

Zerovalent palladium and platinum complexes of aminomethylphosphines. Crystal structure of the palladium(0) dibenzylideneacetone complex $[\text{Pd}(\text{PhCH}=\text{CHCOCH}=\text{CHPh})\{((\text{C}_6\text{H}_{11})_2\text{PCH}_2)_2\text{NMe}\}]$

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Abstract

Tris(dibenzylideneacetone)dipalladium and bis(dibenzylideneacetone)platinum react with *N,N*-bis(dicyclohexylphosphinomethyl)methylamine, $(\text{Cy}_2\text{PCH}_2)_2\text{NMe}$ (Cy = cyclohexyl), and with *N,N*-bis(diphenylphosphinomethyl)methylamine, $(\text{Ph}_2\text{PCH}_2)_2\text{NMe}$ (Ph = phenyl), to give the complexes $[\text{M}(\text{dba})\{(\text{R}_2\text{PCH}_2)_2\text{NMe}\}]$ (M = Pd or Pt, dba = dibenzylideneacetone), R = Cy or Ph. The zerovalent platinum complex $[\text{Pt}(\text{PPh}_3)\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ can be obtained by hydrazine hydrate reduction of a mixture of $[\text{PtCl}_2\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ and triphenylphosphine or one of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and $(\text{Cy}_2\text{PCH}_2)_2\text{NMe}$. The crystal structure of $[\text{Pd}(\text{dba})\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ has been determined and some reactions of the complexes are reported.

Keywords: Palladium; Platinum; Aminomethylphosphines; Dibenzylideneacetone; Crystal structure

1. Introduction

Our interest in aminomethylphosphines [1] prompted us to explore some chemistry of zerovalent palladium and platinum complexes of these novel phosphine ligands. Some complexes of palladium(II) and platinum(II) have been described [2] but the isolation of some zerovalent complexes would provide the opportunity to develop further the chemistry of these systems [3]. Herein we describe new palladium(0) and platinum(0) complexes of the aminomethylphosphines $(\text{Cy}_2\text{PCH}_2)_2\text{NMe}$ (**1a**) and $(\text{Ph}_2\text{PCH}_2)_2\text{NMe}$ (**1b**) [4].

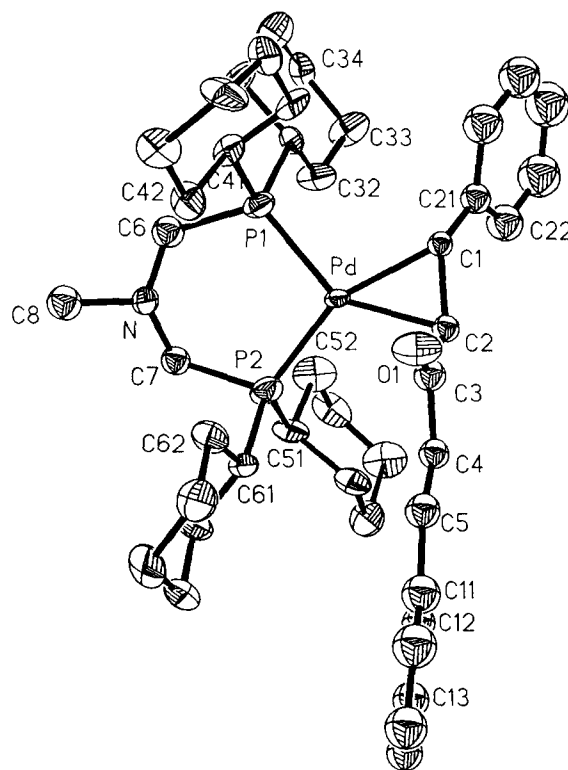
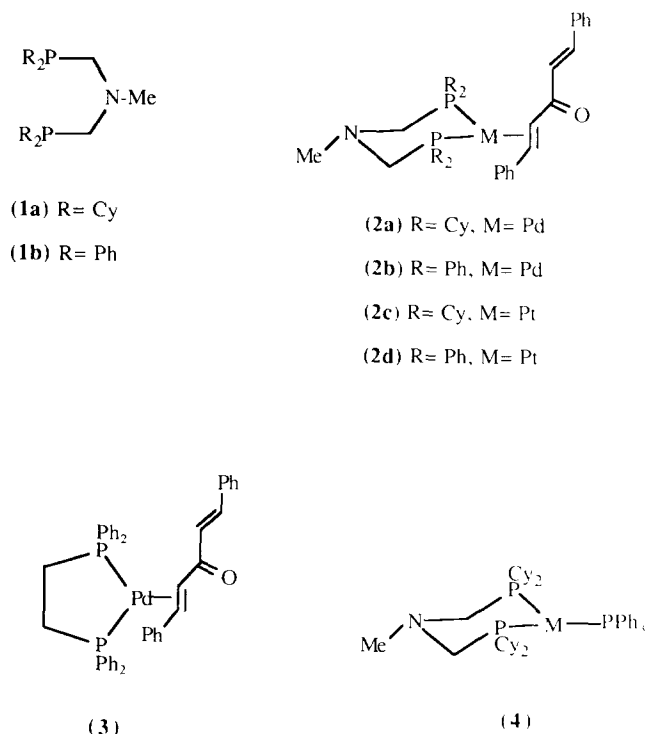
2. Results and discussion

Treatment of the zerovalent palladium complex $[\text{Pd}_2(\text{dba})_3]$, CHCl_3 (dba = dibenzylideneacetone) [5] in benzene with the phosphine (**1a**) affords in high yield a yellow microcrystalline air-stable solid formulated as

the palladium(0) dibenzylidene alkene complex (**2a**) on the basis of microanalysis, spectroscopic properties, and a single crystal X-ray structure determination. The palladium complex (**2b**) can be prepared similarly from the phosphine (**1b**), and analogous platinum complexes (**2c**) and (**2d**) are readily formed by the reaction of $[\text{Pt}(\text{dba})_2]$ [6] with the appropriate phosphine.

The availability of a range of zerovalent dba complexes made it possible to examine the effect of a bulky chelating phosphine on the palladium olefin bond. Accordingly a single crystal X-ray diffraction study was undertaken on the complex $[\text{Pd}(\text{dba})\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ (**2a**); the results are summarised in Table 1 and the molecular structure is shown in Fig. 1. The palladium is three coordinate, with the dba bonding through one double bond in a “W” conformation. The C=C bond (1.52(3) Å) is significantly longer than those in the two molecules of the complex $[\text{Pd}(\text{dba})(\text{bipy})]$ [C=C, 1.42(1); 1.45(1) Å] [7] and in $[\text{Pd}(\text{dba})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ (**3**) [C=C, 1.407(8) Å] [8], suggesting that there is more back-bonding in the aminomethylphosphine complex (**2a**), but because of the low accuracy of the structure determination those comparisons should be

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Treatment of a mixture of $[\text{PtCl}_2\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ and triphenylphosphine with hydrazine hydrate affords the three co-ordinate platinum(0) complex $[\text{Pt}(\text{PPh}_3)\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ (**4**). This complex may also be obtained by treating a mixture of *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and (**1a**) with hydrazine hydrate. However, attempts to obtain an analogous complex of $(\text{Ph}_2\text{PCH}_2)_2\text{NMe}$ (**1b**) were unsuccessful. The zerovalent complex (**4**) reacts with mercury(II) chloride and allyl chloride to afford $[\text{PtCl}_2\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$. Reaction with methyl iodide affords $[\text{PtI}_2\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$.

3. Experimental details

The reported phosphines were characterised by microanalytical, NMR, IR and mass spectroscopic data. Microanalysis were carried out by Butterworth Laboratories Ltd., 54–56 Waldegrave Rd., Teddington, Middlesex, TW11 8LG. The melting points were determined with a Reichert hot-stage apparatus. The mass spectra of the solid phosphines were obtained on a Kratos Concept Double Focusing Sector Mass Spectrometer. The ^1H NMR spectra were recorded at room temperature on a Bruker AM 300 spectrometer operating at 300.13 MHz with SiMe_4 (0.0 ppm) as internal reference. The coupling constants, J , are in Hz. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained along with D.E.P.T. spectra in $[\text{D}_2\text{H}_1]\text{chloroform}$ on a Bruker AM 300 spectrometer operating at 75.47 MHz. The ^{31}P NMR were recorded in dichloromethane unless otherwise stated, either on a JEOL JMM-FX60 operating at 24.15 MHz or on a JEOL EM390 spectrometer operating at 36.24 MHz with $[\text{P}(\text{OH})_4]^+$ in D_2O as external reference [9]. The IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer either as KBr discs or Nujol mulls.

The preparations were carried out under a dry oxygen-free nitrogen by use of standard Schlenk tube techniques. The solvents dichloromethane, diethyl ether, acetonitrile and toluene were dried and distilled under nitrogen prior to use from the following drying agents: dichloromethane (calcium hydride); diethyl ether (sodium/benzophenone); toluene (sodium). The compounds $[\text{Pd}_2(\text{dba})_3]\cdot\text{CHCl}_3$ [5] and $[\text{Pt}(\text{dba})_2]$ [6] were prepared by published methods. $(\text{Cy}_2\text{PCH}_2)_2\text{NMe}$ and $(\text{Ph}_2\text{PCH}_2)_2\text{NMe}$ were prepared from methylamine and $[\text{R}_2\text{P}(\text{CH}_2\text{OH})_2]\text{Cl}$, ($\text{R} = \text{Cy}$ or Ph) [1].

3.1. $[\text{Pd}(\text{dba})\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ (**2a**)

The amine $(\text{Cy}_2\text{PCH}_2)_2\text{NMe}$ (0.314 g, 0.71 mmol) was added to a stirred solution of $[\text{Pd}_2(\text{dba})_3]\cdot\text{CHCl}_3$ (0.2 g, 0.35 mmol) in benzene (15 cm^3). The mixture was stirred for a further 1 h. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the mixture showed signals for the product

and for the free phosphine, and so the mixture was stirred for an additional 16 h. The solvent was removed in vacuo and the residual yellow solid was dissolved in dichloromethane and the product precipitated by addition of diethyl ether. Yield 0.47 g (85% based on Pd). M.p. 213–20°C decomp. (Found: C, 63.4; H, 8.04; N, 2.16. $\text{C}_{44}\text{H}_{65}\text{NOP}_2\text{Pd}$. $1/2 \text{CH}_2\text{Cl}_2$ requires: C, 63.3; H, 7.85; N, 1.68.) NMR ^1H : $\delta = 0.88\text{--}2.16$ [m 44H, Cy], 2.27 [s 3H NMe], 2.42 [d 2H CH_2N , $^2J(\text{PH})$ 14 Hz], 2.61 [d 2H CH_2N , $^2J(\text{PH})$ 14 Hz], 4.70 [b 2H $\text{CH}=\text{CH}$] 6.95–7.62 [m, 14H PPh + $\text{CH}=\text{CH}$ (free)] ppm. $^{31}\text{P}\{^1\text{H}\}$ (benzene): $\delta = 15.7$ [d, Pa, $^2J(\text{PaPb})$ 44 Hz], 18.6 [d, Pb,] ppm. IR: $\nu(\text{C}=\text{O})$ 1645s cm^{-1} . Mass spectrum: m/z 791 (M 791), 557 [Pd(dcpam)], 211 $[\text{Cy}_2\text{PCH}_2]$.

3.2. $[\text{Pd}(\text{dba})\{(\text{Ph}_2\text{PCH}_2)_2\text{NMe}\}]$ (**2b**)

The amine $(\text{Ph}_2\text{PCH}_2)_2\text{NMe}$ (0.22 g, 0.52 mmol) was added to a stirred solution of $[\text{Pd}(\text{dba})_2]$ (0.29 g, 0.50 mmol) in dichloromethane (20 cm^3). The mixture was stirred for a further 2 h and the reaction monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The product was precipitated by addition of diethyl ether. Yield 0.33 g (86% based on Pd). (Found: C, 65.2; H, 5.1; N, 1.76. $\text{C}_{44}\text{H}_{41}\text{NOP}_2\text{Pd}$. 0.5 CH_2Cl_2 requires: C, 66.9; H, 5.1; N, 1.73) NMR ^1H : $\delta = 2.37$ [b, 2H $\text{CH}=\text{CH}$], 2.71 [s 3H NMe], 3.63 [d, 4H PCH_2N , $^2J(\text{HP})$ 5.97 Hz], 5.30 [s CH_2Cl_2], 7.30–7.76 [m 34H, Ph + $\text{CH}=\text{CH}$ (free)] ppm. $^{31}\text{P}\{^1\text{H}\}$: $\delta = 3.27$ [d, Pa, $^2J(\text{PaPb})$ 34 Hz], 7.27 [d, Pb] ppm.

3.3. Preparation of $[\text{Pt}(\text{dba})\{(\text{Cy}_2\text{PCH}_2)_2\text{NMe}\}]$ (**2c**)

The amine $(\text{Cy}_2\text{PCH}_2)_2\text{NMe}$ (dcpam) (0.343 g, 0.76 mmol) was added to a stirred suspension of $[\text{Pt}(\text{dba})_2]$ (0.5 g, 0.75 mmol) in benzene (25 cm^3). The mixture was stirred overnight, dichloromethane was then added to dissolve the starting dba complex completely and the mixture stirred for a further 1 h. The solvents were removed to give a green product which was then washed with diethyl ether and dried in vacuo. Yield 0.55 g (83% based on Pt). M.p. 240–45°C (decomp). (Found: C, 58.9; H, 7.11; N, 1.63. $\text{C}_{44}\text{H}_{65}\text{NOP}_2\text{Pt}$ requires: C, 60.0; H, 7.39; N, 1.59) NMR: ^1H : $\delta = 0.85\text{--}2.15$ [m 44H Cy], 2.24 [s, 3H NMe], 2.40 [d 2H CH_2N , $^2J(\text{PH})$ 3.32, $^3J(\text{PtH})$ 25.6 Hz], 2.64 [d 2H, CH_2N , $^2J(\text{PH})$ 4.3, $^3J(\text{PtH})$ 35.6 Hz], 3.97 [b, 2H $\text{Pt}(\text{HC}=\text{CH})$, $^2J(\text{PtH})$ 47.1 Hz, $^3J(\text{PH})$ unresolved], 6.86–7.61 [m 12 H, Ph + $\text{HC}=\text{CH}$ (free)] ppm. $^{13}\text{C}\{^1\text{H}\}$ $\delta = 26.1\text{--}37.1$ [m Cy], 52.3 [s, NMe], 53.3 [d CH_2N , $J(\text{PC})$ 19.6 Hz], 53.6 [d CH_2N , $J(\text{PC})$ 17.6 Hz, 122.8–128.9 [m, Ph + $\text{C}=\text{C}$ (free)], 136.5 $[\text{C}=\text{O}]$ ppm. $^{31}\text{P}\{^1\text{H}\}$: $\delta = 16.4$ [d Pa, $^2J(\text{PaPb})$ 7, $J(\text{PtPa})$ 3135 Hz], 19.5 [d, Pb $J(\text{PtPb})$ 3741 Hz] ppm. IR: $\nu(\text{C}=\text{O})$ 1685m, 1645 cm^{-1} . Mass spectrum: m/z 880 (M 880), 646 [Pt(dcpam)], 211 $[\text{Cy}_2\text{PCH}_2]$.

3.4. $[Pt(dba)\{(Ph_2PCH_2)_2NMe\}]$ (2d)

A solution of $(Ph_2PCH_2)_2NMe$ (0.163 g, 0.381 mmol) in dichloromethane was added from a syringe to a stirred solution of $[Pt(dba)_3]$ (0.250 g, 0.377 mmol) in benzene. The mixture was stirred for a further 2 h. A brown product was obtained on addition of diethyl ether, and was filtered off and dried in vacuo. Yield 0.226 g (70% based on Pt). (Found: C, 50.5; H, 4.0; N, 1.38. $C_{44}H_{41}NOP_2Pt$. 2 $CHCl_2Cl_2$ requires: C, 51.5; H, 4.0; N, 1.36). NMR: 1H ; δ = 2.44 [s 2H, Pt(CH=CH)], 2.53 [s 3H, NMe], 3.27 [d, 2H CH_2N , $^2J(PH)$ 3.39 Hz], 3.34 [d, 2H CH_2N , $J(PH)$ 3.85 Hz.], 5.30 [s CH_2Cl_2], 6.80–7.90 [m, 34H Ph + olefinic H] ppm. ^{31}P - $\{^1H\}$ (benzene): δ = 2.83 [d, Pa, $^2J(PbPa)$ 10, $J(PtPa)$ 3242 Hz.], 6.23 [d Pb, $J(PtPb)$ 3796 Hz.] ppm. IR.: $\nu(C=O)$ 1675s, 1630 cm^{-1} .

3.5. $[Pd((CNCH=CHCN)\{(Cy_2PCH_2)_2NMe\})]$ (4)

The amine $(Cy_2PCH_2)_2NMe$ (0.095 g, 0.214 mmol) and fumaronitrile (0.017 g, 0.214 mmol) were added to a stirred suspension mixture of $[Pd_2(dba)_3]$ (0.1 g, 0.107 mmol) in benzene (10 cm^3). The mixture was stirred for a further 3 h the formation of the product being monitored by ^{31}P - $\{^1H\}$ NMR spectroscopy. The solvent was removed in vacuo and the white residue recrystallised from a dichloromethane/diethyl ether mixture. Yield 0.087 g (64% based on Pd) M.p. 252–5°C (decomp). (Found: C, 59.2; H, 8.36; N, 6.59. $C_{31}H_{53}N_3P_2Pd$ requires: C, 58.5; H, 8.4; N, 6.61). NMR: 1H δ = 1.22–1.98 [m, 44H, Cy], 2.41 [s 3H, NMe], 2.63 [d, 2H, CH_2N , $^2J(PH)$ 14 Hz.] 2.76 [d 2H, HC=CH, $^3J(PH)$ 3.75 Hz.], 2.8 [d, 2H, C, $^2J(PH)$ 12. Hz.] ppm. ^{13}C - $\{^1H\}$: δ = 20.7–35.3 [m, Cy], 51.8 [s, NMe], 53.5 [t PCH_2N , $J(PC)$ 15.1 Hz.], 123 [s, CN] ppm. ^{31}P - $\{^1H\}$; δ = 20.6 ppm. IR: $\nu(CN)$ 2200 $s\ cm^{-1}$.

3.6. Synthesis of $[Pt(PPh_3)\{(Cy_2PCH_2)_2NMe\}]$ (6)

Hydrazine hydrate (0.4 cm^3) was added to a stirred suspension of *cis*- $[PtCl_2(PPh_3)_2]$ (0.2 g, 0.253 mmol) in ethanol (15 cm^3). The mixture was stirred until a clear yellow solution was formed and $(Cy_2PCH_2)_2NMe$ (0.12 g, 0.26 mmol) was then added. The mixture was then heated to 60°C for 10 min during which a yellow precipitate separated and re-dissolved. The solvent was removed in vacuo and the yellow product was recrystallised from a dichloromethane/diethyl ether mixture, washed with diethyl ether, and dried in vacuo. Yield 0.174 g (87% based on Pt). M.p. 70°C (decomp). (Found: C, 54.8; H, 7.32; N, 1.45. $C_{45}H_{66}NP_3Pt$. CH_2Cl_2 requires: C, 54.4; H, 6.85; N, 1.41) NMR: 1H : δ = 0.93–1.23 [m, 44H Cy], 2.52 [s, 3H NMe], 2.88 [d 2H CH_2N , $^2J(PH)$ 2.77, $^3J(PtH)$ 18.0 Hz.], 3.01 [s 2H, $^3J(PtH)$ 20.8 Hz], 5.32 [s, CH_2Cl_2] 7.47–7.69 [m, 15H

PPh_3] ppm. ^{13}C - $\{^1H\}$: δ = 18.8–34.8 [m, CH_2 of Cy], 35.2–37.8 [m, CH of Cy], 51.8 [m, PCH_2N], 65.8 [s NMe], 128.9–134.1 [m, PPh] ppm. ^{31}P - $\{^1H\}$ δ = 8.81 [t, Pa, $^2J(PaPb)$ 24.4, $J(PaPt)$ 2083 Hz], 21.6 [d Pb, $J(PbPt)$ 2613 Hz] ppm. Mass spectrum: m/z 908 (M^+ 908), 646 [$Pt(dcpam)$], 211 [Cy_2PCH_2].

3.7. Reactions of $[Pd(dba)(dcpam)]$

3.7.1. With dimethylacetylene dicarboxylate

Dimethylacetylene dicarboxylate, (dmd), (0.026 g, 0.182 mmol) was added to a stirred solution of $[Pd(dba)\{(Cy_2PCH_2)_2NMe\}]$ (0.144 g, 0.182 mmol) in dichloromethane (15 cm^3). The mixture was stirred for a further 30 min and the volume of solvent then reduced. The product, $[Pd(dmd)\{(Cy_2PCH_2)_2NMe\}]$, was precipitated with diethyl ether, filtered off, and dried. (Found: C, 49.2; H, 6.2; N, 2.37. $C_{33}H_{57}NO_4P_2Pd$. CH_2Cl_2 requires C, 50.5; H, 7.3; N, 1.78) ^{31}P - $\{^1H\}$ NMR: δ = 25.8 ppm. Mass spectrum: m/z 699 (M^+ 699), 557 [$Pd\{(Cy_2PCH_2)_2NMe\}$], 211 [Cy_2PCH_2].

3.7.2. With diphenylacetylene

Diphenylacetylene (0.036 g, 0.20 mmol) was added to a stirred solution of $[Pd(dba)\{(Cy_2PCH_2)_2NMe\}]$ (0.150 g, 0.19 mmol) in dichloromethane (15 cm^3). The mixture was stirred for a further 2 h. The ^{31}P - $\{^1H\}$ NMR spectrum of the mixture showed the presence of unchanged starting compound.

3.8. Reactions of $[Pt(dba)(dcpam)]$

3.8.1. With diphenylacetylene

Diphenylacetylene (0.02 g, 0.114 mmol) was added to a stirred solution of $[Pt(dba)\{(Cy_2PCH_2)_2NMe\}]$ (0.1 g, 0.114 mmol) in dichloromethane. The mixture was stirred for a further 1 h. The ^{31}P - $\{^1H\}$ NMR spectrum of the mixture showed only the presence of starting compound. When the reaction was repeated in refluxing benzene for 1 h, the starting compound was again found to be unchanged.

3.8.2. With tBuNC

After addition of tBuNC (4.7 mg, 0.057 mmol) to a stirred solution of $[Pt(dba)\{(Cy_2PCH_2)_2NMe\}]$ (0.05 g, 0.057 mmol) in toluene (20 cm^3), the mixture was stirred for a further 2 h. The solvent volume was reduced in vacuo. The ^{31}P - $\{^1H\}$ NMR. spectrum of the solution showed that the starting material was unchanged.

3.8.3. With CO in toluene

Carbon monoxide was passed through a stirred solution of $[Pt(dba)\{(Cy_2PCH_2)_2NMe\}]$ (0.05 g, 0.057 mmol) in toluene (25 cm^3) for 1.5 h and the solvent volume was then reduced in vacuo. The ^{31}P - $\{^1H\}$ NMR. spec-

trum of the solution showed the presence only of unchanged starting compound.

3.8.4. With PPh_2Me in toluene

PPh_2Me (0.034 g, 0.17 mmol) was added to a solution of $[Pt(dba)(Cy_2PCH_2)_2NMe]$ (0.075 g, 0.085

mmol) in toluene (20 cm³). The mixture was refluxed for 2 h and the solvent volume then reduced in vacuo. The $^{31}P\{-^1H\}$ NMR spectrum showed the presence of only the starting compound.

3.9. Reactions of $Pt(dcpam)(PPh_3)_2$ with MeI

Methyl iodide (1 cm³) was added to a stirred solution of $[Pt(dcpam)(PPh_3)]$ (0.05 g, 0.055 mmol) in dichloromethane (20 cm³). The solvent volume was reduced in vacuo to afford a yellow solid, which was recrystallised from dichloromethane-diethyl ether. M.p. 280°C (decomp) (Found: C, 35.2; H, 5.50; N, 2.15. $C_{27}H_{51}I_2NP_2Pt$ requires C, 36.0; H, 5.70; N, 1.56%; $^{31}P\{-^1H\}$ NMR, δ 5.18 ppm. [$J(PPt)$ 3312 Hz].

3.9.1. With allyl chloride

Allyl chloride (4.2 mg, 0.055 mmol) was added to a stirred solution of $[Pt(dcpam)(PPh_3)]$ (0.05 g, 0.055 mmol) in benzene (15 cm³). The mixture was stirred for a further 2 h, additional allyl chloride was added, and the mixture was stirred for 1 h. The solution was evaporated to dryness and the white residue was recrystallised from dichloromethane-diethyl ether. (Found: C, 45.2; H, 7.32; N, 1.84. $C_{27}H_{51}Cl_2NP_2Pt$ requires C, 45.2; H, 7.11; N, 1.95%). $^{31}P\{-^1H\}$ NMR, δ 5.86 ppm. [$J(PPt)$ 3458 Hz].

3.9.2. With $HgCl_2$

After addition of $HgCl_2$ (g, 0.057 mmol) to a stirred solution of $[Pt(dcpam)(PPh_3)]$ (0.05 g, 0.055 mmol) in dichloromethane (20 cm³). The mixture was stirred for a further 2 h. The solvent volume was reduced in vacuo to give a white solid, which was identified by its $^{31}P\{-^1H\}$ NMR spectrum as $[PtCl_2(dcpam)]$.

3.9.3. With CO in ethanol

Carbon monoxide was passed through a stirred suspension of $[Pt(dcpam)(PPh_3)]$ (0.03 g, 0.03 mmol) in ethanol (50 cm³) for 1 h. The solvent was removed in vacuo and the residue was dissolved in acetone. The $^{31}P\{-^1H\}$ NMR spectrum showed the presence only of unchanged starting compound.

4. Crystal data

$Pd(C_{27}H_{51}P_2N)(C_{17}H_{14}O).H_2O$ $M = 808.37$ triclinic space group $P1$, $a = 15.804(15)$, $b = 15.501(17)$, $c = 8.806(32)$ Å, $\alpha = 99.4(2)$, $\beta = 89.2(3)$, $\gamma = 91.4(3)$, $U = 2127.5$ Å³, $Z = 2$, $\mu = 4.79$ cm⁻¹, $\lambda(Mo-K_{\alpha}) = 0.7107$ Å, $F(000) = 858$, $D_c = 1.36$ g cm⁻³.

The crystal used for data collection was a orange rectangular block with the approximate dimensions $0.26 \times 0.13 \times 0.07$ mm³. The crystal was mounted on glass fibre.

Table 2

Fractional atomic co-ordinates and thermal parameters for bis(dicyclohexylphosphinomethane)methylamine dibenzylidene acetonepalladium(0)

Atom	x	y	z	U_{eq}
Pd	0.23683(13)	0.25426(16)	0.18797(29)	0.0330(8)
P(1)	0.1426(5)	0.3508(5)	0.3124(10)	0.055(3)
P(2)	0.3166(5)	0.2330(6)	0.3942(11)	0.062(4)
O(1)	0.3676(11)	0.2963(14)	-0.0872(26)	0.078(10)
O(2)	0.5652(12)	0.4504(13)	0.9276(24)	0.074(6) ^a
N	0.2444(14)	0.3806(15)	0.5651(23)	0.060(10)
C(1)	0.1965(14)	0.2352(16)	-0.0545(27)	0.035(6) ^a
C(2)	0.2768(15)	0.1866(17)	-0.0316(29)	0.041(7) ^a
C(3)	0.3577(18)	0.2242(20)	-0.042(3)	0.053(8) ^a
C(4)	0.4287(16)	0.1764(18)	-0.014(3)	0.048(7) ^a
C(5)	0.5099(18)	0.2004(20)	-0.024(3)	0.062(8) ^a
C(6)	0.1567(18)	0.3793(20)	0.528(3)	0.061(8) ^a
C(7)	0.2789(17)	0.2958(17)	0.581(3)	0.049(7) ^a
C(8)	0.2593(19)	0.4463(20)	0.704(4)	0.070(9) ^a
C(11)	0.5876(11)	0.1602(14)	0.0111(24)	0.077(10) ^a
C(12)	0.5845(11)	0.0896(14)	0.0912(24)	0.059(8) ^a
C(13)	0.6593(11)	0.0553(14)	0.1354(24)	0.071(9) ^a
C(14)	0.7373(11)	0.0915(14)	0.0995(24)	0.068(9) ^a
C(15)	0.7403(11)	0.1621(14)	0.0194(24)	0.088(11) ^a
C(16)	0.6655(11)	0.1965(14)	-0.0248(24)	0.094(11) ^a
C(21)	0.1191(11)	0.1939(13)	-0.0924(23)	0.053(8) ^a
C(22)	0.1001(11)	0.1071(13)	-0.0792(23)	0.080(10) ^a
C(23)	0.0216(11)	0.0699(13)	-0.1267(23)	0.116(14) ^a
C(24)	-0.0378(11)	0.1195(13)	-0.1875(23)	0.124(15) ^a
C(25)	-0.0188(11)	0.2064(13)	-0.2007(23)	0.100(12) ^a
C(26)	0.0596(11)	0.2435(13)	-0.1532(23)	0.088(11) ^a
C(31)	0.0327(15)	0.3110(17)	0.294(3)	0.047(11)
C(32)	0.0223(17)	0.2183(18)	0.332(4)	0.073(15)
C(33)	-0.0661(18)	0.1775(20)	0.303(5)	0.084(16)
C(34)	-0.1315(17)	0.2405(21)	0.384(3)	0.064(14)
C(35)	-0.1210(21)	0.3335(23)	0.351(5)	0.085(17)
C(36)	-0.0325(18)	0.3746(17)	0.382(4)	0.066(13)
C(41)	0.1424(17)	0.4583(16)	0.260(4)	0.051(12)
C(42)	0.2308(20)	0.5045(19)	0.285(4)	0.069(14)
C(43)	0.2277(17)	0.5977(21)	0.239(4)	0.076(15)
C(44)	0.1932(21)	0.5995(21)	0.080(4)	0.077(16)
C(45)	0.1185(19)	0.5510(20)	0.056(4)	0.068(14)
C(46)	0.1144(17)	0.4589(16)	0.096(4)	0.057(14)
C(51)	0.3099(17)	0.1255(18)	0.455(4)	0.058(12)
C(52)	0.2149(21)	0.0894(22)	0.448(5)	0.086(17)
C(53)	0.2130(21)	-0.0012(20)	0.502(4)	0.078(16)
C(54)	0.2679(19)	-0.0660(20)	0.406(4)	0.091(13)
C(55)	0.3656(26)	-0.0301(21)	0.400(5)	0.098(20)
C(56)	0.3627(20)	0.0592(21)	0.342(4)	0.068(14)
C(61)	0.4258(15)	0.2603(16)	0.397(4)	0.055(12)
C(62)	0.4384(18)	0.3544(19)	0.365(4)	0.063(13)
C(63)	0.5294(22)	0.3792(21)	0.343(5)	0.090(18)
C(64)	0.5848(20)	0.3643(28)	0.477(5)	0.107(20)
C(65)	0.5758(19)	0.2696(23)	0.514(4)	0.080(16)
C(66)	0.4789(17)	0.2473(20)	0.534(4)	0.068(14)

^a Isotropic thermal parameter, $U_{eq} = 1/3$ trace of the orthogonalised U .

The unit cell parameters were determined from measurements of oscillation and Weissenberg photographs. All crystals examined were small and did not diffract to high angles. As a result the unit cell parameters could not be redetermined by least squares refinement of omega measurements and have high deviations. The intensities of 5317 unique reflections with $2\theta < 54^\circ$ and $(\pm h, \pm k, \pm l)$ were measured on a Stoe STADI-2 Weissenberg diffractometer, with graphite monochromated Mo K_α radiation using an omega-scan technique. The data were corrected for Lorentz and polarisation effects to yield 1854 reflections with $I > 3\sigma(I)$. The structure was solved using the PATT option of SHELXS86 [10]. All subsequent calculations were carried out using the computer program SHELX-76 [11].

The hydrogen atoms of the water molecule were located on a difference Fourier map and then refined as rigid group. The hydrogen atoms on C(1) and C(2) were not located and were not included in the refinement. All other hydrogen atoms were included in calculated positions ($C-H = 1.08 \text{ \AA}$), with a single fixed isotropic thermal parameter. The atoms Pd, P1, P2, N and O1 and all the cyclohexyl carbon atoms were refined with anisotropic thermal parameters. Owing to the constraint of the small number of significant reflections in the data set all other atoms were refined with isotropic thermal parameters.

Final cycles of refinement employed a weighting parameter $g(0.0058) \{w = 1/[\sigma^2(F) + g(F)^2]\}$ and gave the final residual indices $R\{ = \sum | |F_o| - |F_c| | / \sum |F_o| \}$ 0.086 and $R_w\{ = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \}$ 0.091. The final difference Fourier was featureless and an analysis of the weighting scheme over $|F_o|$ and $\sin \theta/\lambda$ was satisfactory.

The geometry of the molecule is shown in Fig. 1. Atom coordinates are listed in Table 2. A complete list of bond lengths and angles and a table of anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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References

- [1] J. Fawcett, P.A.T. Hoyer, R.D.W. Kemmitt, D.J. Law and D.R. Russell, *J. Chem. Soc., Dalton Trans.*, (1993) 2563.
- [2] A.L. Balch, M.M. Olmstead and S.P. Rowley, *Inorg. Chim. Acta*, 168 (1990) 255.
- [3] F.A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 5th edn., 1988, p. 934.
- [4] G. Markl, G. Yu Jin and C. Schoerner, *Tetrahedron Lett.*, 21 (1980) 1845.
- [5] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet and J.A. Ibers, *J. Organomet. Chem.*, 65 (1974) 253.
- [6] W.J. Cherwinski, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1974) 1405.
- [7] C.G. Pierpont, R.M. Buchanan and H.H. Downs, *J. Organomet. Chem.*, 124 (1977) 103.
- [8] W.A. Herrmann, W.R. Thiel, C. Broßmer, K. Ofele, T. Priemeier and W. Scherer, *J. Organomet. Chem.*, 461 (1993) 51.
- [9] T. Glonek and J.R. Van Wazer, *J. Magn. Reson.*, 13 (1974) 390.
- [10] G.M. Sheldrick SHELXS86 Program for Crystal Structure Solution, University of Göttingen, 1986.
- [11] G.M. Sheldrick SHELX76 Program for Crystal Structure Determination., University of Cambridge, 1976.