.74$. The higher-frequency signal was assigned to the phosphorus of the $\text{NHCH}_2\text{PPh}_2$ group (P_X) and the unshifted $\delta_\text{P} = -22.5$ to triarylphosphane (P_A). This assignment was confirmed by single-crystal X-ray diffraction studies of complexes **9** and **11** (see below).

The ^1H NMR spectra of **9–11** show aromatic proton resonances close to the values for the free ligand. The signals for the NH and methylene protons of the complexes are slightly different. Complexes **10** and **11** display a slightly broad quadruplet for NH at ca. $\delta_\text{H} = 4.9$ ($^3J_{\text{NH,CH}} = ^3J_{\text{NH,CP}} = 7$ Hz) and a doublet at $\delta_\text{H} = 4.48\text{--}4.66$ for CH_2 . No coupling between the CH_2 protons and the phosphorus was observed. In complex **9**, the NH proton signal is a well-resolved multiplet at $\delta_\text{H} = 4.95$. The CH_2 group was observed as a doublet of doublets at $\delta_\text{H} = 4.59$. The coupling constants were verified by H/D exchange with D_2O ($^2J_{\text{P,CH}} = 2$, $^3J_{\text{NH,CH}} = 6$ Hz). Complexes **10** and **11** show coupling between (P_X) and the methyl protons of the pentamethylcyclopentadienyl group, [$J_{\text{P--CH}} = 3$ Hz]. The complicated signals of complex **9** were also assigned by a ^1H - ^1H COSY spectrum. The IR spectra of **9–11** show the ν_{NH} absorption at about 3320 cm^{-1} , implying little hydrogen bonding.

Slow evaporation of a dichloromethane solution of **9** gave well-formed deep purple crystals suitable for X-ray analysis. The crystal structure of **9** (Figure 4, Table 6) reveals a monodentate complex coordinated by the $\text{NHCH}_2\text{PPh}_2$ phosphorus atom, whilst the triarylphosphane moiety remains unbound. The Ru(1) centre adopts an approximately trigonal bipyramidal geometry with Cl(1) and Cl(2) occupying the axial sites while P(1) and the two allylic groups occupy the equatorial positions. The arrangement of the allylic groups, which have local C_2 symmetry, is similar to that found in related complexes.^[26] The ligand backbone

P(2)–C(15)–C(14)–N(13), as observed in **2**, **3**, and **8**, is coplanar (mean deviation 0.01 Å). The dangling phosphorus P(2) remains pyramidal as expected.

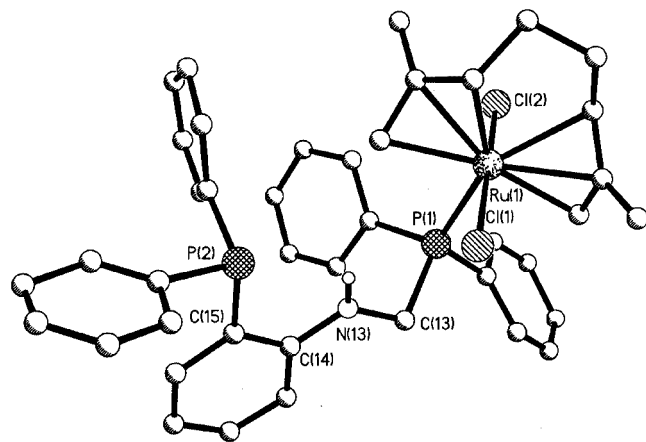


Figure 4. Crystal structure of [RuCl₂(η³:η³-C₁₀H₁₆)(Ph₂PCH₂NHC₆H₄PPh₂-P_X)] (**9**)

enyl top. The bond angles between the “legs” are approximately 90°.

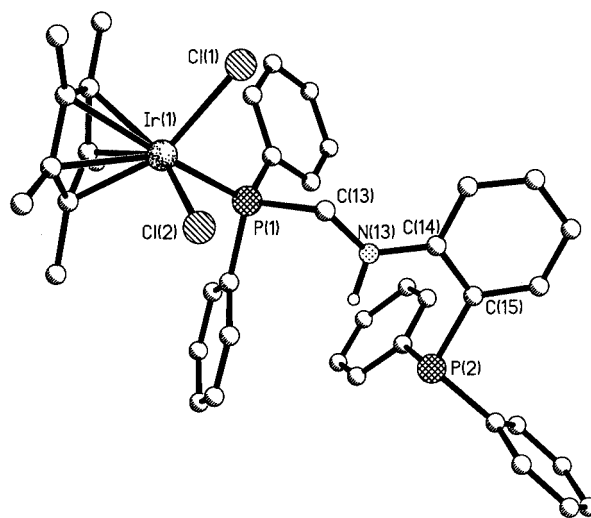


Figure 5. Crystal structure of [IrCl₂(η⁵-C₅Me₅)(Ph₂PCH₂NHC₆H₄PPh₂-P_X)] (**11**)

Table 6. A comparison of the bond lengths (Å) and angles (°) in compounds **9** and **11**

	9	11
M(1)–P(1)	2.393(4)	2.2986(13)
M(1)–Cl(1)	2.413(4)	2.4119(15)
M(1)–Cl(2)	2.387(4)	2.4035(16)
P(1)–C(13)	1.862(11)	1.833(6)
N(13)–C(13)	1.399(14)	1.457(7)
N(13)–C(14)	1.379(15)	1.384(7)
C(14)–C(15)	1.364(16)	1.415(8)
C(15)–P(2)	1.798(12)	1.825(6)
P(2)–C(20)	1.810(16)	1.831(6)
P(2)–C(26)	1.801(13)	1.830(6)
Cl(1)–M(1)–Cl(2)	172.84(15)	88.86(6)
Cl(1)–M(1)–P(1)	89.25(13)	88.27(5)
Cl(2)–M(1)–P(1)	84.01(13)	88.04(5)
M(1)–P(1)–C(13)	114.4(4)	112.50(19)
N(13)–C(13)–P(1)	111.0(8)	112.3(4)
C(14)–N(13)–C(13)	123.7(11)	123.9(5)
N(13)–C(14)–C(15)	120.2(12)	119.3(5)
C(14)–C(15)–P(2)	118.8(10)	117.8(4)
C(20)–P(2)–C(15)	102.4(6)	104.0(3)
C(20)–P(2)–C(26)	101.1(7)	102.2(3)
C(15)–P(2)–C(26)	103.4(6)	102.2(3)

The X-ray structure of **11** (Figure 5) shares many common features with **9**: the pendant triarylphosphane P(2) adopts a pyramidal geometry; the main backbone of the ligand extends in a mean plane P(2)–C(15)–C(14)–N(13) (mean deviation 0.06 Å); the bond lengths and angles (Table 6) are in the expected range; no hydrogen bonding is observed. The geometry around Ir(1) can be viewed as a three-legged “piano stool” with the two chlorides and the phosphorus P(1) supporting the pentamethylcyclopentadi-

Cationic Chelate Complexes

As mentioned above, a cationic chelate complex of iridium(III) **12** formed together with the monodentate species **11**. Other cationic chelate complexes of ligand **1** can be obtained by abstraction of a chloride ligand from the monodentate complexes. For example, abstraction of one chloride from complexes **9** and **10** with AgClO₄ gave the chelate cationic complexes [RuCl(η³:η³-C₁₀H₁₆)(Ph₂PCH₂NHC₆H₄PPh₂-P_X,P_A)] [ClO₄]⁺ (**13**) and [RhCl(η⁵-C₅Me₅)(Ph₂PCH₂NHC₆H₄PPh₂-P_X,P_A)] [ClO₄]⁺ (**14**), respectively. Both complexes gave satisfactory microanalysis and positive FAB mass spectra. Their IR spectra displayed the ν_{NH} at 3272 cm^{−1} and 3332 cm^{−1}, respectively, and the strong band of ClO₄[−] at ca. 1095 cm^{−1}. The ³¹P{¹H} NMR spectrum of **13** showed two singlets at δ_P = 36.89 and δ_P = 21.86 in CDCl₃, which were assigned to the phosphorus atoms of the NHCH₂PPh₂ (P_X) and the triarylphosphane (P_A) groups, respectively, by reference to the other chelate complexes mentioned above. The ¹H NMR spectrum of **13** showed a broad singlet at δ_H = 5.02 for NH and a doublet of doublet of doublets at δ_H = 4.67 for the ligand methylene protons with ³J_{NH,CH} = 6, ³J_{P,CH} = 15 Hz and ²J_{P,CH} = 52 Hz. Characterisation of **14** by multinuclear NMR proved unsuccessful. The ³¹P{¹H} NMR spectrum of **14** exhibited very broad peaks around δ_P = 31 and δ_P = 37, and the ¹H NMR spectrum of this compound also contains broad resonances. The low solubility of **14** in common organic solvents precludes a low temperature NMR study. In solution we believe that there may be an exchange process between several species taking place, possibly the cationic chelate, a monodentate species and perhaps even a cationic bidentate bridging species.

In spite of the uninformative NMR spectroscopic data we were able to obtain single crystals of compound **14** enab-

ling characterisation by X-ray crystallography (Figure 6, Table 7). The crystal structure of **14** reveals that the complex adopts a chair-like seven-membered chelate ring with a ligand bite angle $P(1)-Rh(1)-P(2)$ of $95.12(4)^\circ$. The top mean plane of the “chair”, $C(14)-C(15)-P(2)-N(13)$ (mean deviation $0.02 \text{ \AA}$), is 123° folded back from the “back of the chair”, $N(13)-P(2)-C(13)-Rh(13)$ mean plane (mean deviation $0.12 \text{ \AA}$). The “bottom of the chair”, $P(1)-Rh(1)-C(13)$, is 144° folded forward from the $N(13)-P(2)-C(13)-Rh(13)$ mean plane. Again, the coordination around the rhodium adopts a three-legged “piano stool” geometry. The crystal structure also displays two weak hydrogen bonding interactions between the NH and two of the oxygen atoms of the tetrahedral ClO_4^- anion [$H(13n)\cdots O(1)$: $2.42 \text{ \AA}$; $H(13n)\cdots O(3)$: $2.44 \text{ \AA}$; $N(13)-H(13n)\cdots O(1)$: 145° ; $N(13)-H(13n)\cdots O(3)$: 157°]. The crystal structure also reveals that each molecule of complex **14** crystallises with 0.25 molecules of dichloromethane.

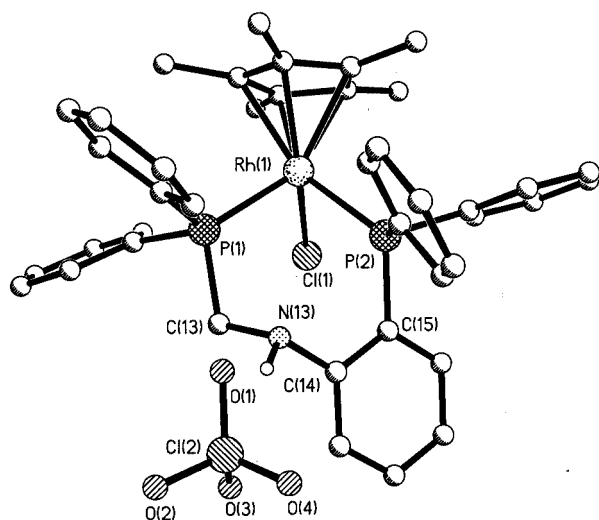


Figure 6. Crystal structure of $[RhCl(\eta^5-C_5Me_5)(Ph_2PCH_2NHC_6H_4PPh_2-P_X,P_A)](ClO_4)$ (**14**); the solvent of crystallisation is omitted for the sake of clarity

Table 7. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) in compound **14**

Rh(1)–P(1)	2.3303(12)	Rh(1)–P(2)	2.3806(11)
Rh(1)–Cl(1)	2.4016(12)	P(1)–C(13)	1.854(4)
N(13)–C(13)	1.452(6)	N(13)–C(14)	1.414(6)
C(14)–C(15)	1.389(6)	C(15)–P(2)	1.836(4)
P(1)–Rh(1)–P(2)	95.12(4)	P(1)–Rh(1)–Cl(1)	89.50(4)
P(2)–Rh(1)–Cl(1)	84.76(4)	C(13)–P(1)–Rh(1)	115.8(2)
N(13)–C(13)–P(1)	113.4(3)	C(14)–N(13)–C(13)	114.4(4)
N(13)–C(14)–C(15)	118.7(4)	C(14)–C(15)–P(2)	117.7(4)
C(15)–P(2)–Rh(1)	120.5(2)		

Bimetallic Complexes

While the Ru^{IV} or Rh^{III} metal centres of the bulky dimers $[\{ RuCl(\mu-Cl)(\eta^3-\eta^3-C_{10}H_{16}) \}_2]$ and $[\{ RhCl(\mu-Cl)(\eta^5-C_5Me_5)_2 \}_2]$ selectively coordinate through the (P_X) or $NHCH_2PPh_2$ moiety of ligand **1**, $[AuCl(tht)]$ displays no such selectivity for either (P_A) or (P_X) of ligand **1**. The reaction between $[AuCl(tht)]$ and **1** in a 1:1 ratio showed two broad peaks at $\delta_P = 33.4$ and 25.0 in the $^{31}P\{^1H\}$ NMR spectrum, implying that both (P_X) and (P_A) were involved in some type of coordination. Workup of this mixture was not attempted. Addition of one more molar equivalent of $[AuCl(tht)]$ to this mixture led to the same bidentate bridging complex **15** as in the one step reaction of $[AuCl(tht)]$ with **1** in a 2:1 molar ratio. Complex **15** exhibits two sharp singlets at $\delta_P = 24.95$ and $\delta_P = 18.64$ which are assigned to (P_X) of the $NHCH_2PPh_2$ group and the (P_A) of the triarylphosphane according to the general trend of the complexes discussed in this paper. The 1H NMR spectrum of **15** showed a well-resolved and well-shaped multiplet at $\delta_H = 4.94$ for the NH proton and a doublet of doublets at $\delta_H = 4.34$ for CH_2 . A $^1H-^1H$ COSY spectrum of the compound in $CDCl_3$ showed no coupling between the NH and aromatic proton 6-H. Therefore it was concluded that both of the phosphorus atoms coupled with the NH group. The coupling constants were obtained through a D_2O exchange reaction in $CDCl_3$ solution ($^2J_{P,CH} = 3$, $^3J_{NH,CH} = 6$, $^3J_{PC,NH} = ^4J_{PCCNH} = 3 \text{ Hz}$).

The reaction of $[\{ RhCl(\mu-Cl)(\eta^5-C_5Me_5) \}_2]$ with **1** in a 1:1 molar ratio gave another bimetallic complex $[\{ RhCl_2(\eta^5-C_5Me_5) \}_2(Ph_2PCH_2NHC_6H_4PPh_2)]$ (**16**). The $^{31}P\{^1H\}$ NMR spectrum of **16** displays two doublets at $\delta_P = 32.44$ ($^1J_{Rh,P} = 138 \text{ Hz}$) and $\delta_P = 27.79$ ($^1J_{Rh,P} = 144 \text{ Hz}$). Upon comparison with the $^{31}P\{^1H\}$ NMR spectrum of **9**, the doublet at $\delta_P = 32.44$ was assigned to the $NHCH_2PPh_2$ group (P_X), and the other at $\delta_P = 27.79$ to the triarylphosphorus atom (P_A). The 1H NMR spectrum of **16** displayed two doublets for the two pentamethylcyclopentadienyl groups. The NH resonance appears at $\delta_H = 5.33$ as a broad triplet and that of the ligand methylene protons at $\delta_H = 4.90$ as a broad doublet of doublets ($^3J_{NH,CH} = 5$, $^2J_{P,CH} = 16 \text{ Hz}$). Both bridging complexes gave satisfactory microanalysis and the anticipated FAB mass spectral patterns. Their IR spectra show vibrations for ν_{NH} at 3309 and 3280 cm^{-1} and ν_{M-Cl} at 329 and 398 cm^{-1} , respectively.

Conclusion

We have shown that the unsymmetrical bisphosphane ligand $Ph_2PCH_2NHC_6H_4PPh_2$ is readily prepared by the condensation of diphenylphosphanylmethanol (Ph_2PCH_2OH) and 2-(diphenylphosphanyl)aniline ($Ph_2PC_6H_4NH_2$), and that treatment of $Ph_2PCH_2NHC_6H_4PPh_2$ with H_2O_2 or elemental sulfur gives rise to the dioxide and disulfide. In addition, we have clearly demonstrated that $Ph_2PCH_2NHC_6H_4PPh_2$ has the potential to ligate in a variety of bonding modes. The different steric properties or ba-

sities of the two phosphorus centres can be exploited to obtain mononuclear complexes where Ph₂PCH₂NHC₆H₄PPh₂ is monodentate (via the Ph₂PCH₂ moiety) or chelating, and this latter bonding mode can also be induced by the use of a halide abstracting agent such as Ag⁺.

Binuclear complexes where Ph₂PCH₂NHC₆H₄PPh₂ adopts a bidentate bridging coordination mode are also readily accessible. The compounds described represent rare examples of either complexes containing PCNC₂P pendant ligands or MPCNC₂P metallacycles. Further studies are currently in progress into the synthesis of heterobimetallic complexes of late transition metals of Ph₂PCH₂NHC₆H₄PPh₂ and the coordination properties of its dichalcogen derivatives Ph₂P(O)CH₂NHC₆H₄P(O)Ph₂ and Ph₂P(S)CH₂NHC₆H₄P(S)Ph₂.

Experimental Section

General: All solvents and reagents were purchased from Aldrich and Lancaster. Dichloromethane was heated to reflux over powdered calcium hydride and distilled under nitrogen. Diethyl ether and tetrahydrofuran were purified by reflux over sodium/benzophenone and distillation under nitrogen. Ligand preparations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Coordination reactions and workup were performed in dry solvents. 2-(Diphenylphosphanyl)aniline,^[16] diphenylphosphanylmethanol,^[27] [MX₂(cod)] (M = Pt, X = Cl or Me; M = Pd, X = Cl, Br; cod = cycloocta-1,5-diene),^[28–30] [Mo(CO)₄(pip)₂] (pip = piperidine),^[31] [AuCl(tht)] (tht = tetrahydrothiophene),^[32] [MCl(μ-Cl)(η⁵-C₅Me₅)₂] (M = Rh, Ir),^[33] and [RuCl(μ-Cl)(η³:η³-C₁₀H₁₆)₂]^[34] were prepared using literature procedures.

Infrared spectra were recorded (KBr discs) on a Perkin–Elmer system 2000 spectrometer, and ¹H NMR spectra (300 MHz) on a Varian Gemini 2000 spectrometer, ³¹P{¹H} NMR spectra at 101.3 MHz with δ referenced to external 85% H₃PO₄. Microanalysis were performed by the University Service within this Department and fast atom bombardment (FAB) or chemical ionization (CI) mass spectra by the Swansea Mass Spectrometer Service. Precious metal salts were provided on loan by Johnson Matthey plc.

2-Ph₂PC₆H₄NHCH₂PPh₂ (1): Ph₂PCH₂OH (3.00 g, 13.87 mmol) was added to a solution of 2-(diphenylphosphanyl)aniline (3.84 g, 13.85 mmol) in toluene (150 cm³). The reaction mixture was stirred at 90–95 °C for 20 h. The solvent was removed in vacuo and the sticky residue was dissolved in 20 cm³ of Et₂O. Degassed absolute ethanol (100 cm³) was then added to the ether solution and the mixture was concentrated in vacuo until a white solid began to precipitate. Storage in the fridge overnight and filtration gave the product as a white solid. Yield: 5.46 g (84.4%). C₃₁H₂₇NP₂ (475.5): calcd. C 78.30, H 5.72, N 2.95; found C 77.17, H 5.48, N 2.75. ³¹P{¹H} NMR (CDCl₃): δ = –22.30 (s, P_A), –18.77 (s, P_X). ¹H NMR (CDCl₃): δ = 3.83 (t, ²J_{P,CH} = ³J_{CH,NH} = 5 Hz, 2 H, CH₂), 4.97 (br. s, 1 H, NH), 6.64 (t, 1 H, ArH), 6.80 (m, 2 H, ArH), 7.40–7.20 (m, 21 H, ArH). IR (KBr disc): ν_{NH} = 3345 cm^{–1}. CI-MS: *m/z* = 476 [M + H]⁺.

Ph₂P(O)CH₂NHC₆H₄P(O)Ph₂ (2): Aqueous hydrogen peroxide (30% w/w, 0.17 cm³, 1.5 mmol) was added dropwise to a solution of **1** (0.355 g, 0.75 mmol) in THF (20 cm³) and the mixture was stirred for 1.5 hours at 0–5 °C. The solvent was then removed in

vacuo to give a viscous oil which was taken up in dichloromethane (20 cm³) and dried over magnesium sulfate. The drying agent was removed by filtration and the filtrate was evaporated to dryness. Addition of diethyl ether to the residue precipitated the product. The product was collected by suction filtration and dried in vacuo. Yield: 0.275 g (73%). C₃₁H₂₇NO₂P₂ (507.5): calcd. C 73.37, H 5.36, N 2.76; found C 71.01, H 5.29, N 2.74. ³¹P{¹H} NMR (CDCl₃): δ = 28.58 (s, P_X), 36.38 (s, P_A). ¹H NMR (CDCl₃): δ = 4.04 (dd, ³J_{NH,CH} = 6, ²J_{P,CH} = 9 Hz, 2 H, CH₂), 6.59–6.53 (m, 1 H, ArH), 6.78–6.70 (m, 2 H, ArH), 7.68–7.26 (m, 22 H, NH + ArH). IR (KBr disc): ν_{NH} = 3315 cm^{–1}, ν_{P=O} = 1179vs, 1167vs, 1118vs cm^{–1}. FAB: *m/z* = 508 [M + H]⁺, 530 [M + Na]⁺.

Ph₂P(S)CH₂NHC₆H₄P(S)Ph₂ (3): Compound **1** (0.582 g, 1.224 mmol) and elemental sulfur (0.079 g, 2.47 mmol) were stirred in THF (20 cm³). A white solid began to precipitate in 10 minutes. Stirring was continued overnight and the product was collected by suction filtration, washed with diethyl ether (3 × 1 cm³) and dried in vacuo. Yield: 0.519 g (78.6%). C₃₁H₂₇NS₂P₂ (539.6): calcd. C 69.00, H 5.04, N 2.60; found C 69.09, H 4.94, N 2.68. ³¹P{¹H} NMR (CD₂Cl₂): δ = 38.46 (s, P_X), 39.35 (s, P_A). ¹H NMR (CD₂Cl₂): δ = 4.12 (dd, ³J_{NH,CH} = 5, ²J_{P,CH} = 7 Hz, 2 H, CH₂), 6.75–6.33 (m, 3 H, ArH), 7.03 (br. q, ³J_{NH,CH} = ³J_{NH,CP} = 5 Hz, 1 H, NH), 7.67–7.27 (m, 21 H, ArH). IR (KBr disc): ν_{NH} = 3287 cm^{–1}. FAB: *m/z* = 540 [M + H]⁺, 562 [M + Na]⁺.

[PdCl₂(Ph₂PC₆H₄NHCH₂PPh₂-P_X,P_A)] (4): [PdCl₂(cod)] (109 mg, 383 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 183 mg, 385 μmol) in CH₂Cl₂ (20 cm³). The reaction mixture was stirred for 25 min and then concentrated in vacuo to about 1 cm³ whereupon diethyl ether (10 cm³) was added to precipitate the product as an orange powder. Yield: 244 mg (98.0%). C₃₁H₂₇Cl₂NP₂Pd: calcd. C 57.12, H 4.17, N 2.15; found C 56.51, H 3.77, N 2.18. ³¹P{¹H} NMR ([D₆]DMSO): δ = 22.98 (s, P_A), 42.72 (s, P_X). ¹H NMR ([D₆]DMSO): δ = 3.96 (t, ²J_{P,CH} = ³J_{NH,CH} = 3 Hz, 2 H, CH₂), 5.53 (br. dt, ³J_{NH,PC} = 10 Hz, 1 H, NH), 6.12–6.07 (m, 1 H, ArH), 6.28 (m, 1 H, ArH), 6.85–6.80 (m, 1 H, ArH), 7.23–7.19 (m, 1 H, ArH), 7.56–7.35 (m, 20 H, ArH). IR (KBr disc): ν_{NH} = 3253s cm^{–1}, ν_{Pd-Cl} = 312m, 293w cm^{–1}. FAB: *m/z* = 616 [M – Cl]⁺, 580 [M – 2Cl]⁺, 674 [M + Na]⁺.

[PdBr₂(Ph₂PC₆H₄NHCH₂PPh₂-P_X,P_A)] (5): [PdBr₂(cod)] (77 mg, 206 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 100 mg, 210 μmol) in CH₂Cl₂ (5 cm³) and the reaction mixture was stirred for 30 min. The orange suspension of [PdBr₂(cod)] dissolved immediately and a yellow solid product precipitated gradually. This precipitate was collected by suction filtration, washed with petroleum ether (60–80, 3 × 1 cm³) and diethyl ether (3 × 1 cm³), yield: 196 mg (68%). C₃₁H₂₇Br₂NP₂Pd (741.7): calcd. C 50.27, H 3.67, N 1.89; found C 50.11, H 3.89, N 1.86. ³¹P{¹H} NMR ([D₆]DMSO): δ = 20.55 (s, P_A), 41.93 (s, P_X). ¹H NMR ([D₆]DMSO): δ = 3.92 (br. t, ²J_{P,CH} = ³J_{NH,CH} = 3 Hz, 2 H, CH₂), 5.44 (br. d, ³J_{P,NH} = 25 Hz, 1 H, NH), 6.08 (m, 1 H, ArH), 6.80 (m, 1 H, ArH), 7.16 (m, 1 H, ArH), 7.55–7.33 (m, 21 H, ArH). IR (KBr disc): ν_{NH} = 3246s cm^{–1}, ν_{Pd,Cl} = 332m, 302vw cm^{–1}. FAB: *m/z* = 663 [M – Br]⁺.

[PtCl₂(Ph₂PC₆H₄NHCH₂PPh₂-P_X,P_A)] (6): This colourless complex was prepared in the same manner as compound **4** using Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 80 mg, 168 μmol) in CH₂Cl₂ (20 cm³) and [PtCl₂(cod)] (62 mg, 168 μmol). Yield: 120 mg (96.0%). C₃₁H₂₇Cl₂NP₂Pt (741.5): calcd. C 50.21, H 3.67, N 1.89; found C 51.42, H 3.70, N 1.75. ³¹P{¹H} NMR (CDCl₃): δ = 1.80 (d, ¹J_{Pt,P_A} = 3573 Hz, P_A), 20.25 (d, ¹J_{Pt,P_X} = 3647 Hz; ²J_{P_A,P_X} = 18 Hz, P_X). ¹H NMR (CD₂Cl₂): δ = 3.55 (dt, ³J_{NH,CP} = 16 Hz, 1 H, NH),

3.96 (dd, $^3J_{\text{NH,CH}} = 6$, $^2J_{\text{P,CH}} = 3$, $^3J_{\text{Pt,CH}} = 36$ Hz, 2 H, CH₂), 6.29–6.25 (m, 1 H, ArH), 6.78–6.72 (m, 1 H, ArH), 7.09–7.06 (m, 1 H, ArH), 7.53–7.27 (m, 17 H, ArH), 7.74–7.66 (m, 4 H, ArH). IR (KBr disc): $\nu_{\text{NH}} = 3265$ cm⁻¹, $\nu_{\text{Pt-Cl}} = 316$ m, 293 m cm⁻¹. FAB: $m/z = 741$ [M]⁺, 705 [M – Cl]⁺, 764 [M + Na]⁺.

[PtMe₂(Ph₂PC₆H₄NHCH₂PPh₂-P_X,P_A)] (7): [PtMe₂(cod)] (50 mg, 149 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 71 mg, 149 μmol) in CH₂Cl₂ (5 cm³). The reaction mixture was stirred for 30 min and then concentrated in vacuo to about 0.5 cm³ and diethyl ether (1 cm³) and petroleum ether (3 cm³, 60–80) were added to precipitate the product as an off-white powder. Yield: 85 mg (82.0%). C₃₃H₃₃NP₂Pt (700.7): calcd. C 56.57, H 4.75, N 2.00; found C 55.68, H 4.49, N 1.93. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 11.91$ (d, $^1J_{\text{Pt,P}_A} = 1720$ Hz, P_A), 30.73 (d, $^1J_{\text{Pt,P}_X} = 1853$ Hz; $^3J_{\text{P}_A,\text{P}_X} = 12$ Hz, P_X). ^1H NMR (CDCl₃): $\delta = 0.34$ (dd, $^3J_{\text{P',CH}} = 7$, $^3J_{\text{P,CH}} = 9$, $^2J_{\text{Pt,CH'}} = 69$ Hz, 3 H, CH₃), 0.60 (dd, $^3J_{\text{P,CH}} = 7$, $^3J_{\text{P',CH}} = 9$, $^2J_{\text{Pt,CH}} = 70$ Hz, 3 H, CH₃), 3.99 (m, $^2J_{\text{P,CH}} = 9$ Hz, 3 H, CH₂ + NH), 6.23 (m, 1 H, ArH), 6.55 (m, 1 H, ArH), 6.80 (m, 1 H, ArH), 6.93 (t, 1 H, ArH), 7.66–7.20 (m, 20 H, ArH). IR (KBr disc): $\nu_{\text{NH}} = 3337$ m cm⁻¹. FAB: $m/z = 700$ [M]⁺, 685 [M – CH₃]⁺, 670 [M – 2CH₃]⁺.

[Mo(CO)₄(Ph₂PC₆H₄NHCH₂PPh₂-P_X,P_A)] (8): [Mo(CO)₄(pip)] (119 mg, 315 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 150 mg, 315 μmol) in CH₂Cl₂ (25 cm³). The reaction mixture was stirred at reflux for 3 h and then filtered through Celite. MeOH (10 cm³) was added to the filtrate, which was then concentrated under vacuum until trace amounts of solid appeared. The solution was stored in a fridge overnight. Filtration, washing with cold MeOH (0.5 cm³) and Et₂O (3 × 0.5 cm³) gave the product as a grey solid. Yield: 105 mg (53%). C₃₅H₂₇MoNO₄P₂ (683.5): calcd. C 61.50, H 3.98, N 2.05; found C 61.15, H 3.86, N 2.14. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 28.31$ (d, P_A), 41.43 (d, $^3J_{\text{P}_A,\text{P}_B} = 25$ Hz, P_X). ^1H NMR (CD₂Cl₂): $\delta = 4.04$ (br. s, 2 H, CH₂), 6.63–6.56 (m, 1 H, ArH), 6.78–6.71 (m, 2 H, ArH), 7.55–7.26 (m, 22 H, ArH + NH). IR (KBr disc): $\nu_{\text{NH}} = 3389$ w cm⁻¹, $\nu_{\text{C=O}} = 2013$ vs, 1914 vs, 1878 vs, 1892 vs cm⁻¹. FAB: $m/z = 684$ [M]⁺, 656 [M – CO]⁺, 628 [M – 2CO]⁺, 600 [M – 3CO]⁺, 572 [M – 4CO]⁺.

[RuCl₂(η³:η³-C₁₀H₁₆)(Ph₂PCH₂NHC₆H₄PPh₂-P_X)] (9): [{RuCl(μ-Cl)(η³:η³-C₁₀H₁₆)}₂] (80 mg, 130 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 124 mg, 261 μmol) in THF (5 cm³). The mixture was stirred for 1.5 h and then concentrated to ca. 0.5 cm³. Addition of Et₂O (2 cm³), filtration and washing with Et₂O (3 × 1 cm³) gave the product as a pale brown solid. Yield: 179 mg (88%). C₄₁H₄₃Cl₂NP₂Ru (783.7): calcd. C 62.84, H 5.53, N 1.79; found C 62.61, H 5.72, N 1.71. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = -22.51$ (s, P_A), 16.80 (s, P_X). ^1H NMR (CD₂Cl₂): $\delta = 2.15$ (s, 6 H, CH₃), 2.65 (m, 2 H, CH₂), 3.18 (m, 2 H, CH₂), 3.43 (d, 2 H, CH), 4.03 (d, 2 H, CH), 4.59 (dd, $^3J_{\text{NH,CH}} = 6$, $^2J_{\text{P,CH}} = 2$ Hz, 2 H, CH₂), 4.95 (m, 1 H, NH), 5.13 (br. m, 2 H, CH), 6.73–6.54 (m, 3 H, ArH), 7.38–6.99 (m, 17 H, ArH), 7.76–7.59 (m, 4 H, ArH). IR (KBr disc): $\nu_{\text{NH}} = 3314$ w cm⁻¹. FAB: $m/z = 784$ [M]⁺, 748 [M – Cl]⁺, 713 [M – 2Cl]⁺.

[RhCl₂(η⁵-C₅Me₅)(Ph₂PCH₂NHC₆H₄PPh₂-P_X)] (10): [{RhCl(μ-Cl)(η⁵-C₅Me₅)}₂] (68 mg, 110 μmol) was suspended in THF (4 cm³) and Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 105 mg, 220 μmol) was added to the stirred suspension as a solid in one portion. The suspension dissolved and after 15 minutes stirring, an orange solid deposited from the deep red solution. After stirring for a total of 2 h the orange solid was collected by suction filtration, washed with diethyl ether (3 × 1 cm³) and dried in vacuo. Yield: 145 mg (87%).

C₄₁H₄₂Cl₂NP₂Rh (784.5): calcd. C 62.77, H 5.40, N 1.79; found C 62.72, H 5.38, N 1.84. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = -22.84$ (s, P_A), 32.74 (d, $^1J_{\text{Rh,P}_X} = 141$ Hz, P_X). ^1H NMR (CD₂Cl₂): $\delta = 1.33$ (d, $^4J_{\text{P',CH}} = 3$ Hz, 15 H, CH₃), 4.66 (d, $^3J_{\text{NH,CH}} = 7$ Hz, 2 H, CH₂), 4.97 (br. q, $^3J_{\text{NH,CH}} = ^3J_{\text{PC,NH}} = 7$ Hz, 1 H, NH; no $^2J_{\text{P,CH}}$ observed), 6.30 (m, 1 H, ArH), 6.40 (m, 1 H, ArH), 6.60 (m, 1 H, ArH), 6.85 (m, 1 H, ArH), 7.77–7.04 (m, 20 H, ArH). IR (KBr disc): $\nu_{\text{NH}} = 3326$ w cm⁻¹. FAB: $m/z = 748$ [M – Cl]⁺, 713 [M – 2Cl]⁺.

[IrCl₂(η⁵-C₅Me₅)(Ph₂PCH₂NHC₆H₄PPh₂-P_X)] (11) and [IrCl(η⁵-C₅Me₅)(Ph₂PCH₂NHC₆H₄PPh₂-P_X,P_A)]Cl (12): [{IrCl(μ-Cl)(η⁵-C₅Me₅)}₂] (70 mg, 88 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 84 mg, 176 μmol) in THF (5 cm³). The mixture was stirred for 1.5 h and the solvent was removed in vacuo. The yellow solid residue was dissolved in CH₂Cl₂ (0.5 cm³) followed by addition of acetone (0.5 cm³). Storage of this solution at room temperature overnight led to the formation of well-shaped orange crystals of **11**. The crystals were collected by suction filtration and washed with acetone (0.5 cm³). Addition of Et₂O (2.0 cm³) to the filtrate caused the precipitation of **12** as an orange powder. **11**: Yield: 30 mg (19.5%). C₄₁H₄₂Cl₂IrNP₂ (873.9): calcd. C 56.35, H 4.84, N 1.60; found C 56.52, H 4.78, N 1.54. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = -22.80$ (s, P_A), 0.10 (s, P_X). ^1H NMR (CD₂Cl₂): $\delta = 1.33$ (d, $^4J_{\text{P',CH}} = 3$ Hz, 15 H, CH₃), 4.66 (d, 2 H, CH₂; no $^2J_{\text{PCH}}$ observed), 4.91 (q, $^3J_{\text{NH,CH}} = ^3J_{\text{PCNH}} = 7$ Hz, 1 H, NH), 6.34 (m, 1 H, ArH), 6.42 (m, 1 H, ArH), 6.61 (m, 1 H, ArH), 7.71–6.91 (m, 21 H, ArH). IR (KBr disc): $\nu_{\text{NH}} = 3328$ w cm⁻¹. FAB: $m/z = 838$ [M – Cl]⁺, 803 [M – 2Cl]⁺.

12: Yield: 29 mg (19%). C₄₁H₄₂Cl₂IrNP₂ (873.9): calcd. C 56.35, H 4.84, N 1.60; found C 48.67, H 4.33, N 1.08. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = -0.32$ (s), 0.48 (s). IR (KBr disc): $\nu_{\text{NH}} = 3283$ w cm⁻¹. FAB: $m/z = 838$ [M – Cl]⁺, 803 [M – 2Cl]⁺.

[RuCl(η³:η³-C₁₀H₁₆)(Ph₂PCH₂NHC₆H₄PPh₂-P_X,P_A)](ClO₄) (13): [{RuCl(μ-Cl)(η³:η³-C₁₀H₁₆)}₂] (64 mg, 103 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 99 mg, 208 μmol) in THF (5 cm³). The mixture was stirred for 1.5 h and then AgClO₄ (43 mg, 207 μmol) was added. Stirring was continued overnight and the precipitated AgCl was removed by filtration through Celite. The dark filtrate was concentrated in vacuo to ca. 0.5 cm³. Addition of Et₂O (5 cm³), filtration and washing with Et₂O (3 × 1 cm³) gave the product as a black solid. Yield: 162 mg (92%). C₄₁H₄₃Cl₂NO₄P₂Ru (847.7): calcd. C 58.09, H 5.11, N 1.65; found C 56.88, H 4.85, N 2.05. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 21.86$ (s, P_A), 36.89 (s, P_X). ^1H NMR (CDCl₃): $\delta = 2.14$ (s, 6 H, CH₃), 2.64 (br. m, 2 H, CH₂), 3.22 (d, 2 H, CH), 3.43 (m, 2 H, CH₂), 4.12 (d, 2 H, CH), 4.67 (ddd, $^2J_{\text{P,CH}} = 52$, $^3J_{\text{P,CH}} = 15$, $^3J_{\text{CH,NH}} = 6$ Hz, 2 H, CH₂), 5.02 (br. s, 1 H, NH), 5.13 (br. m, 2 H, CH), 6.42 (m, 2 H, ArH), 6.63 (m, 1 H, ArH), 7.75–7.05 (m, 21 H, ArH). IR (KBr disc): $\nu_{\text{NH}} = 3272$ w cm⁻¹, $\nu_{\text{ClO}_4^-} = 1099$ vs cm⁻¹. FAB: $m/z = 748$ [M – ClO₄]⁺.

[RhCl(η⁵-C₅Me₅)(Ph₂PCH₂NHC₆H₄PPh₂-P_X,P_A)](ClO₄) (14): This orange product was prepared in the same way as the ruthenium compound **13** from [{RhCl(μ-Cl)(η⁵-C₅Me₅)}₂] (25 mg, 40 μmol), Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 39 mg, 82 μmol) and AgClO₄ (17 mg, 82 μmol). Yield: 63 mg (93%). Red crystals suitable for X-ray analysis were obtained by layering THF and petroleum ether (60–80) on a dichloromethane solution of **14** for four days. C₄₁H₄₂Cl₂NO₄P₂Rh (848.5): calcd. C 58.03, H 4.99, N 1.65; found C 57.49, H 4.87, N 1.52. IR (KBr disc): $\nu_{\text{NH}} = 3332$ m cm⁻¹, $\nu_{\text{ClO}_4^-} = 1095$ vs cm⁻¹. FAB: $m/z = 748$ [M – ClO₄]⁺.

[Ph₂P{AuCl}CH₂NHC₆H₄{AuCl}PPh₂] (15): [AuCl(tht)] (135 mg, 420 μmol) was added to a solution of Ph₂PC₆H₄NHCH₂PPh₂ (**1**;

Table 8. Details of the X-ray data collections and refinements for compounds **2**, **3**, **8**, **9**, **11** and **14**

	2·0.5H₂O	3	8	9	11	14
Empirical formula	C ₃₁ H ₂₇ NO _{2.50} P ₂	C ₃₁ H ₂₇ NP ₂ S ₂	C ₃₅ H ₂₇ MoNO ₄ P ₂	C ₄₁ H ₄₃ Cl ₂ NP ₂ Ru	C ₄₁ H ₄₂ Cl ₂ IrNP ₂	C _{41.25} H _{42.50} Cl _{2.50} NO ₄ P ₂ Rh
Crystal colour, habit	clear, prism	clear, prism	clear, prism	purple, prism	Orange, block	Red, prism
Crystal dimensions/mm	0.21 × 0.1 × 0.1	0.1 × 0.1 × 0.08	0.16 × 0.13 × 0.13	0.12 × 0.1 × 0.06	0.15 × 0.1 × 0.1	0.18 × 0.12 × 0.1
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	C2/c	P $\bar{1}$	P2 ₁ /c	P $\bar{1}$	P2 ₁ /c	P $\bar{1}$
a (Å)	26.754(2)	9.6227(3)	14.3816(3)	10.676(2)	18.5451 (2)	12.3348(5)
b (Å)	9.0619(6)	12.3446(4)	9.9445(2)	13.333(3)	9.1119(1)	12.3577(5)
c (Å)	25.046(2)	13.2192(3)	22.5402(4)	13.646(3)	22.3655(1)	14.1891(6)
α (°)	90	108.7150(10)	90	76.527(5)	90	77.3270(10)
β (°)	119.409(2)	110.4580(10)	103.5250(10)	74.373(4)	92.5500(10)	78.15
γ (°)	90	93.9340(10)	90	79.345(5)	90	81.8740(10)
U (Å ³)	5289.8(7)	1364.24 (7)	3134.25(11)	1803.6(6)	3775.60(6)	2054.6(2)
Z	8	2	4	2	4	2
M	516.48	539.60	683.46	783.67	873.80	724.43
D _c (g cm ⁻³)	1.297	1.314	1.448	1.443	1.537	1.406
μ (mm ⁻¹)	0.196	0.334	0.560	0.702	3.792	0.697
F(000)	2168	564	1392	808	1744	893
Measured reflections	12820	6916	13208	9120	15695	14534
Independent reflections (R _{int})	3756 (0.0806)	3882 (0.0176)	4485 (0.0256)	5066 (0.1443)	5376 (0.0367)	5860 (0.0280)
Final R1, ωR2 [I > 2σ(I)]	0.0566, 0.1316	0.0412, 0.0993	0.0236, 0.0558	0.0842, 0.1770	0.0293, 0.0650	0.0434, 0.1127
Largest difference peak hole (eÅ ⁻³)	0.337, -0.448	0.250, -0.230	0.222, -0.171	0.670, -0.882	0.200, -0.254	0.731, -0.528

100 mg, 210 μmol) in CH₂Cl₂ (10 cm³). The mixture was stirred for 30 minutes and then filtered through Celite. The filtrate was concentrated to ca. 0.5 cm³. Addition of 60–80 petroleum ether (10 cm³), filtration and washing with Et₂O (3 × 1 cm³) gave the product as a white solid. Yield: 176 mg (90%). C₃₁H₂₇Au₂Cl₂NP₂ (940.3): calcd. C 39.60, H 2.89, N 1.49; found C 39.91, H 2.91, N 1.48. ³¹P{¹H} NMR (CDCl₃): δ = 18.64 (s, P_A), 24.95 (s, P_X). ¹H NMR (CDCl₃): δ = 4.34 (dd, ²J_{P,CH} = 3 Hz, 2 H, CH₂), 4.94 (m, ³J_{NH,CH} = 6, ³J_{PCNH} = ⁴J_{PCCNH} = 3 Hz, 1 H, NH), 6.61 (m, 1 H, ArH), 6.79 (m, 1 H, ArH), 6.99 (m, 1 H, ArH), 7.58–7.40 (m, 21 H, ArH). IR (KBr disc): ν_{NH} = 3309 cm⁻¹, ν_{Au-Cl} = 329 cm⁻¹. FAB: m/z = 904 [M – Cl]⁺.

[{RhCl₂(η⁵-C₅Me₅)₂(Ph₂PCH₂NHC₆H₄PPh₂)] (**16**): This compound was prepared in the same way as compound **10** from a 1:1 molar ratio of [{RhCl(μ-Cl)(η⁵-C₅Me₅)₂}]₂ (93 mg, 150 μmol) and Ph₂PC₆H₄NHCH₂PPh₂ (**1**; 73 mg, 151 μmol). Yield: 148 mg (90%). C₅₁H₅₇Cl₄NP₂Rh (1093.6): calcd. C 54.33, H 5.25, N 1.28; found C 56.01, H 4.66, N 1.16. ³¹P{¹H} NMR (CDCl₃): δ = 27.79 (d, ¹J_{Rh,P_A} = 144 Hz, P_A), 32.44 (d, ¹J_{Rh,P_X} = 138 Hz, P_X). ¹H NMR (CDCl₃): δ = 1.23 (d, ⁴J_{P,CH} = 3 Hz, 15 H, CH₃), 1.27 (d, ⁴J_{P,CH} = 3 Hz, 15 H, CH₃), 4.90 (dd, ³J_{NH,CH} = 5, ²J_{P,CH} = 16 Hz, 2 H, CH₂), 5.33 (br. s, 1 H, NH), 5.78 (m, 1 H, ArH), 6.28 (m, 1 H, ArH), 6.52 (m, 1 H, ArH), 6.70 (m, 1 H, ArH), 7.89–6.90 (m, 20 H, ArH). IR (KBr disc): ν_{NH} = 3280 cm⁻¹. FAB: m/z = 1056 [M – Cl]⁺.

X-ray Crystallography: Table 8 lists details of data collections and refinements for **2**, **3**, **8**, **9**, **11** and **14**. Data were collected at room temperature using Mo-K_α radiation with a SMART system. Intensities were corrected for Lorentz polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least-squares based on F² using SHELXTL.^[35] CCDC-172648–172653 (corresponding to compounds **2**, **3**, **8**, **9**, **11**, and **14**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union

Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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