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FORMATION AND REACTIVITY OF PALLADIUM HYDRIDE COMPLEXES, $[(PPh_3)_3PdH]^+$ AND $[(PPh_3)_2Pd(\mu\text{-}H)(\mu\text{-}CO)Pd(PPh_3)_2]^+$, IN AQUEOUS TRIFLUOROACETIC ACID SOLUTIONS

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Summary

Interaction of H_2 with P_2PdX_2 complex ($P = PPh_3$, $X = CF_3COO$) in aqueous trifluoroacetic acid solution at 70°C in excess triphenylphosphine results in the formation of the palladium hydride complex $[P_3PdH]^+$. The same complex is formed by protonation of PdP_4 at 25°C in aqueous CF_3COOH. When treated by carbon monoxide, $[P_3PdH]^+$ is changed to the binuclear palladium carbonyl hydride complex $[P_2Pd(\mu\text{-}H)(\mu\text{-}CO)PdP_2]^+$.

Introduction

The phosphinepalladium(II) complex, P_2PdX_2, in aqueous trifluoroacetic acid solution was shown to be an efficient catalyst for the water gas shift reaction [1] and for the synthesis of dialkyl ketones from olefins (ethylene, propylene), CO and H_2O [2] (or H_2 [3]). These reactions were supposed to proceed via formation and further rearrangement of the palladium hydride complex [3].

In this paper we report the results of ^1H and ^{31}P NMR spectroscopic studies of the formation of the palladium hydride complex in aqueous CF_3COOH solution during the interaction of a phosphinepalladium(II) complex with H_2 and a phosphinepalladium(0) complex with acid.

Results and discussion

The interaction of dihydrogen with the phosphinepalladium(II) complex, P_2PdX_2 (singlet at δ 36.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum), at 70°C in aqueous CF_3COOH solution ($[H_2O] \geq 20\%$ vol.) containing an excess (2–5 mol/mol of Pd^{II} complex) of PPh_3 (singlet at $\delta \approx 8.0$ ppm in the $^{31}P\{^1H\}$ NMR spectrum assigned to Ph_3PH^+) results in the formation of the palladium hydride complex. According to its ^1H and $^{31}P\{^1H\}$ NMR spectra (Table 1, Fig. 1a) this hydride $[P_3PdH]^+$ (I) has a

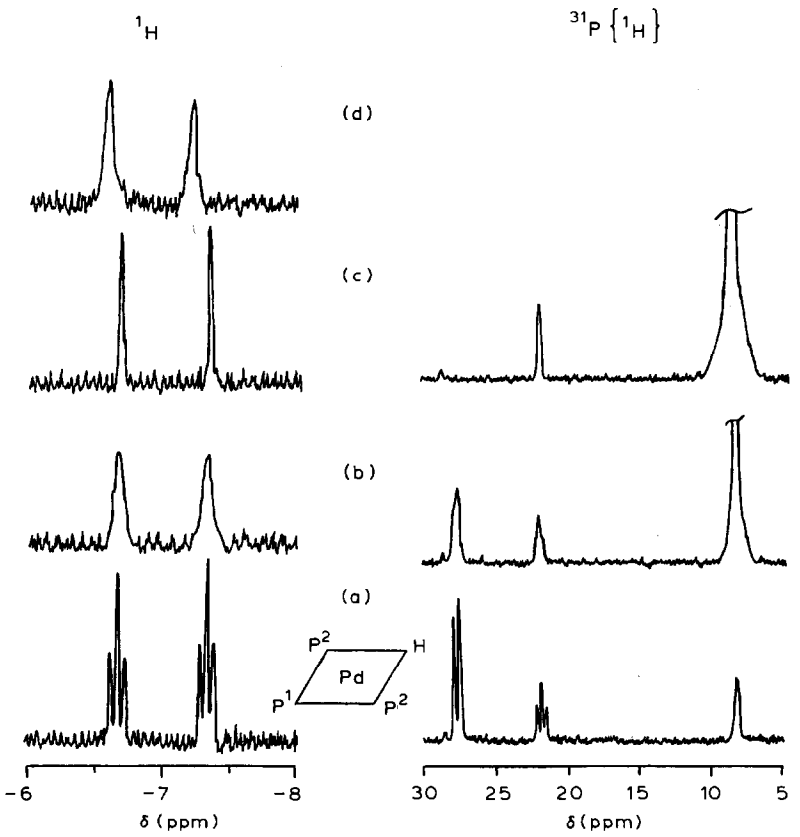


Fig. 1. Hydride region ^{1}H (300 MHz) and ^{31}P{^{1}H} (121 MHz) NMR spectra of a solution of $[(PPh_3)_3PdH]^+$ (0.04 mol/l) in aqueous CF_3COOH ($[H_2O]$ 30% vol.) at 25°C as a function of the amount of added free PPh_3, mol/mol of the complex: (a) 1; (b) 10; (c) 20; (d) 40.

TABLE 1

NMR SPECTRAL PARAMETERS OF THE PALLADIUM HYDRIDE COMPLEXES [a]

Palladium complexes: Observable ligands	Chemical shifts, δ (ppm) [b]				Coupling constant (Hz)
	^{1}H (300 MHz)	^{31}P{^{1}H} (121 MHz)	^{31}P [c] (121 MHz)	^{13}C{^{1}H} (75 MHz)	
(I) $[(PPh_3)_3PdH]^+$					
H^-	−7.0(dt) [d]				$J(^1H-^{31}P(1))$ 174
trans-PPh_3 (P(1))		21.9(t) [e]	21.9(dt)		$J(^1H-^{31}P(2))$ 13.5
cis-PPh_3 (P(2))		27.9(d) [f,g]	27.9(d)		$J(^{31}P(1)-^{31}P(2))$ 28
(II) $[(PPh_3)_2Pd(\mu\text{-}H)(\mu\text{-}CO)Pd(PPh_3)_2]^+$					
H^-	−6.3(q) [h]				$J(^1H-^{31}P)$ 40
PPh_3		23.7(s) [i,j]	23.7(d) [j]		
		23.7(d) [k]			$J(^{13}C-^{31}P)$ 32
CO [k]				230(q)	

[a] Measured at 25°C in aqueous CF_3COOH ($[H_2O]$ 30% vol.), [Pd] 0.04 mol/l. [b] ^{1}H and ^{13}C shifts are referred to TMS, ^{31}P shifts are referred to 85% H_3PO_4. [c] Measured with selective decoupling of the phenyl protons. [d] Double triplet. [e] Triplet. [f] Doublet. [g] Integral intensity ratio of ^{31}P(2) to ^{31}P(1) resonances equals 2. [h] Quintet. [i] Singlet. [j] CO with natural abundance of ^{13}C was used. [k] ^{13}CO (87.5% labelled) was used.

square planar structure, similar to the known complexes $[(PEt_3)_3PdH]^+$ [4,5] and $[(PMe_3)_3PdH]^+$ [6]. Upon treatment of the same solutions of P_2PdX_2 complex with dihydrogen at 25°C traces of complex I are formed.

The palladium hydride complex of the same composition and structure (according to ^1H and $^{31}P\{^1H\}$ NMR data) is readily and quantitatively formed during the dissolution of the phosphinepalladium(0) complex, PdP_4, in aqueous CF_3COOH solution with $[H_2O] \geq 30\%$ vol. at 25°C.

Hydride complex I is stable only in CF_3COOH solutions containing large amounts of water. For example, it is stable for a few days in CF_3COOH solution with $[H_2O]$ 40% vol. and for a few hours in CF_3COOH solution with $[H_2O]$ 30% vol. In more concentrated solutions of CF_3COOH ($[H_2O] < 20\%$ vol.) complex I rapidly decomposes to produce P_2PdX_2 and dihydrogen. Interaction of H_2 with P_2PdX_2 (in the presence of excess phosphine ligand) at 70°C in concentrated CF_3COOH ($[H_2O] <$ 0.3% vol.), or dissolution of PdP_4 in CF_3COOH at 25°C, does not yield complex I, P_2PdX_2 being the only palladium compound observed by $^{31}P\{^1H\}$ NMR.

As was shown previously [7] for the reaction of the PdP_4 complex with aqueous CF_3COOH solution, the rate of dihydrogen evolution decreased considerably with increasing the concentration of water in acidic solution up to 20–25% vol. At $[H_2O] > 30\%$ vol. only traces of H_2 were detected. According to our results, such effect of water concentration can be explained by the different stability of complex I in CF_3COOH solutions of various H_2O concentrations. We propose that this is due to the equilibrium rearrangement of the ionic hydride complex I to the covalent palladium hydride complex (eq. 1).

$$[P_3PdH]^+ X^- \underset{+P}{\overset{-P}{\rightleftharpoons}} P_2Pd(H)X \qquad (1)$$

The possible effect of water concentration on this equilibrium is compatible with the experimental data observed, e.g., in CF_3COOH solutions with $[H_2O] \geq 30\%$ vol. equilibrium 1 is shifted to the left side when the aquated complex I is formed, which is stable to protolysis. In CF_3COOH solutions with $[H_2O] < 20\%$ vol. equilibrium 1 is shifted toward the right side with formation of the $P_2Pd(H)X$ complex which is unstable to protolysis in a strong acidic medium and which readily decomposes with evolution of H_2 (eq. 2).

$$P_2Pd(H)X + HX \rightleftharpoons P_2PdX_2 + H_2 \qquad (2)$$

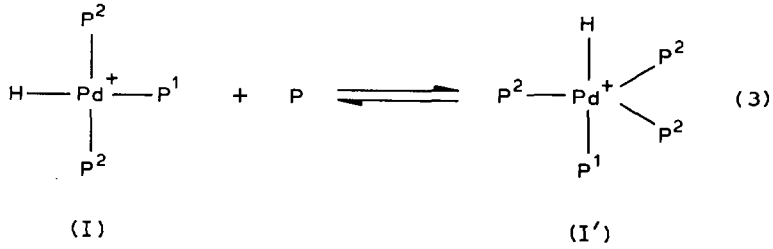
Indeed, the palladium hydride complexes of the $(PR_3)_2Pd(H)Y$ type (R = alkyl or aryl; Y = Cl, CF_3COO) have been prepared by interacting a stoichiometric amount of the acid HY with the corresponding phosphinepalladium(0) complexes, $Pd(PR_3)_n$ ($n = 2$–4), in an inert organic solvent [6,8,9]. It has been shown also [6,8,10,11] that the excess of acid in this reaction results in the formation of $(PR_3)_2PdY_2$ complexes and dihydrogen.

The existence of equilibrium 1 is evidenced also by the fact that addition of even small amounts of strongly coordinating anions (e.g. addition of 1 mol KBr/g-atom Pd) into a solution ($[H_2O]$ 30% vol.) of complex I leads to its rapid decomposition (evolution of H_2, disappearance of the resonances of complex I in ^1H and $^{31}P\{^1H\}$ NMR spectra). The observed phenomena can be explained by a shift of equilibrium 1 to the right side due to the substitution of the *trans*-phosphine ligand P(1) in complex I by bromide ion with formation of $P_2Pd(H)Br$. However, the attempts to

observe this complex by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy were unsuccessful, apparently, due to its rapid protolysis. In this connection note that interaction of H_2 with P_2PdX_2 in aqueous CF_3COOH solution with $[H_2O]$ 30% vol. at 70°C, when there was no excess PPh_3, gave no signals in the hydride region of the ^1H NMR spectrum. In ref. 5 the $(PEt_3)_2Pd(H)Cl$ complex was identified after addition of chloride ions to the moderately acidic aqueous solutions of the $[(PEt_3)_3PdH]^+$ complex.

All the experimental data taken together lead us to conclude that the formation of complex I by interaction of dihydrogen with P_2PdX_2 in aqueous CF_3COOH solutions in the presence of excess PPh_3 proceeds via reactions 2 and 1. Equilibrium 2 at 25–70°C shifts to the right side at any concentration of water.

^1H and $^{31}P\{^1H\}$ NMR spectra of complex I (Fig. 1a) indicate that at 25°C exchange of its hydrido-proton with those from the solvent is slow on the NMR time scale, and that in the absence of excess PPh_3 (> 5 mol per mol of complex I) exchange with participation of the phosphine ligands does not proceed. However, with considerable excess of triphenylphosphine in the solution the coordination sphere in complex I shows dynamic behaviour. For example, gradual addition of excess PPh_3 (up to 20-fold per mol of complex I) to the solution of complex I at 25°C resulted in the broadening of the triplets in the hydride region of the ^1H NMR spectrum and their further sharpening into singlets (Fig. 1b and 1c). At the same time in the $^{31}P\{^1H\}$ NMR spectrum the resonances assigned to *cis*-phosphines (P(2)) strongly broadened and eventually coalesced with the free phosphine resonance, while the resonance assigned to the *trans*-phosphine (P(1)) only slightly broadened. Such a picture of the dynamics of the ^1H and $^{31}P\{^1H\}$ NMR spectra indicates that the presence of an excess of free phosphine (up to 20-fold) in solution of complex I results in rapid intermolecular exchange which affects predominantly the *cis*-phosphine ligands (P(2)). The increase in the exchange rate with addition of the free phosphine means that the exchange proceeds via an associative mechanism (eq. 3).



(I) (I′) (3)

The addition of a 40-fold excess of free phosphine to the solution of the complex I results in further broadening of the resonances of this complex in the hydride region of the ^1H NMR spectrum and in some change in the chemical shift (Fig. 1d). The broadening indicates that at high concentrations of free phosphine in solutions of complex I simultaneously with rapid exchange (eq. 3) of the *cis*-phosphine ligands (P(2)) an exchange of the *trans*-phosphine ligand (P(1)) can be observed. The latter exchange seems to proceed via intermolecular rearrangement of the five-coordinating intermediate (I′). Such a rearrangement, according to ref. 12, is characterized by a small activation energy. However, the reason for the change of the hydride chemical shift has not been established unambiguously. It may be due to the change of the

specific solvation of complex I or its anion at high phosphine concentrations in the solution.

Similar regularities of the phosphine ligand exchange were observed previously for the hydride complexes $[(PEt_3)_3MH]^+$ (M = Pt, Pd, Ni) [13,14].

The addition of other π-acid ligands, such as CO and C_2H_4, to the solution of complex I was not accompanied by an observable ligand exchange of the type shown in eq. 3. Thus, treatment of the solution of complex I with carbon monoxide at 25°C did not enhance the broadening of the hydride resonances in the ^1H NMR spectrum, but resulted in rapid and complete rearrangement of complex I into the new hydride complex II. According to the ^1H, ^{13}C and ^{31}P NMR data (Table 1) complex II contains one hydride, one carbonyl, and four equivalent phosphine ligands in the composition of the molecule. A comparison of the integral intensities of resonances of complex II and a free phosphine in the ^{31}P NMR spectrum indicates that there are only two equivalent phosphine ligands per palladium atom in this complex. Moreover, the integral intensity of the hydride resonance in the ^1H NMR spectrum for complex I is twice as much as that for complex II. From these NMR spectroscopic data one can conclude that a compound produced by the interaction of $[P_3PdH]^+$ with CO represents a binuclear palladium complex containing the bridging hydride and carbonyl ligands with tetrahedral coordination around formally Pd^I ions. Note that recently [15] a similar binuclear carbonyl hydride complex of Pt^I, $[(dpe)Pt(\mu\text{-}H)(\mu\text{-}CO)Pt(dpe)]^+[BF_4]^-$ (dpe = 1,2-bis(diphenylphosphino)ethane), has been prepared.

In contrast to complex I, the phosphine ligands in complex II are not sufficiently labile to observe an exchange in the excess PPh_3 in the solution. Thus addition of 20 mol of PPh_3 per mol of complex II at 25°C in the absence of free CO leads to no broadening of the resonance of complex II in the $^{31}P\{^1H\}$ NMR spectrum. Instead, complex II slowly rearranges to complex I, which is consistent with the existence of the equilibrium shown in eq. 4.

$$2[P_3PdH]^+ + CO \rightleftharpoons [P_2Pd(\mu\text{-}H)(\mu\text{-}CO)PdP_2]^+ + 2P + H^+ \quad (4)$$

Rearrangement of complex II to complex I may involve the stages of acid dissociation of complex I, formation of a carbonylpalladium(0) complex and its interaction with the excess of complex I (eq. 5).

$$[P_3PdH]^+ \overset{-H^+}{\rightleftharpoons} P_3Pd^0 \overset{+CO(-P)}{\rightleftharpoons} P_2Pd^0(CO) \overset{+[P_3PdH]^+(-P)}{\rightleftharpoons} [P_2Pd(\mu\text{-}H)(\mu\text{-}CO)PdP_2]^+ \quad (5)$$

Treatment of the solution of complex I with ethylene at 25°C was also not accompanied by the observable broadening of the hydride resonance line in the ^1H NMR spectrum but resulted in a decrease in their intensity with time. Simultaneously, ethane and a mixture of isomeric butenes were formed as the reaction products of ethylene hydrogenation and dimerization in the presence of complex I.

Treatment of the solution of complex I with a mixture of C_2H_4 and CO as well as the interaction of C_2H_4 with a solution of complex II resulted in rapid formation of diethyl ketone in the solution at 50–70°C. This indicates that complex I (and possibly complex II) takes part in the catalytic reaction of dialkyl ketone synthesis from olefins, CO and H_2O (or H_2) [2,3]. The water gas shift reaction [1], perhaps, also proceeds via intermediate formation and decomposition of complex II.

Results of the detailed investigation of interaction of complex $[P_3PdH]^+$ with ethylene and with a mixture of C_2H_4 and CO will be published elsewhere.

Experimental

Palladium acetate was prepared as described in ref. 16. $Pd(PPh_3)_4$ was prepared by treating an aqueous acetone solution of $Pd(OAc)_2$ with carbon monoxide in excess PPh_3 at 25°C [17]. The phosphinepalladium(II) complex was prepared in situ by means of dissolution of $Pd(OAc)_2$ and PPh_3 (2–7 mol/g-atom Pd) in CF_3COOH with the required amount of water. The PPh_3 and CF_3COOH used ($[H_2O] < 0.3\%$ vol.) were of reactive grade.

For the study of the reactivity of hydride complex I by means of NMR spectroscopy the solution of this complex (0.04 mol/l) which was used was prepared by dissolution of $Pd(PPh_3)_4$ in aqueous CF_3COOH with $[H_2O]$ 30% vol. All treatments of solutions of palladium complexes by gases H_2, CO, and C_2H_4 were carried out by bubbling the gases through the solutions directly in an NMR ampule before recording the spectra.

^1H, ^{13}C and ^{31}P NMR spectra were made on a Bruker CXP-300 spectrometer. ^{13}C and ^{31}P NMR spectra were recorded with proton noise decoupling. In some cases (for the determination of $J(^{31}P-^1H)$ values) ^{31}P NMR spectra were recorded with selective decoupling of the phenyl protons. ^1H chemical shifts were measured against acetone as internal standard, ^{13}C chemical shifts were compared with those of the carboxyl group of CF_3COOH, and in both cases the shifts were referred to TMS. ^{31}P chemical shifts were referred to external 85% H_3PO_4. In all NMR spectra downfield shifts were positive.

Ethane, butenes and diethyl ketone were analyzed by GLC and ^1H NMR.

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