Hydrophosphination of Formaldehyde catalysed by Tris(hydroxymethyl)phosphine Complexes of Platinum, Palladium or Nickel

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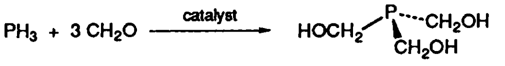
The addition of PH_3 to formaldehyde to give $P(CH_2OH)_3$ is catalysed by a range of platinum-(IV), -(II) and -(0) compounds including $Na_2[PtCl_6]$, $K_2[PtCl_4]$, $[PtCl_2\{P(CH_2OH)_3\}_2]$ **2** and $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ **3**. A large ratio of $P(CH_2OH)_3$ to Pt is present under the conditions in which the catalysis is operated and the hypothesis that a common platinum–$P(CH_2OH)_3$ complex is present under these conditions has been tested. It is shown that $Na_2[PtCl_6]$ is reduced by 3 equivalents of $P(CH_2OH)_3$ to give $[PtCl_2\{P(CH_2OH)_3\}_2]$ **2**, the same species that is formed upon addition of 2 equivalents of $P(CH_2OH)_3$ to $K_2[PtCl_4]$. Addition of 1 equivalent of $P(CH_2OH)_3$ to **2** gives $[PtCl\{P(CH_2OH)_3\}]_3Cl$ **4a** while addition of 2 equivalents of $P(CH_2OH)_3$ to **2** gives an unstable species, tentatively assigned the five-co-ordinate structure $[PtCl\{P(CH_2OH)_3\}_4]Cl$ **5a**. In the presence of further $P(CH_2OH)_3$, **5a** decomposes smoothly to give a mixture of $[PtH\{P(CH_2OH)_3\}_4]Cl$ **3b**, $[P(CH_2OH)_4]Cl$ and the unusual bis(chelate) salts *trans*- and *cis*-$[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ **6a** and **6b**. A mechanism rationalising this reaction is presented. The pH of the reaction medium during the catalysis is *ca*. 9–10 and it is therefore concluded that $[Pt\{P(CH_2OH)_3\}_4]$ **3a** is the main platinum-containing species present during all the platinum catalysed reactions. It is shown that $[Ni\{P(CH_2OH)_3\}_4]$ **18** and $[Pd\{P(CH_2OH)_3\}_4]$ **19** are also catalysts for the hydrophosphination of formaldehyde and a general mechanism is suggested.

In 1958 it was reported[1] that various platinum compounds {*e.g.* $PtCl_2$, $PtCl_4$, $K_2[PtCl_4]$, $Na_2[PtCl_6]$} catalysed the addition of PH_3 to CH_2O to give tris(hydroxymethyl)phosphine **1** [equation (1)]. This reaction attracted our attention because (*i*) it is a homogeneously catalysed addition of a P–H to a C=O bond (*i.e.* the hydrophosphination of formaldehyde); (*ii*) it takes place in water; (*iii*) since the product **1** is known[2–4] to be an excellent ligand for platinum, it was almost certain that water-soluble platinum complexes of **1** were the catalytically active species. In this paper we report our observations on this reaction, discuss the nature of the catalytically active species and suggest a mechanism.


(1)

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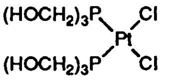
Results and Discussion

In the original procedure[1] for adding PH_3 to CH_2O [equation (1)], a range of platinum-(II) and -(IV) complexes were used as the catalyst precursors. We have shown[4] that with $K_2[PtCl_4]$ as the catalyst, $P(CH_2OH)_3$ **1** can be made very efficiently on a 50 gram scale. We now report that the platinum complexes $[PtCl_2\{P(CH_2OH)_3\}_2]$ **2** and $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ (previously characterised[4] as the equilibrium mixture of **3a** and **3b** in solution [equation (2)]) are also catalyst precursors for this reaction [equation (1)]. It therefore appears that platinum compounds in a variety of oxidation states (IV, II or 0) can function as catalyst precursors. The hypothesis that a common platinum-containing catalyst was present in all of these reactions was probed as described below.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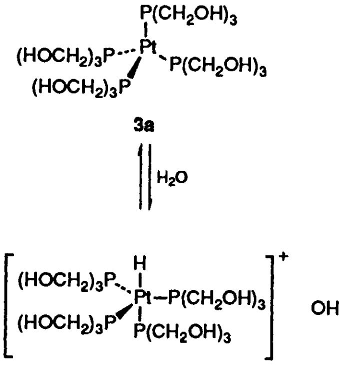


(2)

Under the conditions used, the final mole ratio of product to catalyst is *ca*. 400:1 and therefore the platinum species are in the presence of an excess of $P(CH_2OH)_3$ **1** from the early stages of the reaction. This prompted us to investigate the reaction between platinum-(IV) and -(II) catalyst precursors and an excess of **1**. When aqueous solutions of $Na_2[PtCl_6]$, $K_2[PtCl_4]$, $PtCl_2$ or $[PtCl_2\{P(CH_2OH)_3\}_2]$ were treated with an excess of **1**, the previously reported[4] hydridoplatinum complex $[PtH\{P(CH_2OH)_3\}_4]^+$ **3b** was identified by $^{31}P-\{^1H\}$ NMR spectroscopy as a common product. We have investigated in more detail the complex series of reactions that must have taken place to produce **3b** under these conditions. As would be

Table 1 Phosphorus-31[a] and ^{195}Pt[b] NMR data

Compound	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_X)$	$^1J(PtP_X)$	$^2J(P_AP_X)$	δ(Pt)
1	−24.0					
3b[c]	−11.6	1824	−5.5	2653	29	
4	16.4	3357	16.4	2256	20	−343
5a[d]	10.5	2252				
5b[e]	−30.1	2465				
6a	69.1	2266	169.8	2275	16	520[f]
6b	69.7	2141	167.6	2402	247	522[f]
14a	78.8		184.5		22	
14b	79.8		182.4		254	

[a] Spectra (36.2 MHz) measured in D_2O at 28 °C unless otherwise stated. Chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. Coupling constants (J) in Hz (±3). [b] Spectra (19.2 or 107.0 MHz) measured at 27 °C in D_2O unless stated otherwise. Chemical shifts (δ) in ppm (±0.5) to high frequency of Ξ(Pt) = 21.4 MHz. Coupling constants (J) in Hz (±10). [c] Ref. 4. [d] In CD_3OD at −80 °C. [e] Ref. 6. [f] These are data for the corresponding tetraphenylborates **6c** and **6d** and were measured in CD_3CN.

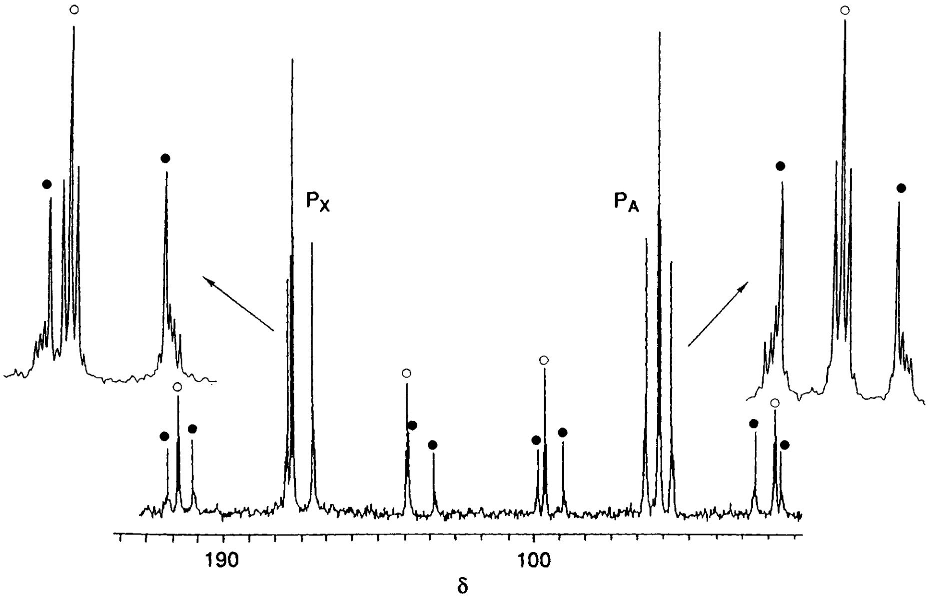


Fig. 1 Phosphorus-31 NMR spectrum (36.2 MHz) of the mixture of salts **6a** (○) and **6b** (●)

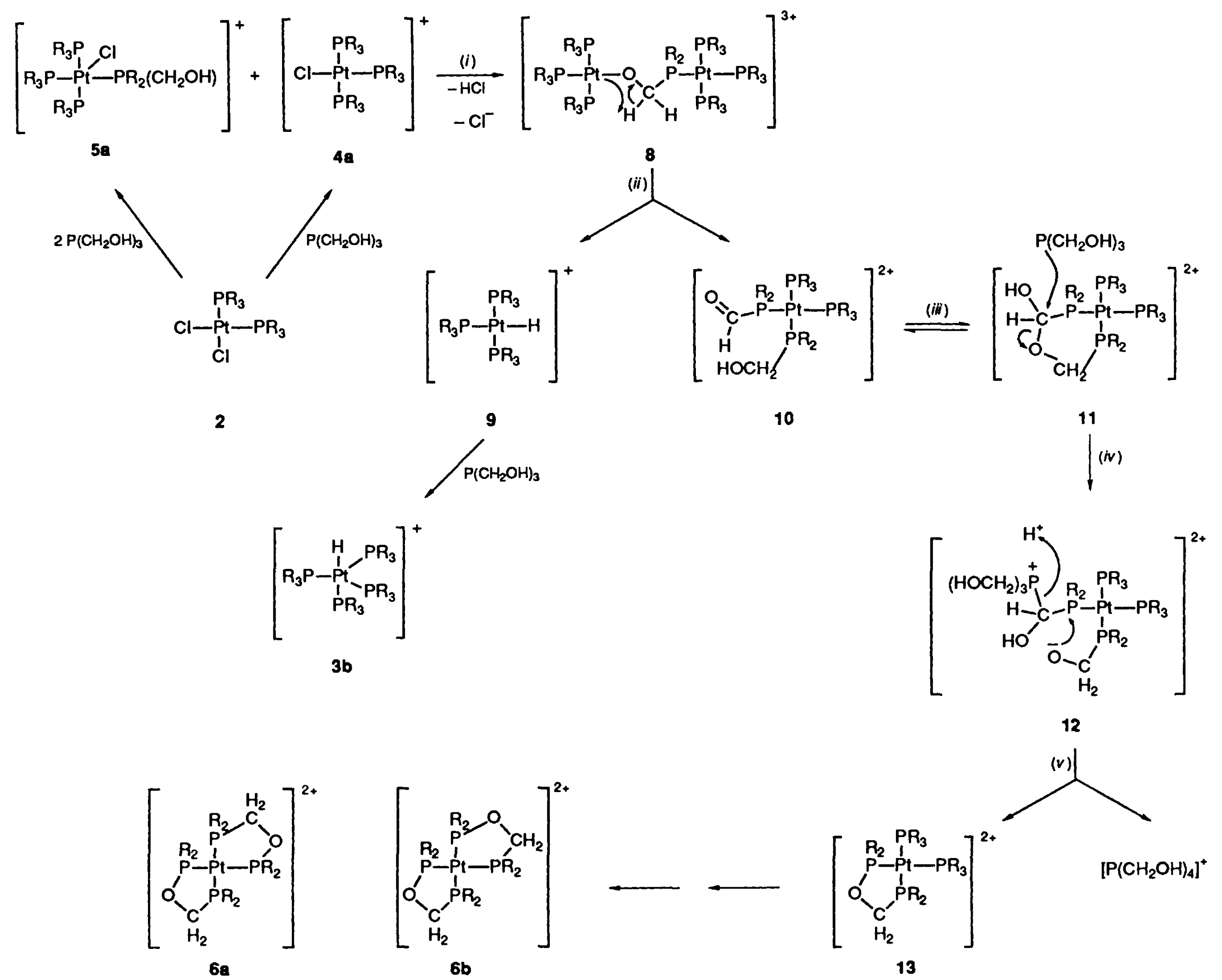
expected of a trialkylphosphine,[5] $P(CH_2OH)_3$ **1** reduces the platinum(IV) in $Na_2[PtCl_6]$ to give the platinum(II) complex $[PtCl_2\{P(CH_2OH)_3\}_2]$ **2** and the oxide $PO(CH_2OH)_3$ stoichiometrically [equation (3)]; the same platinum(II) complex **2** is formed upon addition of 2 equivalents of **1** to $K_2[PtCl_4]$.[3] Therefore the discussion of how all the various platinum compounds are transformed into $[PtH\{P(CH_2OH)_3\}_4]^+$ **3b** reduces to a discussion of the reaction of **2** with phosphine **1**.

$$Na_2[PtCl_6] + 3P(CH_2OH)_3 + H_2O \longrightarrow \underset{\textbf{2}}{[PtCl_2\{P(CH_2OH)_3\}_2]} + PO(CH_2OH)_3 + 2HCl + 2NaCl \quad (3)$$

Treatment of complex **2** with 1 equivalent of phosphine **1** in water gave the cationic complex $[PtCl\{P(CH_2OH)_3\}_3]Cl$ **4** which can be unambiguously identified from its characteristic $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ NMR spectra (see Table 1).

Addition of 2 equivalents of ligand **1** to **2** in methanol gives a yellow species whose ^{31}P NMR spectrum at −80 °C is a broad singlet ($w_{\frac{1}{2}}$ 35 Hz) with ^{195}Pt satellites. As the temperature is raised, this signal broadens further (at −50 °C, $w_{\frac{1}{2}}$ 300 Hz) and then resharpens until at room temperature only a broad singlet ($w_{\frac{1}{2}}$ 58 Hz) is observed and the ^{195}Pt satellites are lost, indicating that intermolecular phosphine exchange is rapid on the NMR time-scale. This new species presumably has composition $PtCl_2\{P(CH_2OH)_3\}_4$ and we tentatively assign it a five-co-ordinate structure $[PtCl\{P(CH_2OH)_3\}_4]Cl$ **5a** because of the similarity of its ^{31}P spectral parameters to the previously reported[6] $[PtCl(PMe_3)_4]Cl$ **5b** (see Table 1); **5b** is also reported to undergo intermolecular phosphine exchange rapidly on the NMR time-scale. Further characterisation of **5a** was not attempted because, unlike $[PtCl(PMe_3)_4]Cl$ **5b**, complex **5a** decomposes at room temperature in aqueous or methanolic solution, particularly in the presence of an excess of phosphine **1** to give a mixture of products which have been fully characterised as described below.

When complex **2** is treated with 3 or more equivalents of **1** in water three products are observed by $^{31}P-\{^1H\}$ NMR spectroscopy: $[P(CH_2OH)_4]^+$, $[PtH\{P(CH_2OH)_3\}_4]^+$, and the isomers of the bis(chelate) dicationic species **6a** (*trans*) and **6b** (*cis*). When this reaction is carried out in methanol, the same products are formed but **6a** and **6b** crystallise from the reaction mixture. The identity of **6a** and **6b** was deduced from the following observations. (*i*) The $^{31}P-\{^1H\}$ NMR spectrum is particularly diagnostic: there are two overlapping $[AX]_2$ patterns, one has triplets and is assigned to the *trans* isomer **6a** and the other is more complex and is assigned to the *cis* isomer **6b** (see Fig. 1 and Table 1). (*ii*) Addition of $Na[BPh_4]$ to an aqueous solution of **6a** and **6b** gave a precipitate of the tetraphenylborate salts **6c** and **6d** for which the $^{31}P-\{^1H\}$ NMR



Scheme 1 Proposed mechanism for the reaction of $P(CH_2OH)_3$ with $[PtCl_2\{P(CH_2OH)_3\}_2]$ (R = CH_2OH or CH_2OCH_2OH)

spectra are almost identical to those of the chlorides. (*iii*) Elemental analyses (C, H and Cl) are consistent for the chlorides and the tetraphenylborate salts. (*iv*) The $^{195}Pt\text{-}\{^1H\}$ NMR spectrum shows two signals one of which is a triplets of triplets, assigned to **6b**, and the other a quintet [because the two $J(PtP)$ values are almost the same] assigned to **6a** (see Table 1). In an attempt to isolate the bidentate phosphine–phosphinite ligand $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ **7**, the mixture of salts **6a** and **6b** was treated with an excess of KCN in water but only $P(CH_2OH)_3$ and $PO(H)(CH_2OH)_2$ were identified as the products, indicating that under these conditions the phosphine–phosphinite ligand **7** was hydrolysed rapidly.

The stoichiometry of the reaction of **1** with $[PtCl_2\{P(CH_2OH)_3\}_2]$ is as shown in equation (4) and the $^{31}P\text{-}\{^1H\}$

$$3[PtCl_2\{P(CH_2OH)_3\}_2] + 8P(CH_2OH)_3 \longrightarrow \underset{\mathbf{3b}}{2[PtH\{P(CH_2OH)_3\}_4]Cl} + \underset{\mathbf{6a}\text{ and }\mathbf{6b}}{[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2} + 2[P(CH_2OH)_4]Cl \quad (4)$$

NMR spectrum of the reaction mixture shows that no other phosphorus-containing products are formed; the reaction is therefore remarkably specific. A mechanism consistent with our observations is shown in Scheme 1. The alcohol protons of co-ordinated $P(CH_2OH)_3$ are acidic[4] which supports the hypothesis that step (*i*) in the mechanism is the formation of a binuclear platinum alkoxide **8** derived from the deprotonation of a co-ordinated $P(CH_2OH)_3$. Platinum(II) alkoxides are known to be unstable[7] with respect to β-hydrogen elimination and thus it is suggested that the next step [step (*ii*)] is β-hydrogen elimination from **8** to generate the four-co-ordinate hydride **9** and the aldehyde–phosphine complex **10**; complex **9** then reacts with a further equivalent of $P(CH_2OH)_3$ to give one of the observed products **3b**. We have observed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy that free or co-ordinated $P(CH_2OH)_3$ readily forms adducts with formaldehyde and therefore we suggest that aldehyde **10** will reversibly form the cyclic adduct **11** [step (*iii*)]. Nucleophilic attack by external $P(CH_2OH)_3$ on the aldehyde carbon in the dication **11** would give **12** [step (*iv*)] and then a ring-closure reaction with concomitant proton capture [step (*v*)] would give one of the observed products $[P(CH_2OH)_4]^+$ and the chelate **13**. If steps (*i*)–(*v*) are repeated with **13** replacing **5** in step (*i*) and intermediates **8**–**13** having the chelating ligand **7** present instead of two $P(CH_2OH)_3$ ligands, the formation of the observed bis(chelates) **6a** and **6b** and the stoichiometry of this reaction [equation (4)] is explained.

A similar reaction takes place between $[PdCl_2\{P(CH_2OH)_3\}_2]$ and an excess of phosphine **1**; the bis(chelates) **14a**, **b** and the corresponding tetraphenylborates **14c**, **d** have been isolated and fully characterised (see Table 1 and Experimental section).

We have thus shown that $[PtH\{P(CH_2OH)_3\}_4]^+$ is the common platinum-containing species formed when platinum-

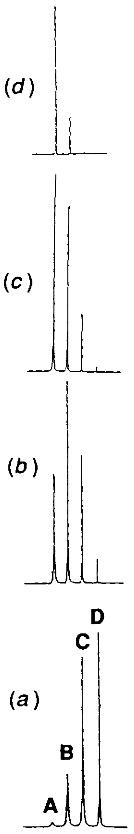
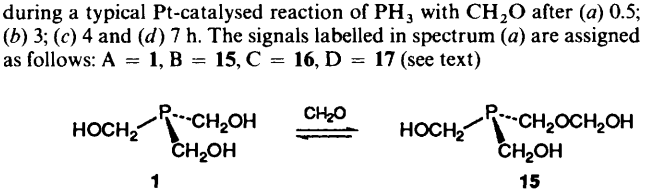


Fig. 2 Phosphorus-31 NMR spectra (162 MHz) of aliquots taken during a typical Pt-catalysed reaction of PH_3 with CH_2O after (*a*) 0.5; (*b*) 3; (*c*) 4 and (*d*) 7 h. The signals labelled in spectrum (*a*) are assigned as follows: A = **1**, B = **15**, C = **16**, D = **17** (see text)



Scheme 2 Hemiacetals formed between $P(CH_2OH)_3$ and CH_2O

(0), -(II) or -(IV) compounds are present under the conditions in which the catalysis operates.

Catalytic Hydrophosphination with $[M\{P(CH_2OH)_3\}_4]$.—The reaction of PH_3 with CH_2O to give $P(CH_2OH)_3$ is a difficult reaction to study quantitatively for the following reasons. (1) The process is kinetically complicated because it involves three consecutive reactions [equations (5)–(7)].

$$PH_3 + CH_2O \longrightarrow PH_2(CH_2OH) \qquad (5)$$

$$PH_2(CH_2OH) + CH_2O \longrightarrow PH(CH_2OH)_2 \qquad (6)$$

$$PH(CH_2OH)_2 + CH_2O \longrightarrow P(CH_2OH)_3 \qquad (7)$$

(2) The reaction medium changes during the course of the reaction from 38% w/w CH_2O solution in water at the beginning to a 50% w/w $P(CH_2OH)_3$ in water at the end; further, the pH of the reaction medium varies from *ca.* 5 to 9 during the reaction (see below). The rate of uptake of PH_3 was observed gradually to increase as the reaction ensued and then decrease again as the reaction approached completion. This may be because the PH_3 is more soluble in aqueous $P(CH_2OH)_3$ than CH_2O.

(3) The reaction was followed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy but under the conditions used we did not detect PH_3, $PH_2(CH_2OH)$ or $PH(CH_2OH)_2$ in solution which suggests that the reactions depicted in equations (5)–(7) are rapid and the rate is therefore strongly dependent on the concentration of dissolved PH_3 (which will depend on the rate of stirring as well as the solubility).

(4) In all the catalyses studied four ^{31}P NMR signals were detected at δ −24.5, −28.7, −33.0 and −37.6 (see Fig. 2); the signal at δ −24.5 can be definitely assigned to $P(CH_2OH)_3$ and the others, which are observed when CH_2O is added to $P(CH_2OH)_3$ **1**, are assigned[8] to the hemiacetals **15**–**17**, shown in Scheme 2. This introduces a further complication to this system: are we following the reaction of $PH_n(CH_2OH)_{3-n}$ with CH_2O, the reaction of $PH_n(CH_2OH)_{3-n}$ with the formaldehyde adducts of $P(CH_2OH)_3$ **15**–**17** or a mixture of all of these reactions?

Hence, for a combination of reasons, our experiments were qualitative and aimed at comparing the relative efficacy of the catalysis.

The relative proportions of **1** and the hemiacetals **15**–**17** is controlled by the concentration of formaldehyde: early in the reaction, when the concentration of formaldehyde is high, the proportion of **17** is high and of **1** low but as the reaction proceeds this situation gradually inverts (see Fig. 2). Hence we were able to follow the progress of the reaction by monitoring the rise and fall of these ^{31}P NMR signals.

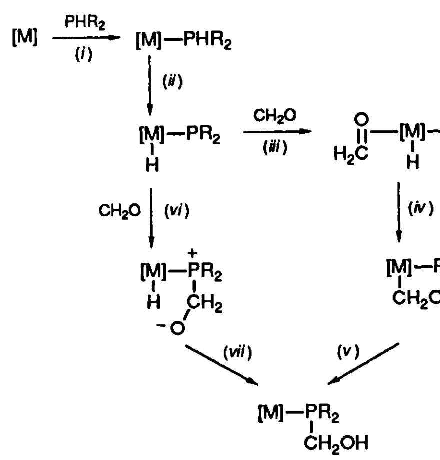
The reaction is catalysed in the presence of the nickel(0) complex $[Ni\{P(CH_2OH)_3\}_4]$ **18** but this was the slowest of all the complexes tested. Recently a nickel–amine complex was also reported to catalyse this reaction.[9]

Similarly the palladium(0) complex $[Pd\{P(CH_2OH)_3\}_4]$ **19** is a catalyst precursor for the reaction and under similar conditions the reaction proceeded *ca.* 10 times faster than in the presence of the nickel analogue, **18**. The palladium(II) compound $Na_2[PdCl_4]$ is not a catalyst precursor, in sharp contrast to $K_2[PtCl_4]$ (see above). This difference in behaviour is explained by the observation that, under the reaction conditions used, $Na_2[PdCl_4]$ is rapidly reduced to palladium metal whereas $K_2[PtCl_4]$ is not reduced to platinum metal.

The platinum complex $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ **3** is similar to the palladium complex **19** in efficiency for the catalysis. Addition of liquid mercury to the reaction mixture had neglible effect on the observed rate of catalysis with **3**, indicating that the catalysis is truly homogeneous.[10]

Since the platinum(0) species **3a** is in equilibrium with the protonated species **3b** [equation (2)], we attempted to measure whether pH has an effect on the rate of reaction by buffering the aqueous solution (see Experimental section). However it was found that the pH of the reaction media always rose to *ca.* 9 during the reaction and only when the reaction was complete did the pH return to *ca.* 6–7 (the normal pH of aqueous solutions of **1**). The explanation of this behaviour is that the buffer is overcome by the alkalinity of the mixture of the hemiacetals **15**–**17** formed during the reaction (see above); this proposal was justified by the observation that addition of formaldehyde to aqueous solution of **1** gave solutions of pH *ca.* 9–10. Under the alkaline conditions prevailing during the catalysis, the platinum species will be predominantly in the zero-valent form **3a**.

The catalysis is very efficient giving exclusively $P(CH_2OH)_3$ as the product, with no trace of the isomeric $P(OCH_3)_3$. A mechanism for the hydrophosphination of formaldehyde is proposed in Scheme 3. The nature of [M] is most likely an ML_2 or ML_3 fragment where L is $P(CH_2OH)_3$ or one of the derivatives **15**–**17**. There is literature support for each of the



Scheme 3 Proposed mechanism for the catalysed addition of PH_3 to CH_2O (R = H, CH_2OCH_2OH or CH_2OH)

subsequent suggested steps. Steps (*i*) and (*ii*) are the co-ordination followed by intramolecular oxidative addition of PH_3.[11] There are then two suggested routes: (*a*) the formation of an η^2-formaldehyde complex[12] [step (*iii*)] and then β-hydrogen migration to give a hydroxymethyl complex[13] [step (*iv*)] followed by intramolecular P–C reductive elimination* [step (*v*)]; (*b*) nucleophilic attack by the co-ordinated PR_2 to give a zwitterionic species [step (*vi*)]† followed by intramolecular proton migration [step (*vii*)].

Metal–phosphine based homogeneous catalysts are normally inhibited by the presence of free phosphine ligand because ligand dissociation to generate the active co-ordinatively unsaturated intermediate is generally the key first step in the process.[16] One remarkable feature of the hydrophosphination catalysis described here is that although the reaction product, $P(CH_2OH)_3$, is potentially a powerful inhibitor, the catalyst still functions efficiently.

Experimental

General methods used were similar to those reported in recent papers from this laboratory.[4] The $P(CH_2OH)_3$ complexes used as catalyst precursors have been previously described.[3,4]

Reaction of $K_2[PtCl_4]$ *with* $P(CH_2OH)_3$.—Tris(hydroxymethyl)phosphine (0.143 g, 1.15 mmol, 5.00 equivalents) was added to a solution of $K_2[PtCl_4]$ (0.094 g, 0.23 mmol) in water (1 cm^3). The initially orange solution paled to yellow after *ca.* 5 min, and then after *ca.* 2 h the solution was colourless. Examination of the resulting product by $^{31}P-\{^1H\}$ NMR spectroscopy showed the presence of each of the species shown in equation (3) (see Results and Discussion). Similar reactions were carried out with $PtCl_2$ and $Na_2[PtCl_6]$ (6 equivalents of **1** used) and in each case the products were those shown in equation (2).

Reaction of $[PtCl_2\{P(CH_2OH)_3\}_2]$ **2** *with* $P(CH_2OH)_3$.—One equivalent of $P(CH_2OH)_3$ (0.007 g, 0.056 mmol) was added to a solution of $[PtCl_2\{P(CH_2OH)_3\}_2]$ (0.028 g, 0.054 mmol) in D_2O (0.4 cm^3) and the solution examined by $^{31}P-\{^1H\}$ NMR spectroscopy. The major species was unambiguously identified as $[PtCl\{P(CH_2OH)_3\}_3]Cl$. Addition of 2 equivalents of $P(CH_2OH)_3$ (0.016 g, 0.129 mmol) to $[PtCl_2\{P(CH_2OH)_3\}_2]$ (0.033 g, 0.064 mmol) in CD_3OD (0.4 cm^3) at −80 °C produced a deep yellow solution which was characterised at low temperatures by ^{31}P NMR spectroscopy and assigned the structure $[PtCl\{P(CH_2OH)_3\}_4]Cl$ (see Results and Discussion). Addition of 3 equivalents of $P(CH_2OH)_3$ (0.023 g, 0.185 mmol) to a solution of $[PtCl_2\{P(CH_2OH)_3\}_2]$ (0.032 g, 0.062 mmol) in D_2O (0.4 cm^3) gave a deep yellow solution which gradually paled to colourless over a period of *ca.* 5 h; $^{31}P-\{H\}$ NMR spectroscopy of the colourless solution revealed the presence of the mixture of products shown in equation (3) (see Results and Discussion).

Preparation of trans- *and* cis-$[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ **6a** *and* **6b**.—Tris(hydroxymethyl)phosphine (0.732 g, 5.90 mmol) was added to a solution of $[PtCl_2\{P(CH_2OH)_3\}_2]$ (1.011 g, 1.97 mmol) in methanol (7 cm^3) to give a yellow solution which was stirred for 15 min after which time it had paled and a white solid had formed. The reaction mixture was then left to stand for 16 h and then the solid product was filtered off, washed with methanol (2 × 10 cm^3) and diethyl ether (30 cm^3), and then dried *in vacuo* (0.391 g, 85%). The same product can be made by treating a suspension of $K_2[PtCl_4]$ (0.087 g, 0.210 mmol) in methanol (2 cm^3) with $P(CH_2OH)_3$ (0.130 g, 1.05 mmol) and stirring the mixture for 5 h and then work-up as above yielded **6a**, **b** (0.032 g, 65%) (Found: C, 17.20; H, 4.40; Cl, 10.15. Calc. for **6a**, **b**: C, 17.20; H, 4.05; Cl, 10.10%).

Preparation of trans- *and* cis-$[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2][BPh_4]_2$ **6c** *and* **6d**.—A solution of $NaBPh_4$ (0.114 g, 0.33 mmol) in hot water (2 cm^3) was added to a solution of $[Pt\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ (0.101 g, 0.14 mmol) in water (2 cm^3) to give an off-white precipitate immediately. The mixture was stirred for 30 min and then the product was filtered off and dried *in vacuo* (0.161 g, 87%) (Found: C, 52.20; H, 5.15. Calc. for **6c**, **d**$\cdot 4H_2O$: C, 52.20; H, 5.65%).

Preparation of trans- *and* cis-$[Pd\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ **14a** *and* **14b**.—Tris(hydroxymethyl)phosphine (1.27 g, 10.20 mmol) was added to a solution of $[PdCl_2\{P(CH_2OH)_3\}_2]$ (1.460 g, 3.43 mmol) in methanol (10 cm^3) to give a yellow solution which was stirred for 10 min after which time a white solid had formed. The reaction mixture was stirred for 3 h and then the solid product was filtered off, washed with methanol (2 × 10 cm^3) and diethyl ether (30 cm^3), and then dried *in vacuo* (0.517 g, 74%). The same product can be made by treating a solution of $Na_2[PdCl_4]$ (0.063 g, 0.214 mmol) in methanol (2 cm^3) with $P(CH_2OH)_3$ (0.130 g, 1.05 mmol) and stirring the mixture for 4 h and then work-up as above yields **14a**, **b** (0.027 g, 62%) (Found: C, 19.75; H, 4.90. Calc. for **14a**, **b**: C, 19.70; H, 5.05%).

Preparation of trans- *and* cis-$[Pd\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2][BPh_4]_2$ **14c** *and* **14d**.—A solution of $NaBPh_4$ (0.158 g, 0.46 mmol) in hot water (2 cm^3) was added to a solution of $[Pd\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_2]Cl_2$ (0.123 g, 0.032 mmol) in water (2 cm^3) to give an off-white precipitate immediately. The mixture was then stirred for 30 min and then the product was filtered off and dried *in vacuo* (0.140 g, 60%) (Found: C, 57.20; H, 5.50. Calc. for **14d**$\cdot 2H_2O$: C, 57.45; H, 5.95%).

Catalytic Hydrophosphination Studies.—**CAUTION**: *Phosphine gas is extremely toxic and should only be handled in a well ventilated fume cupboard.* A 500 cm^3 five-necked flask, equipped with a water condenser (topped with a gas outlet to a chemical phosphine-scrubbing system of ammoniacal copper sulfate), a thermometer, rubber septum, gas inlet sintered tube, and a mechanical stirrer was charged with aqueous formaldehyde

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* The microscopic reverse of this reaction, P–C bond cleavage is well known, see for example, ref. 14.

† Nucleophilic attack by a metal–PH_2 complex has been previously observed.[15]

(200 cm^3, 37.5%, *ca.* 2.5 mol). The solution was purged with nitrogen for 30 min and then the catalyst precursor (0.48 mmol) was added and the solution purged for 10 min. The speed of the mechanical stirrer (*ca.* 1200 revolutions min^{-1}) was the highest possible with our apparatus in order to minimise diffusion effects. The temperature of the external bath (+28 °C) was kept as constant as possible throughout all the catalytic runs. Phosphine was admitted at a slow constant rate, sufficient to prevent suck-back. At regular intervals, an aliquot (*ca.* 4 cm^3) was removed and a ^{31}P-{^{1}H} NMR spectrum recorded. At the end of the run, the solution was purged with nitrogen for 30 min before the apparatus was dismantled. The following complexes were studied: $K_2[PtCl_4]$, $Na_2[PdCl_4]$, $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ **3**, $[Ni\{P(CH_2OH)_3\}_4]$ **18**, $[Pd\{P(CH_2OH)_3\}_4]$ **19**. Commercial (BDH) phosphate-based tablets for pH 6.4 and 7.0 were used in the attempts to buffer the reaction mixture for some of the catalytic reactions but in each case, although the pH began at the value of the buffer, as the reaction ensued the pH rose to a value of *ca.* 9 (see Results and Discussion).

Acknowledgements

We should like to thank Mr. J. W. Ellis (Albright and Wilson Ltd.) for measuring some of the ^{31}P NMR spectra, Albright and Wilson and SERC for financial support and Johnson Matthey for a generous loan of platinum compounds.

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Received 7th July 1992; *Paper* 2/03573A