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METAL COMPLEXES OF FUNCTIONALIZED PHOSPHINES—II.* SYNTHESIS OF HYDROXYMETHYL- AND AMINOMETHYLDIPHENYLPHOSPHINE COMPLEXES OF PLATINUM. CRYSTAL STRUCTURE OF *cis*-[$PtCl_2(Ph_2PCH_2OH)_2$]

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Abstract—The phosphine Ph_2PCH_2OH reacts with $(COD)PtCl_2$ to form *cis*-[$PtCl_2(Ph_2PCH_2OH)_2$], the structure of which has been determined by X-ray crystallography. Similarly, the phosphines Ph_2PCH_2NHR ($R = Bu^t$, C_6H_4Me-4) react with $(COD)PtCl_2$ to form *cis*-[$PtCl_2(Ph_2PCH_2NHR)_2$], although for $R = C_6H_4Me$-4 this complex is unstable and [$PtCl_2\{(Ph_2PCH_2)_2NR\}$] ($R = C_6H_4Me$-4) is isolated. The complexes [$PtCl_2\{(Ph_2PCH_2)_2NR\}$] can be prepared directly from $(COD)PtCl_2$ and $(Ph_2PCH_2)_2NR$.

In recent years functionalized phosphines containing one or more functional groups of various types have been synthesized and their properties investigated.[2] The ligands Ph_2PCH_2XH (X = O, NR) are formally analogous to the diphosphine $Ph_2PCH_2PPh_2$, which is most commonly found as a bridging ligand rather than as a chelate.[3] To our knowledge there are no examples of Ph_2PCH_2XH (X = O, NR) acting as chelates. This is presumably due to the strain involved in forming a four-membered ring since the related ligands $Ph_2PCH_2CH_2XH$ (X = O, NR) will form chelate complexes when bound to platinum.[1,4] Hydroxymethyldiphenylphosphine has been used as a bridging ligand to form early–late heterobimetallic complexes,[5] whilst aminomethyldiphenylphosphine ligands have also been used to form bimetallic platinum complexes.[6]

In this paper we report the synthesis of some hydroxymethyl- and aminomethyldiphenylphosphine complexes of platinum. Reaction of $(COD)PtCl_2$ with Ph_2PCH_2OH resulted in the formation of *cis*-[$PtCl_2(Ph_2PCH_2OH)_2$] (**1**). This complex has been made previously by hydrolysis of [$PtCl_2\{Ph_2PCH_2OCOMe\}_2$] with HCl.[7] The ^1H NMR spectrum exhibits a multiplet due to the phenyl protons at δ 7.6–7.0 and a broad, unresolved multiplet at δ 4.5, which also has broad platinum satellites and is assigned to the methylene protons. A broad signal at δ 3.9 is assigned to the hydroxyl protons. As pointed out previously the absence of P—CH_2 coupling makes determination of the stereochemistry of these complexes in solution difficult from ^1H NMR data. However, we now report the $^{31}P\{^1H\}$ NMR data which allows unequivocal assignment of stereochemistry. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at δ +7.3, with platinum satellites [J(Pt—P) = 3687 Hz]. The magnitude of the coupling constant indicates that the phosphine ligands are *trans* to chloride, in a mutually *cis* configuration.[8]

A single-crystal X-ray diffraction study of **1** was performed to establish the molecular geometry and whether there was any interaction of the hydroxyl groups with platinum or hydrogen bonding with the chlorides. In $Ni(CN)_2$ complexes of this phosphine there were found to be intermolecular hydrogen bonds between the hydroxyl protons and the nitrogens of cyanides in adjacent molecules.[9] The molecular structure of **1** is illustrated in Fig. 1, together with the crystallographic numbering system. A summary of important bond lengths and angles is

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* For part I see ref. 1.

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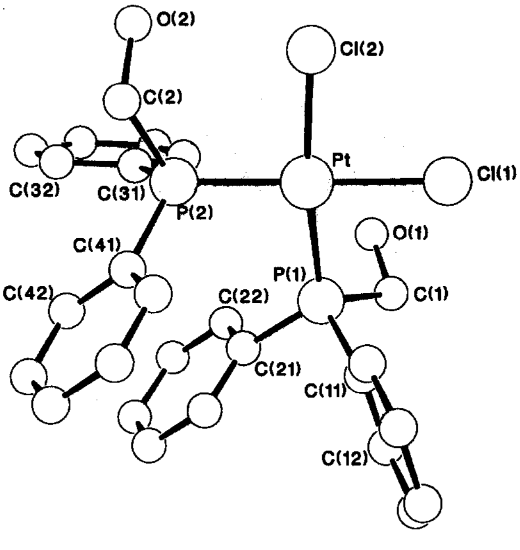
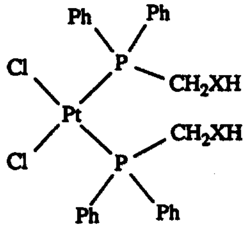


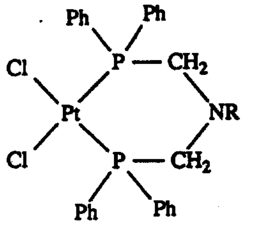
Fig. 1. Molecular structure of *cis*-$[PtCl_2(Ph_2PCH_2OH)_2]$ (**1**).

given in Table 1. The geometry around the platinum is effectively square planar. The molecule exists as the *cis* isomer with the phosphine ligands *trans* to the chloride ligands. The Pt—Cl and Pt—P bond lengths are of a similar magnitude to those reported for *cis*-$[PtCl_2(PPh_3)_2]$,[10] which has average Pt—Cl and Pt—P bond lengths of 2.345(16) and 2.258(10 Å, respectively. The Cl—Pt—Cl and P—Pt—P bond angles are slightly smaller than those recorded for *cis*-$[PtCl_2(PPh_3)_2]$ of 87.1(1)° and 97.8(1)°, respectively. The O(1)—Pt separation of 3.484 Å is too large for any bonding interaction. The hydroxyl hydrogens were located in the difference-Fourier map. The O—H bond lengths are 0.78 [O(1)—H(5)] and 1.39 Å [O(2)—H(6)], respectively. Both these hydrogen atoms have short separations from a chlorine atom. Thus, H(5) is 2.46 Å from a chlorine in an adjacent molecule with an O(1)—H(5)—Cl angle of 164°, both of which are consistent with an intermolecular hydrogen bond. For H(6) the intramolecular distance to Cl(2) is 2.05 Å, which is very short, and the O(2)—H(6)—Cl(2) angle is 123°, suggesting a bent hydrogen bond. This may also explain the rather long O(2)—H(6) bond length mentioned above. Thus, the structure of **1** shows evidence of inter- and intramolecular hydrogen bonding between chlorine atoms and hydroxyl hydrogens.

The reaction of $Ph_2PCH_2NHBu^t$ with (COD) $PtCl_2$ in a 2:1 ratio gave *cis*-$[PtCl_2(Ph_2PCH_2NHBu^t)_2]$ (**2a**). The $^{31}P\{^1H\}$ NMR spectrum of **2a** exhibits a signal at δ +4.0 ppm with platinum satellites [J(Pt—P) = 3710 Hz], consistent with phosphorus coordinated *trans* to chloride; hence, the two phosphorus ligands are in a mutually *cis* configuration. The ^1H NMR spectrum displays a multiplet in the region δ 8.0–7.1 due to the phenyl protons, a multiplet at δ 3.5 due to the methylene protons, as well as signals due to the tert-butyl and N—H protons.



1 X=O
2a X=NBu^t
2b X=NC_6H_4Me-4



3a R=Bu^t
3b R=C_6H_4Me-4

Reaction of $Ph_2PCH_2NHC_6H_4Me$-4 with (COD)$PtCl_2$ gave a mixture of two products, as determined by $^{31}P\{^1H\}$ NMR spectroscopy. It is probable that a signal observed at δ +5.9 [J (Pt—P) = 3693 Hz] is due to *cis*-$[PtCl_2(Ph_2PCH_2$

Table 1. Selected bond lengths (Å) and angles (°) for *cis*-$[PtCl_2(Ph_2PCH_2OH)_2]$

Bond length	(Å)	Bond angle	(°)
Pt—P(1)	2.253(2)	P(2)—Pt—P(1)	96.8(1)
Pt—P(2)	2.249(2)	Cl(2)—Pt—Cl(1)	86.4(1)
Pt—Cl(1)	2.373(2)	Cl(2)—Pt—P(2)	91.1(1)
Pt—Cl(2)	2.358(2)	Cl(2)—Pt—P(1)	172.0(1)
P(1)—C(1)	1.872(10)	Cl(1)—Pt—P(1)	85.8(1)
P(2)—C(2)	1.856(9)	Cl(1)—Pt—P(2)	174.9(1)
C(1)—O(1)	1.385(14)	C(1)—P(1)—Pt	109.7(3)
C(2)—O(2)	1.445(16)	C(2)—P(2)—Pt	115.3(4)
O(1)—H(5)	0.78(11)	P(1)—C(1)—O(1)	108.0(7)
O(2)—H(6)	1.39(11)	P(2)—C(2)—O(2)	113.0(8)

Estimated standard deviations are given in parentheses.

NHC_6H_4Me-4)$_2$] (**2b**), since the chemical shift and size of J(Pt—P) are similar to those found in **2a**. The second signal of δ -6.1 [J(Pt—P) = 3417 Hz] is due to the chelate complex [$PtCl_2\{(Ph_2PCH_2)_2NR\}$] (**3b**), which was identified by comparison of its $^{31}P\{^1H\}$ NMR spectrum with that of an independently prepared sample, see below.

Reaction of (COD)$PtCl_2$ with $(Ph_2PCH_2)_2NR$ (R = Bu^t, C_6H_4Me-4) gave the complexes [$PtCl_2\{(Ph_2PCH_2)_2NR\}$] (**3a,b**). The $^{31}P\{^1H\}$ NMR spectra of **3a** and **3b** each display one signal at δ -5.9 and -6.1, respectively, with J(Pt—P) values of *ca* 3420 Hz. The coupling constant indicates that the phosphine ligands are *trans* to chloride, i.e. in a mutually *cis* configuration. The reduction in magnitude of J(Pt—P) going from complexes **2** to complexes **3** containing a six-membered chelate ring, is consistent with related platinum complexes containing diphenylphosphinoalkyl ligands.[11] The ^1H NMR spectra of **3a** and **3b** display broad multiplets at δ 3.4 and 3.9, respectively, due to the methylene protons, and signals due to the phenyl groups, Bu^t and C_6H_4Me-4, respectively.

The conversion of *cis*-[$PtCl_2(Ph_2PCH_2NHC_6H_4Me$-4)$_2$] (**2b**) to *cis*-[$PtCl_2\{(Ph_2PCH_2)_2NC_6H_4Me-4\}$] (**3b**) is in contrast to the previous reaction of $Ph_2PCH_2NHBu^t$ when only the non-chelate complex *cis*-[$PtCl_2(Ph_2PCH_2NHBu^t)_2$] (**2a**) is formed. The difference in reactivity of the two ligands is unlikely to be due to their nucleophilicity since Bu^t is the more nucleophilic, but it may be that the electron-withdrawing C_6H_4Me-4 group activates the α-C towards nucleophilic attack. It is interesting that complex **3a** can also be formed by refluxing **2a** in toluene with aqueous formaldehyde for 24 h. A similar transformation has been reported for the analogous *cis*-[$Mo(CO)_4(Ph_2PCH_2NHR)_2$] complexes.[12]

Further studies are in progress to investigate the effect of substituents on the reactivity of the phosphines and also the use of complexes **1** and **2a** as precursors to bimetallic species.

EXPERIMENTAL

Petroleum ether and toluene were all dried by refluxing over purple sodium/benzophenone in a nitrogen atmosphere. Dichloromethane was purified by refluxing over calcium hydride. The phosphines[12] and (COD)$PtCl_2$[13] were prepared by the literature methods. The syntheses of phosphorus-containing compounds were performed in deoxygenated solvents under a nitrogen atmosphere. Once isolated as pure solids, all new phosphine compounds are relatively air-stable and precautions for their storage are unnecessary.

^1H NMR spectra were recorded on a Bruker AM300 or Varian EM390 spectrometer as $CDCl_3$ solutions with internal $SiMe_4$ as a reference. $^{31}P\{^1H\}$ NMR spectra were recorded on a Jeol FX60 instrument at 24.15 MHz in CH_2Cl_2 solution and were referenced to external 85% H_3PO_4 with shifts to high frequency being positive. Microanalyses were performed by Butterworth Laboratories Ltd, Middlesex.

Reaction of (COD)$PtCl_2$ *with* Ph_2PCH_2OH

A mixture of Ph_2PCH_2OH (819 mg, 3.79 mmol) and (COD)$PtCl_2$ (650 mg, 1.79 mmol) in dichloromethane (50 cm^3) was stirred for 0.5 h at room temperature, after which time the solvent was removed under vacuum giving a white solid. The solid was crystallized from dichloromethane and petroleum ether to give white crystals of *cis*-[$PtCl_2(Ph_2PCH_2OH)_2$] (**1**) (1.6 g, 85%). Found: C, 44.5; H, 3.7. Calc. for $C_{26}H_{26}Cl_2O_2P_2Pt$: C, 44.7; H, 3.7%. ^1H NMR ($CDCl_3$): δ3.9 (s, br, 2H, OH), 4.5 (m, 4H, CH_2), 7.3 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR: +7.3 [J(Pt—P) 3687 Hz].

Reaction of (COD)$PtCl_2$ *with* $Ph_2PCH_2NHBu^t$

A solution of (COD)$PtCl_2$ (750 mg, 2.0 mmol) in dichloromethane (40 cm^3) was added to a solution of $Ph_2PCH_2NHBu^t$ (0.99 mg, 4.05 mmol) in toluene (4 cm^3). The mixture was stirred for 0.5 h at room temperature, after which time the solvent was removed under vacuum to give a pale yellow solid. Crystallization of the solid from dichloromethane and petroleum ether afforded pale yellow crystals of *cis*-[$PtCl_2(Ph_2PCH_2NHBu^t)_2$] (**2a**) (1.11 g, 69%). Found: C, 50.6; H, 5.6; N, 3.2. Calc. for $C_{34}H_{44}Cl_2N_2P_2Pt$: C, 50.5; H, 5.5; N, 3.5%. ^1H NMR ($CDCl_3$): δ1.00 (s, 18H, Bu^t), 2.00 (s, br, 2H, NH), 3.50 (m, 4H, CH_2), 7.5 (m, 20H, Ph). $^{31}P\{^1H\}$ NMR: +4.0 [J(Pt—P) 3711 Hz].

Reaction of (COD)$PtCl_2$ *with* $Ph_2PCH_2NHC_6H_4Me$-4

A mixture of $Ph_2PCH_2NHC_6H_4Me$-4 (461 mg, 1.51 mmol) and (COD)$PtCl_2$ (221 mg, 0.59 mmol) in dichloromethane (50 cm^3) was stirred for 1 h at room temperature, after which time the solvent was removed under vacuum affording a white solid. The solid consisted of a mixture of two complexes, as determined by $^{31}P\{^1H\}$ NMR spectroscopy, *cis*-[$PtCl_2(Ph_2PCH_2NHC_6H_4Me$-4)$_2$] (**2b**), $^{31}P\{^1H\}$ NMR +5.9 [J(Pt—P) 3693 Hz], and [$PtCl_2\{(Ph_2PCH_2)_2NC_6H_4Me-4\}$] (**3b**) (see below).

Reaction of $(COD)PtCl_2$ *with* $(Ph_2PCH_2)_2NR$ ($R = Bu^t$, C_6H_4Me-4)

A mixture of $(COD)PtCl_2$ (200 mg, 0.54 mmol) and $(Ph_2PCH_2)_2NBu^t$ (251 mg, 0.54 mmol) in dichloromethane (50 cm^3) was stirred for 1 h, after which time the solvent was removed under vacuum giving a white solid. The solid was crystallized from dichloromethane and petroleum ether affording white crystals of $[PtCl_2\{(Ph_2PCH_2)_2NBu^t\}]$ (**3a**) (313 mg, 79%). Found: C, 45.9; H, 4.3; N, 1.8. Calc. for $C_{30}H_{33}Cl_2NP_2Pt\cdot(CH_2Cl_2)$: C, 45.3; H, 4.3; N, 1.7%. ^1H NMR ($CDCl_3$): δ0.8 (s, 9H, Bu^t), 3.4 (m, 4H, CH_2), 7.6 (m, 20H, Ph). $^{31}\{^1H\}$ NMR: -5.9 [J(Pt—P) 3428 Hz].

Using a similar procedure starting from $(COD)PtCl_2$ (100 mg, 0.27 mmol) and $(Ph_2PCH_2)_2NC_6H_4Me$-4 (140 mg, 0.28 mmol) gave, after crystallization from dichloromethane and petroleum ether, $[PtCl_2\{(Ph_2PCH_2)_2NC_6H_4Me\text{-}4\}]$ (**3b**) as white crystals (153 mg, 74%). Found: C, 45.2; H, 3.4; N, 1.5. Calc. for $C_{33}H_{31}Cl_2NP_2Pt\cdot(2CH_2Cl_2)$: C, 44.8; H, 3.8; N, 1.5%. ^1H NMR ($CDCl_3$): δ2.2 (s, 3H, Me), 3.9 (m, 4H, CH_2), 7.5 (m, 24H, Ph). $^{31}P\{^1H\}$ NMR: -6.1 [J(Pt—P) 3418 Hz].

Crystal structure determination

Crystal data for *cis*-$[PtCl_2(Ph_2PCH_2OH)_2]$ (**1**). $M = 698.4$. Monoclinic, space group $P2_1/n$, $a = 17.452(5)$, $b = 15.878(5)$, $c = 9.379(6)$ Å, $\beta = 100.1(1)°$, $U = 2559$ Å^3, $z = 4$, $\mu = 55.89$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $F(000) = 1360$, $D_c = 1.81$ g cm^{-3}. Crystal dimensions $0.08 \times 0.1 \times 0.2$ mm.

The crystal used for data collection was mounted in air and the unit cell parameters were determined by least-squares refinement of ω-measurements of different layers.[14] Data were collected on a Stöe STADI-2 diffractometer with an ω-scan technique in the range $7° < 2\theta < 60°$. The intensities of 4935 unique reflections were measured and these data were corrected for Lorentz and polarization effects to give 4706 unique reflections with $I > 3\sigma(I)$. The structure was solved by conventional Patterson techniques using SHELXS-86 and all subsequent calculations were performed with the computer programme SHELX-76.[15] Scattering factors were taken from ref. 16. An absorption correction was applied to the data, the maximum and minimum transmission factors being 0.7484 and 0.6443, respectively. The phenyl rings were included as rigid groups with D_{6h} symmetry and C—C distances of 1.395 Å. All hydrogen atoms were included in calculated positions (C—H = 0.95 Å) and refined with group isotropic thermal parameters, with the exception of the two hydroxyl hydrogen atoms which were located in a difference-Fourier map and their positional coordinates and isotropic parameters were refined. All non-hydrogen atoms were refined anisotropically. Final cycles of refinement employed a weighting factor w calculated from $w = k/(\sigma^2F + gF^2)$, where $k = 0.95$ and $g = 0.0047$, and gave final values of $R = 0.0580$ and $R_w = 0.0627$.

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