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Preparation and coordination chemistry of $Ph_2P(CH_2)_nNHP^iPr_2$ ($n = 2, 3$)

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Abstract

Unsymmetrical diphosphine ligands of the type $Ph_2P(CH_2)_nNHPPr^i_2$ [$n = 2$ (**1**), 3 (**2**)] have been obtained by reacting the appropriate (diphenylphosphino)alkylamine, $Ph_2P(CH_2)_nNH_2$ with chlorodi-*iso*-propylphosphine, in the presence of triethylamine. Reaction of $Ph_2P(CH_2)_2NHPPr^i_2$ with $PdCl_2(PhCN)_2$, $PtCl_2(PhCN)_2$, $PtMe_2(cod)$ and PtClMe(cod), $NiCl_2\cdot 6H_2O$ and $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$ gives the corresponding chelate complexes, $PdCl_2L$, PtX_2L, $NiCl_2L$ and $Fe(CO)(\eta^5\text{-}C_5H_5)L$. Reaction of $Ph_2P(CH_2)_3NHPPr^i_2$ with $PtCl_2(PhCN)_2$, $PtMe_2(cod)$ and $PdCl_2(PhCN)_2$ yields the chelate complexes and reaction with PtClMe(cod) led to a 50:50 mixture of chelate isomers.

Keywords: $Ph_2P(CH_2)_nNHP^iPr_2$; Diphosphine ligands; Chelate complexes

1. Introduction

Diphosphine ligands have been widely used throughout organometallic and inorganic chemistry, and are particularly important in homogeneous catalysis. Diphosphines in which the two phosphorus atoms are linked by a carbon chain and have the same substituents on each phosphorus such as bis-(diphenylphosphino)ethane (dppe) and bis-(diphenylphosphino)methane (dppm) have been extensively studied. Recently, there has been an increased interest in diphosphines with a hetero atom or bridge linking the two phosphorus atoms. However, in comparison to dppe, dppm and hetero-atom bridged diphosphines, unsymmetrical diphosphines have received relatively little attention [1–6].

Unsymmetrical diphosphines represent an interesting series of compounds because the difference in basicity or steric properties of the two phosphorus atoms could be exploited to obtain different coordination modes, i.e. bidentate versus monodentate. For example, it has already been reported that the reaction of $Ph_2PNHC_6H_4PPh_2$ [7] with η^6-aryl Ru(II), Os(II) and Cp* Rh(III), Ir(III) chloride-bridged dimers leads to mono-metallic, monodentate species where the ligand coordinates via the amino-phosphine. Or cationic chelate complexes. This hemilabile nature of unsymmetrical phosphines has also been further illustrated [8] using $Ph_2PCH_2NHC_6H_4PPh_2$.

The palladium [9] catalyst $Pd(dippp)_2$ [dippp = 1,3-bis(di-isopropylphosphino)propane] is an efficient catalyst for direct formylation of aryl chlorides to aldehydes. More recently the catalytic activity of palladium dichloride complexes [10] with 1,3-bis(dialkylphosphino)propane chelating ligands, $PdCl_2(R_2PCH_2CH_2CH_2PR_2)$, and the cationic derivatives of these complexes, $[(NCCH_3)_2Pd(R_2PCH_2CH_2CH_2PR_2)][BF_4]_2$, have been investigated for alkene/CO copolymerisation reactions. All of these diphosphine catalysts have a three carbon chain linking the two phosphorus atoms and have either phenyl or isopropyl groups bonded to the trivalent phosphorus. With this in mind and the lack of reports on the synthesis and coordination of unsymmetrical diphosphines of the type P–C–C–N–P we set about synthesising the ligands $Ph_2PCH_2CH_2NHPPr^i_2$ and $Ph_2P(CH_2)_3NHPPr^i_2$.

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2. Experimental

2.1. General

Unless otherwise stated, all reactions were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Diethyl ether and thf were purified by reflux over sodium-benzophenone and distillation under nitrogen. Dichloromethane and MeCN were heated to reflux over CaH_2 and distilled under nitrogen. ClP^iPr_2 was from Aldrich. 2-(Diphenylphosphino)ethylamine [11] and 3-(diphenylphosphino)-1-propylamine [12], $MCl_2(PhCN)_2$ (M = Pt, Pd) [13] and PtMeX(cod) (X = Me, Cl) [14] were prepared according to literature methods. IR spectra were recorded as either KBr discs or solutions in the range 4000–200 cm^{-1} on a Perkin–Elmer 2000 FT spectrometer. NMR spectra were recorded on a Gemini 2000 spectrometer (operating at 121.4 MHz for ^{31}P and 300 MHz for ^{1}H). Microanalyses were performed by the St. Andrews University service and EI/FAB mass spectra by the Swansea Mass Spectrometer Service.

2.1.1. $Ph_2PCH_2CH_2NHPPr^i_2$ (1)

Chlorodiisopropyl phosphine (1.04 cm^3, 0.998 g, 6.54 mmol) was added dropwise over a period of 20 min to a stirred solution of $Ph_2PCH_2CH_2NH_2$ (1.5 g, 6.54 mmol) and Et_3N (1.09 cm^3, 0.794 g, 7.85 mmol) in Et_2O (50 cm^3). The mixture was stirred at room temperature (r.t.) for 1 h. The white precipitate (triethylamine hydrogen chloride) was filtered off and the solvent removed in vacuo to produce a clear, viscous liquid. Yield: 2.03 g, 90%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ −20.2(s) ppm; $\delta(P_X)$ 66.0(s) ppm. ^{1}H NMR ($CDCl_3$): δ 7.56–7.45 (m, 10H, aromatics), 3.23 (m, 2H, CH_2), 2.41 (m, 2H, CH_2), 1.30 (m, 1H, NH), 1.34 (m, 2H, CH), 1.15 (m, 12H, CH_3) ppm. MS: m/z 345 [M^+].

2.1.2. $Ph_2PCH_2CH_2CH_2NHPPr^i$ (2)

Chlorodiisopropyl phosphine (1.01 cm^3, 0.971 g, 6.37 mmol) was added dropwise over a period of 20 min to a stirred solution of $Ph_2PCH_2CH_2CH_3NH_2$ (1.548 g, 6.36 mmol) and Et_3N (1.01 cm^3, 0.773 g, 7.59 mmol) in Et_2O (50 cm^3). The mixture was stirred at r.t. for 1 h. The white precipitate (triethylamine hydrogen chloride) was filtered off and the solvent removed in vacuo to produce a white solid. Yield: 1.359 g, 60%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ −14.7(s) ppm; $\delta(P_X)$ 66.9(s) ppm. ^{1}H NMR ($CDCl_3$): δ 7.52–7.43 (m, 10H, aromatics), 3.13 (m, 2H, CH_2), 2.17 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 1.10 (m, 12H, CH_3) ppm.

2.1.3. $PdCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (3)

$Ph_2PCH_2CH_2NH_2$ (1) (0.113 g, 0.327 mmol) and $PdCl_2(PhCN)_2$ (0.125 g, 0.327 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 20 min. A cream precipitate started to form. The solvent was removed in vacuo until about 2 cm^3 remained. Diethyl ether was added dropwise to fully precipitate the cream solid which was collected by suction filtration. Yield: 0.093 g, 54%. *Anal*. Found (Calc. for $C_{20}H_{29}Cl_2NP_2Pd$): C, 45.67 (45.95); H, 5.51 (5.59); N, 2.65 (2.68)%. $^{31}P\{H\}$NMR ($CDCl_3$): $\delta(P_A)$ 20.9(d) ppm; $\delta(P_X)$ 90.3(d) ppm, $^{2}J(^{31}P-^{31}P) = 7$ Hz. MS: m/z 545 [$M+Na$]$^+$, 487 [$M-Cl$]$^+$. IR (KBr): 3244s (νNH), 3072w, 1638w, 287m, 217s cm^{-1}.

2.1.4. $PtCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (4)

$Ph_2PCH_2CH_2NHPPr^i_2$ (1) (0.079 g, 0.22 mmol) and $PtCl_2(PhCN)_2$ (0.108 g, 0.22 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 20 min. The solvent was removed in vacuo until product just started to precipitate; ether (10 cm^3) was added dropwise to aid precipitation. The cream solid was collected by suction filtration. Yield: 0.105 g, 75%. *Anal*. Found (Calc. for $C_{20}H_{29}Cl_2NP_2Pt$): C, 39.60 (39.29); H, 4.53 (4.78); N, 2.25 (2.29)%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ −1.4(d) ppm, $^{1}J(^{195}Pt-^{31}P_A) =$ 3584 Hz; $\delta(P_X)$ 57.8(d) ppm, $^{1}J(^{195}Pt-^{31}P) = 3595$ Hz, $^{2}J(^{31}P_A-^{31}P_X) = 17$ Hz. MS: m/z 576 [$M-Cl$]$^+$. IR (KBr): 3273s (νNH), 3027w, 303w, 278w cm^{-1}.

2.1.5. $PtMe_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (5)

$Ph_2PCH_2CH_2NH_2$ (1) (0.117 g, 0.34 mmol) and $PtMe_2$(cod) (0.113 g, 0.34 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 20 min. The solvent was removed in vacuo until a white solid started to precipitate; then Et_2O was added dropwise to aid precipitation. The solid was collected by suction filtration. Yield: 0.061 g, 32%. *Anal*. Found (Calc. for $C_{22}H_{35}NP_2Pt$): C, 46.06 (46.36); H, 6.03 (6.18); N, 2.30 (2.45)%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ 7.1(d) ppm, $^{1}J(^{195}Pt-^{31}P_A) = 1849$ Hz; $\delta(P_X)$ 68.3(d) ppm, $^{1}J(^{195}Pt-^{31}P_X) = 1990$ Hz, $^{2}J(^{31}P_A-^{31}P_X) = 22$ Hz. ^{1}H NMR ($CDCl_3$): δ 7.69–7.39 (m, 10H, aromatics), 3.20 (m, 2H, CH_2), 2.35 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 1.29–1.03 (m, 12H, CH_3), 0.78–0.67 (m, 6H, CH_3) ppm. MS: m/z 555 [$M-Me$]$^+$. IR (KBr): 3384s (νNH), 3070w, 2959s, 2864s, 1589w, 1098s cm^{-1}.

2.1.6. $PtClMe(Ph_2PCH_2CH_2NHPPr^i_2)$ (6)

$Ph_2PCH_2CH_2NH_2$ (1) (0.113 g, 0.33 mmol) and PtClMe(cod) (0.116 g, 0.33 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 20 min. The solvent was removed in vacuo until a white solid started to precipitate. Diethyl ether was added dropwise to aid precipitation. The solid was collected by suction filtration. Yield: 0.141 g, 73%. *Anal*. Found (Calc. for $C_{21}H_{32}ClNP_2Pt$): C, 42.31 (42.68); H, 5.53 (5.46); N, 2.09 (2.37)%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ 6.4(d) ppm, $^{1}J(^{195}Pt-^{31}P_A) =$ 1879 Hz; $\delta(P_X)$ 63.8(d) ppm, $^{1}J(^{195}Pt-^{31}P_X) = 4626$ Hz, $^{2}J(^{31}P_A-^{31}P_X) = 18$ Hz. ^{1}H NMR ($CDCl_3$): δ 7.85–7.38 (m, 10H, aromatics), 3.45 (m, 2H, CH_2), 2.25 (m, 2H, CH_2), 1.38 (m, 2H, CH), 1.2 (m, 12H,

CH_3), 0.76 (m, 3H, CH_3) ppm. MS: *m/z* 555 $[M-Cl]^+$. IR (KBr): 3277s (*v*NH), 3052w, 2962s, 2867s, 1435s, 1100s, 274w cm^{-1}.

2.1.7. $Fe(CO)(\eta^5\text{-}C_5H_5)(Ph_2PCH_2CH_2NHPPr^i_2)I$ (7)

$Ph_2PCH_2CH_2NHPr_2$ (**1**) (0.114 g, 0.33 mmol), $Fe(CO)_2(\eta^5\text{-}C_5H_5)I$ (0.091 g, 0.30 mmol) and catalyst $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ (0.010 g, 0.057 mmol) were refluxed in MeCN (15 cm^3). Reaction followed by IR to completion. The reaction mixture was allowed to cool to r.t., before the solvent was removed in vacuo, producing a green precipitate. The precipitate was re-dissolved in CH_2Cl_2 and precipitated with 60–80 pet ether. The solid was collected by suction filtration. Yield: 0.107 g, 57%. *Anal*. Found (Calc. for $C_{26}H_{34}FeINOP_2$): C, 50.59 (50.27); H, 5.65 (5.52); N, 2.30 (2.25)%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ 53.0(d) ppm; $\delta(P_X)$ 119.8(d) ppm, $^2J(^{31}P_A-^{31}P_X) = 67$ Hz. ^1H NMR ($CDCl_3$): δ 7.96–7.37 (m, 10H, aromatics), 4.99 (m, 5H, Cp), 3.57 (m, 2H, CH_2), 2.73 (m, 2H, CH_2), 2.27 (m, 2H, CH), 1.50–1.21 (m, 12H, CH_3) ppm. MS: *m/z* 494 $[M^+]$. IR (KBr): 3179m (*v*NH), 3048m, 1954s.

2.1.8. $NiCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (8)

$Ph_2PCH_2CH_2NHPr_2$ (**1**) (0.273 g, 0.79 mmol) and $NiCl_2\cdot 6H_2O$ (0.188 g, 0.79 mmol) were stirred in thf (10 cm^3) at r.t. for 20 min. A dark orange solid started to precipitate. The solvent was removed in vacuo and Et_2O added dropwise to aid precipitation. The orange solid was collected by suction filtration. Yield: 0.263 g, 70%. *Anal*. Found (Calc. for $C_{20}H_{29}Cl_2NNiP_2$): C, 50.22 (50.57); H, 6.65 (6.15); N, 2.94 (2.95)%. IR (KBr): 3263s (*v*NH), 326m, 287m.

2.1.9. $PdCl_2[Ph_2P(CH_2)_3NHPPr^i_2]$ (9)

$Ph_2P(CH_2)_3NHPPr^i_2$ (**2**) (0.125 g, 0.45 mmol) and $PdCl_2(PhCN)_2$ (0.133 g, 0.45 mmol) were stirred at r.t. in CH_2Cl_2 (10 cm^3) for 20 min. Cream solid started to precipitate. Solvent was removed in vacuo until approximately 2 cm^3 remained. Diethyl ether was added dropwise to fully precipitate solid. The solid was collected by suction filtration. Yield: 0.159 g, 85%. *Anal*. Found (Calc. for $C_{21}H_{31}Cl_2NP_2Pd$): C, 47.03 (47.14); H, 5.61 (5.84); N, 2.78 (2.62)%. No NMR as very insoluble. MS: *m/z* 500 $[M-Cl]^+$, 463 $[M-2Cl]^{2+}$. IR (KBr): 3262s (*v*NH), 3052w, 1435s, 297m, 282m cm^{-1}.

2.1.10. $PtCl_2[Ph_2P(CH_2)_3NHPPr^i_2]$ (10)

$Ph_2P(CH_2)_3NHPPr^i_2$ (**2**) (0.248 g, 0.69 mmol) and $PtCl_2(PhCN)_2$ (0.326 g, 0.69 mmol) were stirred at r.t. in CH_2Cl_2 (10 cm^3) for 20 min. The solvent was removed in vacuo until a white solid started to precipitate. Diethyl ether was added dropwise to precipitate the white solid. The solid was collected by suction filtration. Yield: 0.356 g, 92%. *Anal*. Found (Calc. for $C_{21}H_{31}Cl_2NP_2Pt$): C, 40.24 (40.41); H, 4.42 (5.01); N, 2.58 (2.24)%. MS: *m/z* 590 $[M-Cl]^+$, 552 $[M-2Cl]^+$. IR (KBr): 3330s (*v*NH), 3053w, 1700w, 1653w, 304m, 297, 282 *v*(M–Cl) cm^{-1}.

2.1.11. $PtMe_2[Ph_2P(CH_2)_3NHPPr^i_2]$ (11)

$Ph_2P(CH_2)_3NHPPr^i_2$ (**2**) (0.105 g, 0.29 mmol) and $PtMe_2$(cod) (0.097 g, 0.29 mmol) were stirred at r.t. in CH_2Cl_2 (10 cm^3) for 60 min. Solvent was removed in vacuo until precipitate started to form. Diethyl ether was added to aid precipitation. White solid was collected by suction filtration. Yield: 0.122 g, 71%. *Anal*. Found (Calc. for $C_{23}H_{37}NP_2Pt$): C, 47.05 (47.29); H, 6.12 (6.38); N, 2.48 (2.4)%. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta(P_A)$ 7.3 ppm, $^1J(^{195}Pt-^{31}P_A) = 1823$ Hz; $\delta(P_X)$ 94.4 ppm, $^1J(^{195}Pt-^{31}P_X) = 2164$ Hz, $^2J(^{31}P_A-^{31}P_X) = 15$ Hz. ^1H NMR ($CDCl_3$): δ 7.83–7.46 (m, 10H, aromatics), 3.31–3.22 (m, 2H, CH_2), 2.88–2.75 (m, 2H, CH_2), 2.41–2.26 (m, 2H, CH_2), 1.65–1.52 (m, 2H, CH), 1.35–1.24 (m, 12H, CH_3), 0.77–0.48 (m, 3H, CH_3), 0.37–0.08 (m, 3H, CH_3) ppm. MS: *m/z* 584 $[M]^+$, 569 $[M-Me]^+$, 554 $[M-2Me]^+$. IR (KBr): 3377s (*v*NH), 3073w, 1434s.

2.1.12. $PtMeCl[Ph_2P(CH_2)_3NHPPr^i_2]$ (12)

$Ph_2P(CH_2)_3NHPPr^i_2$ (**2**) (0.126 g, 0.49 mmol) and PtMeCl(cod) (0.124 g, 0.49 mmol) were stirred at r.t. in CH_2Cl_2 (10 cm^3) for 60 min. Solvent was removed in vacuo until a precipitate started to form. Diethyl ether was added dropwise to fully precipitate solid. The white solid was collected by suction filtration. Yield: 0.155 g, 73%. *Anal*. Found (Calc. for $C_{22}H_{34}ClNP_2Pt$): C, 43.75 (43.74); H, 5.51 (5.67); N, 2.41 (2.32)%. $^{31}P\{H\}$ NMR ($CDCl_3$): δ 8.8 ppm, $^1J(^{195}Pt-^{31}P) = 1655$ Hz, $^2J(^{31}P-^{31}P) = 12$ Hz; δ 23.2 ppm, $^1J(^{195}Pt-^{31}P) = 3042$ Hz; δ 67.5 ppm, $^1J(^{195}Pt-^{31}P) = 2945$ Hz; δ 82.2 ppm, $^1J(^{195}Pt-^{31}P) = 4575$ Hz, $^2J(^{31}P-^{31}P) = 13$ Hz. MS: *m/z* 604 $[M]^+$, 569 $[M-Cl]^+$. IR (KBr): 3280s (*v*NH), 3052m, 1588w, 279w cm^{-1}.

2.2. Crystallography

X-ray diffraction studies were performed at 293 K using a Rigaku Mercury CCD for **8** and a Bruker SMART diffractometer for **11** with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were 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 ΔF map. Structural refinements were by the full-matrix least-squares method on F^2 using SHELXTL [15]. Compound **8** was only obtained as poorly diffracting very thin plates.

*2.2.1. $NiCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (**8**)*

$C_{20}H_{29}Cl_2N_1Ni_1P_2$, $M = 474.99$, monoclinic, space group $P2_1/n$, $a = 8.979(3)$, $b = 15.115(6)$, $c = 16.688(6)$ Å, $\beta = 91.903(5)^\circ$, $U = 2264(1)$ Å^3, $Z = 4$, $D_{calc} = 1.394$ Mg m^{-3}, $\mu = 1.239$ mm^{-1}, $F(000) = 992$, crystal size = $0.23 \times 0.10 \times 0.02$ mm. Of 14 456 measured data, 4774 were unique ($R_{int} = 0.0517$) and observed to give R_1 [$I > 2\sigma(I)$] = 0.1153.

*2.2.2. $PtMe_2[Ph_2P(CH_2)_3NHPPr^i_2]$ (**11**)*

$C_{23}H_{37}N_1P_2Pt$, $M = 584.57$, monoclinic, space group $P2_1/c$, $a = 9.4476(2)$, $b = 15.5972(3)$, $c = 16.1970(1)$ Å, $\beta = 91.161(1)^\circ$, $U = 2386(1)$ Å^3, $Z = 4$, $D_{calc} = 1.627$ Mg m^{-3}, $\mu = 6.022$ mm^{-1}, $F(000) = 1160$, crystal size = $0.10 \times 0.10 \times 0.13$ mm. Of 10 219 measured data, 2965 were unique ($R_{int} = 0.0192$) and observed to give R_1 [$I > 2\sigma(I)$] = 0.0159.

3. Results and discussion

Surprisingly, there are relatively few examples of unsymmetrical diphosphines in which the two phosphorus atoms have different substituents. One limiting factor in the synthesis has been the inconvenient routes involving highly air sensitive intermediates. Grim et al. [15–18] have synthesised a number of diphosphines of the types $RPhP(CH_2)_nPPh_2$ ($n = 1$–3, R = Me, Et, Pr, Pr^i, Bu^t, Bu) and $R_2P(CH_2)_nPPh_2$ ($n = 1$, R = Me, Pr^i, $n = 3$, R = Me), but their route is experimentally difficult. Briggs and coworkers [19] reported an easier synthesis of diphosphines of the type $RPhP(CH_2)_nPPh_2$ ($n = 3$–6, R = Me, Et, c-C_6H_{11}) via the stepwise formation of the mono- and di-phosphonium salts, using a non-polar solvent in the first stage and a polar solvent for the second stage, and on the loss of phenyl in preference to alkyl at the hydrolysis stage. More recently a one-pot synthesis to unsymmetrical 1,2-bis(phosphanyl)ethanes has been developed [20]. We have been interested in the use of P–N bond forming reactions for phosphine synthesis and have developed strategies for the synthesis of unsymmetrical aryl backbone phosphines from amines [21–26]. Here we have extended our methods to alkyl backbone systems. Thus $Ph_2PCH_2CH_2NHPPr^i_2$ (**1**) and $Ph_2P(CH_2)_3NHPPr^i_2$ (**2**), were obtained by direct reaction of the appropriate amine, and chlorodiisopropylphosphine. The presence of slightly more than 1 M equivalent of triethylamine ensures complete removal of the hydrogen chloride by-product (Eq. (1)).

$$Ph_2P(CH_2)_nNH_2 + {}^iPr_2PCl + Et_3N \rightarrow Ph_2P(CH_2)_nNHP^iPr_2 + NEt_3HCl \quad (1)$$

$n = 2$ (**1**); 3 (**2**)

The structure of **1** was confirmed by mass spectrometry and $^{31}P\{H\}$ and ^1H NMR. MS gave a M^+ peak at 345. $^{31}P\{H\}$ NMR revealed the predicted AX spectrum. The peak at $\delta(P_A)$ −20.2 ppm was assigned to the diphenyl phosphorus, as the peak in the starting material was at −20.5 ppm and $\delta(P_X)$ 65.9 ppm was assigned to the di-isopropyl phosphorus. There is no observable coupling between the 2 inequivalent. phosphorus nuclei. Compound **2** is a white solid whilst **1** is a clear, viscous liquid. In **2** the P_A peak corresponding to the diphenyl phosphorus is at −14 ppm [similar to the starting material at −14.6 ppm]; the $\delta(P_X)$ peak assigned to the di-isopropyl phosphorus, like that of **1**, occurs at $\delta(P)$ 67 ppm.

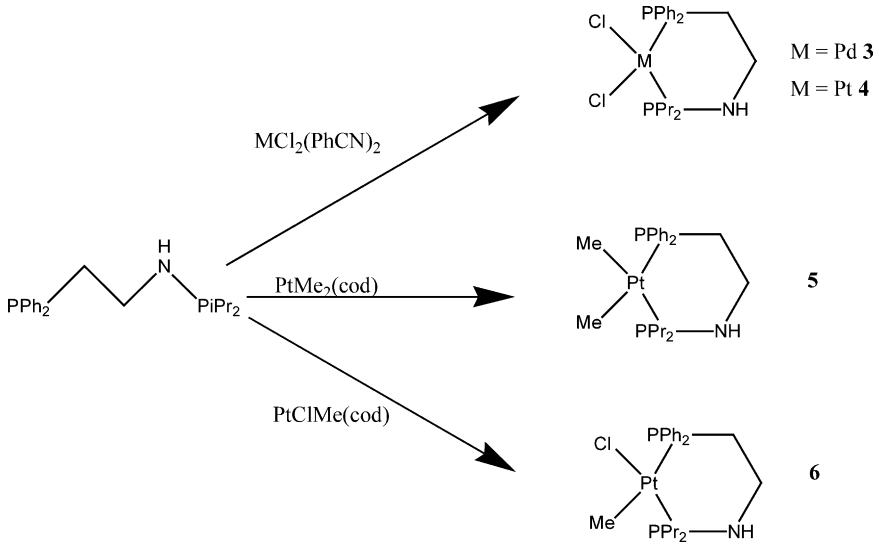
Further evidence for the above assignment is that **1** reacts with 1 equiv. of elemental selenium at the most basic and therefore most reactive phosphorus atom, the di-isopropyl phosphorus atom since $\delta(P_A)$ −20 ppm remains in the same place, whilst $\delta(P_X)$ 65.9 ppm in **1** shifts to 89 ppm in $Ph_2PCH_2CH_2NHP(Se)Pr^i_2$.

We examined some simple coordination chemistry of **1** and **2**. Complexation reactions were straightforward, with coordination to platinum, palladium and nickel all being carried out at room temperature. Coordination to iron required refluxing in acetonitrile in the presence of a catalyst. All complexes were formed as fine powders. The spectroscopic data for the complexes are readily interpreted and consistent with chelate monomeric systems though we noted some weak high value m/z peaks in some of the mass spectra which could suggest dimer formation in the mass spectrometer at least.

The palladium dichloride complex **3** was formed by direct reaction of **1** with $PdCl_2(PhCN)_2$. Mass spectroscopy gave the $M+Na^+$ peak at 545, corresponding to a monomeric complex and microanalysis was in good agreement with the proposed structure. In its $^{31}P\{^1H\}$ NMR the diphenyl phosphorus group is observed at $\delta(P_A)$ 20.9 ppm whilst $\delta(P_X)$ 90.3 ppm, the coupling constant, $^2J(P_X–P_A) = 7$ Hz, is very small. The two peaks in the IR spectrum assigned as ν(M−Cl) 297, 282 cm^{-1} suggest the ligand coordinates in a *cis*-geometry and therefore the complex has a six-membered PdP_2NC_2 chelate ring. The dichloro-, dimethyl- and chloromethylplatinum complexes were all formed by similar ligand substitution reactions (Scheme 1).

The geometry of complexes **4**–**6** was confirmed by examination of the Pt–P coupling constants in their $^{31}P\{H\}$ NMR summarised below (Table 1). The mass spectrum of **4** has a major peak at 576 corresponding to $[M-Cl]^+$. The $^{31}P\{H\}$ NMR of complex **6** has $\delta(P_A)$ 6.4 ppm, $^1J(Pt–P_A) = 1879$ Hz and $\delta(P_X)$ 63.8 ppm, $^1J(Pt–P_X) = 4626$ Hz. The $\delta(P_A)$ peak is assigned to the diphenyl phosphorus group *trans* to methyl with the PPr^i_2 group is *trans* to chloride.

Coville et al. [27] found $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ reacts with diphosphines (L–L) in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalyst to produce $[(\eta^5\text{-}C_5H_5)Fe(CO)(L–$



Scheme 1. Formation of palladium and platinum complexes of **1**.

L)]I. The reaction for each of the diphosphines, L–L = $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4), was followed by IR and in each case $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L\text{–}L)]I$ was readily identified by the characteristic ν(CO) at 2050, 2000 cm^{-1}. We have found that reaction of **1** under the same conditions as above gives $[(\eta^5\text{-}C_5H_5)Fe(CO)(Ph_2PCH_2CH_2NHPPr^i_2)]I$ (**7**) identified by ν(CO) 1954 cm^{-1}, microanalysis and mass spectrometry. The ^{31}P NMR of **7** contains the expected AX spectrum, with a large change in chemical shift on coordination to the iron ($\delta(P_A)$ 53.0 ppm, $\delta(P_X)$ 119.8 ppm) compared to the free ligand values of $\delta(P_A)$ −20.2 ppm and $\delta(P_X)$ 66.0 ppm. The spectrum also shows a large P–P coupling, $^2J(P_X\text{–}P_A) = 67$ Hz. In a separate experiment in which no catalyst was used, the intermediate $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2NHPPr^i_2)]I$ was observed after 16 h [ν(CO) 2951, 2006 cm^{-1}] which is consistent with Coville's work [27].

$NiCl_2\cdot 6H_2O$ reacts with **1** to give $NiCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (**8**). Microanalyses are consistent with this formulation and its IR spectrum contains peaks at 287 and 326 cm^{-1}, confirming the presence of *cis* Ni–Cl bonds. We were unable to obtain a satisfactory NMR spectrum of **8** since it is poorly soluble and appears to be paramagnetic in solution which suggests at least some tetrahedral character in solution. X-ray crystallography reveals the solid state structure of **8** (Fig. 1) with the nickel in an approximate square planar geometry and the two phosphorus atoms coordinating in a *cis* fashion. The diphosphine ligand forms a six-membered metallacycle, which can best be described as having a half-boat conformation, $NiP_2NC(13)$ are approximately coplanar with C(14) at the prow of the boat. Hydrogen bonding between the amine proton N(2) and Cl(2) of the adjacent complex [Cl···H 2.40, Cl···N 3.37 Å, N–H···Cl 170°) results in an infinite chain motif (Fig. 2).

As with **1** complexation of $Ph_2P(CH_2)_3NHPPr^i_2$ (**2**) involves straight forward ligand substitution reactions, we established coordination to platinum and palladium for illustrative purposes. All complexes were produced as fine powders. In the ^{31}P NMR of **11** the spectrum is again the expected AX type, with satellites due to coupling to platinum. $\delta(P_A)$ 7.3 ppm is assigned to

Table 1
$^{31}P\{H\}$ NMR data

	δP_A (PPh_2) (ppm)	δP_B (PPr_2) (ppm)	$^1J(P_A\text{–Pt})$ (Hz)	$^1J(P_X\text{–Pt})$ (Hz)	$^2J(P_A\text{–}P_X)$ (Hz)
$Ph_2PCH_2CH_2NHPPr^i_2$ (**1**)	−20.2	66.0			0
$Ph_2PCH_3CH_3CH_3NHPPr^i$ (**2**)	−14.7	66.9			0
$PdCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (**3**)	20.9	90.3			7
$PtCl_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (**4**)	−1.4	57.8	3584	3595	17
$PtMe_2(Ph_2PCH_2CH_2NHPPr^i_2)$ (**5**)	7.1	68.3	1849	1990	22
$PtClMe(Ph_2PCH_2CH_2NHPPr^i_2)$ (**6**)	6.4	63.8	1879	4626	18
$Fe(CO)(\eta^5\text{-}C_5H_5)(Ph_2PCH_2CH_2NHPPr^i_2)I$ (**7**)	53.0	119.8			67
$PtMe_2[Ph_2P(CH_2)_3NHPPr^i_2]$ (**11**)	7.3	94.4	1823	2164	15
$PtMeCl[Ph_2P(CH_2)_3PPr^i_2]$ (**12A**)	8.8	82.2	1655	4575	12
$PtMeCl[Ph_2P(CH_2)_3PPr^i_2]$ (**12B**)	23.2	67.5	3042	2945	13

No spectra were obtained for **8**, **9** and **10** because of insolubility.

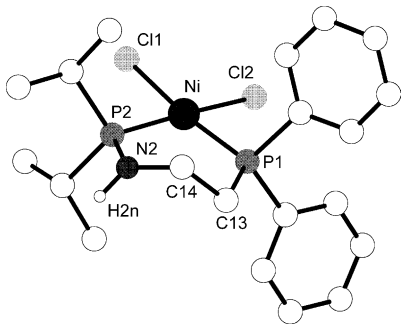


Fig. 1. X-ray structure of $NiCl_2(PH_2PCH_2CH_2NHPPr^i_2)$ (**8**). Selected bond lengths (Å) and angles (°) Ni–P(1) 2.173(2), Ni–P(2) 2.186(2), Ni–Cl(1) 2.196(2), Ni–Cl(2) 2.226(2), P(1)–C(13) 1.822(6), C(13)–C(14) 1.524(9), C(14)–N(2) 1.448(8), N(2)–P(2) 1.668(6); P(1)–Ni–P(2) 96.1(1), Cl(1)–Ni–Cl(2) 90.1(8), N(2)–P(2)–Ni 117.3(2), C(14)–Ni–P(2) 125.7(4).

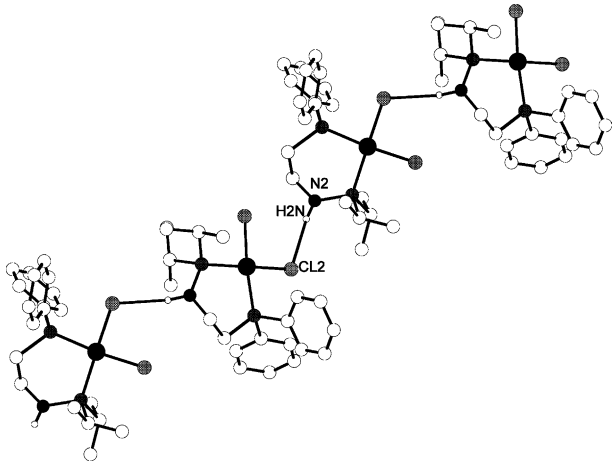


Fig. 2. Hydrogen bonding between the amine proton and chloride of the adjacent complex resulting in an infinite chain motif in $NiCl_2(PH_2PCH_2CH_2NHPPr^i_2)$ (**8**).

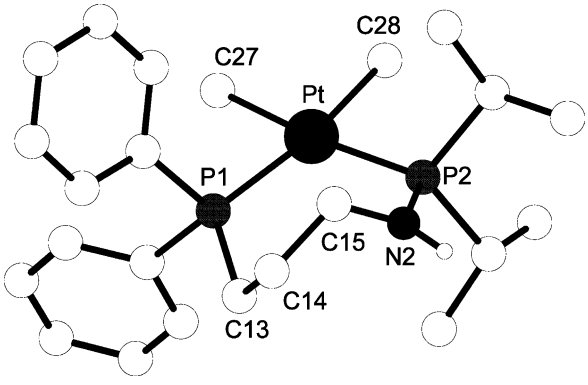


Fig. 3. The X-ray structure of $PtMe_2[Ph_2P(CH_2)_3NHPPr^i_2]$ (**11**). Selected bond lengths (Å) and angles (°) Pt–P(1) 2.285(1), Pt–P(2) 2.285(1), Pt–C(27) 2.124(3), Pt–C(28) 2.110(3), P(1)–C–(!3) 1.844(3), C(13)–C(14) 1.524(5), C(14)–C(15) 1.508(5), C(15)–N(2) 1.455(4), N(2)–P(2) 1.684(3); P(1)–Pt–P(2) 100.0(1), C(27)–Pt–C(28) 82.8(1), N(2)–P(2)–Pt 115.5(1), C(15)–N(6)–P(2) 123.8(2).

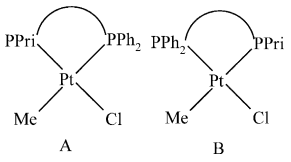


Fig. 4. Different isomers of **12**.

PPh_2 and $\delta(P_X)$ 94.4 ppm is assigned to PPr^i_2. The proton NMR clearly shows the different environments of the two methyl groups on the platinum, both methyl groups are coupled to the phosphorus to give an apparent quartet $J(^1H–^{31}P) = 7.7$ Hz with satellite peaks either side due to coupling to the platinum. Crystallography confirmed the structure of **11** (Fig. 3) to be monomeric with the diphosphine ligand coordinating as a chelate. The geometry around the platinum is distorted square planar, [P(1)–Pt(1)–P(2) 100.0(1)° and C(28)–Pt(1)–C(27) 82.8(1)°] with the ligand displaying a significantly larger bite angle than **1** in **8** as a consequence of the extra methylene group in the backbone here and since the *trans* methyl groups are less sterically demanding than the chlorides in **8**. The conformation of the ring is a distorted 'chaise longue'.

Complex **12** was formed by reaction of ligand **2** with PtMeCl(cod). ^{31}P NMR (Table 1) shows the presence of equal proportions of two isomers (Fig. 4). If $\delta(P_A)$ is assigned to PPh_2 and $\delta(P_X)$ is assigned to PPr^i_2 then in isomer A the PPh_2 moiety is *trans* to methyl and has a small coupling constant to platinum, $^1J(^{31}P_A–^{195}Pt) =$ 1665 Hz, and the PPr^i_2 moiety is *trans* to chloride and therefore has a large coupling constant with platinum, $^1J(^{31}P_X–^{195}Pt) = 4575$ Hz.

This work clearly illustrates the ease of formation of unsymmetrical phosphines and should allow the effect of variation of the two phosphorus centres on a range of catalytic processes to be studied.

4. Supplementary material

Full lists of structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen atom parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 188819 (**8**), 188820 (**11**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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