# Preparation and Coordination Chemistry of *n*-Allylaminophosphane

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Reaction of allylamine with 1 equiv. of $Ph_2PCl$ in the presence of $NEt_3$, proceeds in THF to give (allylamino)phosphane **1**. **1** has been coordinated as a monodentate *P* ligand with Au, Pd, Pt, Ru, Rh, Ir and as a bidentate *P,allyl* ligand to Pt. Reaction of KO*t*Bu with $[PtCl_2\{Ph_2PNH(C_3H_5)\}_2]$ in methanol gives $[Pt\{Ph_2PNH(C_3H_8O)\}_2]$. The X-ray structures of **1**.Se and four demonstrative monodentate complexes all reveal intramolecular N–H···Cl hydrogen bonding. The structure of $[Pt\{Ph_2PNH(C_3H_8O)\}_2]$ consists of an N–H···O hydrogen-bonded dimer in the solid state.

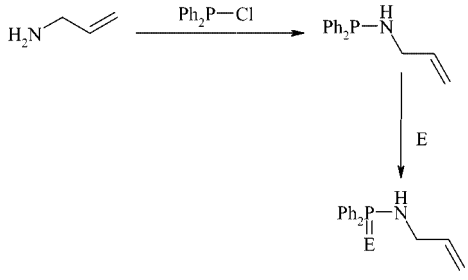

## Introduction

Phosphane–alkenes have the potential to coordinate with the phosphorus atom or through the olefin moiety. For example, Coutinho et al.[1] treated a variety of phosphido-bridged complexes, $[(OC)_4M(\mu\text{-}PPh_2)_2RhH(CO)(PPh_3)]$, with the phosphanylalkenes $Ph_2P(CH_2)_nCH{=}CH_2$ (M = Cr, Mo or W; $n$ = 1–3); in these reactions the olefin undergoes hydroformylation, which is of great interest today in commercial processes including the Rhone-Poulenc/Ruhr Chemie aqueous-based system.[2] Furthermore, work continues to prepare ligands that lead to greater regioselectivity and/or enantioselectivity.[3] It is of interest to investigate other potentially hemilabile ligands to increase the success and efficiency of current processes and in early work the olefinic fragment was used as a stabilising group with strongly bonding phosphane ligands.[4] More recently the study of phosphane–alkene ligands has focused on the weakly ligating nature of the alkene, for example, Brookes[4] displaced the olefinic groups of a rhodium complex with a tetraphenylborate anion to yield a piano stool metal complex. Lindner et al.[5] showed that the furan ring in (phopshanylalkyl)furan ligands could ligate to metal centres in an $\eta^1$-fashion through the oxygen atom or by an $\eta^2$-fashion through the C=C double bonds. The most favoured coordination mode of these types of phosphane–alkene ligands was shown to be the $\eta^2$-fashion as the partial donation of the lone pair from the oxygen atom makes the $\eta^1$-fashion coordination less favourable due to the oxygen atom being a poorer σ-donor than the olefinic groups. Diphenyl(vinyl) phosphane (DPVP) was shown by the Barthel-Rosa research group to be a hemilabile ligand when coordiniated to ruthenium(II) centres.[5] They showed that the ($\eta^3$-DPVP) ruthenium(II) complex could react both reversibly and irreversible depending on the small molecule that was used in the reaction. A reversible reaction was observed when acetonitrile was used; however, in the presence of CO the reaction was found to be irreversible but in both instances the DPVP ligand underwent an $\eta^3$- to $\eta^1$-shift that opened up a coordination site on the metal centre. It is clear that there is a potentially rich and diverse coordination chemistry available for phosphane–alkenes.

Here, we report the preparation of an aminophosphane which contains an olefinic side chain and thus the potential to act as a hemilabile ligand. Illustrative coordination complexes have been prepared.

## Results and Discussion

Reaction of allylamine with 1 equiv. of $Ph_2PCl$ in the presence of $NEt_3$, proceeds in THF to give **1** which was isolated (41 % yield) by filtration from $Et_3NH^+Cl^-$ as a colourless oil that was purified by distillation (132 °C/0.2 Torr). After storing under nitrogen at –18 °C a colourless waxy solid formed (41 % yield). The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a singlet at $\delta_P$ = 42.5 ppm. The $EI^+$ mass spectrum gave the expected fragmentation pattern and parent ion observed at *m*/*z* 242. The microanalysis gave satisfactory results for the suggested structure. The chalcogenides of $Ph_2PNH(C_3H_5)$ were prepared easily [Equation (1)].

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The oxide $Ph_2P(O)NH(C_3H_5)$ (**2**) was prepared by addition of urea/hydrogen peroxide to a dichloromethane solution of **1** whilst the sulfur and selenium analogues **3** and **4** were prepared by the addition of elemental S or Se to the ligand in toluene. Microanalysis and $EI^+$ mass spectroscopic data for all the chalcogenides prepared were satisfactory and the $^{31}P\{^1H\}$ NMR showed single resonances ($CDCl_3$) at $\delta_P$ = 24.4 and 60.5 ppm for the oxide and sulfide, respectively. The selenium analogue exhibited a single $^{31}P\{^1H\}$ NMR resonance ($CDCl_3$) at $\delta_P$ = 58.1 ppm with selenium satellites [$^1J(^{31}P\text{-}^{77}Se)$ = 756 Hz] which is typical for a P=Se group.[6]

The crystal structure of **4** (Figure 1, Table 1). shows that in the solid state the molecule forms hydrogen-bonded dimers. The NH proton of one molecule is hydrogen-bonded to the selenium atom of a second and the selenium atom of the second interacts with the NH proton of the first, leading to a head to tail type arrangement of the molecules [H(2)···Se(1A) 2.63, N(2)···Se(1A) 3.61 Å, N(2)–H(2)···Se(1A) angle of 174°].

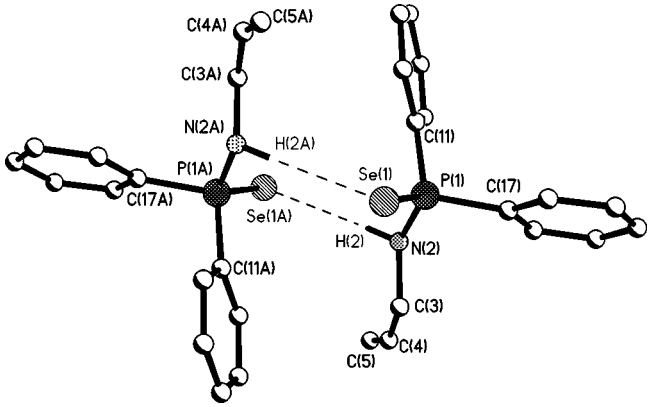



Figure 1. The X-ray structure of $Ph_2P(Se)NH(C_3H_5)$ (**4**) showing hydrogen bonding

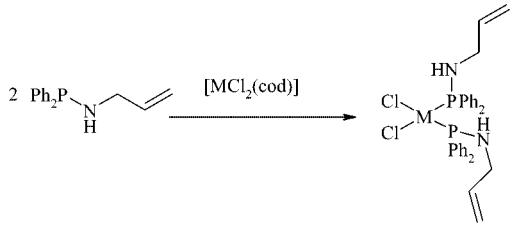
Table 1. Selected bond lengths [Å] and angles [°] for $Ph_2P(Se)NH(C_3H_5)$ (**4**)

| | **4** |
|---|---|
| P(1)–N(2) | 1.657(4) |
| Se(1)–P(1) | 2.1082(12) |
| P(1)–C(11) | 1.806(4) |
| P(1)–C(17) | 1.814(4) |
| N(2)–P(1)–C(11) | 103.30(19) |
| N(2)–P(1)–C(17) | 103.49(18) |
| C(11)–P(1)–C(17) | 105.86(18) |
| C(11)–P(1)–Se(1) | 113.32(13) |
| C(17)–P(1)–Se(1) | 112.20(14) |
| N(2)–P(1)–Se(1) | 117.48(15) |
| P(1)–N(2)–H(2) | 116(3) |

Coordination of **1** as a monodentate ligand was established in a number of cases. Thus, reaction of [AuCl(tht)] with **1** gave the expected product [$AuCl\{Ph_2PNH(C_3H_5)\}$] (**5**) [Table 2 summarises spectroscopic data], and reaction of [$PtCl_2$(cod)] with **1** in a 1:2 molar ratio gave [$PtCl_2\{Ph_2PNH(C_3H_5)\}_2$] (**6**) in very good yield (90 %). The FAB mass spectrum of **6** showed the expected parent ion and fragmentation pattern and the complex displays a single resonance with platinum satellites in the $^{31}P\{^1H\}$ NMR spectrum [$\delta_P$ = 34.8 ppm, $^1J(^{31}P\text{-}^{195}Pt)$ = 3949 Hz, Table 2] which indicates the presence of $Cl^-$ *trans* to P. The IR spectrum has $\nu_{NH}$ at 3054 $cm^{-1}$, $\nu_{C=C}$ and $\nu_{PN}$ at 1642 and 1000 $cm^{-1}$, respectively, and two $\nu_{PtCl}$ bands at 305 and 288 $cm^{-1}$ which support the *cis* geometry.

The crystal structure of **6** (Table 3, Figure 2) shows that the molecule is square-planar at Pt. The P(21)–Pt(1)–P(1) [98.81(4)°] and Cl(1)–Pt(1)–Cl(2) [84.53(4)°] angles are significantly distorted from the ideal 90° due to the bulky phosphane groups. The Pt–P bond lengths are in the normal range. In the solid state the X-ray structure displays two intramolecular N–H···Cl hydrogen bonds that result in two five-membered rings [N(13)–H(13)···Cl(1) 2.34(4) Å N(13)–H(13)···Cl(1) 127(4)°, N(33)–H(33)···Cl(2) 2.34(4) Å, N(33)–H(33)···Cl(2) angle of 128(4)°].

[$PdCl_2\{Ph_2PNH(C_3H_5)\}_2$] (**7**) was prepared in a similar way to **6**. The expected fragmentation pattern and parent ion was observed in the FAB mass spectrum whilst the $^{31}P\{^1H\}$ NMR spectrum showed two peaks at $\delta$ = 58.8 and 46.2 ppm which is indicative of a mixture of *cis* and *trans* isomers. The IR bands observed at 3054, 1643 and 997 $cm^{-1}$ represent $\nu_{NH}$, $\nu_{C=C}$ and $\nu_{PN}$, respectively [Equation (2)].




M = Pt **6**, Pd **7**
cod = 1,5-cyclooctadiene (2)

Reaction of of [{PtCl(μ-Cl)($PEt_3$)}$_2$] with **1** gave [$Pt(PEt_3)Cl_2\{Ph_2PNH(C_3H_5)\}$] (**8**) in a yield of 59 %; $\delta_{PA}$ = 34.2 ppm, $\delta_{PX}$ = 7.3 ppm, $^1J(^{31}P_A\text{-}^{195}Pt)$ = 3979, $^1J(^{31}P_X\text{-}^{195}Pt)$ = 3479, $^2J(^{31}P_A\text{-}^{31}P_X)$ = 19 Hz, which is typical for complexes of this type. The $PMe_2Ph$ analogue **9** was obtained in a similar fashion. The molecular structures of **8** and **9** (Table 4, Figure 3) confirm that the complexes contain one ligand bound to the platinum atom through the phosphorus atom; the hydrogen bonding motif is observed [in **8**: N(2)–H(2)···Cl(2) 2.74(4) Å, N(2)–H(2)···Cl(2) angle of 110(3)°].

[$PdCl(C_{10}H_8N)\{Ph_2PNH(C_3H_5)\}$] (**10**) was prepared from **1** and [{$PdCl(C_{10}H_8N)\}_2$] ($C_{10}H_8N$ = metallated naphthylamine ligand) whilst [RuCl(μ-Cl)($\eta^6$-*p*-$MeC_6H_4$-*i*Pr)$\{Ph_2PNH(C_3H_5)\}$] (**11**) was prepared from [{RuCl(μ-Cl)($\eta^6$-*p*-$MeC_6H_4$ *i*Pr)}$_2$] and **1** (85 % yield). The X-ray structure of **11** (Table 5, Figure 4) confirms that the complex contains one ligand and is bound to the ruthenium

Table 2. Characterisation data for $Ph_2PNH(C_3H_5)$ and its derivatives

| Compound | $^{31}P\{^1H\}$ NMR | IR [$cm^{-1}$] | | | | | Microanalysis: found (calcd.) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\delta_P$ [ppm] | $\nu_{PN}$ | $\nu_{NH}$ | $\nu_{C=C}$ | $\nu_{P=E}$ | $\nu_{MCl}$ | C | H | N |
| $Ph_2PNH(C_3H_5)$ (**1**) | 42.5 | | | | – | – | 72.27 (74.67) | 7.37 (6.68) | 5.58 (5.81) |
| $Ph_2P(O)NH(C_3H_5)$ (**2**) | 24.4 | 993 | 3189 | 1641 | 1181 | – | 69.74 (70.03) | 6.22 (6.27) | 5.15 (5.44) |
| $Ph_2P(S)NH(C_3H_5)$ (**3**) | 60.5 | 997 | 3170 | 1642 | 689 | – | 66.01 (65.91) | 6.09 (5.90) | 5.11 (5.12) |
| $Ph_2P(Se)NH(C_3H_5)$ (**4**) | 58.1[a] | 991 | 3177 | 1644 | 573 | – | 55.97 (56.07) | 5.25 (5.02) | 4.43 (4.36) |
| $[AuCl\{Ph_2PNH(C_3H_5)\}]$ (**5**) | 64.9 | 996 | 3069 | 1643 | – | 323 | 37.98 (38.03) | 2.76 (3.40) | 3.07 (2.96) |
| $[PtCl_2\{Ph_2PNH(C_3H_5)\}_2]$ (**6**) | 34.8[b] | 1000 | 3054 | 1642 | – | 305, 288 | 48.23 (48.14) | 4.10 (4.31) | 3.65 (3.74) |
| $[PdCl_2\{Ph_2PNH(C_3H_5)\}_2]$ (**7**) | 58.8, 46.2 | 997 | 3054 | 1643 | – | 297, 277 | 54.80 (54.61) | 4.67 (4.89) | 4.06 (4.25) |
| $[Pt(PEt_3Cl_2\{Ph_2PNH(C_3H_5)\}]$ (**8**) | 34.2, 7.3[f] | 1002 | 3072 | 1641 | – | 309, 283 | 40.61 (40.38) | 4.38 (5.01) | 2.49 (2.24) |
| $[Pt(PMe_2Ph)Cl_2\{Ph_2PNH(C_3H_5)\}]$ (**9**) | 35.3, –14.2[g] | 1000 | 3053 | 1642 | – | 313, 283 | 42.99 (42.85) | 2.26 (4.22) | 2.08 (2.17) |
| $[PdCl(C_{10}H_8N)\{Ph_2PNH(C_3H_5)\}]$ (**10**) | 65.0 | 993 | 3049 | 1639 | – | 289 | 56.93 (57.16) | 3.93 (4.60) | 5.24 (5.33) |
| [Ru Cl(μ-Cl)($\eta^6$-p-$MeC_6H_4$ *i*Pr) $\{(Ph_2PNH(C_3H_5)\}]$ (**11**) | 61.3 | 996 | 3051 | 1642 | – | 290, 283 | 55.71 (54.85) | 5.62 (5.52) | 2.71 (2.56) |
| $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\{(Ph_2PNH(C_3H_5)\}]$ (**12**) | 66.4[e] | 995 | 3063 | 1642 | – | 279, 267 | 54.32 (54.56) | 5.78 (5.68) | 2.44 (2.55) |
| $[IrCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\{(Ph_2PNH(C_3H_5)\}]$ (**13**) | 34.5 | 994 | 3058 | 1640 | – | 291, 280 | 47.07 (46.95) | 4.85 (4.89) | 2.13 (2.19) |
| $[PdCl_2\{Ph_2PNH(C_3H_5)\}]$ (**14**) | 93.6 | 996 | 3054 | – | – | 318, 281 | 43.95 (43.04) | 4.26 (3.85) | 2.70 (3.35) |
| $[PtCl_2\{Ph_2PNH(C_3H_5)\}]$ (**15**) | 63.5[c] | 998 | 3055 | 3051 | – | 328, 289 | 36.53 (35.52) | 2.99 (3.18) | 2.60 (2.76) |
| $[Pt\{Ph_2PNH(C_4H_8O)\}_2]$ (**16**) | 91.4[d] | 997 | 3069 | – | – | – | 52.06 (51.96) | 4.60 (5.18) | 3.70 (3.79) |

[a] $^1J\{^{31}P\text{-}^{77}Se\} = 756$ Hz. [b] $^1J\{^{31}P\text{-}^{195}Pt\} = 3949$ Hz. [c] $^1J\{^{31}P\text{-}^{195}Pt\} = 3481$ Hz. [d] $^1J\{^{31}P\text{-}^{195}Pt\} = 2294$ Hz. [e] $^1J\{^{31}P\text{-}^{103}Rh\} = 148$ Hz. [f] $^1J\{^{31}P_A\text{-}^{195}Pt\} = 3979$, $^1J\{^{31}P_X\text{-}^{195}Pt\} = 3479$, $^2J(^{31}P_A\text{-}^{31}P_X) = 19$ Hz. [g] $^1J\{^{31}P_A\text{-}^{195}Pt\} = 3878$, $^1J\{^{31}P_X\text{-}^{195}Pt\} = 3625$, $^2J(^{31}P_A\text{-}^{31}P_X)$ 19 Hz.

Table 3. Selected bond lengths [Å] and angles [°] for $[PtCl_2\{Ph_2PNH(C_3H_5)\}_2]$ (**6**)

| | **6** |
|---|---|
| Pt(1)–Cl(1) | 2.3644(10) |
| Pt(1)–Cl(2) | 2.3649(12) |
| Pt(1)–P(1) | 2.2625(10) |
| Pt(1)–P(21) | 2.251(9) |
| P(1)–N(13) | 1.663(3) |
| P(21)–N(33) | 1.660(4) |
| N(13)–C(14) | 1.457(5) |
| N(33)–C(34) | 1.463(6) |
| N(13)···Cl(1) | 3.039(3) |
| N(33)···Cl(2) | 3.050(4) |
| P(1)–Pt(1)–Cl(1) | 88.22(4) |
| Cl(1)–Pt(1)–Cl(2) | 84.53(4) |
| N(13)–P(1)–M(1) | 108.03(12) |
| P(21)–Pt(1)–P(1) | 98.81(4) |
| P(21)–Pt(1)–Cl(1) | 172.97(3) |
| P(21)–Pt(1)–Cl(2) | 88.45(4) |
| P(1)–Pt(1)–Cl(2) | 172.59(4) |
| C(14)–N(13)–P(1) | 125.3(3) |
| N(33)–P(21)–Pt(1) | 109.64(13) |
| C(34)–N(33)–P(21) | 123.0(3) |

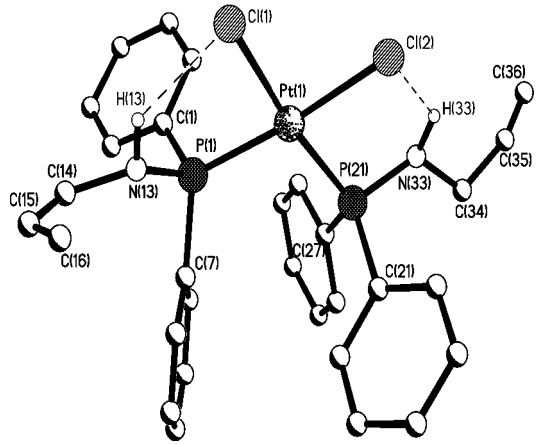



Figure 2. The X-ray structure of $[PtCl_2\{Ph_2PNH(C_3H_5)\}_2]$ (**6**)

atom through the phosphorus atom with a P(1)–Ru(1) bond length of 2.3404(11) Å and similar intramolecular hydrogen bonding to **8**.

Table 4. Selected bond lengths [Å] and angles [°] for [Pt(PEt)$_3$-Cl$_2${Ph$_2$PNH(C$_3$H$_5$)}] (**8**) and [Pt(PPhMe$_2$)Cl$_2${Ph$_2$PNH(C$_3$H$_5$)}] (**9**)

| | **8** | **9** |
|---|---|---|
| Pt(1)–Cl(1) | 2.3496(19) | 2.3481(17) |
| Pt(1)–Cl(2) | 2.3716(17) | 2.3741(16) |
| Pt(1)–P(1) | 2.2587(18) | 2.2505(17) |
| Pt(1)–P(2) | 2.2520(18) | 2.2487(16) |
| P(1)–N(2) | 1.658(6) | 1.677(5) |
| P(1)–C(11) | 1.822(6) | 1.824(6) |
| P(1)–C(17) | 1.820(7) | 1.820(6) |
| P(1)–Pt(1)–P(2) | 96.82(6) | 96.14(6) |
| Cl(2)–Pt(1)–Cl(1) | 85.09(6) | 86.45(6) |
| N(2)–P(1)–C(11) | 110.6(3) | 109.1(3) |
| N(2)–P(1)–C(17) | 100.9(3) | 100.3(3) |
| C(11)–P(1)–C(17) | 105.8(3) | 105.8(3) |
| N(2)–P(1)–Pt(1) | 106.4(2) | 108.4(2) |
| C(11)–P(1)–Pt(1) | 111.9(2) | 110.9(2) |
| C(17)–P(1)–Pt(1) | 120.5(2) | 121.5(2) |

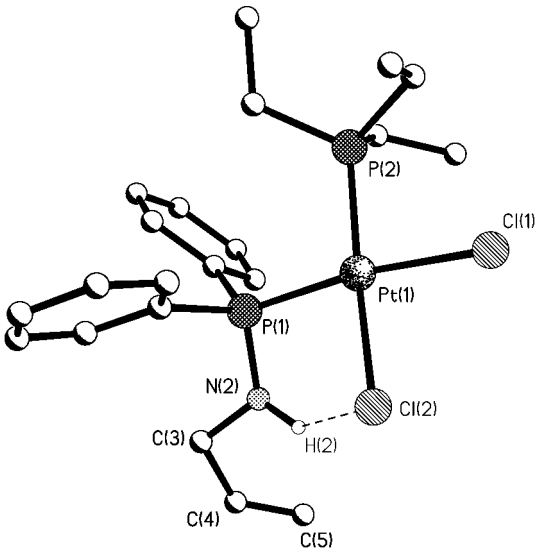
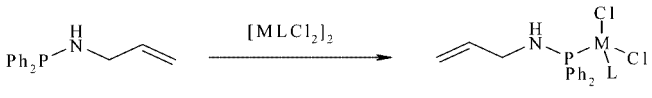



Figure 3. The X-ray structure of [Pt(PEt)$_3$Cl$_2${Ph$_2$PNH(C$_3$H$_5$)}] (**8**), the structure of [Pt(PPhMe$_2$)Cl$_2${Ph$_2$PNH(C$_3$H$_5$)}] (**9**) is very similar and is not illustrated

The reaction of Ph$_2$PNH(C$_3$H$_5$) with [{RhCl(μ-Cl)(η$^5$-C$_5$Me$_5$)}$_2$] and [{IrCl(μ-Cl)(η$^5$-C$_5$Me$_5$)}$_2$] proceeded in similar fashion to give [RhCl(μ-Cl)(η$^5$-C$_5$Me$_5$){Ph$_2$PNH-(C$_3$H$_5$)}] (**12**) and [IrCl(μ-Cl)(η$^5$-C$_5$Me$_5$){Ph$_2$PNH(C$_3$H$_5$)}] (**13**) in good yields [67 % and 65 % respectively, Equation (3), Table 2].




M = Rh **12**, Ir **13**
L = Cp*

(3)

In order to obtain a bidentate complex we treated **1** with 1 equiv. of [MCl$_2$(cod)] to give **14** and **15** [Equation (4),

Table 5. Selected bond lengths [Å] and angles [°] for [RuCl(μ-Cl)(η$^6$-*p*-MeC$_6$H$_4$ *i*Pr){Ph$_2$PNH(C$_3$H$_5$)}] (**11**)

| | **11** |
|---|---|
| Ru(1)–Cl(1) | 2.4314(11) |
| Ru(1)–Cl(2) | 2.4037(12) |
| Ru(1)–P(1) | 2.3404(11) |
| P(1)–N(2) | 1.657(3) |
| P(1)–C(11) | 1.823(4) |
| P(1)–C(17) | 1.827(4) |
| N(2)···Cl(2) | 3.202(3) |
| P(1)–Ru(1)–Cl(1) | 88.54(4) |
| P(1)–Ru(1)–Cl(2) | 85.35(4) |
| Cl(2)–Ru(1)–Cl(1) | 87.06(4) |
| N(2)–P(1)–C(11) | 105.94(18) |
| N(2)–P(1)–C(17) | 106.69(17) |
| C(11)–P(1)–C(17) | 104.36(18) |
| N(2)–P(1)–Ru(1) | 112.64(12) |
| C(11)–P(1)–Ru(1) | 111.88(12) |
| C(17)–P(1)–Ru(1) | 114.61(13) |

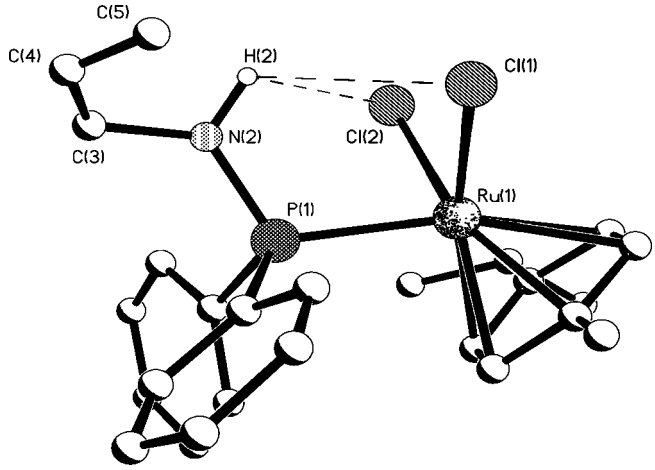
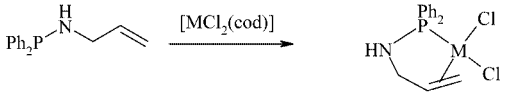



Figure 4. The X-ray structure of [RuCl(μ-Cl)(η$^6$-*p*-MeC$_6$H$_4$ *i*Pr){Ph$_2$PNH(C$_3$H$_5$)}] (**11**) showing hydrogen bonding

Table 2]. The magnitude of the Pt-P coupling constants strongly indicates the coordination of both phosphane and alkene group.




M = Pt **14**, Pd **15**
cod = 1,5-cyclooctadiene

(4)

In an interesting transformation, [Pt{Ph$_2$PNH(C$_3$H$_8$O)}$_2$] (**16**), was obtained by reaction of KO*t*Bu in methanol with **6** (51 % yield). The reaction probably proceeds by nucleophillic attack of methoxide though we have not observed this reaction for other complexes. The $^{31}$P{$^1$H} NMR spectrum showed a single peak at $\delta_P$ = 91.4 ppm with platinum satellites at $^1J(^{31}P\text{-}^{195}Pt)$ = 2294 Hz. The IR spectrum shows absorptions at 2873–2809 cm$^{-1}$, which corre-

spond to $\nu_{OMe}$ vibrations along with vibrations at 3069 and 997, which are assigned to $\nu_{NH}$ and $\nu_{PN}$, respectively. The FAB mass spectral analysis gave the appropriate parent ion and fragmentation pattern and the microanalysis shows good results for the suggested structure. The crystal structure of **16** (Table 6, Figure 5) shows that in the solid state the molecule occurs as hydrogen-bonded dimers. [H(1N)···O(5) 2.241(19) Å, N(1)···O(5) 3.164(4) Å, N(1)–H(1N)···O(5) angle of 157(4)°].

Table 6. Selected bond lengths [Å] and angles [°] for [Pt{$Ph_2PNH(C_3H_5OMe)_2$}] (**16**)

| | **16** |
|---|---|
| Pt(1)–C(3) | 2.113(4) |
| Pt(1)–P(1) | 2.2743(9) |
| P(1)–N(1) | 1.664(3) |
| P(1)–C(7) | 1.832(4) |
| P(1)–C(13) | 1.827(4) |
| N(1)–C(2) | 1.451(5) |
| C(3)–Pt(1)–P(1) | 81.56(11) |
| N(1)–P(1)–C(13) | 105.68(18) |
| N(1)–P(1)–C(7) | 106.47(18) |
| C(13)–P(1)–C(7) | 102.15(17) |
| N(1)–P(1)–Pt(1) | 104.19(12) |
| C(13)–P(1)–Pt(1) | 119.72(11) |
| C(7)–P(1)–Pt(1) | 117.51(12) |
| C(2)–N(1)–P(1) | 117.6(3) |

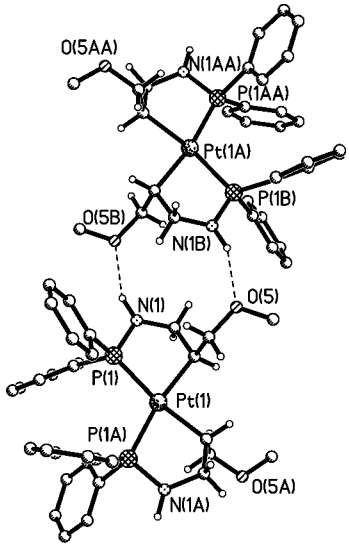



Figure 5. The X-ray structure of [Pt{$Ph_2PNH(C_3H_5OMe)_2$}] (**16**) showing hydrogen bonding

This paper clearly demonstrates the ability of (allylamino)phosphane to behave as a monodenate and bidentate ligand and illustrates a potentially useful nucleophilic addition at the allyl group.

## Experimental Section

**General:** General conditions were as described previously.[7] Unless otherwise stated, all reactions were carried out under oxygen-free nitrogen using standard Schlenk techniques. Diethyl ether and THF were purified by reflux in the presence of sodium/benzophenone and distillation under nitrogen. Dichloromethane was heated to reflux in the presence of calcium hydride and distilled under nitrogen. Toluene and hexane were heated to reflux in the presence of sodium and distilled under nitrogen. The complexes [PtMeX(cod)] (X = Cl or Me),[8] [{Pd(μ-Cl)($\eta^3$-$C_3H_5$)}$_2$],[9] [Cu(MeCN)$_4$][$PF_6$],[10] [AuCl(tht)] (tht = tetrahydrothiophene),[11] [$MCl_2$(cod)] (M = Pt or Pd),[12,13] [{RuCl(μ-Cl)($\eta^6$-p-$MeC_6H_4$-*i*Pr)$_2$}],[14] [{Rh(μ-Cl)(cod)}$_2$],[15] [{MCl(μ-Cl)($\eta^5$-$C_5Me_5$)}$_2$] (M = Rh or Ir),[16] [{PtCl(μ-Cl)($PMe_2Ph$)}$_2$],[17] [{PtCl(μ-Cl)($PMe_2$-Ph)}$_2$][18] and [{Pd(μ-Cl)($C_{10}H_8N$)}$_2$][19] were prepared according to literature procedures. Chlorodiphenylphosphane and allylamine were distilled prior to use. $Et_3N$ (99 % purity), *t*BuOK (95 % purity), $H_2O_2$ (30 wt.% in $H_2O$) and reagent grade KBr were used without further purification. IR spectra were recorded as KBr discs in the range 4000–200 $cm^{-1}$ with a Perkin–Elmer 2000 FTIR/RAMAN spectrometer. NMR spectra were recorded with a Gemini 2000 spectrometer (operating at 121.4 MHz for $^{31}P$ and 300 MHz for $^1H$). Microanalyses were performed by the St. Andrews University service and mass spectra by the Swansea Mass Spectrometer Service.

**$Ph_2PNH(C_3H_5)$ (1):** Allylamine (3.671 g, 64.3 mmol) and triethylamine (6.831 g, 67.5 mmol) were added together in dry THF (50 mL). Chlorodiphenylphosphane (14.894 g, 67.5 mmol) in dry THF (50 mL) was added dropwise with stirring overnight. Triethylamine hydrochloride was removed by filtration under nitrogen and the solvent removed in vacuo to yield a colourless oil which was purified by distillation (132 °C/0.2 Torr) and storing under nitrogen in the freezer which yielded a colourless waxy solid. Yield 6.283 g, 41 %. $C_{15}H_{16}NP$ (241.3): calcd. C 74.67, H 6.68, N 5.81; found C 74.27, H 7.37, N 5.58. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 42.5 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.8 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$) and 1.9 (s, 1 H, NH) ppm. $EI^+$ MS: *m*/*z* = 242 $[M + 1]^+$.

**$Ph_2P(O)NH(C_3H_5)$ (2):** $Ph_2PNH(C_3H_5)$ (461 mg, 1.9 mmol) was dissolved in dichloromethane (10 mL). Urea/hydrogen peroxide (180 mg, 1.9 mmol) was added and the reaction mixture was stirred overnight. The product was extracted from the $CH_2Cl_2$ by addition of distilled water, washed with $CH_2Cl_2$ (3 × 5 mL), dried with magnesium sulfate and the solvents were evaporated to dryness to yield a colourless solid. Yield 338 mg, 67 %. $C_{15}H_{16}NOP$ (257.3): calcd. C 70.03, H 6.27, N 5.44; found C 69. 74, H 6.22, N 5.15. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 24.4 ppm. $^1H$ ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.9 (m, 1 H, CH), 5.3 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$) and 2.9 (br.s, 1 H, NH) ppm. $EI^+$ MS: *m*/*z* = 257 [M]. IR (KBr disc): $\tilde{\nu}$ = 3189, 1641, 1181, 993 $cm^{-1}$.

**$Ph_2P(S)NH(C_3H_5)$ (3):** $Ph_2PNH(C_3H_5)$ (420 mg, 1.7 mmol) and elemental sulfur (56 mg, 1.7 mmol) were dissolved in dry toluene (10 mL) to yield a yellow solution which was stirred overnight. The solvent was reduced to 1 mL before addition of hexane (10 mL) to precipitate a colourless solid that was isolated by filtration. Yield 246 mg, 52 %. $C_{15}H_{16}NPS$ (273.3): calcd. C 65.91, H 5.90, N 5.12; found C 66.01, H 6.09, N 5.11. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 60.5 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.9 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$) and 2.4 (br. s, 1 H, NH) ppm. $EI^+$ MS: *m*/*z* = 273 [M]. IR (KBr disc): $\tilde{\nu}$ = 3170, 1642, 997, 689 $cm^{-1}$.

**$Ph_2P(Se)NH(C_3H_5)$ (4):** $Ph_2PNH(C_3H_5)$ (235 mg, 1.0 mmol) and grey selenium (77 mg, 1.0 mmol) were refluxed in dry toluene (10 mL) for 1 h before cooling to room temperature and filtering through a Celite plug to remove any insoluble material. The solvent was reduced to 1 mL to yield a colourless solid that was isolated by suction filtration and dried in vacuo. Yield 269 mg, 86 %.

$C_{15}H_{16}NPSe$ (320.2): calcd. C 56.07, H 5.02, N 4.36; found C 55.97, H 5.25, N 4.43. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 58.1 ppm [$^1J(^{31}P\text{-}^{77}Se)$ = 756 Hz]. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.9 (m, 1 H, CH), 5.3 (q, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$) and 2.3 (br. s, 1 H, NH) ppm. $EI^+$ MS: *m*/*z* = 322 [M]. IR (KBr disc): $\tilde{\nu}$ = 3177, 1644, 991, 573 $cm^{-1}$.

**[AuCl{Ph$_2$PNH(C$_3$H$_5$)}] (5):** $Ph_2PNH(C_3H_5)$ (78 mg, 0.3 mmol) and [AuCl(tht)] (103 mg, 0.3 mmol) were dissolved in $CH_2Cl_2$ (5 mL) and the mixture stirred overnight in the dark. Hexane (20 mL) was added to precipitate a colourless solid that was isolated by suction filtration. Yield 44 mg, 29 %. $C_{15}H_{16}AuClPN$ (473.7): calcd. C 38.03, H 3.40, N 2.96; found C 37.98, H 2.76, N 3.07. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 64.9 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.4 (m, 10 H, aromatic), 5.9 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.6 (m, 2 H, $NCH_2$), 2.5 (br.s, 1 H, NH) ppm. $FAB^+$ MS: *m*/*z* = 496 [M + Na]$^+$, 473 [M]$^+$, 438 [M – Cl]$^+$. IR (KBr disc): $\tilde{\nu}$= 3069, 1643, 996, 323 $cm^{-1}$.

**[PtCl$_2${Ph$_2$PNH(C$_3$H$_5$)}$_2$] (6):** $Ph_2PNH(C_3H_5)$ (161 mg, 0.7 mmol) and [$PtCl_2$(cod)] (125 mg, 0.3 mmol) were dissolved in dry $CH_2Cl_2$ (10 mL) to yield a colourless solution which was stirred overnight before reducing the solvent volume to 0.5 mL and addition of diethyl ether (20 mL) to precipitate a colourless solid which was isolated by suction filtration and dried in vacuo. Yield 226 mg, 90 %. $C_{30}H_{32}P_2N_2PtCl_2$ (748.5): calcd. C 48.14, H 4.31, N 3.74; found C 48.23, H 4.10, N 3.65. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 34.8 ppm [$^1J(^{31}P\text{-}^{195}Pt)$ 3949 Hz]. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.4 (m, 20 H, aromatic), 5.5 (m, 2 H, CH), 5.0 (m, 2 H, $CH_2$), 4.9 (m, 2 H, $CH_2$), 4.1 (br.s, 2 H, NH) and 3.5 (m, 4 H, $NCH_2$) ppm. $FAB^+$ MS: *m*/*z* = 713 [M – Cl]$^+$, 677 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$= 3054, 1642, 1000, 305, 288 $cm^{-1}$.

**[PdCl$_2${Ph$_2$PNH(C$_3$H$_5$)}$_2$] (7):** $Ph_2PNH(C_3H_5)$ (179 mg, 0.7 mmol) and [$PdCl_2$(cod)] (106 mg, 0.4 mmol) were dissolved in $CH_2Cl_2$ (10 mL) and stirred overnight. The solvent volume was reduced to 0.5 mL before addition of hexane (20 mL) to precipitate a yellow solid that was isolated by filtration and dried in vacuo. Yield 224 mg, 91 %. $C_{30}H_{32}Cl_2N_2P_2Pd$ (659.9): calcd. C 54.61, H 4.89, N 4.25; found C 54.80, H 4.67, N 4.06. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 58.8 and 46.2 ppm, *cis* and *trans* isomers. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.5–7.2 (m, 20 H, aromatic), 5.6 (m, 2 H, CH), 5.2 (m, 2 H, $CH_2$), 5.1 (m, 2 H, $CH_2$), 3.5 (m, 4 H, $NCH_2$) and 4.1 (br.s, 2 H, NH) ppm. $FAB^+$ MS: *m*/*z* = 624 [M – Cl]$^+$, 588 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$= 3054, 1643, 997, 297, 277 $cm^{-1}$.

**[Pt(PEt$_3$)Cl$_2${Ph$_2$PNH(C$_3$H$_5$)}] (8):** To a $CH_2Cl_2$ (10 mL) solution of [{PtCl(μ-Cl)($PEt_3$)}$_2$] (56 mg, 0.07 mmol) was added dropwise a $CH_2Cl_2$ (10 mL) solution of $Ph_2PNH(C_3H_5)$ (35 mg, 0.1 mmol) with stirring to yield a pale yellow solution. After 30 minutes the solvent was reduced to 1 mL before addition of diethyl ether (20 mL) to precipitate a colourless solid that was isolated by suction filtration. Yield 54 mg, 59 %. $C_{21}H_{31}Cl_2NP_2Pt$ (625.4): calcd. C 40.38, H 5.01, N 2.24; found C 40.61, H 4.38, N 2.49. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P_A)$ = 34.2 (d) ppm [$^1J(^{31}P_A\text{-}^{195}Pt)$ = 3979 Hz]; $\delta(P_X)$ = 7.3 (d) ppm [$^1J(^{31}P_X\text{-}^{195}Pt)$ = 3479 Hz, $^2J(^{31}P_A\text{-}^{31}P_X)$ =19 Hz]. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.7 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.0 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$), 3.2 (br.s, 1 H, NH), 1.5 (m, 6 H, $PCH_2$) and 0.9 (m, 9 H, Me) ppm. $ES^+$ MS: *m*/*z* = 590 [M – Cl]$^+$. IR (KBr disc): $\tilde{\nu}$= 3072, 1641, 1002, 309, 283 $cm^{-1}$.

**[Pt(PMe$_2$Ph)Cl$_2${Ph$_2$PNH(C$_3$H$_5$)}] (9):** $Ph_2PNH(C_3H_5)$ (33 mg, 0.1 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a $CH_2Cl_2$ (10 mL) solution of [{PtCl(μ-Cl)($PMe_2Ph$)}$_2$] 56 mg, 0.07 mmol) over 10 minutes with stirring. The solution was stirred for a further 30 minutes before reduction of the solvent to 1 mL and addition of diethyl ether (20 mL) to precipitate a colourless solid that was isolated by suction filtration and dried in vacuo. Yield 55 mg, 62 %. $C_{23}H_{27}Cl_2NP_2Pt$ (645.4): calcd. C 42.85, H 4.22, N 2.17; found C 42., H 2.26, N 2.08. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P_A)$ = 35.3 (d) ppm [$^1J(^{31}P_A\text{-}^{195}Pt)$ = 3878 Hz]; $\delta(P_X)$ = –14.2 (d) ppm [$^1J(^{31}P_X\text{-}^{195}Pt)$ = 3625 Hz. $^2J(^{31}P_A\text{-}^{31}P_X)$ 19 Hz]. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.4 (m, 15 H, aromatic), 5.6 (m, 1 H, CH), 5.1 (m, 1 H, $CH_2$), 4.9 (m, 1 H, $CH_2$), 4.5 (br.s, 1 H, NH), 3.1 (m, 2 H, $NCH_2$) and 1.7 [d, 6 H, $^3J(^{195}Pt\text{-}^1H)$ = 32 Hz, $^2J(^{31}P\text{-}^1H)$ = 11 Hz, PMe] ppm. $ES^+$ MS: *m*/*z* 645 = [M + H]$^+$, 610 [M – Cl]$^+$, 575 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$= 3053, 1642, 1000, 313, 283 $cm^{-1}$.

**[PdCl(C$_{10}$H$_8$N){Ph$_2$PNH(C$_3$H$_5$)}] (10):** To a $CH_2Cl_2$ (10 mL) suspension of [{PdCl($C_{10}H_8N$)}$_2$] (61 mg, 0.1 mmol) was added dropwise a $CH_2Cl_2$ solution of $Ph_2PNH(C_3H_5)$ (52 mg, 0.2 mmol) over 10 minutes to yield a colourless solution. After stirring for a further 30 minutes the solution was filtered through a Celite plug to remove any insoluble material remaining before reducing the solvent volume to 1 mL and addition of diethyl ether (20 mL) to precipitate a tan coloured microcrystalline solid that was isolated by filtration. Yield 78 mg, 69 %. $C_{25}H_{24}ClN_2PPd$ (525.3): calcd. C 57.16, H 4.60, N 5.33; found C 56.93, H 3.93, N 5.24. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 65.0 ppm. $^1H$ NMR ($CDCl_3$): $\delta$ = 9.6–7.8 (m, 6 H, naphthalene aromatic), 7.3 (m, 10 H, aromatic), 5.7 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.0 (m, 1 H, $CH_2$), 4.5 (br.s, 1 H, NH), 3.4 (m, 2 H, $NCH_2$), 2.8 [d, $^2J(^{31}P\text{-}^1H)$ 5 Hz, 2 H, $CH_2$] ppm. $ES^+$ MS: *m*/*z* = 489 [M – Cl]$^+$. IR (KBr disc): $\tilde{\nu}$= 3049, 1639, 993, 28 $cm^{-1}$.

**[RuCl(μ-Cl)(η$^6$-*p*-MeC$_6$H$_4$ *i*Pr){Ph$_2$PNH(C$_3$H$_5$)}] (11):** $Ph_2PNH(C_3H_5)$ (170 mg, 0.7 mmol) and [{RuCl(μ-Cl)(η$^6$-*p*-$MeC_6H_4$ *i*Pr)}$_2$] (54 mg, 0.1 mmol) were dissolved in $CH_2Cl_2$ (5 mL) to yield a dark red solution that was stirred for 30 min. The solvent was reduced to 0.5 mL before addition of hexane (10 mL to precipitate an orange microcrystalline solid that was isolated by suction filtration and dried in vacuo. Yield 82 mg, 85 %. $C_{25}H_{30}Cl_2NPRu$ (547.5): calcd. C 54.85, H 5.52, N 2.56; found C 55.71 54.85, H 5.62, N 2.71. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 61.3 ppm. $^1H$ NMR: $\delta$ = 7.3 (m, 14 H, aromatic), 5.5 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$), 2.9 (br. s, 1 H, NH), 2.6 (m, 1 H, CH), 1.2 (m, 3 H, $CH_3$), 0.8 (m, 6 H, $CH_3$) ppm. $FAB^+$ MS: *m*/*z* = 570 [M + Na]$^+$, 547 [M]$^+$, 512 [M – Cl]$^+$, 476 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$ = 3051, 1642, 996, 290, 283 $cm^{-1}$.

**[RhCl(μ-Cl)(η$^5$-C$_5$Me$_5$){Ph$_2$PNH(C$_3$H$_5$)}] (12):** $Ph_2PNH(C_3H_5)$ (45 mg, 0.2 mmol) and [{RhCl(μ-Cl)(η$^5$-$C_5Me_5$)}$_2$] (58 mg, 0.1 mmol) were dissolved in $CH_2Cl_2$ (10 mL) to yield a blood red solution that stirred for 30 min before reducing the solvent to 1 mL and addition of diethyl ether (20 mL) to precipitate a red microcrystalline solid that was isolated by suction filtration and dried in vacuo. Yield 69 mg, 67 %. $C_{25}H_{31}Cl_2NPRh$ (550.3): calcd. C 54.56, H 5.68, N 2.55; found C 54.32 , H 5.78, N 2.44. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 66.4 ppm [$^1J(^{31}P\text{-}^{103}Rh)$ = 148 Hz]. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.6 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.3 (m, 2 H, $NCH_2$), 3.2 (br. s, 1 H, NH), 1.3 (s, 15 H, $CH_3$) ppm. $FAB^+$ MS: *m*/*z* = 572 [M + Na]$^+$, 514 [M – Cl]$^+$, 474 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$ = 3063, 1642, 995, 279, 267 $cm^{-1}$.

**[IrCl(μ-Cl)(η$^5$-C$_5$Me$_5$){Ph$_2$PNH(C$_3$H$_5$)}] (13):** $Ph_2PNH(C_3H_5)$ (42 mg, 0.2 mmol) and [{IrCl(μ-Cl)(η$^5$-$C_5Me_5$)}$_2$] (69 mg, 0.1 mmol) were dissolved in $CH_2Cl_2$ (10 mL) to yield an orange solution. The solvent was reduced to 1 mL before diethyl ether was added to precipitate a yellow microcrystalline solid that was isolated by filtration and dried in vacuo. Yield 72 mg, 65 %. $C_{25}H_{31}Cl_2IrNP$ (639.6): calcd. C 46.95, H 4.89, N 2.19; found C 47.07, H 4.85, N 2.13. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 34.5 ppm. $^1H$

Table 7. Crystal data for $Ph_2PNH(C_3H_5)$ and derivatives

| Compound | **4** | **6** | **8** | **9** | **11** | **16** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{17}H_{16}N_3PSe$ | $C_{30}H_{32}Cl_2N_2P_2Pt$ | $C_{21}H_{31}Cl_2NP_2Pt$ | $C_{23}H_{27}Cl_2NP_2Pt$ | $C_{25}H_{30}Cl_2NPRu$ | $C_{32}H_{38}N_2O_2P_2Pt$ |
| $M$ | 320.22 | 748.51 | 625.40 | 649.39 | 547.44 | 739.67 |
| Crystal system | monoclinic | monoclinic | triclinic | triclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ | $C2/c$ |
| $a$ [Å] | 12.246(3) | 10.012(3) | 8.835(2) | 9.2943(12) | 9.918(3) | 20229(3) |
| $b$ [Å] | 9.317(2) | 15.065(4) | 9.741(2) | 9.7402(13) | 13.782(4) | 10.8193(17) |
| $c$ [Å] | 12.711(3) | 19.717(6) | 14.634(3) | 14.1561(19) | 17.566(5) | 16.926(3) |
| $\alpha$ [°] | 90 | 90 | 87.302(4) | 90.661(2) | 90 | 90 |
| $\beta$ [°] | 92.261(5) | 91.56(10) | 87.343(4) | 94.862(2) | 94.880(5) | 123.002(2) |
| $\gamma$ [°] | 90 | 90 | 71.362(3) | 112.151(2) | 90 | 90 |
| $Z$ | 4 | 4 | 2 | 2 | 4 | 4 |
| $\mu$ [mm$^{-1}$] | 2.684 | 5.029 | 6.254 | 6.311 | 0.958 | 4.650 |
| Reflections measured | 5982 | 12495 | 5879 | 5970 | 10269 | 8848 |
| Independent reflections | 2066 | 4181 | 3327 | 3353 | 3421 | 2765 |
| Final $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0381, 0.0917 | 0.0214, 0.0515 | 0.0361, 0.0967 | 0.0317, 0.0788 | 0.0343, 0.0783 | 0.0229, 0.0473 |

NMR ($CDCl_3$): $\delta$ = 7.3 (m, 10 H, aromatic), 5.6 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$), 3.2 (br. s, 1 H, NH), 1.3 (s, 15 H, $CH_3$) ppm. FAB$^+$ MS: $m/z$ = 604 [M – Cl]$^+$, 568 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$ = 3058, 1640, 994, 291, 280 cm$^{-1}$.

**[$PdCl_2${$Ph_2PNH(C_3H_5)$}] (14):** $Ph_2PNH(C_3H_5)$ (52 mg, 0.2 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise to $CH_2Cl_2$ (5 mL) solution of [$PdCl_2$(cod)] (53 mg, 0.2 mmol). After stirring for 30 min, the solvent was reduced in vacuo to 0.5 mL before precipitating a yellow microcrystalline solid upon addition of hexane (10 mL) and isolation by suction filtration. Yield 65 mg, 83 %. $C_{15}H_{16}PNPdCl_2$ (418.6): calcd. C 43.04, H 3.85, N 3.35; found C 43.95, H 4.26, N 2.70. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 93.6 ppm. $^1H$ NMR ($CD_2Cl_2$): $\delta$ = 7.35 (m, 10 H, aromatic), 5.6 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$) and 4.1 (br. s, 1 H, NH) ppm. FAB$^+$ MS: $m/z$ = 382 [M – Cl]$^+$, 347 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$ = 3054, 996, 318, 281 cm$^{-1}$.

**[$PtCl_2${$Ph_2PNH(C_3H_5)$}] (15):** $Ph_2PNH(C_3H_5)$ (43 mg, 0.2 mmol) in $CH_2Cl_2$ (5 mL) was added dropwise to a $CH_2Cl_2$ (5 mL) solution of [$PtCl_2$(cod)] (58 mg, 0.2 mmol) over 2.5 h. The solvent was reduced to 1 mL before addition of hexane (10 mL) to yield an off-white sticky solid on reduction of solvent. The sticky solid was subsequently dissolved in $CH_2Cl_2$ (0.5 mL) before addition of petroleum ether (40–60°C) (10 mL) to yield a colourless solid that was isolated by suction filtration. Yield 51 mg, 65 %. $C_{15}H_{16}Cl_2NPPt$ (507.2): calcd. C 35.52, H 3.18, N 2.76; found C 36.53, H 2.99, N 2.60. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ = 63.5 ppm [$^1J(^{31}P\text{-}^{195}Pt)$ = 3481 Hz]. $^1H$ NMR ($CD_2Cl_2$): $\delta$ = 7.35 (m, 10 H, aromatic), 5.5 (m, 1 H, CH), 5.2 (m, 1 H, $CH_2$), 5.1 (m, 1 H, $CH_2$), 3.5 (m, 2 H, $NCH_2$) and 4.1 (br. d, $J$ = 8 Hz, 1 H, NH) ppm. FAB$^+$ MS: $m/z$ = 472 [M – Cl]$^+$, 436 [M – 2 Cl]$^{2+}$. IR (KBr disc): $\tilde{\nu}$ = 3055, 998, 328, 289 cm$^{-1}$.

**[Pt{$Ph_2PNH(C_4H_8O)$}$_2$] (16):** To a $CH_3OH$ (10 mL suspension of [$PtCl_2${$Ph_2PNH(C_3H_5)$}$_2$] (100 mg, 0.1 mmol) was added potassium *tert*-butoxide (30 mg, 0.2 mmol) with stirring to yield a colourless precipitate after 1 h. This microcrystalline solid was subsequently isolated by suction filtration and dried in vacuo. Yield 46 mg, 51 %. $C_{32}H_{38}N_2O_2P_2Pt$ (739.7): calcd. C 51.96, H 5.18, N 3.79; found C 52.06, H 4.60, N 3.70. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 91.4 ppm [$^1J(^{31}P\text{-}^{195}Pt)$ = 2294 Hz]. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.4 (m, 20 H, aromatic), 5.9 (m, 2 H, CH), 5.2 (m, 2 H, $CH_2$), 5.1 (m, 2 H, $CH_2$), 3.6 (m, 4 H, $NCH_2$), 2.5 (br. s, 2 H, NH), 1.5 (s, 6 H, MeO) ppm. FAB$^+$ MS: $m/z$ = 740 [M]$^+$. IR (KBr disc): $\tilde{\nu}$ = 3069, 3045, 2873–2809 (m), 997 cm$^{-1}$.

**X-ray Crystallography:** X-ray diffraction studies were performed using a Bruker SMART diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation. The structures were solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon atoms were idealised, the NH protons were located by a $\Delta F$ map. Structural refinements were made by the full-matrix least-squares method on $F^2$ using SHELXTL.[20] Details are given in Table 7. 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-239884 to –239889 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.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