

## Water Soluble, Zero-valent, Platinum-, Palladium-, and Nickel-P(CH<sub>2</sub>OH)<sub>3</sub> Complexes: Catalysts for the Addition of PH<sub>3</sub> to CH<sub>2</sub>O

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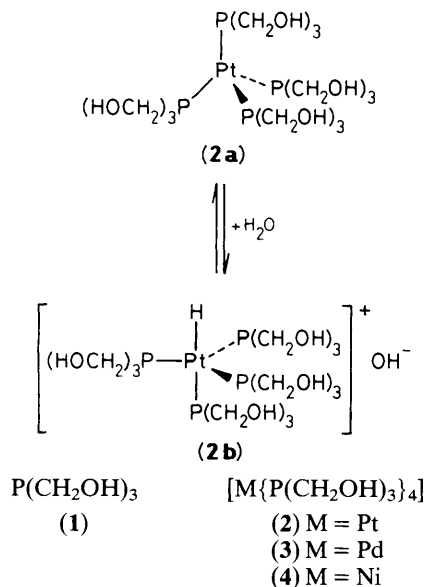
The phosphine P(CH<sub>2</sub>OH)<sub>3</sub> forms water soluble complexes of the type [M{P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>4</sub>] (M = Pt, Pd, or Ni) which are catalysts for the addition of PH<sub>3</sub> to CH<sub>2</sub>O and the Pt complex is readily protonated by water; the crystal structure of the Pd complex is also described.

Water soluble phosphines and their complexes have attracted great interest because of their potential as immobilised homogeneous catalysts.<sup>1,2</sup> Tris(hydroxymethyl)phosphine (**1**) is an unusual trialkylphosphine in being moderately air-stable and water soluble. Surprisingly its co-ordination chemistry has been little studied.<sup>3,4</sup> In this paper we show that (**1**) forms water soluble, zero-valent platinum, palladium, and nickel complexes which are catalysts for the production of the ligand itself from PH<sub>3</sub> and aqueous CH<sub>2</sub>O.

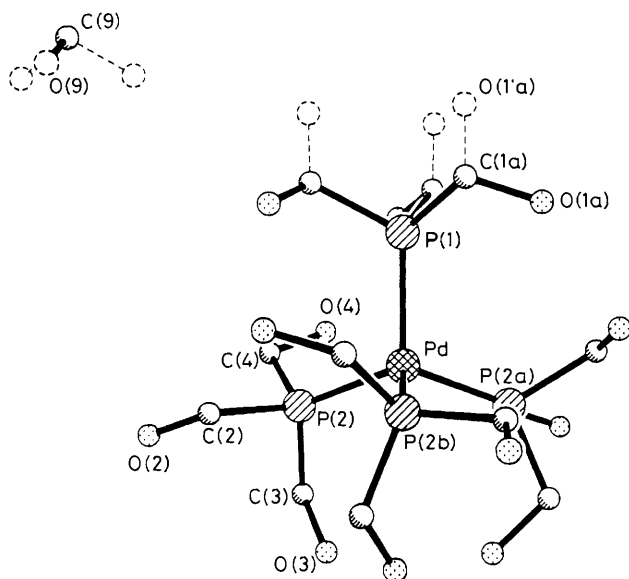
It has been reported<sup>5</sup> that platinum compounds (*e.g.* PtCl<sub>4</sub>) are the best catalysts for the addition of PH<sub>3</sub> to CH<sub>2</sub>O to form P(CH<sub>2</sub>OH)<sub>3</sub>. We have found that treatment of K<sub>2</sub>[PtCl<sub>4</sub>] or Na<sub>2</sub>[PtCl<sub>6</sub>] with an excess of (**1**) in H<sub>2</sub>O gives a platinum complex of composition [Pt{P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>4</sub>·H<sub>2</sub>O (**2**) and the

same species can be made by addition of stoichiometric quantities of (**1**) to the zero-valent complexes [Pt(cod)<sub>2</sub>] (cod = 1,5-cyclo-octadiene) or [Pt(PPh<sub>3</sub>)<sub>4</sub>] in the presence of H<sub>2</sub>O.

Aqueous or alcoholic solutions of (**2**) are equilibrium mixtures of the zero-valent platinum complex (**2a**) and the five-co-ordinate, hydridoplatinum(II) complex (**2b**) (Scheme 1), as indicated by the following spectroscopic observations. There is a distinctive i.r. band at 2103 cm<sup>-1</sup> (in methanol) assigned to ν(PtH). Aqueous solutions of (**2**) are strongly alkaline (10<sup>-2</sup> M solutions have pH 10–11). The <sup>31</sup>P-<sup>1</sup>H} n.m.r. spectrum of (**2**) in D<sub>2</sub>O is a slightly broadened singlet at δ +1.0 p.p.m. with <sup>1</sup>J(PtP) 3202 Hz, but upon addition of one equivalent of aqueous HCl this signal is shifted to -6.5 p.p.m. with <sup>1</sup>J(PtP) 2460 Hz. The low temperature (-78 °C) <sup>31</sup>P-<sup>1</sup>H}



Scheme 1



**Figure 1.** Molecular structure of  $[\text{Pd}\{\text{P}(\text{CH}_2\text{OH})_3\}_4]\cdot\text{MeOH}$  (**3**). Selected bond distances: Pd–P(1) 2.320(2), Pd–P(2) 2.318(1) Å. Selected bond angles: P(1)–Pd–P(2) 108.5(1), P(2)–Pd–P(2a) 110.4(1)°. Hydroxy group on C(1a) suffers a two-fold disorder as illustrated, and the solvent is disordered about a three-fold axis.

n.m.r. spectrum of (**2**) in acidified  $\text{CD}_3\text{OD}$  has an  $\text{AB}_3$  pattern with satellites, confirming the five-co-ordinate structure (**2b**) [ $\delta(\text{P}_A)$   $-5.0$  (d),  $^1J(\text{PtP})$  2670 Hz;  $\delta(\text{P}_B)$   $-12.0$  (q),  $^1J(\text{PtP})$  1809 Hz,  $J(\text{P}_A\text{P}_B)$  30 Hz]. As expected, at ambient temperatures (**2b**) is fluxional; the time-averaged  $^1J(\text{PtP})$  should be 2455 Hz, close to that observed in the acidified solutions, but the much larger  $^1J(\text{PtP})$  values observed in the basic solutions are consistent with the presence of the zero-valent complex (**2a**) in rapid equilibrium with (**2b**) (Scheme 1). Hence complex (**2a**) undergoes protonation by water under mild conditions. Five-co-ordinate complexes of the type  $[\text{HPt}(\text{PR}_3)_4]^+$  are known<sup>6</sup> only for R = Et at  $-137^\circ\text{C}$ , being detected in equilibrium with the more familiar four-co-ordinate species  $[\text{HPt}(\text{PR}_3)_3]^+$ . Ligand (**1**) therefore stabilises the

five-co-ordinate structure (**2b**); we have no evidence for the presence of four-co-ordinate tris(phosphine)platinum(II) hydrides in solutions of (**2**).

The isolated complex (**2**) is a catalyst† for the addition of  $\text{PH}_3$  to  $\text{CH}_2\text{O}$  in water and since (**2**) is the ultimate product of the addition of  $\text{P}(\text{CH}_2\text{OH})_3$  to the  $\text{Pt}^{\text{II}}$  or  $\text{Pt}^{\text{IV}}$  compounds used as catalysts (see above) we conclude that (**2**) is the major species present in all the platinum complex catalysed  $\text{PH}_3$  additions to  $\text{CH}_2\text{O}$ . Clearly further work is necessary to elucidate the  $\text{PH}_3$ ,  $\text{CH}_2\text{O}$ , or  $\text{CH}_2\text{OH}$  complexes that are likely intermediates in this reaction.

The palladium(0) complex (**3**) can be made from  $[\text{Pd}(\text{PPh}_3)_4]$  or  $[\text{Pd}(\text{dba})_2]$  (dba = dibenzylideneacetone) with the stoichiometric amount of ligand (**1**). In contrast to the platinum complex (**2**), aqueous solutions of (**3**) are almost neutral ( $10^{-2}\text{ M}$  solutions have pH 7–8), addition of aqueous HCl had little effect on the  $^{31}\text{P}$  chemical shift, and no Pd–H stretch could be detected in the i.r. spectrum. Hence protonation of (**3**) by water does not take place to an observable extent. The X-ray crystal structure‡ of (**3**)·MeOH confirms the neutral, tetrahedral palladium(0) structure (see Figure 1) and furthermore it can be seen why (**3**) is water soluble; the palladium atom is sheathed by the twelve alcohol groups which present a highly hydrophilic surface to an approaching solvent. To our knowledge this is the first crystal structure of a water soluble palladium(0)–phosphine complex; indeed (**3**) is the first isolated example of such a complex.

Interestingly (**3**) is also a catalyst for the addition of  $\text{PH}_3$  to  $\text{CH}_2\text{O}$ , whereas simple palladium salts (e.g.  $\text{Na}_2\text{PdCl}_4$ ) rapidly decompose to palladium metal under the reaction conditions used. Further catalytic properties for (**3**) are expected.

Finally, preliminary results indicate that the nickel(0) complex (**4**) is formed when phosphine (**1**) is added to  $[\text{Ni}(\text{cod})_2]$  in toluene/methanol. The product is an off-white, air-stable, water soluble solid with microanalytical and spectroscopic properties consistent with the formulation as (**4**); this compound also catalyses the addition of  $\text{PH}_3$  to  $\text{CH}_2\text{O}$ .

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† Catalytic studies were carried out as follows:  $\text{PH}_3$  was bubbled through 37% aqueous formaldehyde ( $100\text{ cm}^3$ ) containing ca.  $10^{-4}$  mol. equiv. of catalyst. The reaction was complete when absorption of  $\text{PH}_3$  ceased.

‡ Crystal data:  $\text{C}_{13}\text{H}_{40}\text{O}_{13}\text{P}_4\text{Pd}$ ,  $M = 634.8$ , trigonal, space group  $R\bar{3}c$  (No. 167);  $a = 10.203(3)$ ,  $c = 86.937(25)$  Å,  $U = 7842(4)$  Å<sup>3</sup>,  $Z = 12$ ,  $D_c = 1.61\text{ g cm}^{-3}$ ,  $F(000) = 3720$  electrons,  $\mu(\text{Mo-K}\alpha) = 9.88\text{ cm}^{-1}$ ,  $\lambda = 0.71069$  Å. The final  $R$  is 0.052 for 1237 unique observed [ $I < 2\sigma(I)$ ] reflections collected at room temperature for  $4 < 2\theta < 50^\circ$  on a Nicolet P3m diffractometer using graphite-monochromated X-radiation for over a quadrant of reciprocal space. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.