Water Soluble, Zero-valent, Platinum–, Palladium–, and Nickel–$P(CH_2OH)_3$ Complexes: Catalysts for the Addition of PH_3 to CH_2O

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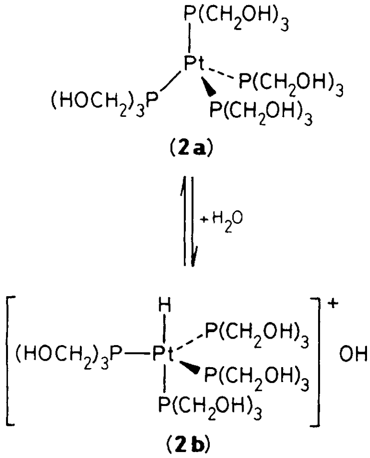
The phosphine $P(CH_2OH)_3$ forms water soluble complexes of the type $[M\{P(CH_2OH)_3\}_4]$ (M = Pt, Pd, or Ni) which are catalysts for the addition of PH_3 to CH_2O and the Pt complex is readily protonated by water; the crystal structure of the Pd complex is also described.

Water soluble phosphines and their complexes have attracted great interest because of their potential as immobilised homogeneous catalysts.[1,2] 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.[3,4] 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_3 and aqueous CH_2O.

It has been reported[5] that platinum compounds (*e.g.* $PtCl_4$) are the best catalysts for the addition of PH_3 to CH_2O to form $P(CH_2OH)_3$. We have found that treatment of $K_2[PtCl_4]$ or $Na_2[PtCl_6]$ with an excess of (**1**) in H_2O gives a platinum complex of composition $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ (**2**) and the same species can be made by addition of stoicheiometric quantities of (**1**) to the zero-valent complexes $[Pt(cod)_2]$ (cod = 1,5-cyclo-octadiene) or $[Pt(PPh_3)_4]$ in the presence of H_2O.

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^{-1} (in methanol) assigned to ν(PtH). Aqueous solutions of (**2**) are strongly alkaline (10^{-2} M solutions have pH 10—11). The ^{31}P-$\{^1H\}$ n.m.r. spectrum of (**2**) in D_2O is a slightly broadened singlet at δ +1.0 p.p.m. with $^1J(PtP)$ 3202 Hz, but upon addition of one equivalent of aqueous HCl this signal is shifted to −6.5 p.p.m. with $^1J(PtP)$ 2460 Hz. The low temperature (−78 °C) ^{31}P-$\{^1H\}$



$P(CH_2OH)_3$
(1)

$[M\{P(CH_2OH)_3\}_4]$
(2) M = Pt
(3) M = Pd
(4) M = Ni

Scheme 1

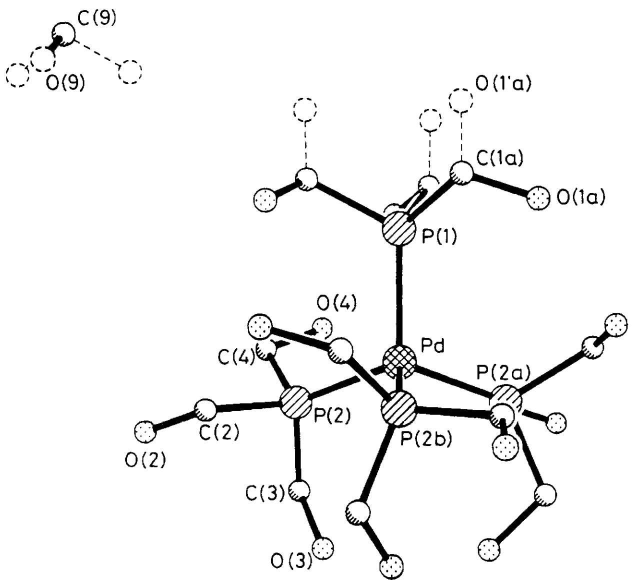


Figure 1. Molecular structure of $[Pd\{P(CH_2OH)_3\}_4]\cdot MeOH$ (**3**). Selected bond distances: Pd–P(1) 2.320(2), Pd–P(2) 2.318(1) Å. Selected bond angles: P(1)–Pd–P(2) 108.5(1), P(2)–Pd–P(2a) 110.4(1)°. Hydroxy group on C(1a) suffers a two-fold disorder as illustrated, and the solvent is disordered about a three-fold axis.

n.m.r. spectrum of (**2**) in acidified CD_3OD has an AB_3 pattern with satellites, confirming the five-co-ordinate structure (**2b**) [$\delta(P_A)$ −5.0 (d), $^1J(PtP)$ 2670 Hz; $\delta(P_B)$ −12.0 (q), $^1J(PtP)$ 1809 Hz, $J(P_AP_B)$ 30 Hz]. As expected, at ambient temperatures (**2b**) is fluxional; the time-averaged $^1J(PtP)$ should be 2455 Hz, close to that observed in the acidifed solutions, but the much larger $^1J(PtP)$ 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 $[HPt(PR_3)_4]^+$ are known[6] only for R = Et at −137 °C, being detected in equilibrium with the more familiar four-co-ordinate species $[HPt(PR_3)_3]^+$. 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 PH_3 to CH_2O in water and since (**2**) is the ultimate product of the addition of $P(CH_2OH)_3$ to the Pt^{II} or Pt^{IV} compounds used as catalysts (see above) we conclude that (**2**) is the major species present in all the platinum complex catalysed PH_3 additions to CH_2O. Clearly further work is necessary to elucidate the PH_3, CH_2O, or CH_2OH complexes that are likely intermediates in this reaction.

The palladium(0) complex (**3**) can be made from $[Pd(PPh_3)_4]$ or $[Pd(dba)_2]$ (dba = dibenzylideneacetone) with the stoicheiometric amount of ligand (**1**). In contrast to the platinum complex (**2**), aqueous solutions of (**3**) are almost neutral (10^{-2} M solutions have pH 7—8), addition of aqueous HCl had little effect on the ^{31}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 PH_3 to CH_2O, whereas simple palladium salts (*e.g.* Na_2PdCl_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 $[Ni(cod)_2]$ 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 PH_3 to CH_2O.

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† Catalytic studies were carried out as follows: PH_3 was bubbled through 37% aqueous formaldehyde (100 cm^3) containing *ca.* 10^{-4} mol. equiv. of catalyst. The reaction was complete when absorption of PH_3 ceased.

‡ *Crystal data*: $C_{13}H_{40}O_{13}P_4Pd$, M = 634.8, trigonal, space group $R\bar{3}c$ (No. 167); a = 10.203(3), c = 86.937(25) Å, U = 7842(4) $Å^3$, Z = 12, D_c = 1.61 g cm^{-3}, $F(000)$ = 3720 electrons, $\mu(Mo\text{-}K_\alpha)$ = 9.88 cm^{-1}, λ = 0.71069 Å. The final R is 0.052 for 1237 unique observed [$I < 2\sigma(I)$] reflections collected at room temperature for $4 < 2\theta < 50°$ 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.