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MECHANISM OF THE FORMATION OF PALLADIUM COMPLEXES SERVING AS CATALYSTS IN HYDROGENATION REACTIONS

II *. REACTIVITY OF PALLADIUM PHOSPHINE HALIDES TOWARDS MOLECULAR HYDROGEN

A.S. BERENBLYUM, A.P. ASEEVA, L.I. LAKHMAN

All-Union Scientific Research Institute of Petroleum Processing (Elektrogorsk Branch), Elektrogorsk (U.S.S.R.)

and I.I. MOISEEV *

Institute of General and Inorganic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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Summary

$[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl$, benzene and aniline hydrochloride were isolated as products of the reactions of $(PPh_3)_2PdCl_2$ or $[(PPh_3)PdCl_2]_2$ with H_2 in organic amines (Am). Similar products were obtained when $(Ph_3P)_2Pd(Ph)Br$ was treated with H_2 both in amines and aromatic solvents. The reaction between H_2 and $[(PBu_3)PdCl_2]_2$ resulted in the formation of $[(PBu_3)(PBu_2)PdCl]_2 \cdot 2\,Am$. The kinetic data for H_2 absorption by solutions of palladium(II) complexes are consistent with the heterolytic mechanism of cleavage of the H—H bond in the coordination sphere of palladium(II); the function of the H^+ acceptor being performed by the bases (e.g. Am or Ph). The reaction between the palladium complexes and H_2 is autocatalytic. Reduction of the initial Pd^{II} complexes leads to lower oxidation state palladium complexes, which catalyse the reduction of Pd^{II} complexes. In the coordination sphere of the lower oxidation state palladium complexes, the oxidative addition of PR_3 to Pd takes place with formation of compounds containing a Pd—R bond. It is the reaction between these complexes and H_2 that yields palladium compounds with PR_2 ligands.

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* For part I see ref. 1.

Introduction

Phosphine complexes of palladium halides, unlike the acetate ones [1], do not react with H_2 under mild conditions. For example, $(Ph_3P)_2PdX_2$ and $[Ph_3PPdX_2]_2$ (X = Cl, Br) practically do not absorb H_2 in aromatic solvents (benzene, diphenyl) in the temperature range of 20 to 90°C * and at a pressure of 1 atm H_2.

As can be inferred from the available data, the observed differences in the reactivity of halide and acetate complexes can be attributed to the susceptibility of the complexes to the heterolytic dissociation of molecular H_2, under the effect of palladium and the attached ligand [2]. The available ESCA data show a marked decrease in the effective positive charge on the Pd atom when OAc^- is substituted by Cl^- ($E\ Pd_{3d_{5/2}} = 338.5$ eV in the case of $[Pd_3Pd(OAc)_2]_2$ [3] and 338.2 eV in the case of $[PPh_3PdCl_2]_2$). This is in agreement with quantum chemical calculations of phosphine complexes of palladium by the CNDO method, which indicate that when Cl^- is replaced by OAc^- or OH^-, the positive charge on the Pd atom and the negative one (in absolute value) on the acid ligands increase [4]. On the other hand, although the heterolytic cleavage of the Pd—Cl bond requires less energy than that of the Pd—OR (R = Ac, H) bond, the basicity of OAc^- and OH^- exceeds that of Cl^- to such an extent that this difference is much greater than that involved in the heterolysis of the Pd—X (X = Cl, OR) bonds. Moreover, calculations of some model systems simulating the transition state for the hydride formation have shown [4] that the strength of the H—H bond in the transition state decreases as follows: $Cl^- > CH_3COO^- > OH^-$. These seem to be the factors responsible for the relatively low reactivity of phosphine halide complexes of Pd towards H_2. This communication discusses the mechanism of their interaction with H_2.

Results and discussion

Introduction into the palladium coordination sphere of ligands forming a relatively weak bond with the central atom and having a pronounced basicity, i.e. ligands tending to accept a proton during heterolytic cleavage of the H—H bond, may enhance the activity of palladium(II) complexes in reactions with H_2 [5]. Such ligands may be neutral (organic amines) or acidic (phenyl or other organic ligands).

Indeed, our experiments have shown that complexes of the $(Ph_3P)AmPdX_2$ type formed when $[(Ph_3P)PdX_2]_2$ is dissolved in aniline or *p*-, *m*- and *o*-toluidines react with H_2 at 30°C absorbing 1 to 1.2 mol H_2 per mole of the complex (Figs. 1 and 2).

The kinetics of the reaction between H_2 and $[(Ph_3P)PdCl_2]_2$ (complex I) or $[(Ph_3P)Pd(OAc)_2]_2$ (complex II), are described by S-shaped curves. The induction period (τ)** increases with increasing concentration of the complex I, P_{H_2}, and decreasing temperature (Fig. 2). As in the case of II, τ decreases when

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* At temperatures above 90°C these complexes decompose in the presence of H_2, liberating Pd.

** Special experiments indicate that τ is not related to the time of formation of $Ph_3P(Am)PdX_2$.

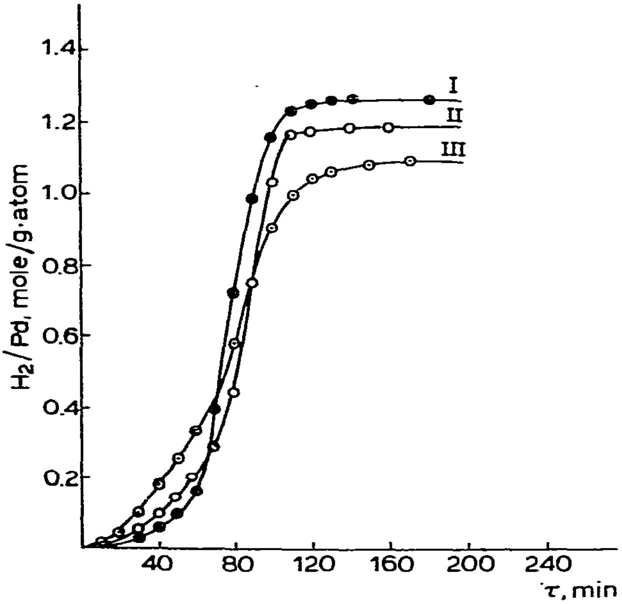

Fig. 1. Kinetic curves for the absorption of H_2 in toluidines. I. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C, solvent *m*-toluidine. II. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C, solvent *o*-toluidine. III. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C, solvent *p*-toluidine.

a certain amount of $[(Ph_3P)PdCl_2]_2$ solution pretreated with H_2 is introduced into the solution of I prior to contact with H_2. As soon as the ratio of Ph_3P to Pd exceeds unity, the hydrogenation rate of both the chloride and acetate com-

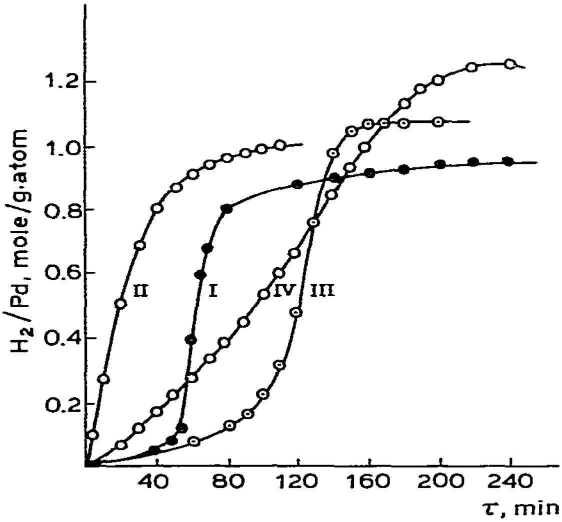

Fig. 2. Kinetic curves for the absorption of H_2 in aniline. I. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C. II. $[[(PPh_3)PdBr_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C. III. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C, volume ratio $H_2 : Ar = 1 : 1$. IV. $[[(PPh_3)PdCl_2]_2] = 1.2 \times 10^{-3}$ mol/l, 50°C. V. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 50°C, with addition of the hydrogenated complex. VI. $[[(PPh_3)PdCl_2]_2] = 2.4 \times 10^{-3}$ mol/l, 30°C.

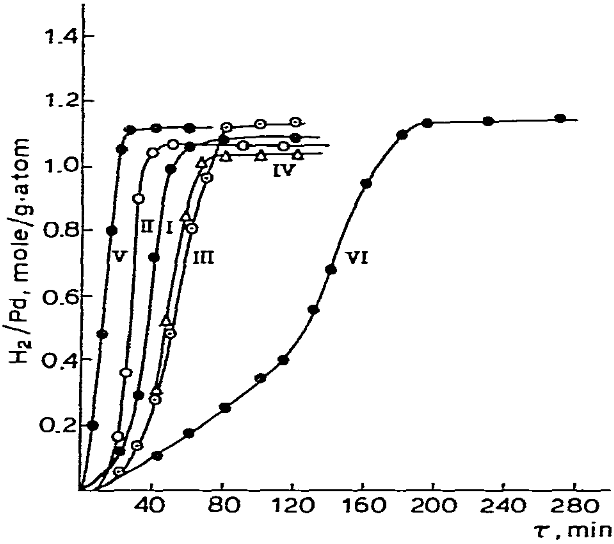

Fig. 3. Kinetic curves for the absorption of H_2 in aniline and biphenyl. I. $[(PPh_3)_2Pd(Br)Ph] = 4.7 \times 10^{-3}$ mol/l, 50°C, solvent biphenyl. II. $[[p(OPh)_3]_2PdCl_2] = 4.7 \times 10^{-3}$ mol/l, 50°C, solvent aniline. III. $[(PPh_3)_2Pd(Br)Ph] = 4.7 \times 10^{-3}$ mol/l, 70°C, solvent aniline. IV. $[(PPh_3)_2PdCl_2] = 4.7 \times 10^{-3}$ mol/l, 90°C, solvent aniline.

plexes decreases. For example, the reaction between $(Ph_3P)_2PdCl_2$ (complex III) and H_2 proceeds in amines at perceptible rates only at 90° C (Fig. 3). The interaction with H_2 is presumably preceded by one of the phosphine ligands being replaced by Am:

$$(PPh_3)_2PdCl_2 + Am \rightarrow PPh_3(Am)PdCl_2 + PPh_3 \qquad (1)$$

It should be noted that all of the above-mentioned characteristics of the reaction between the chloride complex of palladium and H_2 apply also to its bromide analog.

In spite of the similarity of the kinetic curves of the reactions of H_2 with $[(Ph_3P)PdX_2]_2$ or $[(PPh_3)Pd(OAc)_2]_2$, there are some differences in reactivity for both complexes. For example, from reaction (1) with H_2 in aniline we obtained $[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl$ (complex IV) instead of $(Ph_3P)_2Pd_2$ [1], with an almost quantitative yield, in accordance with the following stoichiometric equation *:

$$5\,[(PPh_3)PdCl_2]_2 + 10\,H_2 \rightarrow 2\,[(Ph_3P)_3(PPh_2)_2Pd_3Cl]Cl + 4\,Pd + 16\,HCl + 4\,C_6H_6 \qquad (2a)$$

In case of complex III, the following reaction proceeds:

$$3\,(PPh_3)_2PdCl_2 + 3\,H_2 \rightarrow [(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl + 4\,HCl + 2\,C_6H_6 + PPh_3 \qquad (2b)$$

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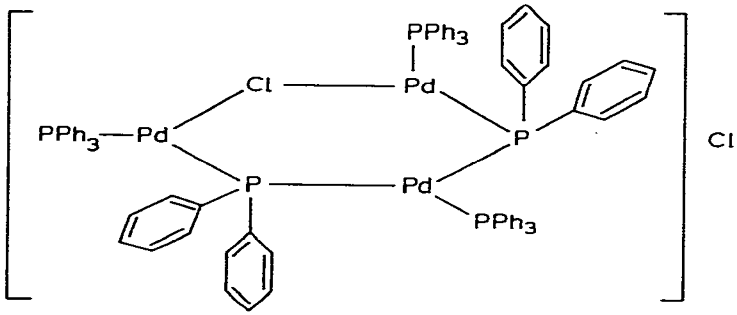
[*] In addition to the compounds listed in equation 2a the reaction yielded a mixture of unidentified black complexes (about 4% with respect to the weight of the initial complex).

Electric conductivity measurements have shown that a solution of IV in CH_3NO_2 is an electrolyte. The $^{31}P\{^1H\}$ NMR spectrum of complex IV in aniline is of the AB_2X_2 type and is characterized by the following parameters *: $\delta_{AA'} = 11.80$ ppm, $\delta_{BB'} = 18.77$ ppm, $\delta_{XX'} = 220.59$ ppm, $J_{AB} = 88.5$ Hz, $J_{ax} = |12.2|$ Hz, $1/2|J_{BX} + J_{BX'}| = 17.1$ Hz, which correspond to the corresponding parameters of the $[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl$ complex obtained by heating $[(PPh_3)_2PdCl]BF_4$ in THF with subsequent replacement of BF_4^- by Cl^- [6]. This complex differing from IV in the presence of three PEt_3 instead of PPh_3 groups is, according to X-ray analysis data, a trinuclear cluster of Pd [7] in which two PPh_2 groups and one Cl ion serve as bridging ligands. According to ESCA data the single bond energy value ($Pd(3d_{5/2}) = 337.1$) corresponds to three Pd atoms in IV, and approaches that observed in cases of Pd^I compounds [3].

The above data suggest that complex IV has a structure similar to:



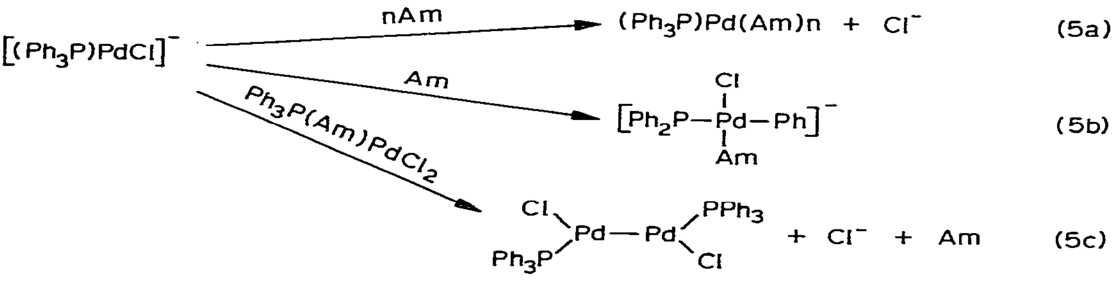
The first step in reactions 2a and 2b is presumably an interaction between H_2 and $Ph_3P(Am)PdCl_2$, during which Am accepts H^+ formed in the course of heterolytic cleavage of H_2, and a hydride complex of Pd is formed:

$$(Ph_3P)AmPdCl_2 + H_2 \rightarrow HAm^+[(Ph_3P)Pd(H)Cl_2]^- \qquad (3)$$

The resulting hydride complex is unstable in Am medium and, eliminating HCl [8], converts into a Pd^0 compound.

$$HAm^+[(Ph_3P)Pd(H)Cl_2]^- \rightarrow HAm^+[(Ph_3P)PdCl]^- + HCl \qquad (4)$$

In the $[(Ph_3P)PdCl]^-$ anion thus formed the vacancies at Pd can be occupied by Am molecules. The following paths of transformation of this unstable anion are possible:



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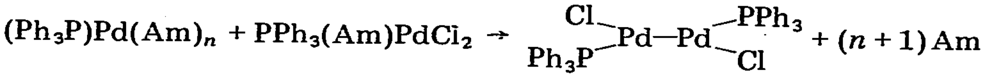
* Chemical shifts relative to 85% H_3PO_4.

We have no data from which we can evaluate the contribution of each of the above paths of transformation of the $[(Ph_3P)PdCl]^-$ anion, but we assume that, as in the case of acetate complexes [1], complexes of Pd^I are yielded either by reaction 5c or as a result of interaction of $(Ph_3P)Pd(Am)_n$ yielded by reaction 5a with the initial complex:

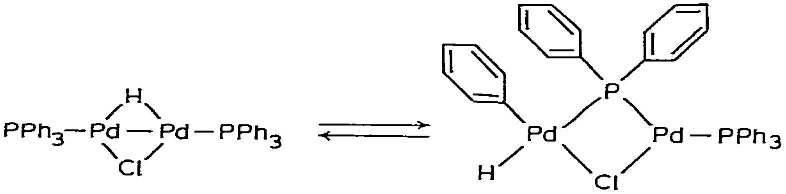


$$(Ph_3P)Pd(Am)_n + PPh_3(Am)PdCl_2 \rightarrow \overset{Cl}{\underset{Ph_3P}{}}{>}Pd{-}Pd{<}\overset{PPh_3}{\underset{Cl}{}} + (n+1)Am \qquad (6)$$

Just as in the case of $(Ph_3P)_2Pd_2(OAc)_2$ [1], the halide complex of Pd^I seems to react rapidly with H_2, generating a respective hydride complex:

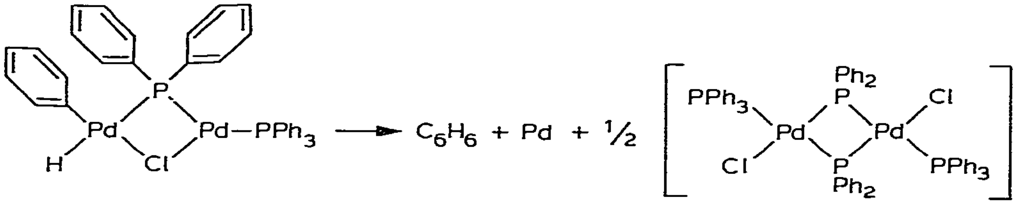
$$(PPh_3)_2Pd_2Cl_2 + H_2 \rightarrow (PPh_3)_2Pd_2(H_2)Cl_2 \rightarrow (PPh_3)_2Pd_2(H)Cl + HCl \qquad (7)$$

The resulting hydride complex of Pd^I, as well as the Pd^0 complex (reaction 5b), seems to be capable of participating in the equilibrium oxidative addition of the phosphine ligand to the Pd atom [9], yielding a phosphide derivative with a σ-bonded phenyl:



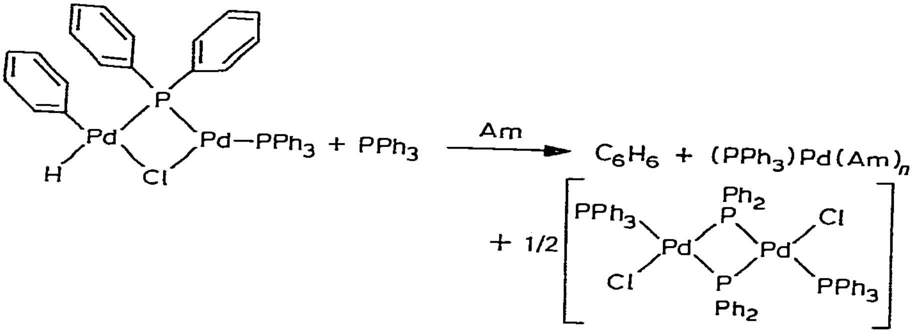
(8)

Due to the more pronounced basicity of the phenyl ligand, as compared to Cl^-, the resulting hydride complex of Pd^{II} will eliminate C_6H_6 rather than HCl, thereby generating the stable complex $[(Ph_3P)Pd(PPh_2)Cl]_2$ [10] and Pd metal observed in reaction 2:



(9)

When $(Ph_3P)_2PdCl_2$ is used as the starting compound with free PPh_3 present in the solution, the hydride complex of Pd^{II} formed in reaction 8 does not yield metallic Pd: $(Ph_3P)Pd(Am)_n$ is formed in addition to $[(Ph_3P)Pd(PPh_2)Cl]_2$ (compound V):



(10)

Another possible path of C_6H_6 formation is hydrogenation of the $(Ph_2P)Pd(Ph)Cl^-$ complex formed in reaction 5b by molecular H_2.

Insertion of the $(Ph_3P)Pd(Am)$ complex into the Pd—PPh_2 bond of complex V results in the formation of complex IV:

$$(PPh_3)Pd(Am)_n + [(PPh_3)Pd(PPh_2)Cl]_2 \rightarrow \underset{(VI)}{[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl} + n\,Am \quad (11)$$

Complex IV, containing Pd in the formal oxidation state +4/3, as well as other compounds of low-valent Pd may react with palladium(II) compounds according to the following scheme:

$$[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl + (PPh_3)Pd(Am)Cl_2 \rightarrow (PPh_3)_2Pd_2Cl_2 + [(PPh_3)Pd(PPh_2)Cl]_2 + Am \quad (12)$$

Thus, the above reactions give an insight into the paths of formation of benzene, aniline hydrochloride and complex IV. Owing to the ability of $(Ph_3P)_2Cl_2Pd_2$ to react rapidly with H_2, the addition of IV to solutions of palladium(II) compounds accelerates the H_2 uptake.

Hydrogenation of $[(Bu_3P)PdCl_2]_2$ yields other products than in case of $[(Ph_3P)PdCl_2]_2$. For example, instead of a trinuclear cluster the reaction with H_2 yields a brown complex, a complex of composition $[(Bu_3P)(Bu_2P)PdCl]_2 \cdot 2\,Am$ * and butane (identified by LGO). The $^{31}P\{^1H\}$ NMR spectrum of this complex features two singlets with $\delta = 10.1$ and 28.1 ppm (with respect to 85% H_3PO_4) corresponding to the phosphorus atoms in the PR_2 and PR_3 groups [11]. The results of chemical analysis and NMR data (δ, ppm): 0.93 (CH_3—), 1.6 (—CH_2—), 4.3 (H_2N—), and 6.8 (C_6H_5—) also agree with the proposed formula.

The hydrogenation of the triphenylphosphine and tributylphosphine complexes presumably involves the common steps 3—9. The observed difference in the composition of the resulting complexes seems to be due to the difference in the ability of $(Bu_3P)Pd(Am)_n$ and $(Ph_3P)Pd(Am)_n$ to participate in the reaction 11.

The replacement of one of the halide ions by a ligand exhibiting higher proton affinity allows hydrogenation of the Pd^{II} complex under mild conditions, even in the absence of amine. For instance, $(Ph_3P)_2Pd(Ph)Br$ (compound VI) reacts with H_2 both in aniline and in biphenyl, unlike $(Ph_3P)_2PdX_2$ and $[(PPh_3)PdX_2]_2$ (where X = Cl, Br), which interact with H_2 only in aniline. The solutions of VI absorb about 1 mol H_2 per mol of the initial complex. Just as in the case of solutions of dihalide complexes in amines, the kinetic curves for the absorption of H_2 by a solution of VI in amines and aromatic hydrocarbons show an induction period, and the final products of the reaction include benzene and a trinuclear complex of palladium

$$3\,(Ph_3P)_2Pd(Ph)Br + 3\,H_2 \rightarrow [(Ph_3P)_3(PPh_2)_2Pd_3Br]Br + HBr + 5C_6H_6 + PPh_3 \quad (13)$$

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[*] The reaction products also include $(Am)_2PdCl_2$ and unidentified Pd complexes.

Reaction 13 proceeds much faster in biphenyl than in aniline (Fig. 3). This may be due to the fact that incorporation of Am into the coordination sphere of palladium(II) leads to a decrease in the effective charge at Pd.

Comparison of Figs. 2 and 3 indicates that under identical conditions the phenylbromide complex in aniline reacts with H_2 at a much lower rate than the dibromide complex in aniline. Being a stronger electron donor than Br^-, Ph^- probably decreases the effective positive charge at Pd in a more pronounced manner.

The above data suggests that the phenyl halide complex of Pd reacts with H_2 through the same mechanism as the dihalide complexes. The reaction probably starts with hydrogenolysis of the Pd—Ph bond, which may result in formation of complexes of both Pd^0 and Pd^I

$$(PPh_3)_2Pd(Ph)Br + H_2 \rightarrow (PPh_3)_2Pd(solv)_m + HBr + C_6H_6 \qquad (14a)$$

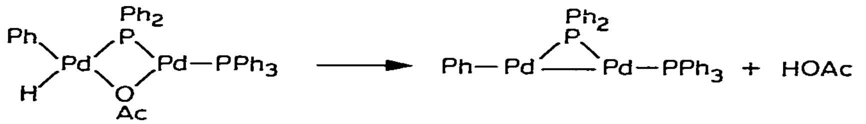
$$(PPh_3)_2Pd(Ph)Br + H_2 \rightarrow 1/2\,(PPh_3)_2Pd_2Br_2 + C_6H_6 + PPh_3 \qquad (14b)$$

The reactions of $(Ph_3P)_2Pd_2Br_2$ and $(Ph_3P)_2Pd(solv)_m$ with H_2 yield the trinuclear cluster $[(PPh_3)_3(PPh_2)_2Pd_3Br]Br$ as mentioned above (reactions 7—11).

Comparison of the data obtained for the reaction of H_2 with phosphine halide and phosphine acetate complexes reveals similarities as well as some differences. The reactions of both types of complexes with H_2 are characterized by autocatalysis and formation of RH (in particular, C_6H_6 and C_4H_{10}) as a result of hydrogenolysis of the P—R bond. However, different complexes are formed in the systems compared. For example, in cases of acetate complexes, Pd compounds free of acid ligand were produced, while in the case of halide complexes compounds with a Pd—halide bond were formed.

The common steps for both systems are the reactions yielding Pd^I complexes as well as the reactions involving oxidative addition of a phosphine ligand (with the rupture of the P—C bond) to the palladium hydride or the Pd^0 complex with subsequent hydrogenolysis of the Pd—R bond.

The differences in behaviour of the compared complexes stems from the fact that the stronger base OAc^- (in comparison to X^-) is able to compete with a multiply bonded phenyl group in the intraspheric attack on the coordinated hydride ion in the Pd^I hydride complex, which leads [1] to reductive elimination of HOAc:



(15)

ortho-Palladation of PPh_2 (or PPh_3) in VII results in formation of a new hydride complex, which in a subsequent intraspheric reaction eliminates C_6H_6 [1].

In contrast, in the case of halide complexes, reaction 9 takes place because of the lower basicity of X^-, as a result of which C_6H_6 and $(R_3P)_2Pd_2(PR_2)_2X_2$ are formed. These complexes cannot react with H_2 because of the low charge on Pd (due to the effect of the basic phosphide group) and the low basicity of the halide ligand. As a result these comparatively stable complexes, in the case of a triphenylphosphine ligand, react with Pd^0 compounds (reaction 11), yielding the above trinuclear clusters, and are the main products of the reaction in the case of a trialkylphosphine ligand.

It should be noted that the reactivity of the palladium complex with triphenylphosphite ligands, $[(PhO)_3P]_2PdCl_2$, is radically different from that observed for complexes with phosphines (Fig. 3). The reaction is as follows:

$$2\,[(PhO)_3P]_2PdCl_2 + 2\,H_2 \rightarrow [(PhO)_3P]_4Pd + Pd + 4\,HCl \qquad (16)$$

It seems that the weak donor $P(OPh)_3$ is not capable of stabilizing complexes of the $(PhO)_3PPd(solv)_m$ type. This leads to their disproportionation with formation of the observed $[(PhO)_3P]_4Pd$ and metallic palladium. On the other hand, the increased strength of the P—O bond, as compared to the P—C bond, prevents oxidative addition with cleavage of the P—OR bond. Hence the formation of complexes with a $P(OPh)_2$ ligand is not observed. The major products of the reaction of phosphine complexes of palladium halides with H_2 are those in which the ratio $P/Pd \geqslant 1$.

On the other hand, the mixture of unidentified Pd complexes formed in small amounts as by-products of reaction 2, in which $P/Pd < 1$ according to chemical analysis, catalyzes the hydrogenation of 1,3-pentadiene in aniline solutions at 20°C and 1 atm at a rate of 1.7×10^{-4} mol/min (the amount of the catalytic solution is 10 ml; the diene concentration is 2×10^{-1} mol/l; the amount of the complex is 0.011 g). These data suggest that the observed catalytic activity of phosphine halide complexes of palladium [12] stems from the formation of cluster complexes with $P/Pd < 1$ as by-products of the reaction between these compounds and H_2.

Experimental

The solvents were purified by described methods [13]. The complexes $[PPh_3PdCl_2]_2$, $[PPh_3PdBr_2]_2$, $PdCl_2(PBu_3)_2$, $(PPH_3)PdBrPh$, and $[P(OPh_3)]_2PdCl_2$ were synthesized as described [14—18].

Synthesis of $[(PBu_3)PdCl_2]_2$

A solution of 0.74 g (2.5×10^{-3} mol) of Na_2PdCl_4 in 45 ml of ethyl alcohol was added to a solution of 1.45 g (2.5×10^{-3} mol) of $PdCl_2(PBu_3)_2$ in 45 ml of ethyl alcohol. The mixture was refluxed under argon for 45 min. The dark brown solution was filtered off and evaporated to dryness. The residue was dissolved in benzene and filtered. The benzene filtrate was evaporated to dryness. The orange precipitate was carefully washed with hexane and dried in vacuum. Found: C, 38.2; H, 7.3. $C_{12}H_{27}PCl_2Pd$ calcd.: C, 38.0; H, 7.15%.

Synthesis of $[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl$ by the reaction between $(PPh_3PdCl_2)_2$ and H_2

A suspension of 1.5 (3.4×10^{-3} mol) of $(PPh_3PdCl_2)_2$ in 20 ml of degassed aniline was stirred in an H_2 atmosphere at 50°C. After 95 ml (3.6×10^{-3} mol) of H_2 had been absorbed 0.8 mol of C_6H_6 was found per mol of the initial complex (identified by GLC). Aniline was evaporated to dryness in vacuum. The resulting brown precipitate was transferred onto a filter in an argon atmosphere, then washed with degassed diethyl ether and benzene. A black product remained on the filter, from which aniline hydrochloride was quantitatively washed out with water and a small amount (ca. 0.06 g) of a dark brown identified Pd complex was washed out with aniline. Metallic Pd formed an insoluble precipitate (ca. 0.05 g). The benzene filtrate was concentrated in vacuum and degassed hexane was added in an argon atmosphere. The dark purplish red precipitate was washed on a filter with degassed hexane and ether, then dried in vacuum. Finally, it was recrystallized under argon from toluene. Yield: 95%. Found: Pd, 21.0; P, 9.0; C, 61.0; H, 4.4; Cl, 4.5. $C_{78}H_{65}P_5Cl_2Pd_3$ calcd.: Pd, 20.6; P, 10.0; C, 60.6; H, 4.2; Cl, 4.0%. The molecular conductivity of the $[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl$ complex (10^{-3} M, 21°C) is 57 ohm^{-1} cm^2 (64 ohm^{-1} cm^2 according to ref. 6).

Synthesis of $[(PPh_3)_3(PPh_2)_2Pd_3Br]Br$ by the reaction between $(PPh_3)_2PdBr(Ph)$ and H_2

A solution of 0.59 g (0.75×10^{-3} mol) of $(PPh_3)_2PdBr(Ph)$ in 20 ml of degassed aniline was stirred in an H_2 atmosphere at 70°C. After 21 ml (0.75×10^{-3} mol) of H_2 had been absorbed, aniline was destilled to dryness in vacuum. The resulting brown precipitate was transferred onto a filter in an argon atmosphere, then washed with degassed diethyl ether and benzene.

A black product remained on the filter, from which aniline hydrobromide was washed out with water. The benzene filtrate was concentrated in vacuum and degassed hexane was added in an argon atmosphere. The dark purplish red precipitate was washed on the filter with degassed hexane and ether, then dried in vacuum. Finally, it was recrystallized under argon from toluene. Yield: 90%. Found: C, 57.8; H, 4.6; Br, 9.4. $C_{78}H_{65}P_5Br_2Pd_3$ calcd.: C, 57.3; H, 4.0; Br, 9.2. The molecular conductivity of the complex (10^{-3} M, 24°C) is 57 ohm^{-1} cm^2 (64 ohm^{-1} cm^2 according to ref. 6).

Synthesis of $[(PPh_3)_3(PPh_2)_2Pd_3Cl]Cl$ by the reaction between $(PPh_3)_2PdCl_2$ and H_2

A solution of 0.49 g (0.7×10^{-3} mol) of $(PPh_3)_2PdCl_2$ in 10 ml of degassed aniline was stirred in an H_2 atmosphere at 90°C. After 21 ml (0.7×10^{-3} mol) of H_2 had been absorbed, aniline was removed under vacuum. The resulting brown precipitate was transferred onto a filter in an argon atmosphere then washed with degassed diethyl ether and benzene. A grey product, remaining on the filter, was almost completely soluble in water. No black precipitate was observed. The benzene filtrate was concentrated in vacuum and degassed hexane was added in argon atmosphere. The dark purplish precipitate was washed on the filter with degassed hexane and diethyl ether, then dried in vacuum. Finally, it was recrystallized under argon from toluene. Yield: 95%. Found: C, 60.4; H, 4.8; Cl, 5.0. $C_{78}H_{65}P_5Cl_2Pd_3$ calcd.: C, 60.6; H, 4.2; Cl, 4.6%. The molecular conductivity (10^{-3} M, 21°C) is 57 ohm^{-1} cm^2.

Synthesis of $[P(OPh)_3]_4Pd$ by the reaction between $[P(OPh)_3]_2PdCl_2$ and H_2

A solution of 0.3 g (0.38×10^{-3} mol) of $[P(OPh)_3]_2PdCl_2$ in 10 ml of degassed aniline was stirred in an atmosphere of H_2 at 50°C. After 11 ml (0.4×10^{-3} mol) of H_2 had been absorbed, the reaction mixtures was cooled to 20°C and filtered in an argon flow. Metallic palladium precipitated on the filter.

Aniline was removed from the filtrate in vacuum at 50° C. The dry residue was dissolved in degassed benzene and filtered off. Water-soluble aniline hydrochloride remained on the filter. Degassed hexane was added to the benzene filtrate. The precipitated white complex was washed on a filter with degassed hexane and dried in vacuum. Yield: 80%. Melting point: 85 to 90° C (lit. 85° to 87° C [18]).

Found: C, 63.8; H, 4.8. $C_{72}H_{60}P_4O_{12}Pd$ calcd.: C, 64.2; H, 4.4%.

Synthesis of [(PBu$_3$)(PBu$_2$)PdCl]$_2$ · 2Am by the reaction between [PBu$_3$PdCl$_2$]$_2$ and H$_2$

A solution of 0.57 g (1.5×10^{-3} mol) of $[PBu_3PdCl_2]_2$ in 20 ml of degassed aniline was stirred in an H_2 atmosphere at 40° C. After 35 ml (1.3×10^{-3} mol) of H_2 had been absorbed, the reaction mixture was cooled to 20° C, degassed ether was added, and the mixture was filtered in an inert atmosphere.

Removal of the solvent from the filtrate resulted in a dark brown oily product. Yield: 45%. Found: C, 54.0; H, 8.2; N, 2.9; Cl, 8.0. $C_{332}H_{104}N_2P_4Cl_2Pd_2$ calcd.: C, 53.5; H, 8.9; N, 2.4; Cl, 6.1%.

The grey precipitate remaining on the filter was washed first with acetone then with dimethylformamide, leaving a pale yellow complex, $(C_6H_5NH_2)_2PdCl_2$, on the filter. Yield: 40%. Found: C, 40.2; H, 3.7; N, 8.3; Cl, 17.8. $C_{12}H_{14}N_2Cl_2Pd$ calcd.: C, 39.6; H, 3.8; N, 7.75; Cl, 19.5%.

After evaporation of dimethylformamide from the DMF extract, about 0.05 g of a dark brown unidentified Pd complex was isolated. Evaporation of acetone off the acetone extract yielded a bright yellow complex, $(PBu_3)PdCl_2(C_6H_5NH_2)$. Found: C, 46.5; H, 6.6; Cl, 16.0. $C_{15}H_{34}NPCl_2Pd$ calcd.: C, 46.0; H, 7.2; Cl, 15.0%.

The reaction between the above complexes and hydrogen and the hydrogenation of the dienes were studied as described earlier [19].

The resistance of the solutions was measured using an NM34-04 conductivity meter complete with a UK-02/1 transducer as an immersible vessel, with blackened platinum electrodes was used as the electrolytic cell. The amount of benzene formed in the reactions between the complexes and H_2 was determined by GLC (LkhM-8 MD chromatograph, 2 m × 0.3 cm column, 10% of polyethylene glycol adipinate on Resorb BLK, carrier gas flow rate 30 ml/min). The presence of butane in the reaction mixture resulting from reactions between the complexes and H_2 was determined by GLC (LKhM-7 MD chromatograph, 9 m × 0.3 cm column, 17% of β,β'-oxydipropionitrile on Celite 545, carrier gas flow rate 20 ml/min).

The IR spectra were determined on a UR-20 instrument in KBr. The ^{31}P NMR spectra were determined on a Bruker HX-90 spectrometer (36.43 MHz).

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