Reduction Chemistry of Hydrido(triethylphosphine) Complexes of Platinum(II) or Palladium(II) and Aqueous Chemistry of Tris(triethylphosphine)palladium(0)

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Sodium or magnesium amalgam reductions of tetrahydrofuran solutions of $[MH(PEt_3)_3][BPh_4]$ (M = Pt or Pd), or of toluene solutions of $[PtH(Cl)(PEt_3)_2]$ in the presence of an excess of PEt_3, produce hydrogen and $[Pt(PEt_3)_3]$ or Pd metal. The mechanism of the reaction is discussed and $[Ru(bipy)_3]^{2+*}$ (bipy = 2,2′-bipyridyl) is shown not to reduce $[PdH(PEt_3)_3]^+$ in aqueous solution. The compound $[Pd(PEt_3)_3]$ dissolves in buffered or acidic water to produce $[PdH(PEt_3)_3]^+$ although it is less nucleophilic than $[Pt(PEt_3)_3]$. In the presence of chloride ion at low pH, $[PdH(Cl)(PEt_3)_2]$ is formed in high yield.

THE current oil crisis has focused the attention of the scientific community upon the need to discover and exploit alternative sources of energy. Amongst these, the storage of solar energy by the photochemical decomposition of water is of considerable interest.

It is now well known[1] that $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl) has excited-state properties which make it a suitable catalyst for the decomposition of water but that, in the absence of further catalysts, neither hydrogen nor oxygen is evolved on irradiating aqueous solutions of $[Ru(bipy)_3]^{2+}$; nor, despite initial claims to the contrary,[2] on irradiating[3-5] monolayers of analogous cationic complexes containing surfactant bipyridyl ligands.

However, in the presence of suitable catalysts, hydrogen can be produced[1] at the expense of a sacrificial reducing agent such as ethylenediaminetetra-acetate (edta) or triethanolamine and a system has recently been reported[6] in which both oxygen and hydrogen (1 : 2 mole ratio) are produced from the same system, although with low efficiency.

In general, hydrogen is produced by a series of reactions in which an electron-transfer catalyst, usually methyl viologen (= 1,1′-dimethyl-4,4′-bipyridinium dichloride),[1] $[Rh(bipy)_3]^{3+}$,[7,8] or an iron–sulphur cluster[9] receives an electron from $[Ru(bipy)_3]^{2+*}$, formed by irradiation of $[Ru(bipy)_3]^{2+}$ with light at 450 nm. The reduced electron-transfer catalyst then reduces protons in the presence of a heterogeneous redox catalyst, such as Pt,[10] PtO_2,[11] Au,[12] RuO_2,[13] or hydrogenase.[14] The $[Ru(bipy)_3]^{3+}$ so formed is then capable[15] of oxidising OH^- to O_2, but this reaction is only sufficiently rapid to compete with back electron transfer from the reduced electron-transfer catalyst if it in turn is catalysed[16] by colloidal RuO_2. In the absence of such a catalyst the hydrogen-producing reaction is driven by removal of $[Ru(bipy)_3]^{3+}$ by the weak reducing agent, edta or triethanolamine. These reactions are outlined for methyl viologen (mv^{2+}) and colloidal RuO_2 in Scheme 1.

The use of heterogeneous redox catalysts leads to problems associated with dispersion and absorption of incident radiation, whilst the use of an electron-transfer catalyst and a redox catalyst causes energy losses associated with multicomponent systems. Furthermore, it has been shown that methyl viologen has a limited lifetime under the reaction conditions, probably because of a platinum-catalysed hydrogenation reaction.[10,17] Very recently, TiO_2 has been used to replace methyl viologen as the electron-transfer catalyst and stable systems of *ca.* 5% efficiency have been produced.[18]

$$[Ru(bipy)_3]^{2+} \xrightarrow{h\nu} [Ru(bipy)_3]^{2+*}$$

$$[Ru(bipy)_3]^{2+*} + mv^{2+} \longrightarrow [Ru(bipy)_3]^{3+} + mv^{+}$$

$$mv^{+} + H^{+} \xrightarrow[\text{catalyst}]{\text{redox}} mv^{2+} + \tfrac{1}{2}H_2$$

$$[Ru(bipy)_3]^{3+} + OH^{-} \xrightarrow{RuO_2} [Ru(bipy)_3]^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O$$

SCHEME 1

We have attempted to discover ways in which the electron-transfer catalyst and the redox catalyst might be combined as a single homogeneous catalyst for the production of hydrogen from $[Ru(bipy)_3]^{2+*}$ and water. In principle, one possible form for such a catalyst would be a hydrido-metal complex which, on reduction by $[Ru(bipy)_3]^{2+*}$, loses hydrogen to give a compound which in turn could be protonated by water to give the starting hydride.

We now report systems which conform to this general pattern but which do not, unfortunately, appear to catalyse the photoproduction of hydrogen from $[Ru(bipy)_3]^{2+}$ and water under any conditions that we have employed.

RESULTS AND DISCUSSION

It has been known[19] for several years that the pyrophoric red oil $[Pt(PEt_3)_3]$ dissolves in water to give a colourless solution containing $[PtH(PEt_3)_3]^+$, and recently a full investigation of the aqueous chemistry of this complex was published.[20] We have also shown (see later) that $[Pd(PEt_3)_3]$ will dissolve in water, although it is less nucleophilic than its platinum analogue. It, thus, seemed reasonable to investigate the reduction chemistry of these cations in the hope that hydrogen and $[M(PEt_3)_3]$ might be formed.

Chemical Reduction of $[MH(PEt_3)_3]^+$ (M = Pt *or* Pd) *and of* [PtH(Cl)$(PEt_3)_2$].—Reduction of [MH$(PEt_3)_3$][BPh_4] in tetrahydrofuran (thf), or of [PtH(Cl)$(PEt_3)_2$] in toluene in the presence of an excess of PEt_3, with such reducing agents as sodium or magnesium amalgam * leads to the evolution of a gas identified mass spectroscopically as hydrogen. Hydrogen evolution is more rapid for M = Pd than for M = Pt, but the resulting solutions have no transition-metal-containing components and the palladium is precipitated in metallic form. However, in the reduction of either of the two hydrido-platinum complexes, hydrogen is produced together with an orange solution. On evaporation to dryness a red oil, identified as [Pt$(PEt_3)_3$], is recovered in high yield. The failure to isolate [Pd$(PEt_3)_3$] from reductions of [PdH$(PEt_3)_3$][BPh_4] with amalgams may reflect the lower intrinsic stability of low-valent palladium complexes with respect to their platinum analogues or may be due to some effect of the mercury. Support for the latter suggestion arises from the observation that stirring [$PdCl_2(PEt_3)_2$] with an excess of sodium amalgam (1%) in thf or benzene containing excess of PEt_3 gives a grey precipitate within a few minutes whilst the use of molten potassium at 65 °C (generally considered to be a stronger reducing agent) slowly reduces[21] [$PdCl_2(PEt_3)_2$] to [Pd$(PEt_3)_4$] in high yield in the presence of excess of PEt_3. The insoluble grey precipitate produced from the sodium-amalgam reduction is believed to be palladium metal, but we cannot rule out the possibility that it is a mercury palladium cluster similar to [$Hg_6Rh_4(PMe_3)_{12}$], which is formed[22] on reduction of [RhCl$(PMe_3)_4$] with excess of sodium amalgam.

Yields of hydrogen produced on reduction of low-valent metal hydrides in thf (40 cm^3)

Complex	(weight/g)	Reducing agent	Reaction time/min	Volume of H_2 produced ^{a}/cm^3	Yield of H_2 (%)
[PtH$(PEt_3)_3$][BPh_4]	(0.125)	Sodium amalgam	60	1.42	88
	(0.258)	Magnesium amalgam	50	0.65	20
[PdH$(PEt_3)_3$][BPh_4]	(0.104)	Sodium amalgam	5	1.35	91
	(0.157)	Magnesium amalgam	30	2.02	90
[PtH(Cl)$(PEt_3)_2$] ^{b}	(0.117)	Sodium amalgam	60	1.52	54

^{a} At normal temperature and pressure. ^{b} In toluene (40 cm^3) + PEt_3 (0.15 cm^3).

Further support for the suggestion that mercury is responsible for our inability to isolate [Pd$(PEt_3)_3$] on amalgam reductions of [PdH$(PEt_3)_3$]$^+$ is afforded by the observation that electrochemical reduction of concentrated solutions of [PdH$(PEt_3)_3$]$^+$ at a mercury cathode initially produces[23] an oil, presumed to be [Pd$(PEt_3)_3$], but that on further stirring the oil disappears and a black insoluble solid is formed.

The isolation of [Pt$(PEt_3)_3$] from reductions of [PtH$(PEt_3)_3$][BPh_4] suggests that half a mole of hydrogen should be produced per mole of metal and direct measurement of evolved gas in a gas burette suggests that up to 90% of the expected hydrogen is evolved (see Table).

In principle, then, we have identified possible catalysts for the production of hydrogen from water by the reactions shown in Scheme 2. However, the utility of such species as catalysts depends very much on the mechanism of hydrogen production, as well as on the redox potential of [MH$(PEt_3)_3$]$^+$.

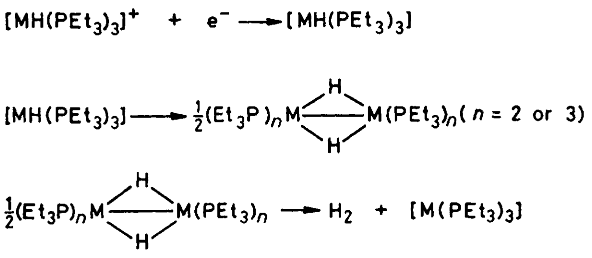
In principle, the reduction of [MH$(PEt_3)_3$]$^+$ could occur by one-electron or two-electron pathways. In the former, the steps would be as in Scheme 3. For the two-electron reduction a sequence such as is shown in Scheme 4 can be envisaged.

$$[M(PEt_3)_3] + H_2O \longrightarrow [MH(PEt_3)_3][OH]$$
$$[MH(PEt_3)_3]^+ + e^- \longrightarrow [M(PEt_3)_3] + \tfrac{1}{2}H_2$$

SCHEME 2

The last step in Scheme 4 can either occur by protonation to give transient [$MH_2(PEt_3)_3$] or *via* the bimetallic hydrido-bridged species assumed to be an intermediate in the one-electron reduction route (Scheme 3). Such a dinuclear species (n = 2) is believed[21] to be formed for palladium when [Pd$(PEt_3)_3$] is pressurised with H_2.

Since the one-electron reduction mechanism involves a free-radical intermediate {[(MH$(PEt_3)_3$]}, whilst the two-electron reduction does not, we have carried out the reduction of [PtH$(PEt_3)_3$][BPh_4] with sodium amalgam in thf in an e.s.r. tube in the hope of detecting radica intermediates. However, although free radicals are observed on freezing freshly shaken mixtures of [PtH$(PEt_3)_3$][BPh_4] and sodium amalgam in thf, these apparently arise from the [BPh_4]$^-$ anion since similar signals are observed when Na[BPh_4] is shaken with sodium amalgam in thf and the resulting solution frozen. We have been unable to detect free radicals in the reaction of [PtH$(PEt_3)_3$][PF_6] with sodium amalgam. The failure to detect free radicals in these reactions does not



SCHEME 3

$$[MH(PEt_3)_3]^+ + 2e^- \longrightarrow [MH(PEt_3)_3]^-$$
$$[MH(PEt_3)_3]^- + [MH(PEt_3)_3]^+ \longrightarrow H_2 + 2[M(PEt_3)_3]$$

SCHEME 4

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* Zinc amalgam does not appear to be capable of reducing [MH$(PEt_3)_3$]$^+$.

rule out the mechanism shown in Scheme **3** since any radical intermediates may be so short-lived that they do not build up sufficient concentration for detection. We are, thus, unable unequivocally to decide which of the two mechanisms is correct.

Of course, if the two-electron reduction mechanism is correct, it is unlikely that these or related complexes will be reduced by photochemical reducing agents such as $[Ru(bipy)_3]^{2+*}$ which can only transfer one electron per quantum of light absorbed.

Electrochemical Studies.—In order to find out whether or not the complexes $[MH(PEt_3)_3]^+$ are thermodynamically capable of being reduced by $[Ru(bipy)_3]^{2+*}$ $\{E^\ominus$ for $[Ru(bipy)_3]^{3+}$–$[Ru(bipy)_3]^{2+*} = -1.1$ V$\}$, we have carried out cyclic voltammetry on aqueous and MeCN solutions containing $[MH(PEt_3)_3]^+$. Although we propose to publish these in detail later,[23] it seems that neither of the cations is reduced at greater than −0.7 V (*cf.* saturated calomel electrode, s.c.e.) but that controlled-potential reduction of $[PdH(PEt_3)_3]^+$ at −0.8 V in water gives hydrogen and $[Pd(PEt_3)_3]$.

Photochemical Studies.—*Quenching studies*. The emission of $[Ru(bipy)_3]^{2+*}$ is not quenched in bulk solution by $[Pd(PEt_3)_3]$. In the presence of polyelectrolytes such as potassium polyvinyl sulphonate, sodium polystyrenesulphonate (pss), or sodium polyanethole sulphonate, $\{\text{-CH}[C_6H_3(SO_3Na)OMe]CH(CH_3)\text{-}\}_n$, which have been shown [24,25] to enhance the quenching of the emission of $[Ru(bipy)_3]^{2+*}$ by Cu^{2+}, small amounts of quenching (*ca.* 10%) are observed, but since $[PdH(PEt_3)_3]^+$ solutions absorb weakly at the excitation frequency (452 nm) we do not feel that genuine quenching occurs.

Using sodium dodecyl sulphate micelles as a means of bringing the positively charged $[PdH(PEt_3)_3]^+$ and $[Ru(bipy)_3]^{2+}$ together on a two-dimensional negatively charged surface has also been unsuccessful, although studies at one wavelength show up to 50% reduction of the emission of $[Ru(bipy)_3]^{2+*}$. Investigation of the complete emission spectra of solutions containing various amounts of $[PdH(PEt_3)_3]^+$, however, show that the loss of intensity of emission of $[Ru(bipy)_3]^{2+*}$ at 630 nm arises from changes in the position of the emission maximum. Thus, at low concentration of $[PdH(PEt_3)_3]^+$ the emission maximum is at 630 nm, the position normally observed [26] for $[Ru(bipy)_3]^{2+*}$ in the presence of micelles, whereas at higher palladium concentrations the position of the maximum moves to 610 nm, that expected for $[Ru(bipy)_3]^{2+*}$ in bulk solution. At intermediate concentrations the emission spectrum consists of overlapping emissions from $[Ru(bipy)_3]^{2+*}$ in the two different environments. Clearly, the main effect of $[PdH(PEt_3)_3]^+$ is to replace $[Ru(bipy)_3]^{2+}$ on the surface of the micelle, although this only occurs at $[PdH(PEt_3)_3]^+$ concentrations $>2 \times 10^{-3}$ mol dm^{-3}.

Even when both cations are present on the micelle, little or no quenching of the emission of $[Ru(bipy)_3]^{2+*}$ occurs.

Prolonged irradiation studies. Despite the lack of quenching of $[Ru(bipy)_3]^{2+*}$ by $[PdH(PEt_3)_3]^+$ reported above, we have studied the prolonged irradiation of solutions containing $[Ru(bipy)_3]^{2+}$, $[PdH(PEt_3)_3]^+$, pss, and triethanolamine {a weak reducing agent capable of reacting with any formed $[Ru(bipy)_3]^{3+}$}. Although small amounts of hydrogen are produced, similar amounts of hydrogen are also evolved [27] if $[Pd(PEt_3)_3]$ is irradiated in water in the absence of $[Ru(bipy)_3]^{2+}$ so we do not feel that $[PdH(PEt_3)_3]^+$ catalyses the photoproduction of hydrogen from $[Ru(bipy)_3]^{2+}$ and water under these conditions.

The Aqueous Chemistry of $[Pd(PEt_3)_3]$.—Although it has been known [19] for several years that $[Pt(PEt_3)_3]$ dissolves in water to form solutions of $[PtH(PEt_3)_3][OH]$, the reaction of $[Pd(PEt_3)_3]$ with water has not been described, although $[PdH(PEt_3)_3][BPh_4]$ can be prepared [21] by addition of $Na[BPh_4]$ to alcoholic solutions of $[Pd(PEt_3)_3]$.

On stirring $[Pd(PEt_3)_3]$ with distilled water for several hours, the pH of the solution rises to 9.5, indicating that solutions *ca.* 10^{-5} mol dm^{-3} in $[PdH(PEt_3)_3]^+$ are obtained. Much more concentrated solutions arise if the water is buffered to pH 7 with phosphate buffer or if dilute acid (H_2SO_4, HCl, or H_3PO_4) is added. Using buffer solutions, the rate at which $[Pd(PEt_3)_3]$ dissolves is low, but the maximum concentration of $[PdH(PEt_3)_3]^+$ appears to be governed only by the buffer capacity {*i.e.* only if the pH rises to 9.5 does $[Pd(PEt_3)_3]$ cease to dissolve}. Interestingly, the solubility of $[Pd(PEt_3)_3]$ in all of these solutions is higher at lower temperatures since the yellow oil $[Pd(PEt_3)_3]$ precipitates on warming its saturated solution, but redissolves on cooling.*

In the absence of co-ordinating anions, n.m.r. studies (^{1}H and ^{31}P) show that the only observable species present at pH 2—9 is $[PdH(PEt_3)_3]^+$ and that exchange of the hydrido-proton with those of free water is slow on the n.m.r. time scale. Indeed, the hydrido-resonance is even observable when the signal from water is being irradiated, suggesting [28] that negligible site exchange between the water and hydrido-protons is occurring. Despite the fact that there is no resonance from $[Pd(PEt_3)_3]$ in the ^{31}P n.m.r. spectra of its aqueous solutions, it is evidently present in low concentration since it can be extracted quantitatively into toluene or diethyl ether. On the basis of their photochemical behaviour we also believe [27] these aqueous solutions to contain low concentrations of $[PdH_2(PEt_3)_3(OH_2)]^{2+}$, although these again are not spectroscopically detectable. Addition of $K[PF_6]$ to these solutions precipitates $[PdH(PEt_3)_3][PF_6]$ essentially quantitatively and we have used this as a method for the gravimetric determination of the concentration of palladium in these solutions.

In the presence of anions other than sulphate or phosphate slightly different behaviour is observed. Thus, attempting to dissolve $[Pd(PEt_3)_3]$ in water buffered to pH 4 with potassium hydrogenphthalate produces a

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* This may simply reflect a shift in the position of the equilibrium $[Pd(PEt_3)_3] + H_2O \rightleftharpoons [PdH(PEt_3)_3]^+ + OH^-$, although at all pH values n.m.r. evidence suggests that the only species *in solution* is $[PdH(PEt_3)_3]^+$.

white solid identified as $[PdH(PEt_3)_3]$[phthalate] by its ^1H n.m.r. spectrum.

Addition of chloride ion to aqueous solutions of $[PdH(PEt_3)_3]^+$ produces a white crystalline precipitate identified[29] as $[PdH(Cl)(PEt_3)_2]$ by its n.m.r. and i.r. spectra. At high pH only small amounts of $[PdH(Cl)(PEt_3)_2]$ are formed in this way, although the same compound crystallises when these solutions are evaporated to low volume. At low pH, on the other hand, large amounts of $[PdH(Cl)(PEt_3)_2]$ are precipitated on addition of Cl^- to $[PdH(PEt_3)_3]^+$. This pH dependence is presumably the result of equilibrium (1) being pulled further

$$[PdH(PEt_3)_3]^+ + Cl^- \rightleftharpoons [PdH(Cl)(PEt_3)_2] + PEt_3 \quad (1)$$

to the right at low pH by the protonation of released PEt_3. Indeed, ^{31}P n.m.r. studies on acidic solutions from which $[PdH(Cl)(PEt_3)_2]$ has been removed by filtration show resonances from $[PdH(PEt_3)_3]^+$ together with a singlet at δ 22.4 p.p.m.* An identical signal is obtained by dissolving PEt_3 in water of the same pH and is attributed to $[PEt_3H]^+$.

This ready formation of $[PdH(Cl)(PEt_3)_2]$ from $[Pd(PEt_3)_3]$, water, and chloride ion has proved the basis of a facile high-yield preparation of $[PdH(Cl)(PEt_3)_2]$, which had only previously been available[29] from the prolonged reaction of $[PdCl_2(PEt_3)_2]$ with $GeHMe_3$ (see Experimental section).

It is worth noting that Nujol mulls of $[PdH(Cl)(PEt_3)_2]$ show two ν(Pd–H) bands at 2 035 and 1 997 cm^{-1} whose relative intensities are time and concentration dependent. In concentrated mulls the main absorption is at 2 035 cm^{-1} but this decreases on standing at the expense of the peak at 1 997 cm^{-1}, which is the major peak if mulls are less concentrated. This clearly arises since $[PdH(Cl)(PEt_3)_2]$ dissolves in Nujol; then the peak at 2 035 cm^{-1} can be assigned to the solid $[PdH(Cl)(PEt_3)_2]$ (2 035 cm^{-1} in a KBr disc) whilst that at 1 997 cm^{-1} comes from dissolved $[PdH(Cl)(PEt_3)_2]$ (1 997 cm^{-1} in hexane solution).

EXPERIMENTAL

Microanalyses were by Butterworth Laboratories. Infrared spectra were recorded on a Perkin-Elmer 577 grating spectrometer, u.v. visible spectra on a Beckmann SP800 spectrophotometer, and ^1H n.m.r. spectra on Varian Associates R12 and R34 spectrometers. Phosphorus-31 n.m.r. spectra were recorded on JEOL FX 90Q (City of London Polytechnic) or FX 60Q spectrometers (ICI Corporate Laboratories) in the Fourier-transform mode with proton-noise decoupling. Fluorescence spectra were recorded on a Perkin-Elmer MPF-43 fluorescence spectrometer and e.s.r. spectra on a Varian E4 *X*-band spectrometer.

Non-aqueous solvents [tetrahydrofuran, toluene, diethyl ether, and light petroleum (b.p. 40–60 °C)] were dried before use by distillation from sodium diphenylketyl, and water was purified by distillation. All solvents were thoroughly degassed before use and manipulations were carried out under nitrogen using standard Schlenk-line and catheter-tubing techniques.

Triethylphosphine, $[Pt(PEt_3)_3]$,[21] $[Pd(PEt_3)_3]$,[21] $[PtH(Cl)(PEt_3)_2]$,[30] and $[MH(PEt_3)_3][BPh_4]$[21] (M = Pt or Pd) were prepared by standard literature methods.

Buffer solutions were prepared from pure $Na_2[HPO_4]$ (0.025 mol dm^{-3}) and $K[H_2PO_4]$ (0.025 mol dm^{-3}) and were halide free (commercial buffer tablets contain KCl as a binder).

Hydrogen evolution was monitored using a gas burette. These measurements were subject to error limits of ±5% since one arm of the gas burette was open to the atmosphere and reaction times were quite long. This made the readings susceptible to changes in atmospheric pressure, although attempts were made to allow for these changes.

(1) *Reduction of* $[MH(PEt_3)_3][BPh_4]$ (M = Pt *or* Pd) *and* $[PtH(Cl)(PEt_3)_2]$.—Reductions using the solutions of the Table were carried out using sufficient sodium (0.5%) or magnesium (1%) amalgams for the sodium or magnesium to be in a three-fold excess.

A 100-cm^3 three-necked flask containing the solutions of metal complex of the Table was connected *via* a greaseless tap to a Schlenk line. The remaining necks were connected to a reservoir containing the reducing agent and a gas burette respectively. The system was degassed and isolated from the Schlenk line. After allowing the system to equilibrate at 1 atm,† the reducing agent was added and the mixture stirred. The volume of gas evolved was measured at 1 atm and identified mass spectroscopically as hydrogen.

For the palladium complexes, the resulting solution was colourless and yielded no product on evaporation to dryness, whereas for platinum the resulting red solution was filtered and evaporated to dryness to leave a red oil identified as $[Pt(PEt_3)_3]$ by comparison with an authentic sample. For $[PtH(PEt_3)_3][BPh_4]$ and magnesium amalgam, the oil was contaminated with a white solid, unreacted starting material. The yields of hydrogen for the various reactions are collected in the Table.

(2) *Reaction of* $[Pd(PEt_3)_3]$ *with Water*.—(*a*) The compound $[Pd(PEt_3)_3]$ (0.2379 g) was stirred with water (40 cm^3) containing $Na_2[HPO_4]$ (1.42 g, 0.25 mol dm^{-3}) and $K[H_2PO_4]$ (1.37 g, 0.25 mol dm^{-3}) (pH 6.88) for 24 h. The resulting pale yellow solution was filtered to remove a small amount of palladium metal and shown to contain $[PdH(PEt_3)_3]^+$ as the only detectable phosphine-containing product. N.m.r. spectra: ^1H, δ −7.3 [d, M–H, *J*(PH) = 180 Hz]; ^{31}P 24.3 (d, 2), 11.0 (t, 1) [*J*(PP) = 31.7 Hz].

(*b*) A similar reaction but with $K[H_2PO_4]$ (0.342 g, 0.025 mol dm^{-3}) and $Na_2[HPO_4]$ (0.355, 0.025 mol dm^{-3}) dissolved only 0.25 g of $[Pd(PEt_3)_3]$ in 100 cm^3 of water.

(*c*) A similar reaction but using water (20 cm^3) containing potassium hydrogenphthalate (0.202 g, 0.05 mol dm^{-3}) (pH 4.0) produced a white solid identified as $[PdH(PEt_3)_3][C_6H_4COO(COOK)]$ by its ^1H n.m.r. spectrum {δ 7.82 [AA′BB′,4, C_6H_4], 1.8 (m, 18, CH_2), 1.2 (m, 27, CH_3), −7.6 [d, M–H, *J*(PH) = 180 Hz]}.

(*d*) A similar reaction to (*b*) but in the presence of KCl (1 mol dm^{-3}) produced small amounts of a white crystalline solid. These were collected and dried *in vacuo*. They were identified as $[PdH(Cl)(PEt_3)_2]$ by their i.r. [ν(M–H) (hexane) at 1 997 cm^{-1} (lit.,[29] 2 009 cm^{-1}), KBr disc 2 035 cm^{-1} (lit.,[29] 2 035 cm^{-1}), ν(Pt–Cl) at 338 cm^{-1} (lit.,[29] 338 cm^{-1})] and ^1H n.m.r. spectra [δ − 13.4 (s, M–H) (lit.,[29] −13.6)].

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* To high frequency of external 85% H_3PO_4.

† Throughout this paper: 1 atm = 101 325 Pa.

Phosphorus-31 n.m.r. studies of the filtered solution showed the presence of only $[PdH(PEt_3)_3]^+$. At lower pH (3.0) larger amounts of $[PdH(Cl)(PEt_3)_2]$ (*ca.* 50%) were precipitated in the presence of chloride ion and ^{31}P n.m.r. spectra showed the presence of $[PdH(PEt_3)_3]^+$ together with a singlet at δ 22.4 p.p.m. identical to that obtained by dissolving PEt_3 in water containing Cl^- at pH 3.0.

(*e*) The compound $[Pd(PEt_3)_3]$ also dissolved readily in dilute H_2SO_4 or H_3PO_4 to give solutions whose ^{31}P n.m.r. spectra only showed the presence of $[PdH(PEt_3)_3]^+$.

(3) *Preparation of* $[PdH(PEt_3)_3][PF_6]$.—A portion (5 cm³) of the solution prepared in (2*a*), above, was treated with $K[PF_6]$ (0.3 g) in water (10 cm³). The resulting white precipitate was collected in a preweighed sintered glass crucible, washed with water (3 × 50 cm³), and dried *in vacuo* over silica gel. Yield: 0.0351 g (89.9%) [ν(Pd–H) at 1 960 cm^{-1}; lit.,[21] 1 966 cm^{-1}]. Stirring the filtrate with toluene left the organic phase uncoloured suggesting that the precipitation was quantitative.

(4) *Extraction of* $[Pd(PEt_3)_3]$ *from its Aqueous Solution.*—The compound $[Pd(PEt_3)_3]$ (0.1 g) was stirred with water (10 cm³) containing $Na_2[HPO_4]$ (0.035 g, 0.025 mol dm^{-3}) and $K[H_2PO_4]$ (0.034 g, 0.025 mol dm^{-3}) (initial pH 6.88) for 16 h. The clear pale yellow solution was filtered from undissolved $[Pd(PEt_3)_3]$ and extracted with toluene (3 × 5 cm³). The toluene phases were combined, dried over $Mg[SO_4]$, and evaporated to dryness to give an orange-yellow oil identified as $[Pd(PEt_3)_3]$ by comparison with an authentic sample.[21] Addition of $K[PF_6]$ to the aqueous phase after extraction with toluene caused only a slight turbidity, suggesting that almost all of the palladium complex had been extracted into toluene.

(5) *Preparation of* $[PdH(Cl)(PEt_3)_2]$.—The compound $[Pd(PEt_3)_3]$ (0.43 g) was stirred with water (100 cm³) containing KCl (0.74 g, 1 mol dm^{-3}), $Na_2[HPO_4]$ (0.355 g, 0.025 mol dm^{-3}), and $K[H_2PO_4]$ (0.342 g, 0.025 mol dm^{-3}) {pH 6.88 before addition of $[Pd(PEt_3)_3]$} for 48 h. Filtration from a small amount of undissolved $[Pd(PEt_3)_3]$ produced a pale yellow solution which was extracted with toluene (3 × 10 cm³). The pale yellow organic phases were combined, dried with $CaCl_2$, and evaporated to dryness to yield a pale yellow oil. This was recrystallised from light petroleum (at −30 °C) to give pale yellow crystals of $[PdH(Cl)(PEt_3)_2]$, identified [29] by their i.r. and ^1H n.m.r. spectra.* Yield: *ca.* 70%. Addition of $K[PF_6]$ to the aqueous phase after toluene extraction caused only slight turbidity.

(6) *Quenching Studies.*—A stock solution of $[Ru(bipy)_3]Cl_2$ (2.9 × 10^{-5} mol dm^{-3}) and potassium polyvinyl sulphonate (0.1% w/w) was degassed. This solution (3.5 cm³) was added to each of two matched anaerobic fluorescence cells, containing $[PdH(PEt_3)_3]^+$ (1.58 × 10^{-2} mol dm^{-3}) in water (1.5 cm³), prepared from $[Pd(PEt_3)_3]$ and HCl (1 mole equivalent) (pH 7.0), and distilled water (1.5 cm³) respectively.

The intensity of fluorescence at 610 nm (irradiation frequency = 452 nm) for the two solutions was measured. Different concentrations of $[PdH(PEt_3)_3]^+$ were obtained by diluting these solutions with aliquots (0.3 cm³) of a solution of identical composition to that which did not contain palladium (3.5 cm³ of the stock solution + 1.5 cm³ of distilled water). Quenching of *ca.* 2% was observed for 2.8 × 10^{-3} mol dm^{-3} $[PdH(PEt_3)_3]^+$. For this solution, absorbances at 452 nm for $[Ru(bipy)_3]^{2+}$ and $[PdH(PEt_3)_3]^+$ were 0.464 and 0.029 respectively. The quenching increased to *ca.* 8% for 4.4 × 10^{-3} mol dm^{-3} $[PdH(PEt_3)]^+$ but above this concentration visible precipitation occurred.

Experiments employing sodium polystyrenesulphonate (0.1%) or sodium polyanethole sulphonate (0.1%) were carried out similarly, with similar results.

A stock solution of $[Ru(bipy)_3]Cl_2$ (2.2 × 10^{-5} mol dm^{-3}) and sodium dodecyl sulphate (0.4%) was degassed. This solution (4 cm³) was added to each of two matched anaerobic fluorescence cells containing $[PdH(PEt_3)_3]^+$ (0.7 × 10^{-2} mol dm^{-3}) in water (0.1 cm³), prepared from $[Pd(PEt_3)_3]$ and H_3PO_4, and water (0.1 cm³) respectively.

The fluorescence spectra of the two solutions were recorded. Different concentrations of $[PdH(PEt_3)_3]^+$ were obtained by adding aliquots (0.1 cm³) of the $[PdH(PEt_3)_3]^+$ solution or water to the two solutions. Little or no quenching was observed at any of the concentrations investigated.

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* Pure samples of $[PdH(Cl)(PEt_3)_2]$ are white but they rapidly become yellow even on storage under nitrogen. This change in colour does not appear to affect the spectroscopic properties.[29]

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