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

I. REACTIONS OF COMPLEXES WITH MOLECULAR HYDROGEN

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Summary

The interaction of $[Ph_3PPd(OAc)_2]_2$ with molecular H_2 yields a binuclear complex of zero-valent palladium, $(Ph_3P)_2Pd_2$. This complex interacts reversibly with H_2 in CH_2Cl_2, yielding $(Ph_3P)_2Pd_2H_2$. In argon atmosphere $(Ph_3P)_2Pd_2$ reacts with $[Ph_3PPd(OAc)_2]_2$ to form a binuclear complex of Pd^I with a metal—metal bond. These data, as well as the results of kinetic studies of the reactions between $[Ph_3PPd(OAc)_2]_2$ and H_2, are in agreement with an autocatalytic mechanism for the process, including catalysis of the reduction of Pd^{II} complexes by the Pd^0 compounds. It has been established that the synthesized compounds of Pd^{II}, Pd^I and Pd^0 with the ratio $P/Pd \geqslant 1$, are inactive in the hydrogenation of unsaturated compounds. The catalytically active complex $(PPh)_2Pd_5$ is formed when palladium acetate reacts with $(Ph_3P)_2Pd_2$ in the presence of H_2. The same compound is formed when a solution of $(Ph_3P)_2Pd_2$ is treated with a mixture of H_2 and O_2 (or H_2O_2 in an atmosphere of H_2). $(PPh)_2Pd_5$ is an effective catalyst for the hydrogenation of olefins, dienes, acetylenes, aldehydes, organic peroxides, quinones, O_2, Schiff bases, and nitro, nitroso, and azo compounds.

Introduction

Reactions between compounds of transition metals and molecular hydrogen often play a key role in the formation of complexes active as catalysts of the

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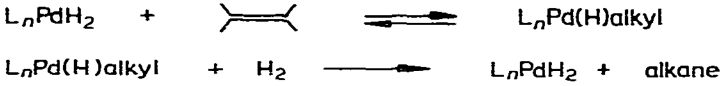
hydrogenation of organic compounds. While rhodium, iridium and cobalt complexes have been investigated in detail [1], those of palladium are relatively less thoroughly investigated. In the majority of the publications on palladium catalysts of hydrogenation it is assumed without any tangible proof that the catalysis is due to palladium hydride formed in situ [2,3]. Insertion of an unsaturated hydrocarbon into the Pd—H bond and hydrogenolysis of the formed alkyl or alkenyl intermediate with regeneration of the Pd—H bond are the factors contributing to the catalytic transformation [4], which may proceed as follows:



There are some indications of the formation of hydride complexes when H_2 reacts with Pd^{II} compounds [2,3,6]. However, there are no experimental data attesting to the role of these hydrides in catalysis.

Therefore, it was the intention of the work reported here to elucidate the nature of the compounds formed when H_2 reacts with phosphinacetate complexes of palladium.

Results and discussion

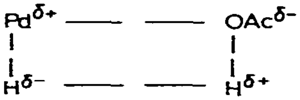
It has been found that solutions of $[Pd(OAc)_2]_3$ and PPh_3 in CH_2Cl_2, HOAc, C_6H_6, $C_6H_5CH_3$, C_6H_5Br, DMFA, DMSO, $(CH_3)_2CO$ in which hydrogenation of unsaturated compounds was studied [6] in the absence of dioxygen absorb 1.0—1.2 mol H_2 per gram atom of Pd at 20°C and 1 atm * (Table 1).

The kinetic curves (Figs. 1 and 2) show clearly the induction periods (τ). The duration of τ depends greatly on the $[PPh_3]/[Pd^{II}]$ ratio. The greater this ratio, the greater the value of τ (Fig. 3). At $[PPh_3]/[Pd^{II}] = 1$, $[Ph_3PPd(OAc)_2]_2$ is predominant in the solution [9]. As the ratio increases, the $(Ph_3P)_2Pd(OAc)_2$ complex is accumulated:

$$6\,PPh_3 + 2\,[Pd(OAc)_2]_3 \rightarrow 3\,[Ph_3PPd(OAc)_2]_2 \qquad (1)$$

$$[Ph_3PPd(OAc)_2]_2 + 2\,PPh_3 \rightleftharpoons 2\,(Ph_3P)_2Pd(OAc)_2 \qquad (2)$$

The increase in τ may be ascribed to the lower reactivity of $(Pd_3P)_2Pd(OAc)_2$ as compared to $[(Ph_3P)Pd(OAc)_2]_2$, in reactions with H_2. It seems that the more PPh_3 ligands are bonded to the Pd atom, the lower the reactivity of the compounds in the reaction under investigation. This may be explained on the basis of the transition state scheme of the initial step of the observed reaction, i.e. the hydrogenolysis of the Pd—OAc bond:



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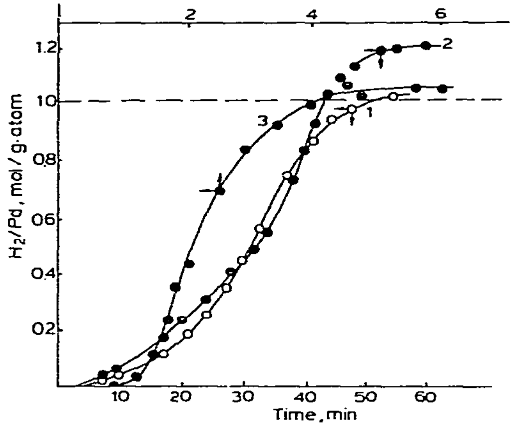
* In CH_2Cl_2 in the concentration range of $[Ph_3PPd(OAc)_2]_2$ 5×10^{-4} to 5×10^{-3} mol/l, IR spectra (ν = 1630 and 1580 cm^{-1}) do not reveal any deviation from the Lambert-Beer law, which is indicative of the absence of measurable amounts of $(Ph_3P)_2Pd(OAc)_2$ or $[Ph_3PPd(OAc)_2]\cdot(Solvent)$.



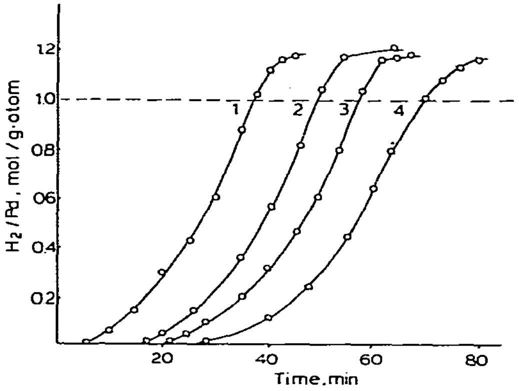


Fig. 1. Kinetic curves for the absorption of H_2 in CH_3COOH (1), in C_6H_5Br (2), $[[Ph_3PPd(OAc)_2]_2]_0 = 3.2 \times 10^{-3}$ mol/l, and in C_6H_6 (3), $[[Ph_3PPd(OAc)_2]_2]_0 = 2 \times 10^{-4}$ mol/l.

Fig. 2. Kinetic curves for the absorption of H_2 in CH_2Cl_2: 1. $[[Ph_3PPd(OAc)_2]_2]_0 = 4.6 \times 10^{-3}$ mol/l with addition of the hydrogenated complex; 2. same, without addition; 3. $[[Ph_3PPd(OAc)_2]_2]_0 = 2.1 \times 10^{-3}$ mol/l; 4. $[[Ph_3PPd(OAc)_2]_2]_0 = 4.9 \times 10^{-3}$ mol/l, volume ratio $H_2 : Ar = 1:1$.

In such a transition state the Pd atom accepts the hydride ion, while the connected nucleophilic ligand promotes this by accepting the proton detached from the H_2 molecule. Obviously, all other conditions being equal, the easier the transition state of such a reaction is attained, the greater the charge at the Pd atom. Since, according to ESCA data, the charge at the Pd atom in $(Ph_3P)_2Pd(OAc)_2$ (E Pd $3d_{5/2}$ = 338.1 eV [10]) is less than in $[Ph_3PPd(OAc)_2]_2$ (E Pd $3d_{5/2}$ = 338.5 eV [10]), the decrease in reactivity when passing from $[Ph_3PPd(OAc)_2]_2$ to $(Ph_3P)_2Pd(OAc)_2$ becomes clear.

The reaction of the acetate complex containing PBu_3 is slower than that of the complex containing PPh_3. For example, at the concentration of $[Pd^{II}] = [PBu_3] = 9.5 \times 10^{-3}$ mol/l in CH_2Cl, no absorption of H_2 is observed for an

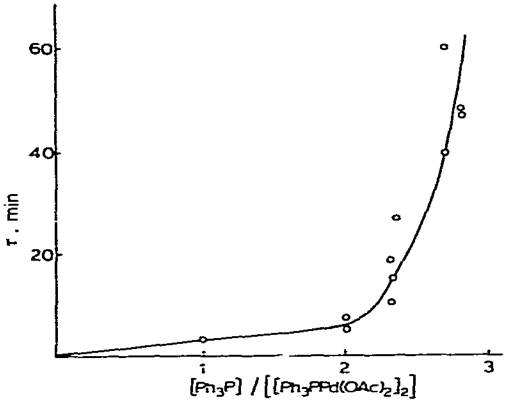


Fig. 3. τ versus molar ratio $Ph_3P : [Ph_3PPd(OAc)_2]_2$. $[[Ph_3PPd(OAc)_2]_2]_0 = 1 \times 10^{-3}$ mol/l, benzene.

TABLE 1

H_2 ABSORBED BY $[Ph_3PPd(OAc)_2]_2$ IN VARIOUS SOLVENTS ($[[Ph_3PPd(OAc)_2]_2]_0 = 2 \times 10^{-3}$ mol/l, 20°C, 1 atm)

Solvent 1	mol H_2/g-atom Pd 2
Benzene	1.0
Ethylbenzene	1.0
Toluene	1.0
Bromobenzene	1.2
Methylene chlroide	1.2
Acetic acid	1.0
1-Butanol	1.0
Acetone	1.1
Acetonitrile	1.0
DMF	1.0
DMSO	1.0

hour. This is in agreement with the more pronounced donor ability of PBu_3 in comparison with those of PPh_3.

The product of the reaction in which 1 mole H_2 is absorbed per gram atom of Pd may be the postulated [3] hydride complex of Pd, i.e.:

$$[Ph_3PPd(OAc)_2]_2 + 2H_2 \rightarrow [Ph_3PPd(H)OAc]_2 + 2\,HOAc \qquad (3)$$

However, instead of the 1 mole HOAc per gram atom of Pd, expected from eq. 3, 2 mol HOAc were found after the reaction of $[Ph_3PPd(OAc)_2]_2$ with H_2. Moreover, instead of the hydride complex a diamagnetic compound, $(Ph_3P)_2Pd_2$*, containing no Pd—H bond (absence of a PMR signal in the range 8 to 60 ppm and absence of absorption in the IR spectra in the region 1700 to 2400 cm^{-1}), was obtained, the reaction being:

$$[Ph_3PPd(OAc)_2]_2 + 2\,H_2 \rightarrow (Ph_3P)_2Pd_2 + 4\,HOAc \qquad (4)$$

The same complex is formed not only during reduction of $[Ph_3PPd(OAc)_2]_2$ with H_2 but also when it is treated with a reducing agent such as sodium amalgam:

$$[Ph_3PPd(OAc)_2]_2 + 4\,Na/Hg \rightarrow (Ph_3P)_2Pd_2 + 4\,NaOAc \qquad (5)$$

Moreover, $[Ph_3PPdCl_2]_2$, which does not react with H_2 at 20°C and 1 atm, is reduced with Na/Hg, yielding $(Ph_3P)_2Pd_2$:

$$[Ph_3PPdCl_2]_2 + 4\,Na/Hg \rightarrow (Ph_3P)_2Pd_2 + 4\,NaCl \qquad (6)$$

Obviously, for $(Ph_3P)_2Pd_2$ to be formed it is important that the initial complex should contain bridging ligands bringing together two palladium atoms and facilitating formation of a Pd—Pd bond in the course of reduction of Pd^{II}.

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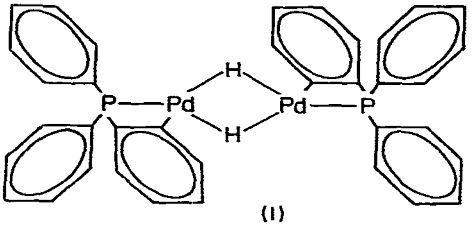
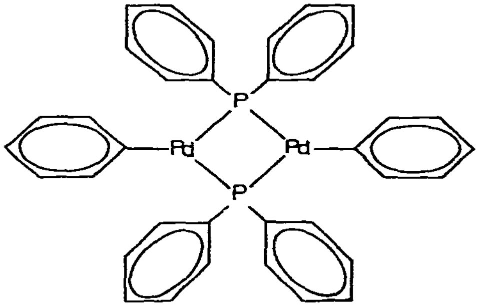
* Reaction 4 proceeds with a maximum yield of $(Ph_3P)_2Pd_2$ in CH_2Cl_2 solutions. In other solvents other processes occur along with this reaction. The nature of these will be discussed later.

Indeed, at the ratio $PPh_3/Pd = 5$ $(Ph_3P)_2Pd(OAc)_2$ reacts with H_2 at 50°C and 40 atm. *

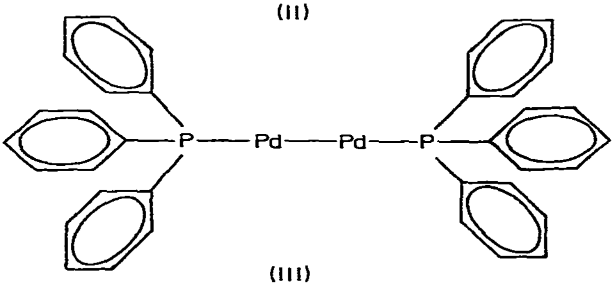
The molecular weight determined for $(Ph_3P)_2Pd_2$ in CH_2Cl_2 is 690, which is in agreement with the calculated one for $(Ph_3P)_2Pd_2$. The isolated compound could be in principle, have one of the following structures:



(I)



(II)



(III)

Because of the lack of any evidence in the PMR and IR spectra for the presence of Pd—H bonds in the complex, structure I can be rejected. Neither structures I nor II are consistent with ESCA data (E Pd $3d_{5/2} = 336.8$ eV [10]), according to which the oxidation state of palladium in $(Ph_3P)_2Pd_2$ approaches zero.

When Br_2 or I_2 act upon solutions of $(Ph_3P)_2Pd_2$ in CH_2Cl_2, the corresponding benzene halide is not formed in perceptible amounts, as opposed to what is observed for phenyl complexes of Pd^{II} [12]. Moreover, when $(Ph_3P)_2Pd_2$ is treated with Br_2, the known complex $[Ph_3PPdBr_2]_2$ is formed in quantitative yield [13]. Hence, $(Ph_3P)_2Pd_2$ lacks Pd—phenyl σ bonds and all phenyl groups are bonded to the P atom. Thus structure II is also rejected.

The available data are incompatible with structure III, in which two Pd

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* The more rigorous conditions in this reaction as compared to reaction 5 stem from the fact that $(Ph_3P)_2Pd(OAc)_2$ practically does not react with H_2 at 20°C and 1 atm.

atoms are linked by a metal—metal bond and are also connected with two P atoms of PPh_3. The Pd—Pd bond in the two-atom Pd_2 molecule is extremely weak ($E_{diss} = 15 \pm 5$ kcal/mol [14]) and, as can be inferred from quantum chemical calculations, the attachment of phosphine ligands does not stabilize it [15]. This suggests that the Pd atoms are linked not only to the P atoms but also to the phenyl rings of PPh_3. The ability of the Pd_2 group to coordinate a benzene ring is well known [16]. Moreover, in the known formally bicoordinated phosphine complexes of Pd^0 of the $(R_3P)_2Pd$ type, the metal interacts with the hydrogen atoms of R [17].

The $(Ph_3P)_2Pd_2$ complex does not attach excess phosphine ligands on treatment with PPh_3 and does not form mononuclear complexes of the $(Ph_3P)_4Pd$ type.

Solutions of $(Ph_3P)_2Pd_2$ in CH_2Cl_2 absorb 0.2 mol H_2 per gram atom of Pd under 1 atm and 20° C:

$$(Ph_3P)_2Pd_2 + H_2 \rightleftharpoons (Ph_3P)_2Pd_2H_2, \qquad (7)$$

which is why the absorption of H_2 exceeds that required by the stoichiometry of reaction 4 *. When a 1:1 mixture (volume ratio) of H_2 and Ar acts upon $(Ph_3P)_2Pd_2$, the amount of H_2 absorbed decreases to about 0.1 mol H_2 per gram atom of Pd (Fig. 4). Reaction 7 is reversible: a solution of $(Ph_3P)_2Pd_2$ in CH_2Cl_2 with about 0.2 mol H_2 per gram atom of Pd absorbed, after flushing with an argon flow to remove H_2, absorbs again 0.2 mol H_2 per gram atom of Pd. As can be seen from Fig. 4, the reaction is of first order in $(Ph_3P)_2Pd_2$ and H_2. In an H_2 atmosphere $k_7 \cdot [H_2] = 0.057$ min^{-1}, whereas in the case of an H_2/Ar mixture (volume ratio 1/1), $k_7[H_2] = 0.030$ min^{-1} and $k_{-7} = 0.079$ min^{-1}.

Solutions of $(Ph_3P)_2Pd_2H_2$ in CH_2Cl_2 do not act as catalysts in hydrogenation of unsaturated compounds. According to quantum-chemical calculations [15], in compounds of the $(R_3P)_2Pd_2H_2$ type H_2 is coordinated as an integral molecular ligand without cleavage of the H—H bond. Molecular hydrogen is probably too weak an oxidizing agent for $(Ph_3P)_2Pd_2$. Molecular oxygen does not oxidize $(Ph_3P)_2Pd_2$ under mild conditions either. For example, at 20° C and 1 atm, no absorption of O_2 by solutions of $(Ph_3P)_2Pd_2$ in CH_2Cl_2 is observed for an hour.

On the contrary, when an oxidizing agent as Br_2 is involved, $[Ph_3PPdBr_2]_2$ is formed almost instantaneously in quantitative yield:

$$(Ph_3P)_2Pd_2 + 2\,Br_2 \rightarrow [Ph_3PPdBr_2]_2 \qquad (8)$$

Moreover, CH_2Cl_2 also oxidizes $(Ph_3P)_2Pd_2$, although this is a slow process. For example, when solutions of $(Ph_2P)_2Pd_2$ in CH_2Cl_2 are allowed to stand for more than 24 hours, $(Ph_3P)_2PdCl_2$ [18] and metallic Pd are formed. $(Ph_3P)_2Pd_2$ is readily oxidized with the Pd^{II} complex $[Pd_3PPd(OAc)_2]_2$, yielding the Pd^I complex $(Ph_3P)_2Pd_2(OAc)_2$. Studies of the stoichiometry of the reaction between $(Ph_3P)_2Pd_2$ and $[Ph_3PPd(OAc)_2]_2$ have shown that these complexes interact in a 1:1 ratio. The IR spectrum taken in CH_2Cl_2 solution reveals

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* According to GLC and mass-spectrometric data, H_2 is not used in the system CH_2Cl_2 -$[Ph_3PPd(OAc)_2]_2$ for the hydrogenation of CH_2Cl_2.

absorption, prior to the reaction, of the terminal carboxyl group $>C{=}O$ at 1630 cm^{-1} and the bridging group at 1580 cm^{-1}. As more $(Ph_3P)_2Pd_2$ in CH_2Cl_2 is added to $[Ph_3PPd(OAc)_2]_2$, the relative intensity of the 1630 cm^{-1} band decreases, and as soon as a molar ratio of 1 : 1 is reached between the components, this band disappears and only the 1580 cm^{-1} band remains:

$$(Ph_3P)_2Pd_2 + [Ph_3PPd(OAc)_2]_2 \rightarrow 2\,(Ph_3P)_2Pd_2(OAc)_2 \tag{9}$$

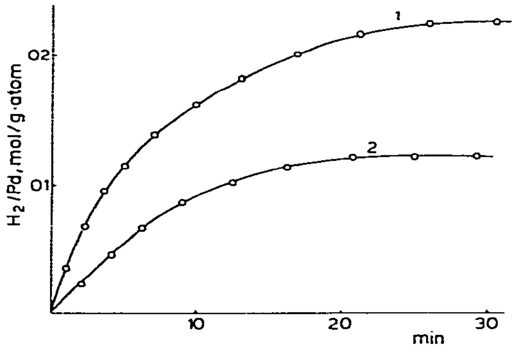
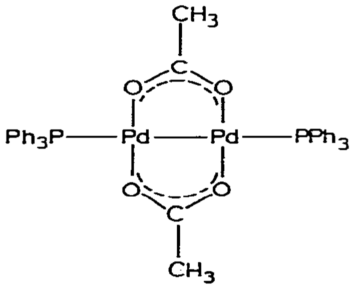


Fig. 4. Kinetic curves for the absorption of H_2 by the complex $(Ph_3P)_2Pd_2$ in CH_2Cl_2: 1. H_2, $[(Ph_3P)_2Pd_2]_0 = 5.1 \times 10^{-3}$ mol/l; 2. $H_2:Ar = 1:1$ mixture, $[(Ph_3P)_2Pd_2]_0 = 6.5 \times 10^{-3}$ mol/l.

The presence in the IR spectra of $(Ph_3P)_2Pd_2(OAc)_2$ of only the 1580 cm^{-1} band typical of vibrations of $>C{=}O$ bridging acetate groups [19], molecular weight measurements versus those estimated, ESCA data (bonding energy Pd $3d_{5/2}$ = 337.1 eV) and the observed diamagnetism suggest that this compound is a dimeric complex of Pd^{I} with bridging acetate groups.



Unlike $[(Ph_3P)Pd(OAc)_2]_2$, this compound rapidly reacts with H_2 yielding $(Ph_3P)_2Pd_2$ and 1 mole HOAc per gram atom of Pd (GLC data):

$$(Ph_3P)_2Pd_2(OAc)_2 + H_2 \rightarrow (Ph_3P)_2Pd_2 + 2\,HOAc \tag{10}$$

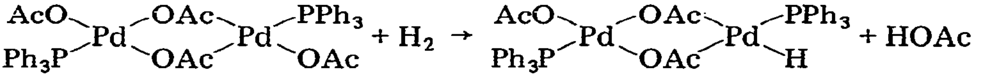
The reaction between $(Ph_3P)_2Pd_2$ and Pd^{II} compounds free of phosphine ligands, such as $[Pd(OAc)_2]_3$, proceeds in an H_2 atmosphere, yielding a cluster compound as the main product, containing phosphene rather than phosphine ligands. For example, at a $[Pd(OAc)_2]_3/(Ph_3P)_2Pd_2$ ratio of 1, the reaction yields 6 mol HOAc and 3 mol C_6H_6 as well as $Pd_5(PPh)_2$ [20] *:

$$(Ph_3P)_2Pd_2 + [Pd(OAc)_2]_3 + 4.5\,H_2 \rightarrow (PPh)_2Pd_5 + 3\,C_6H_6 + 6\,HOAc \qquad (11)$$

This reaction can be observed by means of UV spectra since $(Ph_3P)_2Pd_2$, unlike $Pd_5(PPh)_2$, absorbs at 412 nm. As more $[Pd(OAc)_2]_3$ is added to $(Ph_3P)_2Pd_2$ in the presence of H_2, the intensity of the band at 412 nm diminishes and the band disappears completely at a $[Pd(OAc)_2]_3/(Ph_3P)_2Pd_2$ ratio of 1 (Fig. 7).

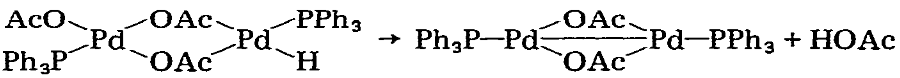
The rate of reduction of $[(Ph_3P)Pd(OAc)_2]_2$ complex with hydrogen depends on the solvents used. For example, in C_6H_6, $C_6H_5CH_3$, DMFA and DMSO with complex concentrations ranging from 10^{-3} to 3×10^{-3} mol/l the reaction is so fast that the rate of hydrogen uptake cannot be studied volumetrically. In CH_2Cl_2, acetic acid, bromobenzene ($[[(Ph_3P)Pd(OAc)_2]_2]_0 = 3\text{—}4 \times 10^{-3}$ mol/l), and benzene ($[[(Ph_3P)Pd(OAc)_2]_2]_0 = 2 \times 10^{-4}$ mol/l) the absorption of H_2 can be observed in the kinetic region (Figs. 1 and 2). It has been established that the absorption of H_2 is represented by S-shaped curves and that τ increases with decreasing concentration of the starting complex and decreasing P_{H_2}. The new complexes resulting from the reaction between $[Ph_3PPd(OAc)_2]_2$ and H_2 seem to catalyze the reaction between the latter two. This is demonstrated by a decrease in τ and even its becoming zero when either a certain amount of an H_2-treated solution or $(Ph_3P)_2Pd_2$ complex is added to the $[Ph_3PPd(OAc)_2]_2$ solution under examination prior to hydrogenation. This indicates that $(Ph_3P)_2Pd_2$ is responsible for the catalysis of the reaction between $[Ph_3PPd(OAc)_2]_2$ and H_2. It should be noted that the introduction of freshly precipitated Pd into the reaction does not affect the H_2 absorption rate. All of the above data suggest the following scheme for the process.

In the first step, one of the Pd—OAc bonds in the dimeric complex $[Ph_3PPd(OAc)_2]_2$ is split by molecular H_2, probably resulting in a hydride complex:



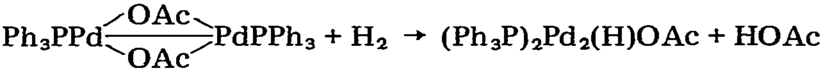
$$(AcO)(Ph_3P)Pd(\mu\text{-}OAc)_2Pd(PPh_3)(OAc) + H_2 \rightarrow (AcO)(Ph_3P)Pd(\mu\text{-}OAc)_2Pd(PPh_3)(H) + HOAc \qquad (12)$$

This compound seems to be unstable relative to reductive elimination of HOAc and loses the HOAc group, forming a Pd^I complex:



$$(AcO)(Ph_3P)Pd(\mu\text{-}OAc)_2Pd(PPh_3)(H) \rightarrow Ph_3P\text{—}Pd(\mu\text{-}OAc)_2Pd\text{—}PPh_3 + HOAc \qquad (13)$$

As mentioned above, unlike $[Ph_3PPd(OAc)_2]_2$, this complex is rapidly hydrogenated, probably through intermediate formation of a hydride-Pd complex, yielding $(Ph_3P)_2Pd_2$:



$$Ph_3PPd(\mu\text{-}OAc)_2PdPPh_3 + H_2 \rightarrow (Ph_3P)_2Pd_2(H)OAc + HOAc \qquad (14)$$

$$(Ph_3P)_2Pd_2(H)OAc \rightarrow (Ph_3P)_2Pd_2 + HOAc \qquad (15)$$

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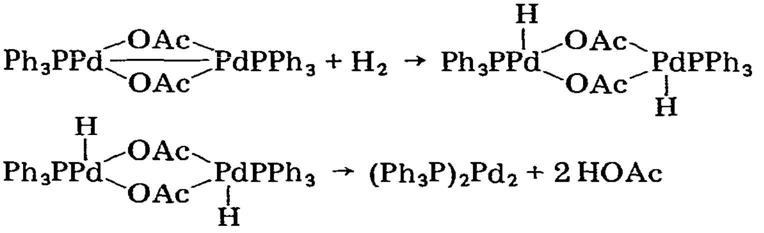
[*] The lower yield of C_6H_6 as compared to that required for formation of $(PhP)_2Pd_5$ must be due to formation, in addition to this compound, of a cluster compounds of the $(Ph_nP)_2Pd_5$ type, where $n = 2$ or 3.

The rapid reaction of $(Ph_3P)_2Pd_2(OAc)_2$ with H_2 despite the low degree of oxidation of Pd suggests that in the case of this complex there is a path for the interaction with H_2 other than the above-mentioned heterolytic mechanism. It is possible that, in the case of Pd^I compounds, H_2 is oxidatively added with the participation of both palladium atoms in the Pd_2^{II} group:



$$Ph_3PPd\begin{matrix}OAc\\OAc\end{matrix}PdPPh_3 + H_2 \rightarrow Ph_3P\overset{H}{Pd}\begin{matrix}OAc\\OAc\end{matrix}\underset{H}{Pd}PPh_3$$

$$Ph_3P\overset{H}{Pd}\begin{matrix}OAc\\OAc\end{matrix}\underset{H}{Pd}PPh_3 \rightarrow (Ph_3P)_2Pd_2 + 2\,HOAc \qquad (16)$$

In the case of mononuclear Pd^0 complexes the oxidative addition of H_2 must increase the oxidation state Pd^{II}. Calculations [15] show that such a reaction is thermodynamically unfavourable. Oxidative addition of H_2 to Pd^{II} complexes is also thermodynamically unfavourable because the Pd^{IV} oxidation state is energetically too high. H_2 is too weak an oxidizing agent for both Pd^0 and Pd^{II}. On the contrary, in the case of the binuclear $Pd^I—Pd^I$ groups, the addition of H_2 is quite possible because Pd^{II} complexes must eventually be formed.

The reaction between $(Ph_3P)Pd_2$ and the initial $[(Ph_3P)Pd(OAc)_2]_2$ again yields a Pd^I compound according to eq. 2. Hence, the presence of an induction period in the reaction between $[(Ph_3P)Pd(OAc)_2]_2$ and H_2 is due to the slow step of Pd^I complex formation (slow step 12 and fast step 13), the latter complex being reduced to $(Ph_3P)_2Pd_2$ more rapidly than the initial Pd^{II} complex. The zero-valent complexes catalyze the reduction of the starting compounds. In reactions 9, 14 and 15 the disappearance of one $(Ph_3P)_2Pd_2$ leads to the formation of two molecules of $(Ph_3P)_2Pd_2$, which is how the observed autocatalysis of the entire process can be explained.

However, there is an alternative mechanism possible for the catalysis of the hydrogeneration of Pd^{II} complexes: through a reaction between these compounds and $(Ph_3P)_2Pd_2H_2$:

$$(Ph_3P)_2Pd_2H_2 + [Ph_3PPd(OAc)_2]_2 \rightarrow$$
$$(Ph_3P)_2Pd_2 + (Ph_3P)_2Pd_2(OAc)_2 + 2\,HOAc \qquad (18)$$

An argument in favour of this possibility is the fact that the rate of reaction is accelerated by hydrides of other metals, such as Rh. For example, addition of a rhodium hydride such as $[(Ph_3P)_2Rh(H)_2Cl]_2$ [21] or $[(Ph_3P)_2Rh(H)_2(OAc)]_2$ [22] to a solution of $[R_3PPd(OAc)_2]_2$ in CH_2Cl_2 accelerates the reaction of both triphenylphosphine and tributylphosphine complexes of Pd^{II} with H_2 (Fig. 5). It should be noted, however, that hydrides such as $(Ph_3P)_4RhH$, whose activity in the hydrogenation of organic substrates is extremely low [1], practically do not catalyze the hydrogenation of $[Ph_3PPd(OAc)_2]_2$.

During the hydrogenation of $[Ph_3PPd(OAc)_2]_2$, as has been mentioned above, the formation of $(Ph_3P)_2Pd_2$ is accompanied by the appearance of C_6H_6 in the system. The yield of benzene depends on the solvent used (Table 2). For example, in CH_3COOH $(Ph_3P)_2Pd_2$ is not formed at all and 1 mol C_6H_6 per mol of

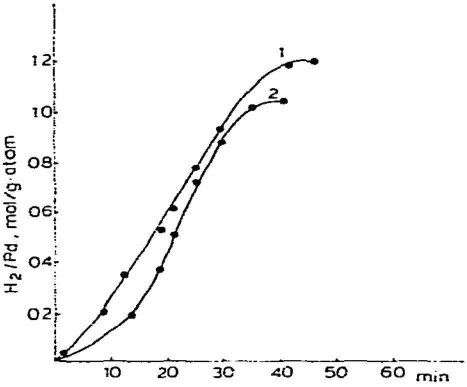


Fig. 5. Absorption of H_2 by phosphine-acetate complexes of palladium in the presence of rhodium hydrides (in CH_2Cl_2): 1. $[[Ph_3PPd(OAc)_2]_2]_0 = 4.6 \times 10^{-3}$ mol/l, $[[(Ph_3P)_2Rh(H_2)OAc]_2]_0 = 10^{-4}$ mol/l; 2. $[[Pd(OAc)_2]_3]_0 = 3.2 \times 10^{-3}$ mol/l, $[P(C_4H_9)_3]_0 = 9.5 \times 10^{-3}$ mol/l, $[[(Ph_3P)_2Rh(H_2)Cl]_2]_0 = 5 \times 10^{-4}$ mol/l.

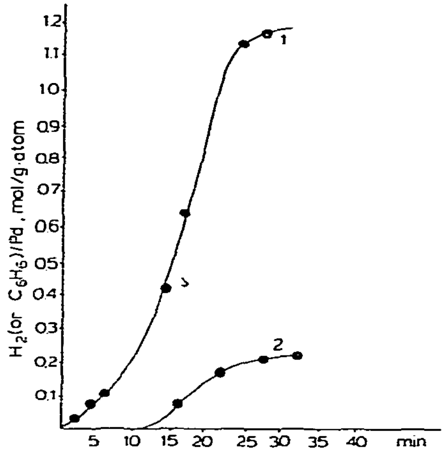


Fig. 6. Kinetic curves for the absorption of H_2 (1) and accumulation of C_6H_6 (2) during the hydrogenation of $[Ph_3PPd(OAc)_2]_2$ (CH_2Cl_2, $[[Ph_3PPd(OAc)_2]_2]_0 = 1.85 \times 10^{-2}$ mol/l).

PPh_3 is produced. The lowest amount of C_6H_6 is formed in CH_2Cl_2 (the yield of C_6H_6 is about 0.2 mol per mol of PPh_3). No benzene is formed when the solutions of the complexes $(Ph_3P)_2Pd_2$, $(Ph_3P)_2Pd_2(OAc)_2$ and $[Ph_3PPd(OAc)_2]_2$ in CH_2Cl_2 or CH_3COOH are exposed to argon for an hour. In addition, when a solution of $(Ph_3P)_2Pd_2$ in CH_2Cl_2 is exposed to H_2, no formation of C_6H_6 is observed at 20°C and 1 atm. At the same time, hydrogenation of $(Ph_3P)_2Pd_2(OAc)_2$ does produce C_6H_6. The kinetics of the accumulation of C_6H_6 during the hydrogenation of $[Ph_3PPd(OAc)_2]_2$ also indicates that C_6H_6 is generated from the intermediate complex $(Ph_3P)_2Pd_2(OAc)_2$. For example, in CH_2Cl_2 the amount of benzene formed increases as more H_2 is absorbed by the solution and both processes stop at the same time (Fig. 6).

In all experiments with hydrogenation of $[(Ph_3P)Pd(OAc)_2]_2$ (see Table 2), 1 ± 0.05 mol H_2 per gram atom of Pd^{II} is absorbed in CH_3COOH, ethylbenzene and DMF; hence, the amount of C_6H_6 generated does not correlate with the

TABLE 2

YIELD OF C_6H_6 IN REACTIONS BETWEEN $[Ph_3PPd(OAc)_2]_2$ AND H_2 IN VARIOUS SOLVENTS ($[[Ph_3PPd(OAc)_2]_2]_0 = 10^{-2}$ mol/l)

Solvent	mol C_6H_6/mol PPh_3
CH_2Cl_2	0.2
DMF	0.4
$C_6H_5C_2H_5$	0.6
HOAc	1.0

amount of absorbed H_2. These data indicate that no H_2 is involved in the formation of C_6H_6.

The yield of CH_3COOH in all solvents corresponds to the stoichiometry of reaction 4 (to within ±5%) without any tendency to decrease with increasing yield of C_6H_6. It seems unlikely that solvents of so dissimilar chemical nature, such as DMF, ethylbenzene and HOAc, could perform the function of H-donors in the formation of C_6H_6 equally well.

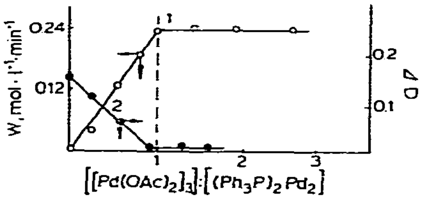
Unfortunately, too few data are available to elucidate the mechanism of this reaction. However, the fact that C_6H_6 is formed as a result of exposure of $(Ph_3P)_2Pd_2(OAc)_2$ to H_2 suggests that C_6H_6 appears as a consequence of transformations of the hydride complex resulting from substitution of the H atom for the acetate group in $(Ph_3P)_2Pd_2(OAc)_2$. The formation of C_6H_6 seems to involve the steps of oxidative addition of the coordinated PPh_3 to the $Pd^I—Pd^I$ group and reductive elimination of CH_3COOH and C_6H_6. The deficiency in H atoms is compensated by *ortho*-palladation of a phenyl ring in PPh_3.

In the case of interaction between H_2 and solutions in which $PPh_3/[Pd(OAc)_2]_3 < 3$, the yield of benzene exceeds 1 mol per mol of PPh_3. The data available and the composition of the resulting complex $Pd_5(PPh)_2$ suggest that under these conditions two P—C bonds are split in the PPh_3, eventually yielding a PPh ligand. It should be noted that when PBu_3 is used as ligand, the formation of butane is also observed under conditions when C_6H_6 is generated from PPh_3. This is indicative of the general nature of the cleavage of the P—C bond during hydrogenation of tertiary phosphine complexes of palladium acetate.

Depending on the ratio between Pd^{II} and PPh_3 and the solvent used, a series of compounds is obtained which are difficult to isolate and identify. However, they can be divided into two groups: complexes in which $P/Pd \geqslant 1$ and those in which $P/Pd < 1$. Neither the solutions containing $[Pd(OAc)_2]_3$ and PPh_3 at ratio $P/Pd \geqslant 1$ in DMF, CH_3COOH, CH_2Cl_2 and other solvents, nor the complexes isolated from these systems after their treatment with H_2, such as $(Ph_3P)_4Pd$, $(Ph_3P)_2Pd_2$, and a mixture of unidentified Pd complexes with *ortho*-palladated PPh_2, exhibit any catalytic activity with respect to the hydrogenation of dienes (1,3-pentadiene, cyclopentadiene) and olefins (1-pentene, cyclohexene) at 20° C and 1 atm.

On the contrary, the systems containing $[Pd(OAc)_2]_3$-PPh_3 in the ratio $P/Pd < 1$ are active in the hydrogenation of unsaturated compounds (Table 3). The lower this ratio (to 1 : 0.4), the greater the activity of the catalytic solutions in the hydrogenation of 1,3-pentadiene (Fig. 7). The maximum activity is attained at $Pd/P = 2.5$, this being the ratio corresponding to the $(PhP)_2Pd_5$ complex. On the other hand, the isolated complex $(PhP)_2Pd_5$ in DMF solution exhibits the same activity at 20° C and 1 atm with respect to 1 gram atom of Pd as dimethylformamide solutions of $[Pd(OAc)_2]_3$ and PPh_3 in which $Pd/P = 2.5$. Complex $(PhP)_2Pd_5$ is also active in the hydrogenation of oxygen. It should be noted that the systems in which $P/Pd = 1$ become active in the hydrogenation of unsaturated compounds only after preliminary contact with an O_2/H_2 mixture (volume ratio 1/2). Separate treatment of the solution first with O_2 and then with H_2 is not conductive to catalytic activity.

The rate of hydrogenation of 1,3-pentadiene increases symbatically with the amount of the O_2/H_2 mixture absorbed before the diene was introduced



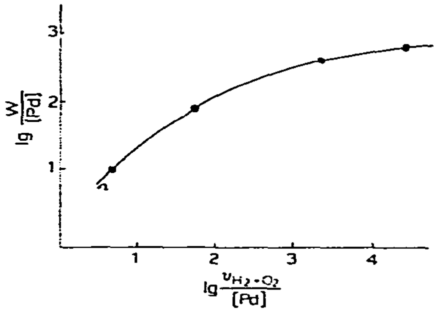


Fig. 7. Hydrogenation rate of 1,3-pentadiene (1) and optical density variations (2) (λ = 412 microns) versus molar ratio $[Pd(OAc)_2]_3$:$(Ph_3P)_2Pd_2$.

Fig. 8. Hydrogenation rate of 1,3-pentadiene versus volume of the absorbed H_2/O_2 mixture, $[(Ph_3P)_2Pd_2]_0 = 5 \times 10^{-5}$ mol/l, DMF.

(Fig. 8). After the O_2/H_2 mixture has been absorbed to more than 10^4 to 10^5 mol/g-atom Pd, unidentified substances precipitate followed by metallic Pd, and the catalytic activity declines.

As was indicated in special experiments in which hydrogenation was conducted in a practically complete absence of O_2 in the system (see Experimental), the solutions are not active in hydrogenation reactions. If the reactor is flushed only with H_2, as is normally done before catalytic experiments, the remaining O_2 in the reactor is sufficient for the formation of active solutions in which the hydrogenation rate of pentadiene is 1 to 10 mol/g-atom Pd min. Since the interaction between H_2 and solutions containing $[Pd(OAc)_2]_3$ and Ph_3P in the ratio Ph_3P:Pd = 1:1 yields primarily $(Ph_3P)_2Pd_2$ and HOAc (reac-

TABLE 3

CATALYTIC PROPERTIES OF $(PPh)_2Pd_5$ IN THE HYDROGENATION OF ORGANIC COMPOUNDS (20°C, 1 atm, DMF)

Class of compounds	Substrate	Product	H_2-uptake mol/g-atom Pd min
Dienes	1,3-Pentadiene	2-Pentene	1000
Olefins	1-Pentene 2-Pentene	Pentane Pentane	100 100
Aldehydes	Salicylaldehyde	Salicyl alcohol	40
Peroxides	Cumene peroxide	Cumene alcohol	2 [a]
Nitro compounds	Picric acid	2,4,6-Triaminophenol	10
Quinones	*p*-Benzoquinone	*p*-Hydroquinone	10
Nitroso compounds	α-Nitroso-β-naphthol	α-Amino-β-naphthol	10
Azo compounds	Azobenzene	Hydrazobenzene	2
Schiff bases	2-Oxybenzylidene-4-methoxyphenylamine	2-Oxybenzyl-4-methoxyphenylamine	2

[a] Hydrogenation at 40°C.

tion 4), the effect of the O_2/H_2 mixture on catalytic activity was studied in dimethylformamide solutions of $(Ph_3P)_2Pd_2$ and HOAc at molar ratio of 1:4. Contact between the O_2/H_2 mixture and the solutions under investigation initiates the following catalytic reaction in accordance with volumetric data:

$$O_2 + 2\,H_2 \rightarrow 2\,H_2O \tag{19}$$

Hydrogen peroxide was also formed in small amounts during the hydrogenation of O_2 as indicated by qualitative reactions on H_2O_2 (see Experimental). The introduction of H_2O into a solution of $(Ph_3P)_2Pd_2$ and HOAc not treated with O_2/H_2 does not give rise to any catalytic activity in the hydrogenation of 1,3-pentadiene. However, H_2O_2 introduced into this system (molar ratio $Pd:H_2O_2 = 1:4$), brings about catalytic activity (the 1,3-pentadiene hydrogenation rate is 100 mol/g-atom Pd min). The observed effect cannot be attributed to the system being affected by an O_2/H_2 mixture which could be formed as a result of decomposition of H_2O_2 in the presence of a Pd complex, since the amount of the O_2 formed in this case should bring about a much lower activity (2 to 3 mol/g-atom Pd min) than that observed.

As a result of relatively short exposure of $(Ph_3P)_2Pd_2$ solutions to hydrogen peroxide in the presence of HOAc, the complex $[(Ph_3P)Pd(OAc)_2]_2$ was isolated from the reaction:

$$(Ph_3P)_2Pd_2 + 2\,H_2O_2 + 4\,HOAc \rightarrow [Ph_3PPd(OAc)_2]_2 + 4H_2O \tag{20}$$

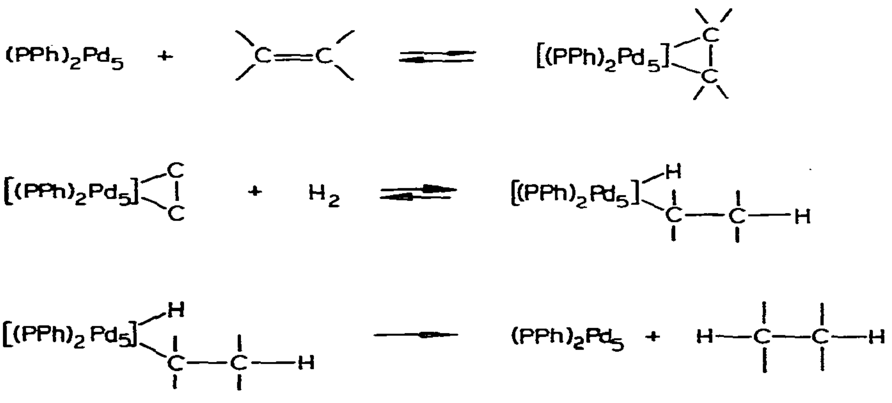
A longer exposure yields $[Pd(OAc)_2]_3$:

$$3\,[Ph_3PPd(OAc)_2]_2 + 6\,H_2O_2 \rightarrow 2\,[Pd(OAc)_2]_3 + 6\,Ph_3PO + 6\,H_2O \tag{21}$$

Thus, the $[Ph_3PPd(OAc)_2]_2$ complex rapidly formed as a result of exposure of the $(Ph_3P)_2Pd_2/HOAc$ system to H_2O_2 is consumed in two reactions: hydrogenation (reaction 4) and oxidation of phosphine (reaction 21).

The resulting $[Pd(OAc)_2]_3$ reacts with $(Ph_3P)_2Pd_2$ in the presence of H_2 (reaction 11), generating $(PhP)_2Pd_5$ which is active in the catalysis of hydrogenation.

According to IR spectra, $(PhP)_2Pd_5$ lacks Pd—H bonds. Moreover, no complexes between $(PhP)_2Pd_5$ and H_2 were found in DMF solutions either volumetrically or spectroscopically. Studies of the kinetics of hydrogenation of unsaturated compounds [23] have shown that a catalytic reaction involves preliminary formation of a complex of $(PPh)_2Pd_5$ with a substrate, followed by interaction between the complex and H_2, in cases of olefins:



Thus, our data cast doubt on the hypothesis that palladium hydrides catalyze the hydrogenation of organic compounds under homogeneous conditions. It is possible that in the systems where Pd complexes were used as catalysts [24—26] responsible for catalysis were in fact clusters, such as $(PhP)_2Pd_5$ isolated by us. We believe that a better understanding of the mechanism of formation of these catalysts and their participation in catalysis will depend on advances in studies into the nature and structure of the clusters appearing in these systems.

Experimental

The solvents were purified by described methods [27]. Chemically pure CH_2Cl_2 intended for chromatography was used without additional purification. H_2 and Ar were freed of O_2 and H_2O by being passed successively through columns with alumina, chromenickel catalyst, and molecular sieves. $[(Ph_3P)Pd(OAc)_2]_2$ was prepared under an Ar atmosphere by a method similar to that described earlier [7].

The complexes $[(Ph_3P)_2RhH_2OAc]_2$ and $[(Ph_3P)_2RhH_2Cl]_2$ were prepared by previously described methods [21,22].

Preparation of $(Ph_3P)_2Pd_2$

A solution of 1.00 g (1.3×10^{-3} mol) of $[(Ph_3P)Pd(OAc)_2]_2$ in 30 ml of CH_2Cl_2 was treated for 40 min with H_2 or 30 g of semi-liquid sodium amalgam (1.5% Na). Then the solution was agitated in a flow of argon for 20 min and about 10 ml of the solvent was distilled off in vacuum (when sodium amalgam was used, the solution was decanted at this stage). About 30 ml of ether was added to the solution, the precipitate containing unidentified palladium complexes was filtered off, and about 30 ml of an ether/pentane mixture (1/1) was added to the filtrate. The precipitated $(Ph_3P)_2Pd_2$ was filtered off, washed with ether and pentane, dried in vacuum, and kept in an argon atmosphere. Yield $\approx$60%. Found: C, 57.7; H, 4.7; P, 8.2; Pd, 28.0. $C_{36}H_{30}P_2Pd_2$ calcd.: C, 58.5; H, 4.1; P, 8.4; Pd, 28.7%. IR spectrum: ν(PC) 495, 515, 525 cm^{-1}. $(Ph_3P)_2Pd_2$ was obtained in a reaction between $[(Ph_3P)PdCl_2]_2$ and sodium amalgam in a similar manner. The treatment with Na/Hg takes 1.5 h.

Reaction of $[(Ph_3P)Pd(OAc)_2]_2$ with H_2 in the presence of Ph_3P

20 ml of toluene, 2.20 g (8.4×10^{-3} mol) of Ph_3P, and 0.30 g (3.1×10^{-4} mol) of $[(Ph_3P)Pd(OAc)_2]_2$ were placed in an autoclave in a flow of H_2 and heated for three hours at 50° C and 40 atm H_2. Then the solution was transferred under argon flow into a flask containing about 100 ml of pentane. The yellow precipitate was washed on a filter with ether and pentane, then dried in vacuum. Yield 90%. Found: C, 74.1; H, 5.4. $C_{72}H_{60}P_4Pd$ calcd.: C, 74.4; H, 5.2%. The IR spectrum of the complex is identical to that of $(Ph_3P)_4Pd$, prepared by a previously described method [11].

Reaction of $(Ph_3P)_2Pd_2$ with Br_2.

A solution of Br_2 in ether (molar ratio $Br_2:(Ph_3P)_2Pd_2 = 10$) was added to a solution of 0.10 g (1.3×10^{-4} mol) of $(Ph_3P)_2Pd_2$ in 5 ml of CH_2Cl_2. The solution almost immediately turned orange. Then another 5 ml of ether was added at once, the precipitate was washed on a filter with a $CH_2Cl_2/(C_2H_5)_2O$ mixture, ether, pentane, and dried in vacuum. Yield 80%. Found: C, 40.0; H, 3.2; Br, 31.2. $C_{36}H_{30}P_2Pd_2Br_4$ calcd.: C, 40.6; H, 2.8; Br, 30.5%. The IR spectrum of the complex and its Debye-Scherrer pattern are identical to those taken for $[(Ph_3P)PdBr_2]_2$ prepared by a method described earlier [12].

Oxiation of $(Ph_3P)_2Pd_2$ with methylene dichloride

0.10 g (1.3×10^{-4} mol) of $(Ph_3P)_2Pd_2$ was dissolved in 10 ml of CH_2Cl_2. Approximately four hours later a dark precipitate fell out. After the solution was allowed to stand for 24 hours, light crystals appeared on the test tube walls, and a dark powder insoluble in organic solvents was formed. 50 ml of CH_2Cl_2 were added to the mixture, which was filtered off. The filtrate was evaporated till crystals fell out, and the latter were washed on a filter with CH_2Cl_2 and pentane, then dried in vacuum. Found: C, 61.0; H, 4.7; Cl, 10.8. $C_{38}H_{30}Cl_2P_2Pd$ calcd.: C, 61.5; H, 4.3; Cl, 10.1%. The IR spectrum is identical with that of $(Ph_3P)_2PdCl_2$, taken by a previously described method [18].

Preparation of $(Ph_3P_2)_2Pd_2(OAc)_2$

A solution of 0.38 g (5×10^{-4} mol) of $(Ph_3P)_2Pd_2$ in 10 ml of CH_2Cl_2 was treated with 0.48 g (5×10^{-4} mol) of $[(Ph_3P)Pd(OAc)_2]_2$ in an atmosphere of Ar for 5 min, and then an ether:pentane (4:1) mixture was added, the precipitate was filtered off, washed with ether and pentane, and dried in vacuum. Yield 80%. Found: C, 56.2, H, 4.6; P, 7.0; Pd, 24.3. Molecular weight: 800. $C_{40}H_{36}P_2O_4Pd_2$ calcd.: C, 56.1; H, 4.2; P, 7.2; Pd, 24.7%. Molecular weight: 856.

Preparation of $(PPh)_2Pd_5$

A mixture of 0.74 g (10^{-3} mol) $(Ph_3P)_2Pd_2$ and 0.67 g (10^{-3} mol) of $[Pd(OAc)_2]_3$ in 60 ml of DMF were treated with H_2 for an hour. The precipitate formed was filtered off in Ar, washed with DMF, toluene and ether, then dried in vacuum. Yield 40%. Found: C, 20.0; H, 1.5; P, 8.2; Pd, 68.0. $C_{12}H_{10}P_2Pd_5$ calcd.: C, 19.6; H, 1.3; P, 8.3; Pd 71.0%.

Detection of H_2O_2 in a catalytic reaction between O_2 and H_2 in the presence of $(Ph_3P)_2Pd_2$

Toluene was added to a solution of 0.01 g of $(Ph_3P)_2Pd_2$ and 0.003 g of HOAc in 20 ml of dimethylformamide, which had absorbed 50 to 60 ml of a H_2/O_2 mixture (molar ratio $H_2/O_2 = 2$) until complete precipitation of the complexes. The precipitate was filtered off. An aqueous starch-containing solution of KI was added to the almost colorless filtrate. The appearance of a deep blue color disappearing after addition of $Na_2S_2O_3$ was indicative of the presence of H_2O_2. Another indication of the presence of H_2O_2 in the filtrate was the appearance of an orange color after addition of a hydrochloric acid solution of $TiCl_4$, which disappeared in the presence of LiF.

Reaction of $(Ph_3P)_2Pd_2$ with H_2O_2 in the presence of HOAc

A solution of 0.50 g (6.8×10^{-4} mol) of $(Ph_3P)_2Pd_2$ in 10 ml of CH_2Cl_2 was treated with 2 ml of 30% H_2O_2 and 0.2 ml of HOAc for 10 min with vigorous stirring. 5 ml of water were added and the water layer was then decanted. 10 ml of H_2O were added to the solution of the complex in CH_2Cl_2, the mixture was stirred, and the water layer was decanted again. 40 ml of ether were added to the solution of the complex in CH_2Cl_2, the precipitate was washed on a filter with toluene, ether and pentane, then dried in vacuum. Yield 60%. Found: C, 54.0; H, 4.5. $Pd_2C_{44}H_{48}O_8P_2$ calcd.: C, 54.2; H, 4.3%. The IR spectrum is identical to that of $[(Ph_3P)Pd(OAc)_2]_2$.

$[Pd(OAc)_2]_3$ was isolated in a similar manner by treating $(Ph_3P)_2Pd_2$ with hydrogen peroxide and HOAc for three hours. Found: C, 21.0; H, 3.0. $C_{12}H_{18}O_{12}Pd_3$ calcd.: C, 21.0; H, 2.6%. The IR spectrum is identical to that of $[Pd(OAc)_2]_3$ [28].

Procedure for hydrogenation experiments

Prior to the experiments, the manometric unit described earlier [29] was evacuated and filled with H_2. This procedure was repeated twice. Then the complex and the substrate were added in the H_2 flow to the solvent degassed by evacuation and the absorption of H_2 was measured.

The IR spectra were measured in KBr, liquid petroleum, and a liquid cell (d = 0.1 cm) on a UR-20 instrument. The molecular weight of the complexes was determined osmometrically in a CH_2Cl_2 solution at 25° C. The PMR spectra were determined using a Bruker HX 90 instrument in $CDCl_3$. The X-ray powder patterns were measured on a DRON-1.5 instrument using Cu-K_α radiation and a graphite monochromator.

References

1 B. James, Homogeneous Hydrogenation (Gomogennoe gidrirovanie), Mir Publishers, Moscow, 1976 (in Russian).
2 E.H. Brooks and F. Glockling, J. Chem. Soc., A (1966) 1241.
3 G. Strukul and G. Carturan, Inorg. Chim. Acta, 35 (1979) 99.
4 E.W. Stern and P.K. Maples, J. Catal., 27 (1972) 120.
5 E.W. Stern and P.K. Maples, J. Catal., 27 (1972) 134.
6 A.S. Berenblyum, L.I. Lakhman, I.I. Moiseev and Ye.D. Radchenko, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 2417.
7 T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 29 (1967) 2122.
8 L.I. Lakhman, Thesis, Moscow, (1977) p. 97.
9 A.S. Berenblyum, A.G. Knizhnik, S.L. Mund and I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 1687.
10 V.I. Nefedov, Ya.V. Salyn, I.I. Moiseev, A.S. Berenblyum, A.G. Knizhnik, S.L. Mund and A.P. Sadovsky, Inorg. Chem., Acta, 35 (1979) 1343.
11 D.V. Nolan, A.N. Hughes, B.C. Hui and K. Wright, Canad. J. Chem., 52 (1974) 2990.
12 T.K. Sukhova and O.N. Temkin, Koordinats. Khimiya, 11 (1976) 1540.
13 D.M. Adams and P.J. Chandler, J. Chem. Soc., (1957) 2351.
14 V.N. Kondratyev (Ed.), Dissociation Energy. Ionization Potentials and Electron Affinity (Energiya rasryva khimicheskikh svyazey. Potentsial ionizatsiy i srodstvo k elektronu), Nauka Publishers, Moscow, 1974, p. 39.
15 O.V. Gritsenko, A.A. Bagaturyants, I.I. Moiseev, V.B. Kazansky and I.V. Kalechits, Kinetika i kataliz, 1980 (in press).
16 G. Allegra, G. Tettamanti Casagrande, A. Immirzi and L. Porri, J. Amer. Chem. Soc., 92 (1970) 289.
17 T. Ioshida, Kagaku no rioiki, 32 (1978) 434 (in Japanese).
18 L. Malatesta and C. Carielo, J. Chem. Soc., (1958) 2323.
19 K. Nakomoto, IR Spectra of Inorganic Compounds (Infrakrasnye spektry neorganicheskikh soedineniy), Mir Publishers, Moscow, 1966 (in Russian).
20 A.S. Berenblyum, A.G. Knizhnik, S.L. Mund and I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2157.

21 J.P. Candlin and A.R. Oldham, Discuss. Faraday Soc., 46 (1968) 60.
22 A.S. Berenblyum, A.G. Knizhnik, L.I. Lakhman and I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2586.
23 A.S. Berenblyum, L.G. Danilova, S.L. Mund and I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (in press).
24 G. Henrici-Olive and S. Olive, Angew. Chem., 86 (1975) 561.
25 J.C. Bailar, Jr. and H. Itatani, J. Amer. Chem. Soc., 89 (1967) 1592.
26 T.W. Russel and D.M. Duncan, J. Org. Chem., 39 (1974) 3050.
27 A. Gordon and R. Ford, The Chemist's Companion (Sputnik khimika), Mir Publishers, Moscow, 1976 (in Russian).
28 S.M. Morehouse, A.R. Powell, J.P. Heffer, T.A. Stephenson and G. Wilkinson, J. Chem. Soc., (1965) 3632.
29 A.S. Berenblyum, A.G. Knizhnik, S.L. Mund and I.I. Moiseev, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 2711.