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FULL PAPER

Synthesis of chelate complexes and the dichalcogen derivatives of the unsymmetrical diphosphine ligand $Ph_2PNHC_6H_4PPh_2$. Molecular structure of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]\cdot 0.75dmso\cdot 0.75CHCl_3$

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$[M(\eta^3\text{-}C_3H_5)(L)][Cl]$ (M = Pt or Pd and L = $Ph_2PNHC_6H_4PPh_2$), $[MX_2(L)]$ (where M = Pt, X = Me, Cl, Br or I and where M = Pd or Ni X = Cl), [PtMeCl(L)], $[Mo(CO)_4(L)]$ and $[(AuCl)_2(L)]$ have been synthesised. In all complexes except $[(AuCl)_2(Ph_2PNHC_6H_4PPh_2)]$ where the diphosphine acts as a bridging ligand between the two metal centres a chelating coordination mode is observed. We have also prepared and characterised the dichalcogen compounds $Ph_2P(E)NHC_6H_4P(E)Ph_2$ (where E = O, S or Se) and found that the disulfide reacts cleanly with $[PdCl_2(PhCN)_2]$ in dichloromethane or $Na_2[PdCl_4]$ in ethanol with elimination of HCl to give the unusual neutral N-metallated species $[PdCl(Ph_2P(S)NC_6H_4P(S)Ph_2\text{-}S,N,S)]$, which contains both S–P–C–C–N–Pd six and N–P–S–Pd four-membered metallacycles. The cationic species $[Pd(PPh_3)(Ph_2P(S)NC_6H_4P(S)Ph_2\text{-}S,N,S)][ClO_4]$ was generated by the sequential addition of first $Ag[ClO_4]$ followed by PPh_3 to the neutral chloride. The molecular structure of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]\cdot 0.75dmso\cdot 0.75CHCl_3$, which reveals a puckered ring and displays hydrogen-bonding interactions between the ligand amine proton and the oxygen atom of the dmso molecule, has been determined by single crystal X-ray diffraction.

Introduction

Throughout inorganic and organometallic chemistry few ligands have been as extensively employed as symmetrical tertiary diphosphines; well known examples being dppm $Ph_2PCH_2PPh_2$ bis(diphenylphosphino)methane, dppe $Ph_2P(CH_2)_2PPh_2$ bis(diphenylphosphino)ethane, dppp $Ph_2P(CH_2)_3PPh_2$ bis(diphenylphosphino)propane and the aromatic backboned $Ph_2PC_6H_4PPh_2$ 1,2-phenylenebis(diphenylphosphine). In comparison there are relatively few examples in the chemical literature of unsymmetrical, potentially bidentate bisphosphines containing P–C–C–X–P backbones, where X = C,[1,2] Si,[3,4] O,[5–11] or S,[12] fewer still where X = N,[13–15] and no examples, to the best of our knowledge, where transition metal complexes have been prepared using preformed P–C–C–N–P backboned ligands. Six-membered P–C–C–O–P–M metallacycles (where M = Pd[16,17] and Pt[17]) and platinum(II) and palladium(II) P–C–C–N–P–M metallacycles have previously been reported[18] but all were formed by intramolecular reactions brought on by high temperature thermolysis. Further examples of P–C–C–O–P–M metallacycles include the photochemical formation of $[W(CO)_4(Ph_2POC(Ph)=CHPPh_2)]$ from $[W(CO)_4(Ph_2PCH(C(O)Ph)PPh_2)]$[19] a series of Group 10 metallacycles formed by reaction of Ph_2PCl or $PhPCl_2$ with phosphino–enolate complexes[20–22] and the elimination/rearrangement reaction of a palladium complex bearing a phosphino–hydroquinone ligand in an acidic medium[23]

We recently described the synthesis of $Ph_2PNHC_6H_4PPh_2$[24] an unsymmetrical diphosphine derived from 2-(diphenylphosphino)aniline[25] and have shown that the difference in basicity or the steric properties of the two different phosphorus atoms of $Ph_2PNHC_6H_4PPh_2$ can be exploited to obtain different coordination modes *i.e.* bidentate *versus* monodentate. We have previously shown that reaction of $Ph_2PNHC_6H_4PPh_2$ with η^6-aryl Ru(II), Os(II) and Cp* (Cp* = η^5-C_5Me_5) Rh(III), Ir(III) chloride-bridged dimers in thf leads to monometallic species in which the diphosphine ligand binds to the metal only *via* the amino–phosphine moiety. Subsequent dissolution of these complexes in other solvents *e.g.* chloroform or methanol/chloroform mixtures resulted in their conversion to the corresponding cationic chelate complexes.[25] In this paper we report the synthesis and characterisation of $Ph_2PNHC_6H_4PPh_2$ chelate compounds of platinum group and other late transition metals in addition to $[Ph_2P(AuCl)NHC_6H_4P(AuCl)Ph_2]$ where the ligand bridges the two (AuCl) groups.

Experimental

General

Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. The compound $Ph_2PNHC_6H_4PPh_2$ was prepared as previously reported.[25] The complexes $[Pt(\mu\text{-}Cl)(\mu\text{-}\eta^2:\eta^1\text{-}C_3H_5)]_4$,[26] $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$,[27] [MX(Y)(cod)] (M = Pt or Pd; X, Y = Me, Cl, Br or I; cod = cycloocta-1,5-diene),[28–31] $[PdCl_2(NCPh)_2]$,[32] $[Mo(CO)_4(pip)_2]$[33] (pip = piperidine) or $[AuCl(tht)]$[34] (tht = tetrahydrothiophene) were prepared according to literature procedures. Aqueous H_2O_2 (30% w/w, Fluka), PPh_3 (Aldrich 99% purity), $NiCl_2\cdot 6H_2O$ (Aldrich) and $Ag[ClO_4]$ (Aldrich 99% purity) were obtained commercially and used without further purification.

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin-Elmer system 2000 Fourier transform spectrometer, ^1H NMR spectra (250 MHz) on a Bruker AC250 FT spectrometer with δ referenced to external $SiMe_4$ and $^{31}P\text{-}\{^1H\}$ NMR spectra (36.2 or 101.3 MHz) either on a JEOL FX90Q or a Bruker AC250 FT spectrometer with δ referenced to external H_3PO_4. Microanalyses were performed by the Loughborough University Service.

Sodium tetrachloropalladate ($Na[PdCl_4]$) along with other precious metal salts were provided on loan by Johnson Matthey plc.

Syntheses

$[Pt(\eta^3\text{-}C_3H_5)(Ph_2PNHC_6H_4PPh_2)][Cl]$ 1. To a stirred thf suspension (10 cm^3) of $[Pt(\mu\text{-}Cl)(\mu\text{-}\eta^2 : \eta^1\text{-}C_3H_5)]_4$ (0.109 g, 0.10 mmol) was added in one portion solid $Ph_2PNHC_6H_4PPh_2$ (0.185 g, 0.40 mmol). The mixture was stirred for 4 hours to give a very pale yellow solution which was filtered through a small plug of Celite to remove a small quantity of dark insoluble material and concentrated under vacuum to half its original volume. Diethyl ether (20 cm^3) was slowly added to the stirred filtrate and the resulting pale yellow precipitate was collected by filtration washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.267 g, 91%. Microanalysis: Found (Calcd. for $C_{33}H_{30}ClNP_2Pt$) C 54.18 (54.09), H 3.87 (4.13), N 1.85 (1.91)%. ^1H NMR (CD_2Cl_2): δ 7.99 (br s, 1 H, NH), 7.72–7.20 (m, 22 H, aromatics), 6.92 (m, 1 H, aromatic), 6.72 (m, 1 H, aromatic), 5.26 (m, 1 H, allyl), 3.99 (v br s, 2 H, allyl), 3.01 (v br s, 2 H, allyl). FAB^+ MS: *m/z* 697 $[M-Cl]^+$ and 656/7 $[M-Cl-(C_3H_5)]^{2+}$. Selected IR data (KBr): 2800w [ν(N–H)] and 919br cm^{-1} [ν(P–N)].

$[Pd(\eta^3\text{-}C_3H_5)(Ph_2PNHC_6H_4PPh_2)][Cl]$ 2. To a stirred toluene (10 cm^3) suspension of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ (0.095 g, 0.26 mmol) was added in one portion solid $Ph_2PNHC_6H_4PPh_2$ (0.240 g, 0.52 mmol). The mixture was stirred for 4 hours to give a pale yellow precipitate which was collected by filtration, washed with toluene (5 cm^3) and diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.291 g, 87%. Microanalysis: Found (Calcd. for $C_{33}H_{30}ClNP_2Pd$) C 61.44 (61.51), H 4.69 (4.69), N 2.04 (2.17)%. ^1H NMR ($CDCl_3$): δ 8.11 (m, 1 H, $^2J(^{31}P\text{–}^1H)$ 7 Hz, NH), 7.60–7.22 (m, 22 H, aromatics), 6.86 (m, 1 H, aromatic), 6.61 (m, 1 H, aromatic), 5.63 (pent, 1 H, $^2J(^1H\text{–}^1H)$ 10.6 Hz, allyl), 3.62 (v br s, 4 H, allyl). FAB^+ MS: *m/z* 608 $[M - Cl]^+$ and 567/8 $[M - Cl - (C_3H_5)]^{2+}$. Selected IR data (KBr): 2786w [ν(N–H)] and 914br cm^{-1} [ν(P–N)].

$[PtCl_2(Ph_2PNHC_6H_4PPh_2)]$ 3. To a stirred dichloromethane (3 cm^3) solution of $[PtCl_2(cod)]$ (0.092 g, 0.25 mmol) was added in one portion solid $Ph_2PNHC_6H_4PPh_2$ (0.116 g, 0.25 mmol) and stirred for 2 hours. The resulting cream coloured microcrystalline product was collected by suction filtration washed with ice cold dichloromethane (2 × 2 cm^3) then petroleum ether (2 × 20 cm^3) followed by diethyl ether (2 × 20 cm^3) and dried *in vacuo*. Yield: 0.170 g, 95%. Microanalysis: Found (Calcd. for $C_{30}H_{25}Cl_2NP_2Pt$) C 50.05 (49.53), H 3.86 (3.46), N 2.06 (1.93)%. ^1H NMR ($CDCl_3$/d_6-dmso): δ 8.30 (m, 1 H, NH), 7.72 (m, 4 H, aromatics), 7.60–7.29 (m, 17 H, aromatics), 7.12 (m, 1 H, aromatic), 6.89 (m, 1 H, aromatic) and 6.55 (m, 1 H, aromatic). FAB^+ MS: *m/z* 692 $[M - Cl]^+$ and 656/7 $[M - 2Cl]^{2+}$. Selected IR data (KBr): 3191br [ν(N–H)], 919br [ν(P–N)] and 313w, 290w cm^{-1} [ν(Pt–Cl)].

$[PtBr_2(Ph_2PNHC_6H_4PPh_2)]$ 4. This was prepared in the same way as the platinum complex **3** using $[PtBr_2(cod)]$ (0.129 g, 0.28 mmol) in dichloromethane (4 cm^3) and $Ph_2PNHC_6H_4PPh_2$ (0.130 g, 0.28 mmol) and stirred for 17 hours (overnight), collected by suction filtration, washed with ice cold dichloromethane (2 × 2 cm^3) then petroleum ether (2 × 10 cm^3) followed by diethyl ether (15 cm^3) to give a cream coloured microcrystalline product. Yield: 0.191 g, 84%. Microanalysis: Found (Calcd. for $C_{30}H_{25}Br_2NP_2Pt$) C 44.97 (44.14), H 3.43 (3.09), N 1.78 (1.72)%. FAB^+ MS: *m/z* 839 $[M + Na]^+$, 816 $[M]^+$, 736 $[M - Br]^+$ and 656/7 $[M - 2Br]^{2+}$. Selected IR data (KBr): 3199br [ν(N–H)], 906br [ν(P–N)] and 305br cm^{-1} [ν(Pt–Br)].

$[PtI_2(Ph_2PNHC_6H_4PPh_2)]$ 5. This was prepared in the same way as the platinum complex **3** using $[PtI_2(cod)]$ (0.136 g, 0.24 mmol) in dichloromethane (4 cm^3) and $Ph_2PNHC_6H_4PPh_2$ (0.116 g, 0.25 mmol) and stirred for 17 hours (overnight), collected by suction filtration, washed with ice cold dichloromethane (2 × 2 cm^3) then petroleum ether (2 × 10 cm^3) followed by diethyl ether (2 × 10 cm^3) to give a pale yellow microcrystalline product. Yield: 0.173 g, 78%. Microanalysis: Found (Calcd. for $C_{30}H_{25}I_2NP_2Pt$) C 39.73 (39.58), H 3.05 (2.77), N 1.48 (1.54)%. FAB^+ MS: *m/z* 933/4 $[M + Na]^+$, 910 $[M]^+$, 783/4 $[M - I]^+$ and 656/7 $[M - 2I]^{2+}$. Selected IR data (KBr): 3199br [ν(N–H)], 899br [ν(P–N)] and 353br cm^{-1} [ν(Pt–I)].

$[PtMe_2(Ph_2PNHC_6H_4PPh_2)]$ 6. This was prepared in the same way as the platinum complex **3** using $[PtMe_2(cod)]$ (0.072 g, 0.22 mmol) in dichloromethane (1.5 cm^3) and $Ph_2PNHC_6H_4PPh_2$ (0.105 g, 0.23 mmol) and stirred for 2 hours to give a clear yellow solution. Light petroleum (10 cm^3) was added and the dichloromethane was removed by slow evaporation to give a cream coloured precipitate. The product was collected by suction filtration and washed with light petroleum (2 × 10 cm^3) followed by diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.122 g, 82%. Microanalysis: Found (Calcd. for $C_{32}H_{31}NP_2Pt$) C 55.39 (55.98), H 4.63 (4.55), N 2.06 (2.04)%. ^1H NMR ($CDCl_3$/d_8-dmso): δ 8.17 (m, 1 H, NH), 7.56–7.49 (m, 4 H, aromatics), 7.41–7.29 (m, 16 H, aromatics), 7.17 (m, 1 H, aromatic), 6.95 (m, 1 H, aromatic), 6.79 (m, 1 H, aromatic), 6.69 (m, 1 H, aromatic) and 0.34 (m, 6 H, $^2J(^{195}Pt\text{–}^1H)$ 69 Hz, PtMe). FAB^+ MS: *m/z* 709 $[M + Na]^+$, 687 $[M + H]^+$, 671 $[M - CH_3]^+$ and 656/7 $[M - 2CH_3]^{2+}$. Selected IR data (KBr): 3314vs [ν(N–H)] and 883vs cm^{-1} [ν(P–N)].

Isomers of $[PtMeCl(Ph_2PNHC_6H_4PPh_2)]$ 7. A dichloromethane (15 cm^3) solution of $Ph_2PNHC_6H_4PPh_2$ (0.123 g, 0.27 mmol) was added drop-wise over a 10 minute period to a rapidly stirred dichloromethane (15 cm^3) solution of [PtMeCl(cod)] (0.094 g, 0.27 mmol) and the mixture was stirred for 1 hour. Light petroleum (10 cm^3) was added and the volume of the reaction solvent was reduced to *ca.* 15 cm^3. The resulting cream coloured precipitate was collected by suction filtration, washed with light petroleum (2 × 10 cm^3) followed by diethyl ether (2 × 5 cm^3) and dried *in vacuo*. Yield: 0.167 g, 89%. Microanalysis: Found (Calcd. for $C_{31}H_{28}ClNP_2Pt$) C 52.39 (52.66), H 3.75 (3.99), N 1.93 (1.98)%. FAB^+ MS: *m/z* 707 $[M]^+$, 672 $[M - Cl]^+$, 692 $[M - CH_3]^+$ and 656/7 $[M - Cl - CH_3]^{2+}$.

$[PdCl_2(Ph_2PNHC_6H_4PPh_2)]$ 8. This was prepared in the same way as the platinum complex **3** using $[PdCl_2(cod)]$ (0.075 g, 0.26 mmol) in dichloromethane (2.5 cm^3) and $Ph_2PNHC_6H_4PPh_2$ (0.125 g, 0.27 mmol). The pale yellow precipitate was collected by suction filtration washed with ice cold dichloromethane (2 × 1 cm^3), then petroleum ether (20 cm^3) followed by diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.159 g, 95%. Microanalysis: Found (Calcd. for $C_{30}H_{25}Cl_2NP_2Pd$) C 56.58 (56.41), H 3.96 (3.94), N 2.18 (2.19)%. ^1H NMR ($CDCl_3$/dmso): δ 8.34 (br t, 1 H, $^2J(^{31}P\text{–}^1H)$ 6 Hz, NH), 7.71 (m, 4 H, aromatics), 7.61–7.32 (m, 17 H, aromatics), 7.19 (m, 1 H, aromatic), 6.87 (m, 1 H, aromatic) and 6.59 (m, 1 H, aromatic). FAB^+ MS: *m/z* 662 $[M + Na]^+$, 604 $[M - Cl]^+$ and 568 $[M - 2Cl]^{2+}$. Selected IR data (KBr): 3125m [ν(N–H)], 925br [ν(P–N)] and 312w, 290w cm^{-1} [ν(Pd–Cl)].

$[NiCl_2(Ph_2PNHC_6H_4PPh_2)]$ 9. Solid $Ph_2PNHC_6H_4PPh_2$ (0.167 g, 0.36 mmol) was added in one portion to a hot stirred ethanol solution (5 cm^3) of $NiCl_2{\cdot}6H_2O$ (0.086 g, 0.36 mmol) causing an immediate colour change from pale green to deep red. The reaction mixture was heated and stirred for a further 10 minutes and then allowed to cool. The resulting bright red crystalline material was collected by suction filtration washed with ethanol (2 × 5 cm^3) and dried *in vacuo*. Yield: 0.154 g, 72%. Microanalysis: Found (Calcd. for $C_{30}H_{25}Cl_2NP_2Ni$) C 60.31 (60.96), H 4.01 (4.26), N 2.15 (2.37)%. FAB^+ MS: *m/z* 591 $[M]^+$,

556 [M − Cl]$^+$ and 520 [M − 2Cl]$^{2+}$. Selected IR data (KBr): 3201m [ν(N–H)], 917m [ν(P–N)] and 330br cm^{-1} [ν(Ni–Cl)].

[Mo(CO)$_4$(Ph$_2$PNHC$_6$H$_4$PPh$_2$)] 10. [Mo(CO)$_4$(pip)$_2$] (0.403 g, 1.07 mmol) and Ph$_2$PNHC$_6$H$_4$PPh$_2$ (0.493 g, 1.07 mmol) were refluxed in dichloromethane (20 cm^3) under an N_2 atmosphere for 1.5 hours. The pale orange solution was cooled to room temperature and methanol (*ca.* 20 cm^3) was added then the mixture was concentrated to *ca.* 30 cm^3 and left to stand at −4 °C overnight. The cream coloured solid was collected by suction filtration washed with methanol (10 cm^3) and diethyl ether (10 cm^3) and dried *in vacuo*. Yield: 0.623 g, 88%. Microanalysis: Found (Calcd. for $C_{34}H_{25}MoNO_4P_2$) C 60.58 (61.00), H 3.50 (3.76), 1.82 (2.09)%. ^{1}H NMR ($CDCl_3$): δ 7.45–7.16 (m, 21 H, aromatics), 6.87 (m, H, aromatic), 6.61 (m, 1 H, aromatic), 6.49 (m, 1 H, aromatic), 4.79 (br d, 1 H, $^2J(^{31}P–^1H)$ 8 Hz, NH). FAB$^+$ MS: *m*/*z* 669/670 [M]$^+$, 641 [M − CO]$^+$, 613 [M − 2CO]$^+$, 585 [M − 3CO]$^+$ and 557 [M − 4CO]$^+$. Selected IR data (KBr): 3331m [ν(N–H)], 893s [ν(P–N)] and 2017s, 1925vs, 1903vs, 1884vs cm^{-1} [ν(CO)].

[(AuCl)$_2$(Ph$_2$PNHC$_6$H$_4$PPh$_2$)] 11. [AuCl(tht)] (0.115 g, 0.36 mmol) was dissolved in dichloromethane (5 cm^3) and solid Ph$_2$PNHC$_6$H$_4$PPh$_2$ (0.082 g, 0.18 mmol) was added in one portion. The mixture was stirred for 30 minutes giving a clear brown coloured solution which was then filtered through Celite to remove a small amount of insoluble material and reduced in volume to *ca.* 2 cm^3. Petroleum ether (bp 60–80 °C) was added drop-wise (30 cm^3) and the colourless microcrystalline product was collected by suction filtration washed with petroleum ether (2 × 10 cm^3) and dried *in vacuo*. Yield: 0.150 g, 91%. Microanalysis: Found (Calcd. for $C_{30}H_{25}Au_2Cl_2NP_2$) C 38.75 (38.90), H 2.59 (2.72), N 1.50 (1.51)%. ^{1}H NMR (CD_2Cl_2): δ 7.65–7.33 (m, 21 H, aromatics), 7.18 (m, 1 H, aromatic), 7.05 (m, 1 H, aromatic), 6.70 (m, 1 H, aromatic) and 5.61 (br t, 1 H, $^2J(^{31}P–^1H)$ 3 Hz, NH). FAB$^+$ MS: *m*/*z* 949 [M + Na]$^+$, 926 [M]$^+$ and 891 [M − Cl]$^+$. Selected IR data (KBr): 3238m [ν(N–H)], 922s [ν(P–N)] and 339w cm^{-1} [ν(Au–Cl)].

Ph$_2$P(O)NHC$_6$H$_4$P(O)Ph$_2$ 12. Aqueous hydrogen peroxide (30% w/w, 0.2 cm^3, 1.76 mmol) was added drop-wise to a solution of Ph$_2$PNHC$_6$H$_4$PPh$_2$ (0.360 g, 0.78 mmol) in thf (10 cm^3) and the mixture was stirred for 30 minutes. The solvent was removed *in vacuo* to give a viscous oil which was dissolved in dichloromethane (30 cm^3) and dried over magnesium sulfate. The drying agent was removed by filtration and the filtrate was evaporated to dryness. The product was recrystallised from the minimum of hot toluene and after storage overnight at −4 °C the colourless crystalline product was collected by suction filtration washed with ice cold toluene (5 cm^3) and dried *in vacuo*. Yield: 0.304 g, 79%. Microanalysis: Found (Calcd. for $C_{30}H_{25}NO_2P_2$) C 72.78 (73.02), H 5.32 (5.11), N 2.74 (2.84)%. ^{1}H NMR ($CDCl_3$): δ 9.43 (br d, 1 H, $^2J(^{31}P–^1H)$ 12 Hz, NH) and 7.73–7.20 (m, 22 H, aromatics) and 6.97–6.79 (m, 2 H, aromatics). FAB$^+$ MS: *m*/*z* 493 [M]$^+$. Selected IR data (KBr): 3149br [ν(N–H)], 1188s, 1173s [ν(P=O)] and 952s cm^{-1} [ν(P–N)].

Ph$_2$P(S)NHC$_6$H$_4$P(S)Ph$_2$ 13. Ph$_2$PNHC$_6$H$_4$PPh$_2$ (0.410 g, 0.89 mmol) and elemental sulfur (0.057 g, 1.78 mmol) were stirred in toluene (20 cm^3) for 90 minutes. The solvent was removed *in vacuo* and the crude product was taken up in dichloromethane (10 cm^3) and filtered through Celite. The filtrate was evaporated to dryness and the crude product was recrystallised from a minimum of warm toluene. The colourless solid was collected by suction filtration washed with ice cold toluene (5 cm^3) and dried overnight *in vacuo*. Yield: 0.402 g, 86%. Microanalysis: Found (Calcd. for $C_{30}H_{25}NP_2S_2$) C 68.45 (68.56), H 4.74 (4.79), N 2.63 (2.66)%. ^{1}H NMR ($CDCl_3$): δ 8.35 (br d, 1 H, $^2J(^{31}P–^1H)$ 8 Hz, NH), 7.78–7.21 (m, 22 H, aromatics) and 6.85–6.71 (m, 2 H, aromatics). FAB$^+$ MS: *m*/*z* 526 [M + H]$^+$ and 548 [M + Na]$^+$. Selected IR data (KBr): 3106m [ν(N–H)], 926s [ν(P–N)] and 642s, 632s cm^{-1} [ν(P=S)].

Ph$_2$P(Se)NHC$_6$H$_4$P(Se)Ph$_2$ 14. Ph$_2$PNHC$_6$H$_4$PPh$_2$ (0.421 g, 0.91 mmol) and grey selenium (0.144 g, 1.82 mmol) were heated to reflux in toluene (20 cm^3) for 30 minutes. The solvent was removed *in vacuo* and the crude product was taken up in dichloromethane (10 cm^3) and filtered through Celite to remove a trace of unreacted selenium. The filtrate was evaporated to dryness and the crude product was recrystallised from the minimum of warm toluene. The colourless crystalline solid was collected by suction filtration washed with ice cold toluene (5 cm^3) and dried overnight *in vacuo*. Yield: 0.463 g, 82%. Microanalysis: Found (Calcd. for $C_{30}H_{25}NP_2Se_2$) C 57.95 (58.17), H 4.16 (4.07), N 2.58 (2.26)%. ^{1}H NMR ($CDCl_3$): δ 8.19 (br d, 1 H, $^2J(^{31}P–^1H)$ 7 Hz, NH), 7.75 (m, 4 H, aromatics), 7.63–7.27 (m, 18 H, aromatics), 6.85 (m, 1 H, aromatic) and 6.67 (m, 1 H, aromatic). FAB$^+$ MS: *m*/*z* 621 [M]$^+$. Selected IR data (KBr): 3081m [ν(N–H)], 921s [ν(P–N)] and 561vs, 543s cm^{-1} [ν(P=Se)].

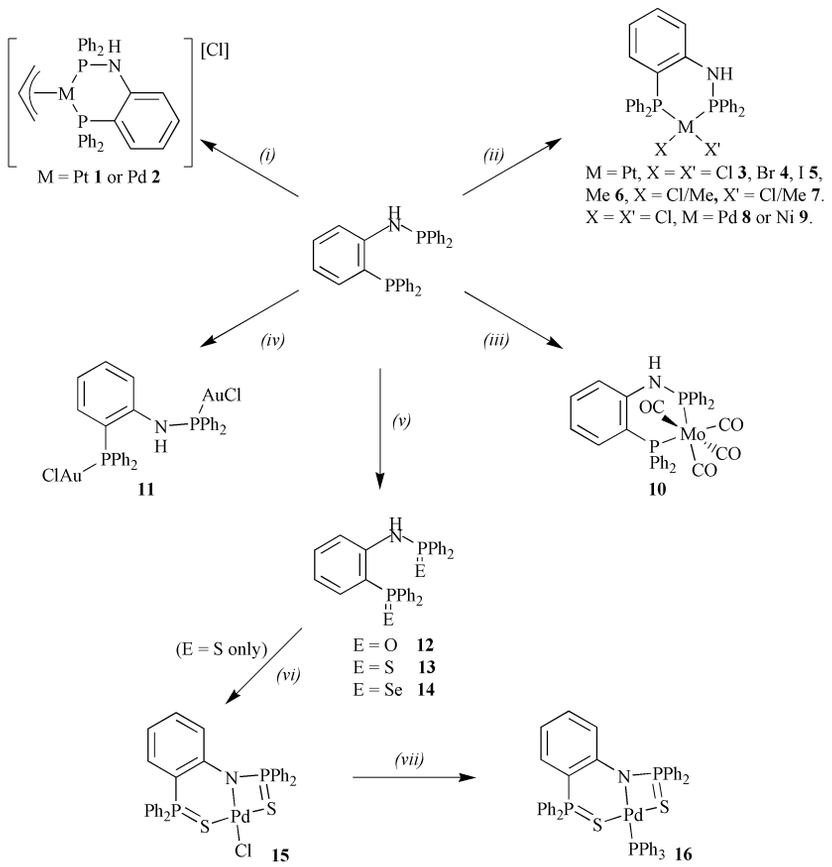
[PdCl(Ph$_2$P(S)NC$_6$H$_4$P(S)Ph$_2$-*S*,*N*,*S*)] 15. *Method (a)*. To an ethanol solution (10 cm^3) of Na_2[PdCl$_4$] (0.073 g, 0.248 mmol) was added Ph$_2$P(S)NHC$_6$H$_4$P(S)Ph$_2$ **13** (0.132 g, 0.251 mmol) as a solid in one go. The reaction mixture was gently heated until the Ph$_2$P(S)NHC$_6$H$_4$P(S)Ph$_2$ had completely dissolved, then stirred for 17 hours. The resulting red solid was collected by filtration, re-dissolved in dichloromethane (10 cm^3) and filtered through a small Celite pad. Slow addition of diethyl ether (50 cm^3) to the stirred filtrate gave **15** as bright red microcrystals, which were collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield 0.129 g, 78%. Microanalysis: Found (Calcd. for $C_{30}H_{24}ClNP_2PdS_2$) C 53.73 (54.14), H 3.53 (3.64), N 2.00 (2.11)%. ^{1}H NMR (CD_2Cl_2): δ 7.84–7.53 (m, 20 H, aromatics), 7.13–7.06 (m, 1 H, aromatic) and 6.79–6.60 (m, 3 H, aromatics). FAB$^+$ MS: *m*/*z*, 666/7 [M]$^+$ and 630/1 [M − Cl]$^+$. Selected IR data (KBr): 809m [ν(P–N)] 634s, 622m [ν(P=S)] and 305w cm^{-1} [ν(Pd–Cl)].

Method (b). Solid Ph$_2$P(S)NHC$_6$H$_4$P(S)Ph$_2$ **13** (0.141 g, 0.268 mmol) was added in one portion to a stirred dichloromethane (15 cm^3) solution of [PdCl$_2$(NCPh)] (0.102 g, 0.266 mmol). The resulting dark red solution was stirred for 17 hours and then filtered through a Celite plug to remove a small quantity of insoluble black material. The filtrate was concentrated *in vacuo* to *ca.* 5 cm^3 and the addition of diethyl ether (30 cm^3) caused the precipitation of a dark red microcrystalline solid. Yield 0.133 g, 75%. The spectroscopic properties of this material were identical to those described above.

[Pd(PPh$_3$)(Ph$_2$P(S)NC$_6$H$_4$P(S)Ph$_2$-*S*,*N*,*S*)][ClO$_4$] 16. To a dichloromethane solution (10 cm^3) of [PdCl(Ph$_2$P(S)NC$_6$H$_4$-P(S)Ph$_2$-*S*,*N*,*S*)] **15** (0.125 g, 0.188 mmol) was added solid Ag[ClO$_4$] (0.040 g, 0.193 mmol). The reaction mixture was stirred for 3 hours and the precipitated AgCl was removed by filtration through a small Celite pad. To the red filtrate was added solid PPh$_3$ (0.050 g, 0.191 mmol) which caused an immediate colour change from red to orange. The slow addition of diethyl ether to the orange solution gave **16** as bright orange microcrystals, which were collected by suction filtration, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. Yield 0.166 g, 89%. Microanalysis: Found (Calcd. for $C_{48}H_{39}ClNO_4$-P_3PdS_2) C 57.97 (58.12), H 3.75 (3.97), N 1.38 (1.41)%. ^{1}H NMR (CD_2Cl_2): δ 7.78–7.49 (m, 20 H, aromatics), 7.10–7.02 (m, 1 H, aromatic) and 6.83–6.67 (m, 3 H, aromatics). FAB$^+$ MS: *m*/*z*, 893 [M − (ClO$_4$)]$^+$. Selected IR data (KBr): 1094vs [ν(ClO$_4$)], 798m [ν(P–N)] and 639s, 622m cm^{-1} [ν(P=S)].

X-Ray crystallography

X-Ray diffraction studies on crystals of **3** grown from chloroform–dimethyl sulfoxide–diethyl ether were performed at 293 K using a Bruker SMART diffractometer with graphite-



Scheme 1 *(i)* $[Pt(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_4$, thf or $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$, C_6H_5Me; *(ii)* [PtXX′(cod)] (X = X′ = Me, Cl, Br, I or X = Cl and X′ = Me), $[PdCl_2(cod)]$, CH_2Cl_2, or $NiCl_2{\cdot}6H_2O$, EtOH; *(iii)* $[Mo(CO)_4(pip)_2]$, CH_2Cl_2; *(iv)* [AuCl(tht)], CH_2Cl_2; *(v)* H_2O_2(aq), thf or S_8/Se_8, C_6H_5Me; *(vi)* $[PdCl_2(NCPh)_2]$, CH_2Cl_2 or Na_2PdCl_4, EtOH, *(vii)* $Ag[ClO_4]$, CH_2Cl_2, PPh_3.

monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealised and fixed (C–H 0.95 Å), the NH protons were located by a ΔF map and allowed to refine anisotropically. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL.[35]

$C_{32.35}H_{30.25}Cl_{4.25}NO_{0.75}P_2PtS_{0.75}$, $M = 875.56$, monoclinic, space group $P2_1/n$, $a = 12.2267(2)$ Å, $b = 21.7198(3)$ Å, $c = 14.1548(2)$ Å, $\beta = 98.8060(10)^o$, $U = 3714.66(10)$ Å^3, $Z = 4$, $D_c = 1.566$ Mg m^{-3}, $\mu = 4.236$ mm^{-1}, $F(000) = 1716$, crystal size = 0.2 × 0.3 × 0.4 mm. Of 16141 measured data, 5310 were unique (R_{int} 0.0217) to give $R1[I > 2\sigma(I)] = 0.0330$ and $wR2 = 0.0893$.

CCDC reference number 159100.

See http://www.rsc.org/suppdata/dt/b1/b101772l/ for crystallographic data in CIF or other electronic format.

Results and discussion

Chelate complexes of $Ph_2PNHC_6H_4PPh_2$

$Ph_2PNHC_6H_4PPh_2$ reacts with $[Pt(\mu\text{-}Cl)(\mu\text{-}\eta^2 : \eta^1\text{-}C_3H_5)]_4$ in thf and $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ in toluene at room temperature to give the cationic chelate complexes $[M(\eta^3\text{-}C_3H_5)(Ph_2PNHC_6H_4PPh_2)][Cl]$ (where M = Pt **1** or Pd **2**) in excellent yields (91% and 87% respectively) (Scheme 1). The attempted synthesis of **1** in chloroform resulted in the isolation of a mixture of the desired product and the dichloride complex $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]$ **3** ($^{31}P\text{-}\{^1H\}$ NMR evidence, Table 1) which we were unable to separate. The decomposition of the platinum allyl complex **1** is presumably a result of reaction with free HCl in the chloroform resulting in the loss of propene and formation of the observed dichloride species.[36] The $^{31}P\text{-}\{^1H\}$ NMR spectra for complexes **1** and **2** are of the AX type and show two sharp doublets and small $^2J(^{31}P\text{–}^{31}P)$ couplings of 35 (**1**) and 71 Hz (**2**), with corresponding platinum satellites for compound **1**. The $NHPPh_2$ (P_X) high frequency resonance is observed at δ (P) 62.9 [$^1J(^{195}Pt\text{–}^{31}P_X)$ 4058 Hz], for **1** and δ (P) 74.3 for **2** while the low frequency signal occurs at δ (P) 4.5 [$^1J(^{195}Pt\text{–}^{31}P_A)$ 3529 Hz], and δ (P) 14.7 for **1** and **2** respectively. The ^1H NMR spectra are consistent with the proposed structures and include amine δ 7.99 (**1**), δ 8.11 (**2**) and allyl δ 5.26 (m) and broad singlets at 3.99 and 3.01 for **1** and δ 5.63 [pent, $^2J(^1H\text{–}^1H)$ 10.6 Hz] and a very broad singlet at δ 3.62 for **2**. Further supporting data includes IR (KBr) bands at 2800 (**1**), 2786 (**2**) and a band at 919 (**1**), 914 cm^{-1} (**2**) assigned as ν(NH) and ν(PN) respectively. The reduction in the ν(NH) band energies in the IR spectra of complexes **1** and **2** compared to for example complex **3** [3191 cm^{-1}] is characteristic of a strong hydrogen-bonding interaction between the amine proton of the ligand and the chloride counter ion, causing a significant reduction in the NH stretching frequency. Treatment of $[PtCl_2(cod)]$ with $Ph_2PNHC_6H_4PPh_2$ in dichloromethane gives a cream coloured solid in excellent yield (95%). The product was characterised as the expected chelate species. The $^{31}P\text{-}\{^1H\}$ NMR spectrum (in $CDCl_3$/dmso) of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]$ **3** is an AX type spectrum and contains two sharp doublets at δ (P_A) −0.4 [$^1J(^{195}Pt\text{–}^{31}P_A)$ 3508 Hz] and δ (P_X) 53.8 [$^1J(^{195}Pt\text{–}^{31}P_X)$ 3932 Hz], assigned to the PPh_3 and the $NHPPh_2$ centres respectively, with a small $^2J(^{31}P_A\text{–}^{31}P_X)$ coupling of 21 Hz. The large $^1J(^{195}Pt\text{–}^{31}P_A)$ and $^1J(^{195}Pt\text{–}^{31}P_X)$ coupling constants are in agreement with values previously found for platinum(II) complexes where phosphorus is *trans* to chloride.[37] The ^1H NMR spectrum (in $CDCl_3$/d_6-dmso) shows a multiplet at δ 8.30, which we have assigned to the amine proton – as an exchange reaction with D_2O causes the resonance to disappear. Further evidence in support of the *cis* chelate structure comes from the IR spectrum which shows two distinct ν(Pt–Cl) stretches at 313 and 290 cm^{-1} which are also consistent with a *cis*-$PtCl_2$ geometry. The IR spectrum also

Table 1 ^{31}P-{^{1}H} NMR [a] data for complexes of $Ph_2PNHC_6H_4PPh_2$ (where P_A = triarylphosphine {PPh_3} and P_X = diarylaminophosphine {$NHPPh_2$})

	Chemical shifts (ppm)		Coupling constants/Hz		
Complex	$\delta(P_A)$	$\delta(P_X)$	$^{1}J(Pt–P_A)$	$^{1}J(Pt–P_X)$	$^{2}J(P_A–P_X)$
1	4.5	62.9	3529	4058	35
2 [b]	14.7	74.3	—	—	71
3 [c]	−0.4	53.8	3508	3932	21
4	—	—	—	—	—
5	—	—	—	—	—
6 [c]	10.7	70.6	1808	2063	26
7(A) [d]	11.9	63.2	1696	4615	23
7(B) [d]	11.1	71.5	4126	1965	28
8 [c]	18.1	77.8	—	—	5
9	—	—	—	—	—
10 [c]	33.6	91.7	—	—	35
11	20.1	60.9	—	—	—
12 [b]	36.5	18.4	—	—	n.o. [e]
13 [b]	39.9	57.3	—	—	n.o. [e]
14 [b,f]	27.2 (691)	47.0 (787)	—	—	n.o. [e]
15	42.6	79.4	—	—	3
16 [g]	38.5	76.1	—	—	3

[a] Spectra (101.3 MHz) measured in CD_2Cl_2 unless otherwise stated. [b] Spectra (101.3 MHz) measured in $CDCl_3$. [c] Spectra (36.2 MHz) measured in $CDCl_3$/dmso. [d] Spectra (101.3 MHz) measured in $CDCl_3$/dmso. [e] n.o. = not observed. [f] Values in parentheses denote $^{1}J(^{77}Se–^{31}P)$/Hz. [g] Other ^{31}P-{^{1}H} spectral parameters for **16** $\delta(PPh_3)$ 34.3 $^{3}J(PPh_3–P_A)$ 6 Hz, $^{3}J(PPh_3–P_X)$ 18 Hz.

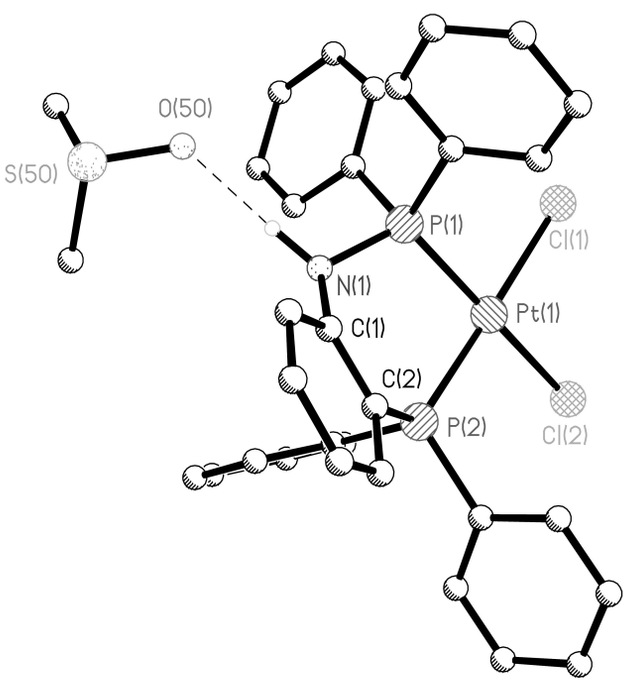


Fig. 1 Crystal structure of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]\cdot0.75dmso\cdot0.75CHCl_3$ **3**.

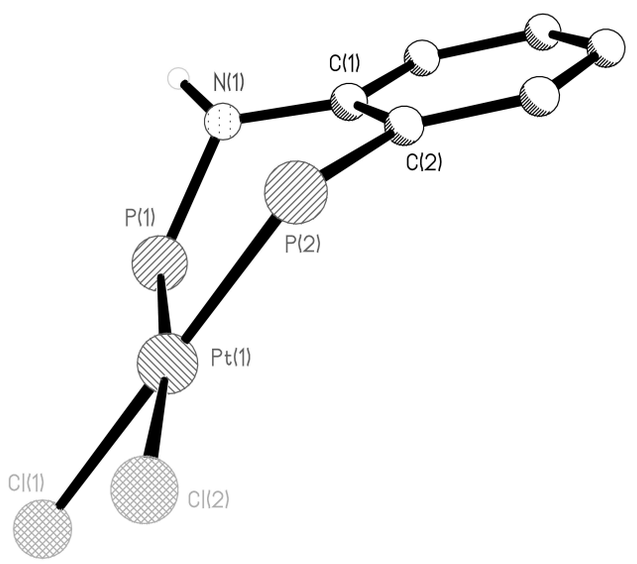


Fig. 2 Core geometry in $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]\cdot0.75dmso\cdot0.75CHCl_3$ **3**.

Table 2 Selected bond lengths (Å) and angles (°) for $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]\cdot0.75dmso\cdot0.75CHCl_3$

P(1)–Pt(1)	2.2126(13)	P(2)–Pt(1)	2.2319(13)
Pt(1)–Cl(1)	2.3664(14)	Pt(1)–Cl(2)	2.358(2)
P(1)–N(1)	1.689(4)	N(1)–C(1)	1.407(7)
C(1)–C(2)	1.404(8)	P(2)–C(2)	1.821(5)
P(1)–Pt(1)–P(2)	91.03(5)	Cl(1)–Pt(1)–Cl(2)	89.45(6)
P(1)–Pt(1)–Cl(2)	172.80(6)	P(2)–Pt(1)–Cl(1)	178.36(5)
P(1)–Pt(1)–Cl(1)	87.38(5)	P(2)–Pt(1)–Cl(2)	92.18(6)
Pt(1)–P(1)–N(1)	113.90(2)	Pt(1)–P(2)–C(2)	114.10(2)
P(1)–N(1)–C(1)	120.70(4)	P(2)–C(2)–C(1)	119.00(4)
N(1)–C(1)–C(2)	120.50(5)		

shows a broad band at 3191 cm^{-1} and a band at 919 cm^{-1} assigned as ν(NH) and ν(PN) respectively. Crystals of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]\cdot0.75dmso\cdot0.75CHCl_3$ suitable for X-ray crystallography were grown in approximately 2 hours by layering a $CDCl_3$/dmso solution of $[PtCl_2Ph_2PNHC_6H_4PPh_2]$ **3** with diethyl ether. The crystal structure of the complex (Fig. 1) along with its core geometry (Fig. 2) and selected bond lengths and angles (Table 2) confirm the proposed *cis* chelate geometry. The crystal structure shows that the $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]$ **3** molecule is approximately square planar at platinum [maximum deviations from Pt(1)–P(1)–P(2)–Cl(1)–Cl(2) mean plane 0.06 Å above for Pt(1)]. The bite angle of the chelating phosphine is close to the ideal 90° [P(1)–Pt(1)–P(2) 91.03(5)]. The Pt(1)–P(1)–N(1)–C(1)–C(2)–P(2) six-membered ring can be considered as two planes of four atoms with two atoms, N(1) and P(2) in common. The N(1)–C(1)–C(2)–P(2) atoms are planar whilst the Pt(1)–P(1)–P(2)–N(1) plane shows a mean deviation of only 0.04 Å. The 'hinge angle' between the N(1)–C(1)–C(2)–P(2) and Pt(1)–P(1)–P(2)–N(1) planes is approximately 46°. The crystal structure also reveals that each molecule of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]$ **3** crystallises with 0.75 molecules of $CDCl_3$ and 0.75 molecules of dimethyl sulfoxide, the oxygen atom of which is hydrogen-bonded to the amine proton of **3** [H(1n)···O(50) 1.93 Å, O(50)···N(1) 2.86 Å, N(1)–

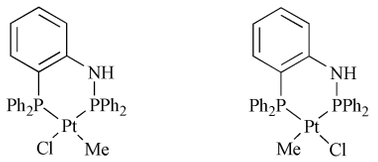


Fig. 3 Products obtained by reaction of $Ph_2PNHC_6H_4PPh_2$ with [PtClMe(cod)].

H(1n)···O(50) 159°]. The dibromo- **4** and diiodo- **5** derivatives of $[PtCl_2(Ph_2PNHC_6H_4PPh_2)]$ can be prepared by reaction of $Ph_2PNHC_6H_4PPh_2$ with $[PtBr_2(cod)]$ and $[PtI_2(cod)]$ or by metathesis of the dichloride with an excess of the appropriate halide ion in refluxing acetone. Microanalytical data obtained for the dibromo and diiodo complexes are in good agreement with calculated values. Also in agreement were the positive-ion FAB mass spectra which displayed the expected parent-ion peaks and fragmentation patterns. {For **4** *m*/*z* 839 $[M + Na]^+$, 816 $[M]^+$, 736 $[M - Br]^+$ and 656/7 $[M - 2Br]^{2+}$}, {for **5** *m*/*z* 933/4 $[M + Na]^+$, 910 $[M]^+$, 783/4 $[M - I]^+$ and 656/7 $[M - 2I]^{2+}$}, with appropriate isotope distributions. Satisfactory ^{31}P-$\{^1H\}$ NMR data could not be collected due to the insolubility, even in neat d_6-dmso, of the diiodo complex and the rapid halide exchange reaction of the dibromide which takes place in $CDCl_3$/dmso, resulting in multiplets around the mean δ (P) values observed for the dichloride **3**. A $CDCl_3$/dmso solution of $[PtBr_2(Ph_2PNHC_6H_4PPh_2)]$ reverts back to the dichloride if left to stand for approximately one week. Reaction of $Ph_2PNHC_6H_4PPh_2$ with $[PtMe_2(cod)]$ in dichloromethane produces an off-white powder, characterised as the dimethyl complex $[PtMe_2(Ph_2PNHC_6H_4PPh_2)]$ **6**, as is evidenced by the ^{31}P-$\{^1H\}$ NMR spectrum (in $CDCl_3$/dmso). The much smaller $^1J(^{195}Pt–^{31}P_A)$ couplings associated with doublet resonances at δ (P_A) 10.7 [$^1J(^{195}Pt–^{31}P)$ 1808 Hz] (PPh_3) and δ (P_X) 70.6 [$^1J(^{195}Pt–^{31}P_X)$ 2063 Hz] ($NHPPh_3$) are consistent with those found in complexes where phosphorus is *trans* to a methyl group.[38–40] The two inequivalent methyl group proton resonances in the ^1H NMR spectrum of complex **6** (in $CDCl_3/d_6$-dmso) appear as overlapping multiplets at approximately δ 0.30 flanked by platinum satellites [$^2J(^{195}Pt–^1H)$ 69 Hz]. Due to the complexity of the splitting pattern the *cis* and *trans* $^3J(^{31}P–^1H)$ coupling constants could not be confidently assigned. The NH signal appears as a multiplet at δ 8.17, confirmed by an exchange reaction with D_2O. A dilute dichloromethane solution of $Ph_2PNHC_6H_4PPh_2$ added drop-wise over 10 minutes, (extension of the addition time to 2 hours gave the same products in the same ratio), to a dilute solution of [PtClMe(cod)] in the same solvent gives two products (Fig. 3). Structural assignment is based on comparison of the ^{31}P-$\{^1H\}$ NMR spectrum (in $CDCl_3$/dmso) of the isolated material, shown in (Fig. 4), to those of the dichloro **3** and the dimethyl **6** analogues. The ^{31}P-$\{^1H\}$ NMR spectrum ($CDCl_3$/dmso) (Fig. 4) showed that isomer **B** constituted approximately 80–85% of the isolated material (89% yield overall). The same NMR sample stored at room temperature was run two and four weeks after the initial ^{31}P-$\{^1H\}$ NMR experiment. Comparison of the spectra showed that the isomer ratio had not changed. A sample of the same material heated to approximately 60 °C in toluene failed to alter the ratio of products, but, instead, gave rise to several new ones. Isolation and characterisation of these products was not attempted.

$[PdCl_2(Ph_2PNHC_6H_4PPh_2)]$ **8** was prepared and isolated in the same manner as its platinum analogue **3**. The expected AX type ^{31}P-$\{^1H\}$ NMR spectrum was obtained, δ (P_A) 18.1 for the Ph_2P group and δ (P_X) 77.8 for the $NHPPh_2$ moiety, where both of the phosphorus centres have been shifted significantly down field ($\Delta\delta$ = 37.6 and 48.2 ppm respectively), indicating that both phosphorus atoms have coordinated. However, the $^2J(^{31}P_A–^{31}P_X)$ coupling constant of 5 Hz is very small when compared to those of the platinum complexes (**3**, **6** and **7** {**A** and **B**}) (Table 1). The coupling is only slightly larger than the $^4J(^{31}P_A–^{31}P_X)$ coupling of 4 Hz observed for the free ligand and smaller than those found in complexes where the ligand is acting as a monodentate phosphorus donor which have an average $^4J(^{31}P_A–^{31}P_X)$ coupling of 9 Hz.[25] The positive-ion FAB mass spectrum failed to give the anticipated parent-ion peak but showed the expected $[M - Cl]^+$ and $[M - 2Cl]^{2+}$ fragments. The IR spectrum of the complex shows two distinct ν(Pd–Cl) stretches at 313 and 290 cm^{-1} which are consistent with a *cis*-$PdCl_2$ geometry. The IR spectrum also shows a band at 3125 cm^{-1} and a band at 925 cm^{-1} assigned as ν(NH) and ν(PN) respectively. The addition of solid $Ph_2PNHC_6H_4PPh_2$ to a hot ethanol solution of $NiCl_2{\cdot}6H_2O$ after cooling gives $[NiCl_2(Ph_2PNHC_6H_4PPh_2)]$ **9** as a bright-red crystalline solid. No ^{31}P-$\{^1H\}$ or ^1H NMR spectra for this complex were observed, indicating that in solution $[NiCl_2(Ph_2PNHC_6H_4PPh_2)]$ **9** is paramagnetic. Since square planar Ni(II) complexes are expected to be diamagnetic, this observation indicates that **9** exhibits distortions from idealised square-planar geometry. As measurement of NMR parameters was not possible, complex **9** was characterised by IR spectroscopy, mass spectrometry and microanalysis only. The IR spectrum showed bands at 3201, 917 and 330 cm^{-1} assigned as ν(NH), ν(PN) and ν(NiCl) respectively. The positive-ion FAB mass spectrum gave the correct parent-ion peak, *m*/*z* 591 $[M]^+$ and the appropriate $[M - Cl]^+$ and $[M - 2Cl]^{2+}$ fragments and microanalytical data were in good agreement with the proposed $[NiCl_2(Ph_2PNHC_6H_4PPh_2)]$ **9** formulation (Experimental section).

$Ph_2PNHC_6H_4PPh_2$ reacts with $[Mo(CO)_4(pip)_2]$ in refluxing dichloromethane by displacement of the piperidine molecules to give the anticipated six-membered ring molybdenum complex as shown in Scheme 1. The ^{31}P-$\{^1H\}$ NMR spectrum of $[Mo(CO)_4(Ph_2PNHC_6H_4PPh_2)]$ **10** showed two sharp doublets at δ (P_A) 33.6 and δ (P_X) 91.7 with a $^2J(^{31}P_A–^{31}P_X)$ coupling of 35 Hz which is consistent with that of other molybdenum unsymmerical chelating bis-phosphine tetracarbonyl complexes.[41] Microanalytical data were in good agreement with calculated values (Experimental section) as was the positive-ion FAB mass spectrum which gave the anticipated parent-ion peak at *m*/*z* 669/670 and showed successive loss of one, two, three and four CO groups. IR data (KBr pellet) gave further support to the proposed structure showing four distinct ν(CO) absorptions in the range 2017–1884 cm^{-1} which are characteristic of molybdenum *cis*-tetracarbonyl derivatives.[42,43]

Bidentate bridging coordination chemistry of $Ph_2PNHC_6H_4PPh_2$

As well as the chelating mode of coordination, resulting in the formation of six-membered metallacycles $Ph_2PNHC_6H_4$-PPh_2 can act as a bridging ligand between two metal centres. The reaction of two equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) with $Ph_2PNHC_6H_4PPh_2$ in dichloromethane gave $[(AuCl)_2(Ph_2PNHC_6H_4PPh_2)]$ **11** as a colourless solid in excellent yield (91%). The complex displays two single resonances in its ^{31}P-$\{^1H\}$ NMR spectrum [δ (P_X) 60.9 and δ (P_A) 20.1 for the $NHPPh_2$ and PPh_3 coordinating centres respectively] and the ^1H NMR spectrum showed the amine proton as a broad triplet at δ 5.61 [$^2J(^{31}P–^1H)$ 3 Hz]. Microanalytical data were in good agreement with calculated values (Experimental section) and the positive-ion FAB mass spectrum gave the correct, though very weak, parent-ion peak at *m*/*z* 926 along with a strong peak corresponding to $[M - Cl]^+$. Assignment of the IR spectrum is difficult, but we can identify ν(NH) at 3238 cm^{-1} and ν(PN) at 922 cm^{-1}.

Synthesis of $Ph_2P(E)NHC_6H_4P(E)Ph_2$

The generation of $Ph_2P(E)NHC_6H_4P(E)Ph_2$ (where E = O **12**, S **13** and Se **14**) from $Ph_2PNHC_6H_4PPh_2$ is straightforward. Reaction of $Ph_2PNHC_6H_4PPh_2$ with a small excess of H_2O_2

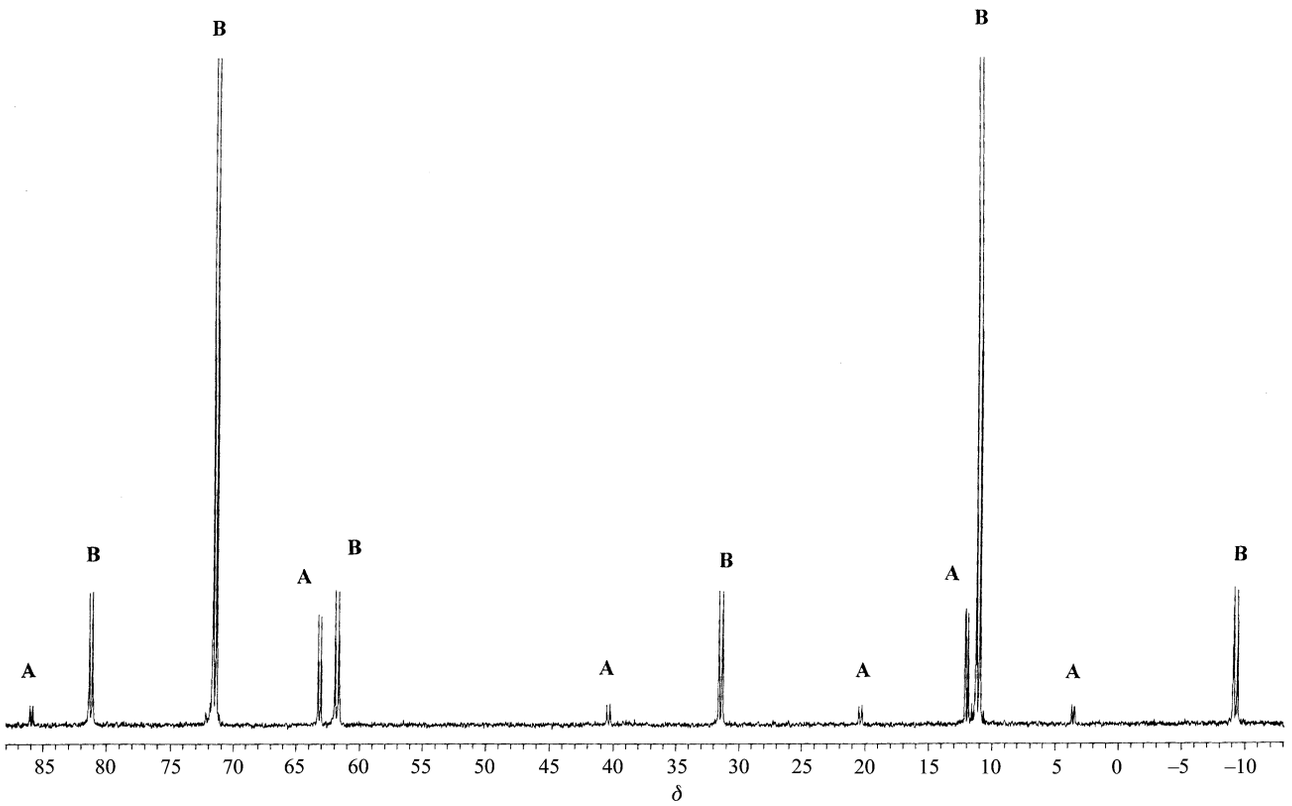


Fig. 4 ^{31}P-{^{1}H} NMR spectum (101.3 MHz) of isolated material from reaction of $Ph_2PNHC_6H_4PPh_2$ with [PtClMe(cod)]. Peaks denoted with the letters **A** and **B** respectively.

Table 3 Selected IR [KBr pellet] (cm^{-1}) spectroscopic data for $Ph_2PNHC_6H_4PPh_2$ and compounds **12**–**14**

Compound	*ν*(NH)	*ν*(PN)	*ν*(P=E)
$Ph_2PNHC_6H_4PPh_2$	3300s	891s	—
12	3149br	952s,	1188s, 1173s*
13	3106m	926s,	642s, 632s*
14	3081m	921s,	561vs, 543s*

Bands highlighted * are assigned to E=$PPh_2(C_6H_4)$.

(aq) in thf, or stoichiometric quantities of S_8 in toluene, or Se_8 in refluxing toluene, lead to good yields (79%, 86% and 82% respectively) of the dioxidised species (Scheme 1). Compounds **12**, **13** and **14** were all isolated as colourless solids, soluble in thf, acetonitrile, dichloromethane and chloroform, less so in toluene, methanol and ethanol and slightly in petrol. The $^{4}J(^{31}P_A–^{31}P_X)$ coupling constants were not observed in the ^{31}P-{^{1}H} NMR spectra (in $CDCl_3$) for any of the dioxidised ligand species, displaying instead two single phosphorus resonances (Table 1). The chalcogens of $Ph_2PC_6H_4NH_2$ 2-(diphenylphosphino)aniline were prepared and characterised by ^{31}P-{^{1}H} NMR ($CDCl_3$). The following ^{31}P-{^{1}H} NMR data were generated for the oxide [δ (P) 35.1], sulfide [δ (P) 39.7] and selenide [δ (P) 26.9, $^{1}J(^{31}P–^{77}Se)$ 695 Hz], allowing unambiguous assignment of the two phosphorus environments of the dichalcogen species. The ^{1}H NMR spectra (in $CDCl_3$) of compounds **12** [δ 9.43 $J(P_X–H)$ 12 Hz], **13** [δ 8.35 $J(P_X–H)$ 8 Hz] and **14** [δ 8.19 $J(P_X–H)$ 7 Hz] all display the anticipated doublets for the amine protons. Assignment of the IR spectra of **12**–**14** is difficult but those bands we can identify along with those of $Ph_2PNHC_6H_4PPh_2$ for comparative purposes are collected in Table 3. Oxidation of $Ph_2PNHC_6H_4PPh_2$ causes significant increases in *ν*(PN) band energies, which accompanies a large decrease in *ν*(NH) energy, which may be an indication of intermolecular hydrogen bonding. The *ν*(P=E) bands highlighted with an asterisk* have been assigned to the $PPh_2(C_6H_4)$ phosphorus chalcogen bonds. Assignment is based upon comparison of the IR spectra of the oxide *ν*(P=O) 1173 cm^{-1}, sulfide *ν*(P=S) 632 cm^{-1} and selenide *ν*(P=Se) 545 cm^{-1} of 2-(diphenylphosphino)aniline to the IR spectra of the dioxidised bis-phosphines $Ph_2P(E)NHC_6H_4P(E)Ph_2$ **12**–**14**.

Coordination chemistry of $Ph_2P(S)NHC_6H_4P(S)Ph_2$

$Ph_2P(S)NHC_6H_4P(S)Ph_2$ **13** reacts with $[PdCl_2(PhCN)_2]$ in dichloromethane and $Na_2[PdCl_4]$ in ethanol by elimination of HCl to give the same N-metallated species, [PdCl($Ph_2P(S)$-$NC_6H_4P(S)Ph_2$-*S*,*N*,*S*)] **15**, which was isolated as a bright-red crystalline solid in 75 and 78% respectively (Scheme 1). The material is soluble in dichloromethane and chloroform but insoluble in methanol, ethanol, diethyl ether and petroleum ether. The ^{31}P-{^{1}H} NMR spectrum (in CD_2Cl_2) is, like that of the free ligand **13**, an AX type but, unlike **13**, displays a small $^{4}J(^{31}P_A–^{31}P_X)$ coupling of 3 Hz. The low frequency resonance at δ (P_A) 42.6 assigned to the Ph_3P=S phosphorus centre is comparable to that of the free ligand value δ (P) 39.9 but the $NHPh_2P$=S resonance at δ (P) 79.4 has been significantly shifted to higher frequency when compared to the $NHPh_2P$=S resonance of **13** δ (P) 57.3. This shift to higher frequency occurs as a result of ring strain and is observed in other complexes containing Pd–S–P–N rings. A similar coordination mode to **13**, (*i.e.* four- and six-membered ring formation), is observed when the symmetrically substituted urea ligand *N*,*N*′-bis(diphenylphosphino)urea disulfide [{$Ph_2P(S)NH$}$_2$CO] is reacted with $[PdCl_2(PhCN)_2]$ in dichloromethane.[44] The ^{31}P-{^{1}H} NMR value (in $CDCl_3$) of the free ligand is δ (P) 52.2,[45] the chemical shift of the phosphorus atoms within the six-membered Pd–S–P–N–C–N metallacycle is δ (P_A) 56.1 whilst that of the phosphorus centre contained in the four-membered ring is δ (P) 91.6, although no $^{4}J(^{31}P_A–^{31}P_X)$ coupling was observed. Further examples of four-membered metallacycles containing anionic P–S–N moieties (where M = Al,[46] Ni,[47–50] Pd,[51] Pt[52] and Ti[53]) rings have been reported along with [Ph_2P-

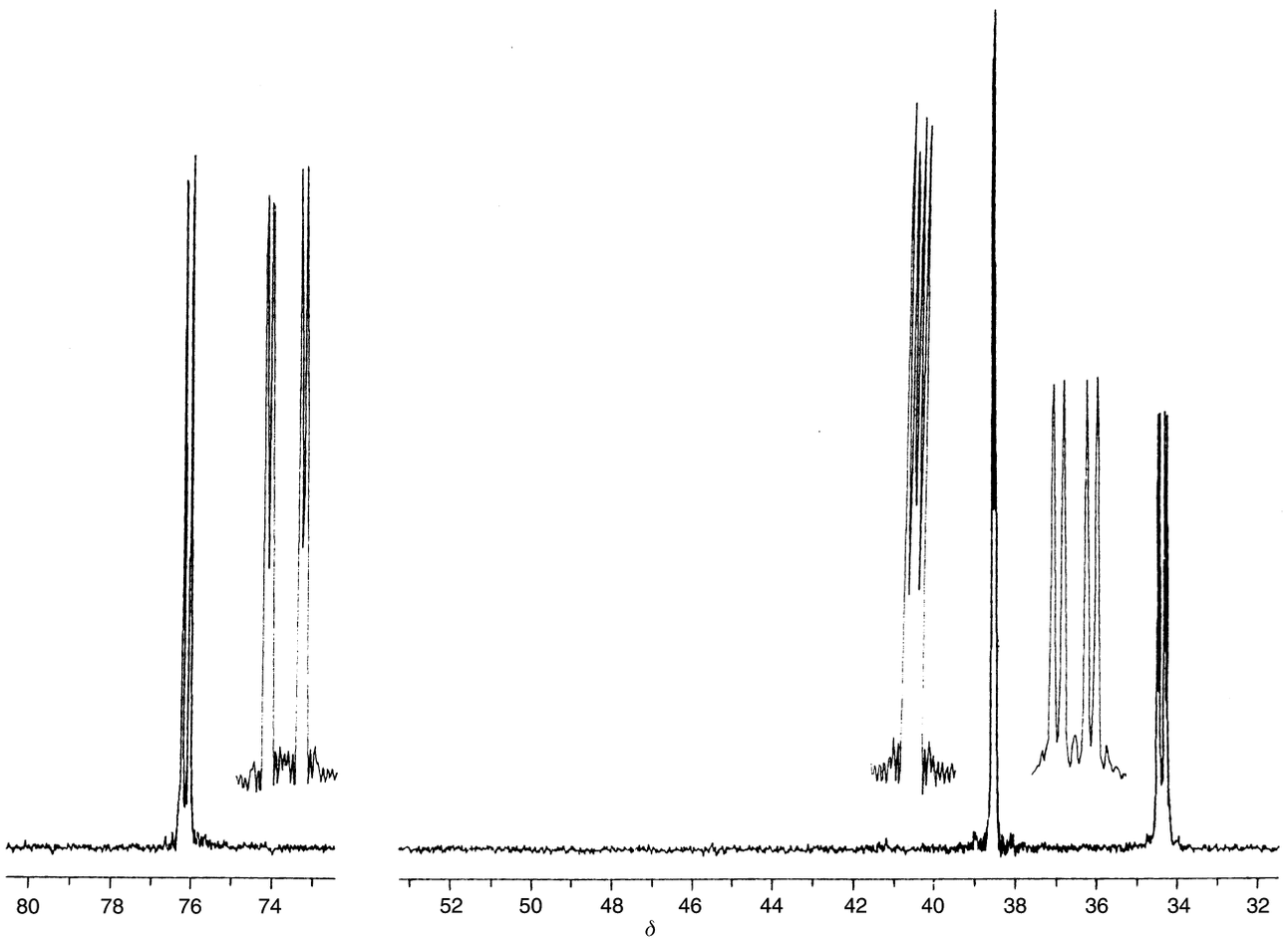


Fig. 5 ^{31}P-{^{1}H} NMR spectrum (101.3 MHz) of $[Pd(PPh_3)(Ph_2P(S)NC_6H_4P(S)Ph_2$-*S*,*N*,*S*)][$ClO_4$] **16**.

(S)NH_2]Mn(CO)$_3$Br[54] which contains the neutral bidentate PN donor $Ph_2P(S)NH_2$. Further evidence for the proposed anionic tridentate S,N,S coordination mode is given by the IR and ^1H NMR spectra which indicate the absence of the amine proton. Positive-ion FAB mass spectral and microanalytical data were in excellent agreement with the proposed structure. We also found that treatment of [PdCl($Ph_2P(S)NC_6H_4P(S)Ph_2$-*S*,*N*,*S*)] **15** in dichloromethane with Ag[ClO_4], followed by PPh_3 gave the cationic species [Pd(PPh_3)($Ph_2P(S)NC_6H_4P(S)Ph_2$-*S*,*N*,*S*)][ClO_4] **16** as a bright-orange crystalline solid in 89% yield (Scheme 1). The ^{31}P-{^{1}H} spectrum (in CD_2Cl_2) of **16** (AMX spin system) (Fig. 5) clearly reveals three unique phosphorus environments. The lowest frequency resonance at δ (P_A) 34.4 is assigned to the coordinated PPh_3 group and displays two distinct couplings [$^3J(^{31}P_A$–$^{31}P_M)$ 6 and $^3J(^{31}P_A$–$^{31}P_X)$ 18 Hz]. The resonance at δ (P_M) 38.5 [$^3J(^{31}P_M$–$^{31}P_A)$ 6 and $^4J(^{31}P_M$–$^{31}P_X)$ 3 Hz] is assigned to the Ph_3P=S phosphorus atom and the high-frequency resonance at δ (P_X) 76.1 [$^3J(^{31}P_X$–$^{31}P_M)$ 3 and $^4J(^{31}P_X$–$^{31}P_A)$ 18 Hz] to the $NHPh_2P$=S group. Again, there is good supporting evidence for anionic tridentate S,N,S coordination behaviour from the IR, ^1H NMR and positive-ion FAB mass spectra in addition to good microanalytical data.

Conclusion

We have shown that a range of transition-metal complexes with $Ph_2PNHC_6H_4PPh_2$ are readily accessible with either chelating or bridging ligand coordination modes. Furthermore we have demonstrated that oxidation of $Ph_2PNHC_6H_4PPh_2$ with H_2O_2, S_8 or elemental selenium give rise to other potential ligand systems. Although preliminary studies into the coordination chemistry of $Ph_2P(S)NHC_6H_4P(S)Ph_2$ **13** have shown that it can act as an anionic tridentate S,N,S donor by N-metallation as in [PdCl($Ph_2P(S)NC_6H_4P(S)Ph_2$-*S*,*N*,*S*)] **15**, the related compounds $Ph_2P(O)NHC_6H_4P(O)Ph_2$ **12** and $Ph_2P(Se)NHC_6H_4P(Se)Ph_2$ **14** remain, as yet, unexplored. Further investigations into the coordination chemistry of $Ph_2PNHC_6H_4PPh_2$ and $Ph_2P(E)NHC_6H_4P(E)Ph_2$ (E = O, S or Se) are currently underway.

References

1 M. Davis and F. G. Mann, *J. Chem. Soc.*, 1964, 3786.
2 H. P. Abicht and K. Issleib, *Z. Chem.*, 1984, **11**, 414.
3 P. Aslanidis and J. Grobe, *J. Organomet. Chem.*, 1983, **249**, 103.
4 J. Grobe, S. Göbelbecker, B. Krebs and M. Läge, *Z. Anorg. Allg. Chem.*, 1992, **611**, 11.
5 R. Schmutzler, D. Schomburg, R. Bartsch and O. Stelzer, *Z. Naturforsch., Teil B*, 1984, **39**, 1177.
6 M. J. Baker and P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, 1993, 314.
7 J. Heinicke, R. Kadyrov, M. Koesling and U. Jux, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1996, **109**, 501.
8 J. Heinicke, R. Kadryov, M. K. Kindermann, M. Koesling and P. G. Jones, *Chem. Ber.*, 1996, **127**, 1547.
9 J. Heinicke, R. Kadryov, M. K. Kindermann, M. Kloss, A. Fischer and P. G. Jones, *Chem. Ber.*, 1996, **129**, 1061.
10 S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.
11 R. H. Crabtree and R. J. Uriarte, *Inorg. Chem.*, 1983, **22**, 4152.
12 J. Heinicke, E. Nietzschmann and A. Tzschach, *J. Organomet. Chem.*, 1983, **243**, 1.
13 J. Heinicke and A. Tzschach, *J. Prakt. Chem.*, 1983, **325**, 232.
14 K. Rauzy, M. R. Mazières, P. Page, M. Sanchez and J. Bellen, *Tetrahedron Lett.*, 1990, **31**, 4463.
15 M. R. Mazières, K. Rauzy, J. Bellen, M. Sanchez, G. Pfister-Guillouzo and A. Senio, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **76**, 45.
16 S. E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.

17 D. A. Knight and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1990, 3051.
18 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1993, 3653.
19 S. Al-Jibori, M. Hall, A. T. Hutton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 863.
20 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *J. Chem. Soc., Chem. Commun.*, 1987, 488.
21 P. Braunstein, D. Matt, D. Nobel and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1987, 1530.
22 F. Balegroune, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1988, **27**, 3320.
23 S. B. Sembiring, S. B. Colbran, D. C. Craig and M. L. Scudder, *J. Chem. Soc., Dalton Trans.*, 1995, 3731.
24 S. M. Aucott, A. M. Z. Slawin and J. D. Woollins, *J. Organomet. Chem.*, 1999, **582**, 83.
25 M. K. Copper, J. M. Downes and P. A. Duckworth, *Inorg. Synth.*, 1989, **25**, 129.
26 J. Lukas, *Inorg. Synth.*, 1974, **15**, 75.
27 A. L. Balch and L. S. Benner, *Inorg. Synth.*, 1990, **28**, 340.
28 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.
29 E. Costa, P. G. Pringle and M. Ravetz, *Inorg. Synth.*, 1997, **31**, 284.
30 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 47.
31 J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
32 G. K. Anderson and M. Lin, *Inorg. Synth.*, 1990, **28**, 60.
33 J. D. Woollins (Editor), *Inorganic experiments*, VCH, Weinheim, 1994.
34 R. Uson, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
35 SHELXTL, Structure Solution and Determination Package, Bruker AXS, Madison, WI, 1999.
36 H. C. Volger and K. Vrieze, *J. Organomet. Chem.*, 1968, **13**, 495.
37 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 4567.
38 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Chem. Commun.*, 1996, 2095.
39 A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1997, 3397.
40 S. Chatterjee, D. C. R. Hockless, G. Salam and P. Waring, *J. Chem. Soc., Dalton Trans.*, 1997, 3889.
41 S. D. Perera, B. L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 1469.
42 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432.
43 M. S. Balakrishna, T. K. Prakasha, S. S. Krishnamurthy, U. Siriwardane and N. S. Hosmane, *J. Organomet. Chem.*, 1990, **390**, 202.
44 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2000, 1545.
45 P. Bhattacharyya, A. M. Z. Slawin, M. B. Smith, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 3647.
46 K. Urata, T. Yogo, K. Itoh and Y. Ishii, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 2709.
47 W. Peters, M. Fuchs, H. Sicius and W. Kuchen, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 231.
48 M. Fuchs, W. Kuchen and W. Peters, *Chem. Ber.*, 1986, **119**, 1569.
49 A. Deeg, W. Kuchen, D. Langsch, D. Mootz, W. Peters and H. Wunderlich, *Z. Anorg. Allg. Chem.*, 1991, **606**, 119.
50 T. Froemmel, W. Peters, H. Wunderlich and W. Kuchen, *Angew. Chem.*, 1992, **104**, 632.
51 P. Z. Zak, M. Fofana, J. Kamenícek and T. Głowiak, *Acta. Crystallogr., Sect. C*, 1989, **45**, 1689.
52 W. Henderson, R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1992, 59.
53 M. Fuchs, W. Kuchen and W. Peters, *Z. Anorg. Allg. Chem.*, 1987, **545**, 75.
54 E. Lindner and H. M. Ebinger, *J. Organomet. Chem.*, 1973, **47**, 133.