

CATALYTIC REACTION
MECHANISMS

Palladium(II, I, 0) Complexes in Catalytic Reactions of Oxidative Carbonylation

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Abstract—The mechanisms of carbonylation of alkenes, alkynes, and alcohols, including the mechanism of oxidative carbonylation of alkynes in the regime of self-oscillations catalyzed by Pd(II), Pd(I), or Pd(0) complexes, are analyzed. It is shown that the main reasons for the appearance of self-oscillations in the oxidation reactions are nonlinear and autocatalytic steps of generation and termination of active centers. The results of studying the functions of *para*-benzoquinone as an oxidant, ligand, and catalyst in the oxidative reactions are generalized. It is found that Pd(0) complexes with *para*-benzoquinone can catalyze oxidation reactions.

Catalysis by palladium complexes is a well developed area of homogeneous catalysis covering diverse reactions. Classical works by J. Smidt [1], I. Moiseev [2], R. Heck [3, 4], P. Maithis [5], P. Henry [6], D. Tsuji and co-workers [7, 8], and many other researchers laid the foundation for catalysis by palladium complexes. Examples of numerous reactions catalyzed by Pd(II) and Pd(0) complexes are given in [1–9].

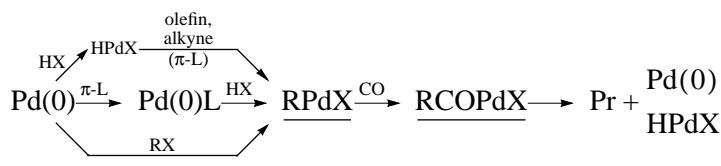
For example, Pd(II) is active in olefin oxidation; oxidative carbonylation of olefins, alkynes, amines, alcohols, and phenols; oxidative coupling and oxidative arylation of olefins; hydrocarboxylation and hydrocarbalkoxylation of olefins and alkynes; copolymerization of CO and olefins; dimerization of alkynes and polymerization of alkenes; cyclopropanation of olefins; and various tandem reactions.

Pd(0) complexes are active in the Heck reactions, cross-coupling, hydroarylation, hydrovinylation and hydrometallation of alkenes and alkynes, hydrocarboxylation and hydrocarbalkoxylation of alkenes and alkynes, telomerization of dienes, carbonylation of aryl halides, nucleophilic substitution in allylic (All) com-

pounds of the AllX type, and numerous tandem processes. Pd(II) complexes are often used as precursors (initial reactants) in Pd(0)-catalyzed reactions.

The theory of mechanisms of reactions involving CO (carbonylation and oxidative carbonylation) considers two fairly well substantiated hypotheses (or dogmas) on the mechanism of catalysis of Pd complexes. Let us consider them using examples of reactions of CO with alcohols, olefins, alkynes, and aryl halides.

Dogma no. 1. A Pd(0) complex reacts (via the formation of an intermediate hydride complex HPdX) with olefins, alkynes, or directly with RX to form a key intermediate RPdX, which reacts with CO and transforms into the final products (e.g., RCOOR) with the formation of HPdX or Pd(0) (Scheme 1) [10, 11]. The protonation of the Pd(0) π -complex with an unsaturated substrate (π -L) by an acid from a solution is also possible with the formation of RPdX. The main point in this hypothesis is the formation of the Pd–C bond from an organic substrate (olefin, alkyne, RX (where X is halide), OAc, OC(O)OR, and others) preceding C–C bond formation.



Scheme 1.

According to Scheme 1, the Pd(II) acyl complexes (RCOPdXL₂) were synthesized from olefins and CO in alcohols [12–15], and their transformations into hydrocarboxylation and hydrocarbalkoxylation products were studied. Recent studies (see the works by E.S. Petrov, Yu.G. Noskov, and others) refined information on the elementary steps, composition, and struc-

ture of complexes involved in the hydride mechanism in several catalytic systems of alkene hydrocarboxylation and hydrocarbalkoxylation and provided data on the factors determining the regioselectivity of processes proceeding via this mechanism and kinetic substantiation of Scheme 1 [15–24]. In particular, it was shown that data on isotope exchange of hydrogen in the initial

olefin in the $\text{PdCl}_2\text{--PPh}_3\text{--H}_2\text{O}$ system (and with SnCl_2 additives) can only be consistent with the hydride mechanism [16].

The important role of the acid formed upon palladium reduction was established for styrene carboxylation [17]. Additives of HCl increase the rate and decrease the regioselectivity of the process. Additives of alkali and $\text{Pd}(\text{PPh}_3)_4$ result in the opposite effect. In the authors' opinion, the role of the acid lies in the influence on the distribution of palladium complexes over the catalytic system due to the participation of HCl in the step of oxidative addition to different palladium(0) complexes and, perhaps, in steps of hydrolysis of acyl compounds [17].

Information on the composition and structure of palladium complexes was mainly obtained by *in situ* IR spectroscopy under the conditions of ethylene and styrene hydrocarboxylation ($100\text{--}110^\circ\text{C}$, $0.8\text{--}2.4$ MPa) [17, 18]. Most carbonyl complexes are mono- $(\text{Pd}(\text{CO})(\text{PPh}_3)_2$, 1980 cm^{-1}) and dicarbonyl $(\text{Pd}(\text{CO})_2(\text{PPh}_3)_2$, $2024, 1986\text{ cm}^{-1}$) compounds. They seem to be in equilibrium with complexes without carbonyl groups ($\text{Pd}(\text{PPh}_3)_3$ and $\text{Pd}(\text{PPh}_3)_2$).

The distribution of $\text{Pd}(0)$ complexes $(\text{Pd}(\text{CO})_x\text{L}_y$ and hydride complexes HPdClL_2 , $\text{HPdCl}(\text{CO})\text{L}$, and $\text{HPdCl}(\text{CO})_2$) depending on P_{CO} [L], and $[\text{HCl}]$, determines the regioselectivity of hydrocarboxylation and hydrocarbalkoxylation of alkenes described by the kinetic models of multiroute reactions [15, 19–23]. The $\text{Pd}(\text{PPh}_3)_2$ complex catalyzes the formation of products with a normal structure, and the carbonyl complexes, except for $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, contribute greatly to the formation of branched products.

In the $\text{Pd}(\text{dba})_2\text{--PPh}_3\text{--toluenesulfonic acid}$ system (dba is dibenzylideneacetone), the key intermediate of the hydride mechanism is cationic palladium hydride $\text{HPd}(\text{PPh}_3)_3^+$ formed by the protonation of $\text{Pd}(\text{PPh}_3)_3$, whereas palladium(0) carbonyl complexes, which are present in the system, practically are not involved in styrene hydrocarbalkoxylation (the formation of both linear and branched products is inhibited when the partial pressure of carbon oxide increases) [24]. All intermediates were characterized by NMR in ethylene hydrocarbomethoxylation in the presence of the $\text{C}_6\text{H}_4(\text{CH}_2\text{PBu}_2^t)_2$ bidentate ligand. The relatively stable cationic $\text{Pd}(\text{II})$ hydride complex was synthesized by the reaction of the $\text{Pd}(\text{L--L})(\text{dba})$ complex with HBF_4 or $\text{CF}_3\text{SO}_3\text{H}$ in methanol [25].

Dogma no. 2. The interaction of $\text{Pd}(\text{II})$ with CO and ROH leads to the formation of a key intermediate: the alkoxy carbonyl complex XPdCOOR , whose reactions with alcohols, olefins, or alkynes result in various products of carbonylation or oxidative carbonylation of organic compounds (Scheme 2).

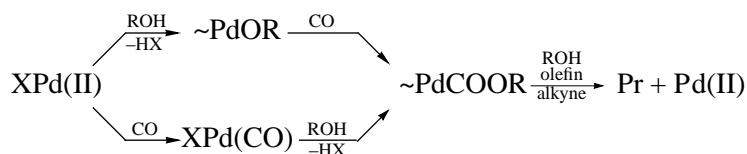
Scheme 2 proposed in [26, 27] was kinetically substantiated for the synthesis of butyl acrylate from acetylene in a solution of the *cis*- $\text{PdBr}_2[\text{P}(\text{OPh})_3]_2$ complexes [26, 28] and by the results of chemical [29] and physicochemical [30] studies. The kinetic equation describing the rate of butyl acrylate synthesis,

$$r = \frac{k P_{\text{CO}} P_{\text{C}_2\text{H}_2} [\text{Pd}]_\Sigma}{[\text{H}^+](1 + k_1 P_{\text{CO}} + k_2 P_{\text{CO}} P_{\text{C}_2\text{H}_2})}, \quad (1)$$

indicates the existence of a reversible step of formation of a key intermediate (for example, $\text{XPd}(\text{COOR})\text{L}_2$). The alkoxy carbonyl complexes were prepared by different methods from different X and L [31], including ROH and CO [14, 32], and by the reaction of AcOHgCOOMe with PdCl_2 [33]. The structures of the key intermediates $\text{ClPd}(\text{COOMe})(\text{PPh}_3)_2$ [33] and $\text{AcOPd}(\text{COOMe})(\text{PPh}_3)_2$ [34] were studied by X-ray diffraction analysis.

It is interesting that the involvement of the methoxy carbonyl intermediate in diene hydrocarbalkoxylation was also substantiated for the $\text{Co}_2(\text{CO})_8\text{--Py}$ system [35] for which the formation of alkyl and acyl derivatives of $\text{Co}(\text{I})$ was always considered as the only one possible (dogma no. 1).

The studies of catalytic properties of palladium complexes in the past 25 years have shown that the important role in the catalytic chemistry of palladium belongs to $\text{Pd}(\text{I})$ complexes, mainly clusters containing the Pd_2^{2+} fragment [36, 37] or Pd_n^{m+} [37], including giant clusters with $n = 561$ [38–40]. It has recently been shown that $\text{Pd}(\text{IV})$ complexes can be involved in processes similar to the Heck reaction [41, 42] and $\text{Pd}(0)$ complexes with *para*-benzoquinone can participate in the oxidative carbonylation of alkynes [43, 44]. Oscillatory reactions of alkyne carbonylation of diesters of α,β -unsaturated acids [45–47] in which the $\text{Pd}(\text{I})$ and HPdX complexes play an important role were discovered. This article is devoted to some new aspects of the catalytic chemistry of palladium: oxidative carbonylation of alcohols and alkynes catalyzed by the $\text{Pd}(\text{I})$ and $\text{Pd}(0)$ complexes with *para*-benzoquinone and the rea-



Scheme 2.

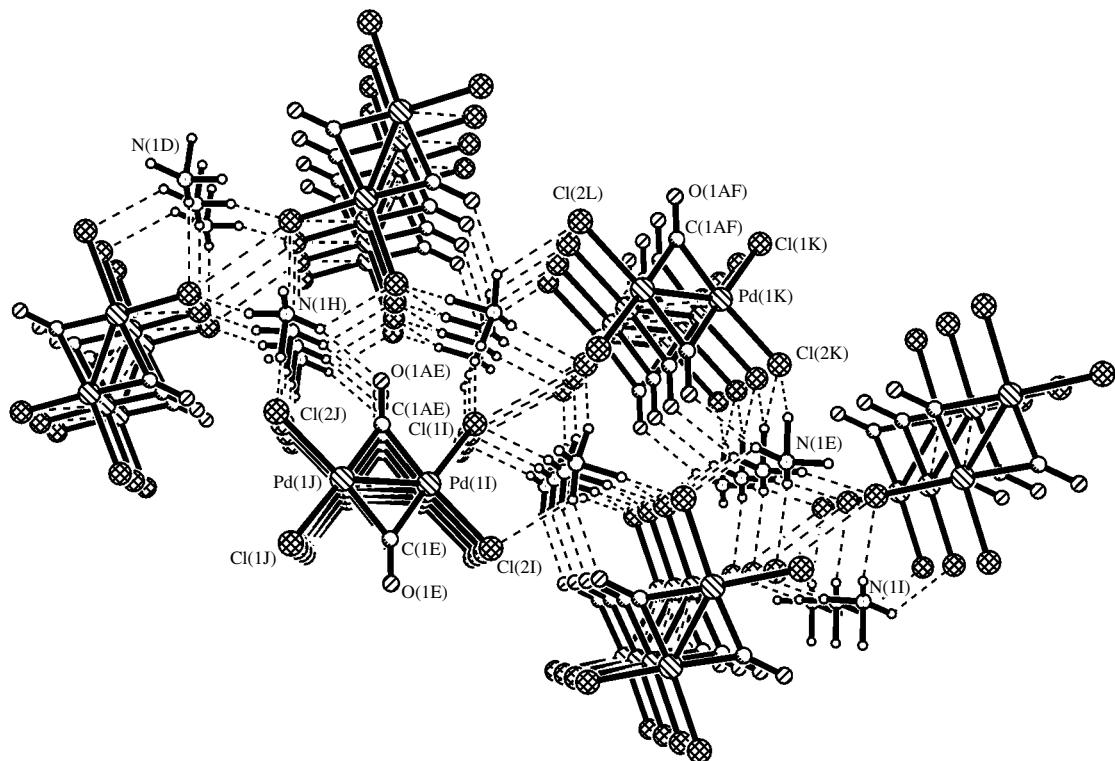


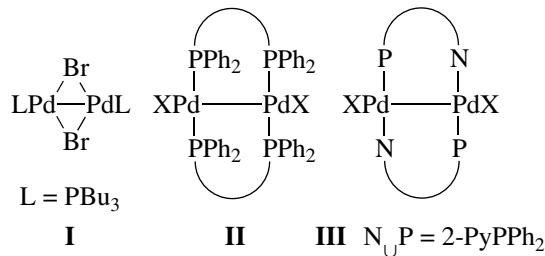
Fig. 1. Structure of the Gel'man complex $(\text{NH}_4)\text{Pd}_2(\mu\text{-CO})_2\text{Cl}_4$ [57].

sions behind the appearance of self-oscillations in oxidation processes.

SYNTHESIS AND STRUCTURE OF Pd(I) COMPLEXES

Currently, the chemistry of carbonyl complexes [36, 48] is a well developed area of coordination chemistry of palladium.

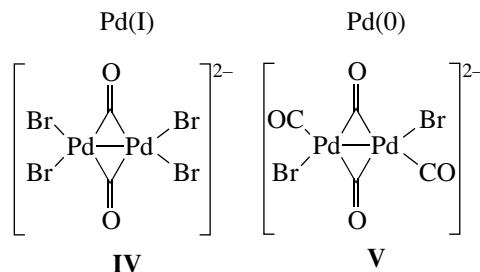
Among the halide phosphine complexes, only three complexes are worth mentioning in the present study: **I** [49], **II** [50], and **III** [51], which have characteristic structural motives and are of interest for catalysis.



Palladium(I) carbonyl complexes with reliably established compositions were synthesized for the first time by Manchot ($[\text{Pd}(\text{CO})\text{X}]_n$, 1926) [52] and Gel'man ($(\text{NH}_4)_2\text{Pd}_2(\text{CO})_2\text{Cl}_4$, 1942) [53]. These were followed by the complexes synthesized by Colton ($\text{Pd}_2(\mu\text{-CO})(\text{dppm})_2\text{X}_2$) [36, 54] and Stromnova and Moiseev [55] (the synthesis and structure of the first Pd(I) carbonyl acetate cluster $\text{Pd}_4(\text{CO})_4(\text{OAc})_4$). The

structure of the $(\text{Bu}_4^{\text{t}}\text{N})_2\text{Pd}_2(\mu\text{-CO})_2\text{Cl}_4$ complex was studied in [56]. We have recently succeeded in isolating the crystals of the Gel'man complex and establishing the structure of this cluster [57], which is often used in catalytic reactions. The intriguing layered structure of this complex with hydrogen bonds formed by the NH_4^+ ions is shown in Fig. 1. Palladium(I) carbonyl complexes with one CO group, namely, $\text{Pd}_2(\mu\text{-CO})\text{L}_2\text{X}_2$ [58], $\text{Pd}_2(\mu\text{-CO})\text{L}_3\text{Cl}_2$ [59], and $\text{Pd}_2(\mu\text{-H})(\mu\text{-CO})\text{L}_2^+$ [60], are worth noting.

An attempt to synthesize the bromide analog of the Gel'man complex resulted in the diamagnetic $(\text{PPN})_2\text{Pd}_2(\mu\text{-CO})_2(\text{CO})\text{Br}_3$ complex (PPN is $\text{PPN}^+ \text{Ph}_3\text{PNPPh}_3^+$), whose X-ray photoelectron spectrum contained two bands at $E_{\text{Pd}} = 337.3$ and 335.0 eV. To explain its composition and structure (X-ray diffraction data [61]), one has to assume that the complex is a mixture of two anions (**IV** and **V**) in a ratio of $1 : 1$,



Anion **IV** is the Pd(I) analog of the Gel'man complex, while anion **V** is the Pd(0) complex.

Carbonyl iodide complexes cannot be isolated. Complexes with unknown structures containing a Pd_2^{2+} fragment were prepared: $\text{LiPdI}_2 \cdot 2\text{H}_2\text{O}$, CsPdI_2 [82], and KPd_4I_5 [47]. The cationic complexes containing the $\text{Pd}_2(\text{CO})_2^{2+}$ fragment are also known [63, 64].

Pd(I) COMPLEXES IN CATALYSIS

The first hypotheses on the catalytic activity of Pd(I) complexes appeared in the works of I.I. Moiseev [65, 66], J. Davidson [67], and G. Chiusoli [68]. The study of positional isomerization of butenes in aqueous solutions of PdCl_2 showed [65, 66] that an intermediate complex in the oxidation of butenes to methyl ethyl ketone (presumably, $\text{Pd}_2\text{Cl}_4^{2-}$) catalyzed butene isomerization, and this process was terminated by *para*-benzoquinone additives, whereas oxidation was not affected by these additives. This hypothesis, which agrees with kinetic studies, was confirmed later [62] for the $[\text{Pd}(\text{CO})\text{Cl}]_n\text{-LiCl-DMF}$ system and *para*-benzoquinone additives.

It was established after these studies that Pd(I) is the catalyst of various reactions (oxidation of CO; oxidative carbonylation of alcohols, amines, phenols, and alkynes; carbonylation of alkenes; dimerization of olefins; polymerization of alkynes; and other processes). Let us consider some reactions in more detail.

Oxidative Carbonylation of Methanol

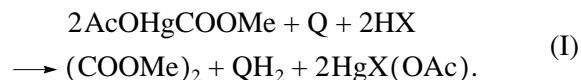
The main products of oxidative carbonylation of methanol are dimethyl carbonate (DMC) and dimethyl oxalate (DMO) [69, 70].

1.1. $\text{PdCl}_2\text{-LiCl-Q-MeOH}$ [72].

It has been established [31, 71, 72] that the use of *para*-benzoquinone (Q) in the oxidative carbonylation of methanol (instead of CuCl_2 or FeCl_3) in system 1.1 decreases the rate of DMC formation and increases the rate of DMO formation [31, 72]. Under the optimal conditions (30°C , $P_{\text{CO}} = 1$ atm, $\text{C}_6\text{H}_5\text{COOH-C}_6\text{H}_5\text{COONa}$ buffer with $\text{pH} \approx 4$), the selectivity to DMO is $> 96\%$. System 1.2 with Pd(I) is more active.

1.2. $[\text{Pd}(\text{CO})\text{Cl}]_n\text{-LiCl-Q-MeOH}$ [73].

In systems 1.1 and 1.2 containing Pd(II) and Pd(I), respectively, the kinetic dependences on P_{CO} and $[\text{Pd}]_\Sigma$ differ indicating the absence of the remarkable oxidation of Pd(I) to Pd(II) by quinone at $\text{pH} \approx 4$ provided that Pd(I) is more active. A similar situation is observed for the synthesis of DMO in the absence of CO [72, 73]:



Plots of the reaction rate (I) vs. [Q] are described by the equations

$$\text{Pd(II)} \quad r_{\text{DMO}} = \frac{k_1[\text{Q}]}{1 + k_2[\text{Q}]}, \quad (2)$$

$$\text{Pd(I)} \quad r_{\text{DMO}} = k_3[\text{Q}]. \quad (3)$$

A kinetic study of DMO synthesis [72, 73] and possible intermediate compounds [31, 32], including $\text{L}_2\text{Pd}(\text{COOR})_2$ [32], provided the scheme of the mechanism (Scheme 3), which assumes the involvement of Q in steps of formation and transformation of intermediates of dogma no. 2, that is, as a ligand, determining the selectivity of the process, and an oxidant.

Nonoxidative and Oxidative Carbonylation of Alkynes at a C≡C Bond

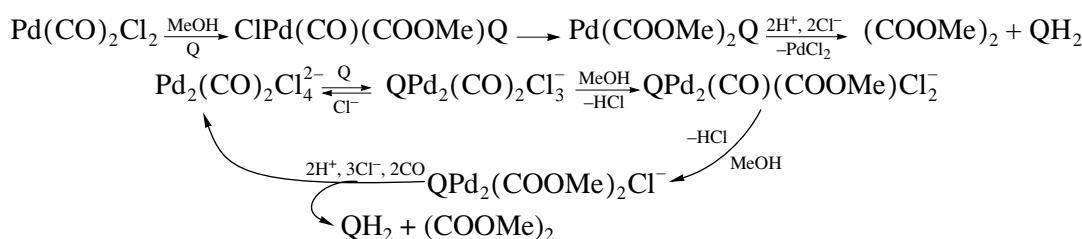
Our study of the behavior of different catalytic systems in alkyne carbonylation suggests that, in most cases, except for the $\text{PdBr}_2\text{-P(OPh)}_3\text{-HBr-}n\text{-BuOH}$ system [26, 28], the active forms of the catalyst are Pd(I) complexes formed during the process from the initial PdX_2 [36, 74, 75] (systems 1.3-1.8).

1.3. $\text{PdI}_2\text{-LiI(KI)-HCl-n-BuOH}$ [28, 74-76]

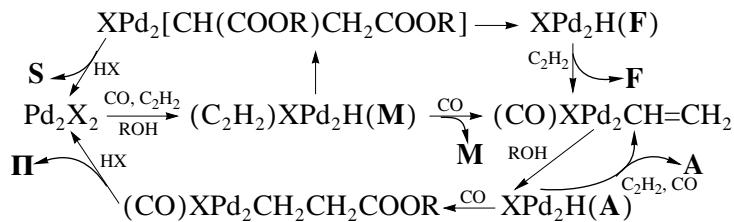


where A, S, P, M, and F are butyl acrylate, dibutyl succinate, butyl propionate, dibutyl maleate, and dibutyl fumarate, respectively.

The overall selectivity based on acetylene is $\sim 80\%$, the selectivity to butyl acrylate is $\sim 50\%$, and the overall productivity is $200 \text{ g l}^{-1} \text{ h}^{-1}$ (70°C , $P = 1$ atm).



Scheme 3.



Scheme 4.

1.4. $\text{PdBr}_2\text{-PPh}_3\text{-HBr-DMF-ROH}$ [77]

$\text{L/Pd} = 1$, 50–90°C, $P = 1$ atm. Selectivity to acrylates is 60–85%.

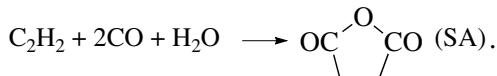
1.5. $\text{PdBr}_2\text{-HBr-}n\text{-BuOH-(CH}_3\text{)}_2\text{CO}$ [78]

S

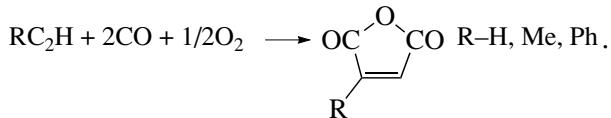
40°C, $P = 1$ atm, the selectivity to is >90%, the productivity is ~50 g l⁻¹ h⁻¹.

1.6. $\text{PdBr}_2\text{-HBr-(CH}_3\text{)}_2\text{CO-H}_2\text{O}$ [78]

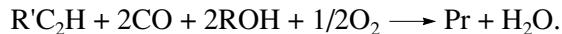
40°C, $P = 1$ atm, the selectivity to succinic acid is >95%, the productivity is ~80 g l⁻¹ h⁻¹.

1.7. $\text{PdBr}_2\text{-(CH}_3\text{)}_2\text{CO-CH}_3\text{CN-H}_2\text{O}$ [74, 75, 79, 80]

40°C; $P = 1$ atm; the selectivities are as follows: succinic anhydride (SA), ~70%; succinic acid, ~15%, and maleic anhydride (MA), ~5%.

1.8. $\text{PdBr}_2\text{-CH}_3\text{CN-H}_2\text{O}$ [74, 75, 81, 82]

40°C, $P = 1$ atm, for R = H the selectivity is >85%.

1.9. $\text{PdI}_2\text{-KI-ROH}$ [83]

Pr are Z, E-diesters of α , β -unsaturated acids, 20°C, $P_{\text{CO}} = 20$ atm.

In systems 1.7, 1.8, and, probably, 1.9 (see below), it is Pd(I) that catalyzes carbonylation even in the presence of O_2 .

The study of the kinetics and mechanism of carbonylation in systems 1.3, 1.5, and 1.6 made it possible to establish the sequence of formation of the A, S, P, M, and F products in the complicated multiroute reaction and find the mechanism of conjugation of oxidative, reductive, and nonoxidative processes in acetylene (alkyne) carbonylation [28, 75, 76, 78, 79] (Scheme 4).

In systems 1.3, 1.5, and 1.6 as in the case of butene isomerization [62, 65, 66], *para*-benzoquinone additives inhibit the process [75].

Palladium hydride complexes are involved in acrylate formation (dogma no. 1) as well as in propionate and succinate formation. However, the regularities of the synthesis of maleate contradict the two dogmas.

The mechanisms of formation of SA and MA were studied in more detail in [80–82]. It was found that

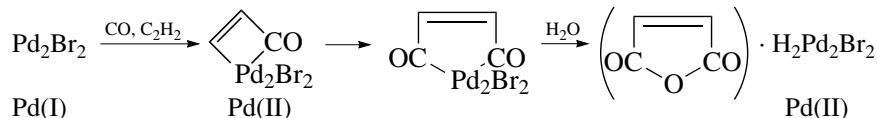
–MA is an intermediate in the synthesis of SA;

–Intense isotope exchange of MA with D_2O and doubly deuterated maleic anhydride prepared from C_2D_2 with H_2O is observed;

–Kinetic isotope effects ($r_{\text{H}}/r_{\text{D}}$) are close to unity for SA and MA,

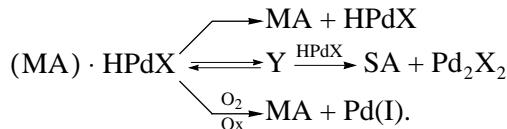
	SA	MA
$\text{CH}_3\text{CN}(\text{CD}_3\text{CN}), \text{C}_2\text{H}_2, \text{H}_2\text{O}(\text{D}_2\text{O})$	1.13 ± 0.05	0.9 ± 0.1
$\text{CH}_3\text{CN}(\text{CD}_3\text{CN}), \text{C}_2\text{H}_2(\text{C}_2\text{D}_2), \text{H}_2\text{O}(\text{D}_2\text{O})$	1.10 ± 0.05	0.9 ± 0.1

–Hypothesis no. 3 was proposed for the mechanism of MA synthesis:



The idea of this hypothesis is the formation of the C–C and Pd–C bonds before the formation of C–H and C–O bonds.

–The routes of transformation of the MA complex with palladium hydrides can be described by the reactions



Hypothesis no. 3 for alkyne carbonylation catalyzed by Co(0) clusters was proposed in 1970 by Y. Iwashita and coworkers [84]. We proposed the same hypothesis for reactions catalyzed by Pd(I) clusters in [36, 71, 79, 85].

In addition to the kinetic and physicochemical experiments [80–82], the grounds for hypothesis no. 3 can be found in the chemistry of Pd(I) complexes [36] and organometallic chemistry of other metals [86–88].

The coupling of routes of MA and SA formation with the routes of by-product formation (acrylic (AA) and propionic (PA) acids) is presented in Scheme 5. The kinetic isotope effects for AA and PA confirm the hydride mechanism of AA synthesis (dogma no. 1) and the hydride mechanism of AA reduction to PA [81].

	AA	PA
$r_{\text{H}}/r_{\text{D}}$	1.83 ± 0.15	2.5 ± 0.3

Polyfunctional catalytic systems 2.0 and 2.1 [89] were used to accelerate the steps of oxidation of hydride complexes in the synthesis of maleic anhydride

(Pc* is bis(dibutylsulfomayl)phthalocyanine, and Pc is phthalocyanine).

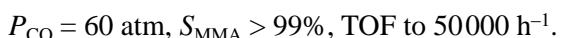
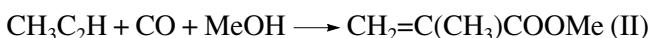
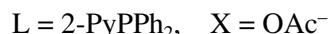
2.0. $\text{PdBr}_2\text{LiBr}\text{Pc}^*\text{Fe-CH}_3\text{CN}$

2.1. $\text{PdBr}_2\text{LiBr}\text{PcCo}_{(\text{sol})}\text{CH}_3\text{CN}$

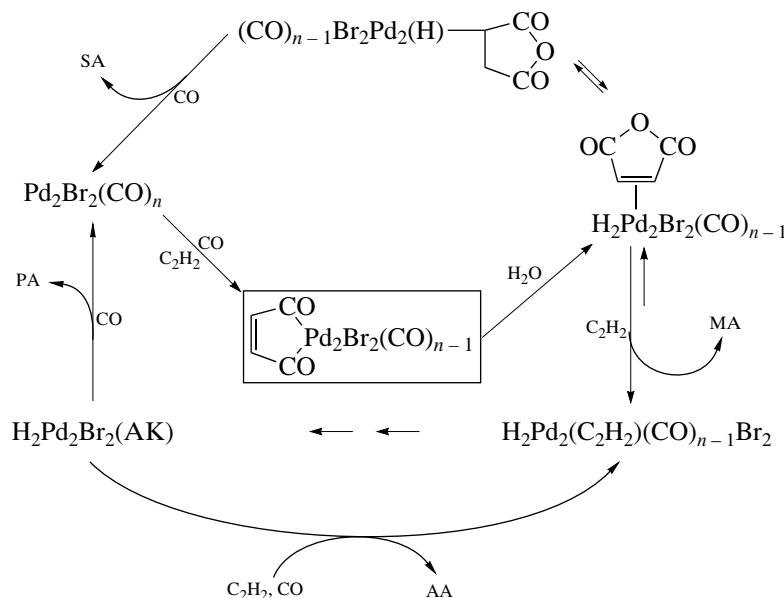
In the homogeneous (2.0) and heterogeneous (2.1) systems at $P_{\text{O}_2} = 0.04$ atm, the selectivity (S) to MA reaches 98% at a productivity of $\sim 80 \text{ g l}^{-1} \text{ h}^{-1}$. The rate of MA synthesis increases with an increase in P_{O_2} (Figs. 2, 3) and the PcM concentration (Figs. 4, 5). As a result, we conclude that the process is catalyzed by the Pd(I) complex on the solid PcCo surface and by the Pd(II) complex in a solution in the presence of Pc^*Fe .

System 2.2 evokes a great interest and discussions on possible mechanisms of carbonylation. In this system, methyl methacrylate (MMA) is synthesized from methylacetylene with a high selectivity and a great turnover frequency (TOF) of the catalyst [90, 91].

2.2. $\text{PdX}_2\text{L}_2\text{CH}_3\text{SO}_2\text{H-MeOH}$

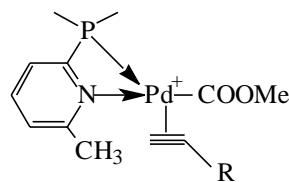


The authors of this system [91] believe that the mechanism of catalysis by the Pd(II) complex corresponds to dogma no. 2 and includes the stereo- and regioselective insertion of alkyne into the Pd–COOMe



Scheme 5.

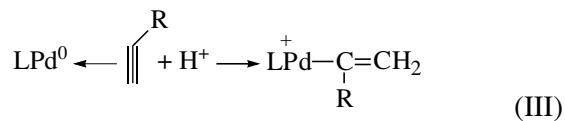
bond of the Pd(II) π -complex



The proposed mechanism is not substantiated by any convincing kinetic and physicochemical arguments [90, 91]. It seems difficult to rationalize the variable order with respect to HX in the region of low acid concentrations (an increase in the rate with an increase in the HX concentration) and the zero order with respect to HX at $[HX]/[Pd]_{\Sigma} > 10$ [91] with the limiting step of protolysis of the Pd(II) σ -alkenyl derivative (the kinetics was studied without analyzing the mass balance with respect to the ligand, palladium, and HX). The existence of cationic Pd(II) complexes in a strongly reductive medium (MeOH, CO, 2-PyPPh₂) is most surprising. Since this scheme of the mechanism was poorly substantiated, other hypotheses appeared.

The kinetic, isotope, and NMR studies of the carbonylation of phenylacetylene and methylacetylene in the Drent system 2.2 [92] and phenylacetylene in the Pd₂(dba)₃-CF₃COOH-PPh₃-MeOH [93] and Pd(η^2 -olefin)(P^N)-CH₃SO₃H-MeOH systems [94] (P^N is iminophosphine) provided the scheme of the mechanism (dogma no. 1), according to which the alkenyl derivative of palladium(II) was formed due to the addition of a proton to the Pd(0) π -complex with alkyne (from a solution [93] or from the protonated pyridine-

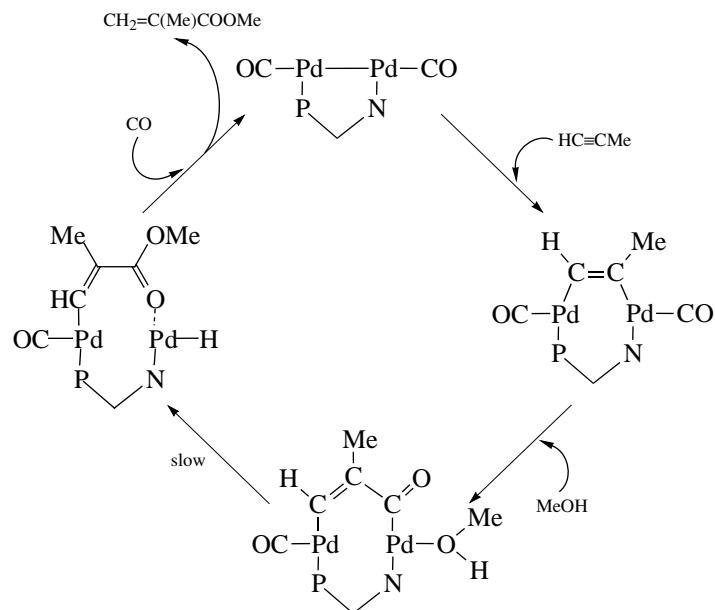
phosphine ligand coordinated by palladium at the phosphorus atom [92])



The high regioselectivity, kinetic isotope effect $k_H/k_D = 6.4$, isotope exchange $\equiv C-H(D)$ in alkyne and in the methyl group of methyl methacrylate, an increase in the reaction rate with an increase in P_{CO} , and the presence of the vinyl group bound to Pd(II) in a solution (¹H NMR) [92] agree satisfactorily with the proposed hypothesis.

At the same time, when discriminating the hypotheses, one has to take into account that Pd(I) complexes can be involved in this process. Such a hypothesis proposed by I.I. Moiseev [95, 96] (Scheme 6) includes the formation of an intermediate with the Pd-CH=CHCOPd fragment from the Pd(I) cluster, acetylene, and CO (hypothesis no. 3 according to our classification). This hypothesis does not contradict the results in [51] in which the Pd₂(2-PyPPh₂)₂X₂ complex was prepared from Pd(OAc)₂ and 2-PyPPh₂ in the presence of different strong acids HX (CF₃COOH, CH₃SO₃H, CF₃SO₃H, and others). This complex was characterized by X-ray diffraction data, and alkyne insertion into the Pd-Pd bond was demonstrated for MeOC(O)C≡CC(O)OMe.

The formation of Pd(I) complexes in system 2.2 provides various routes for different mechanisms of carbonylation, including hybrid variants, which combine the hypotheses (dogma nos. 1 and 2, for example, Scheme 7).



Scheme 6.

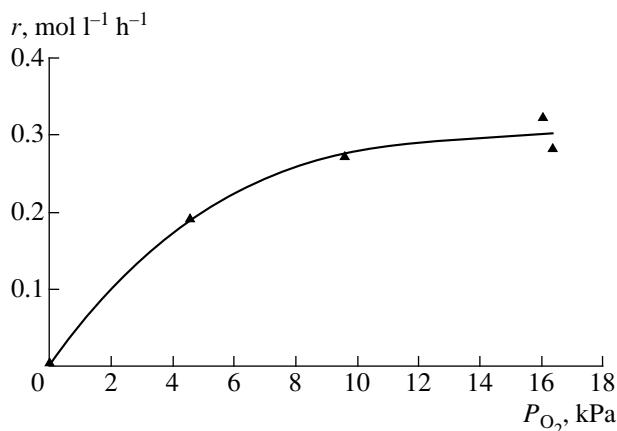


Fig. 2. Plot of the rate of MA formation vs. P_{O_2} in the $PdBr_2$ – $LiBr$ – Pc^*Fe –adipodinitrile system at $40^\circ C$ [89].

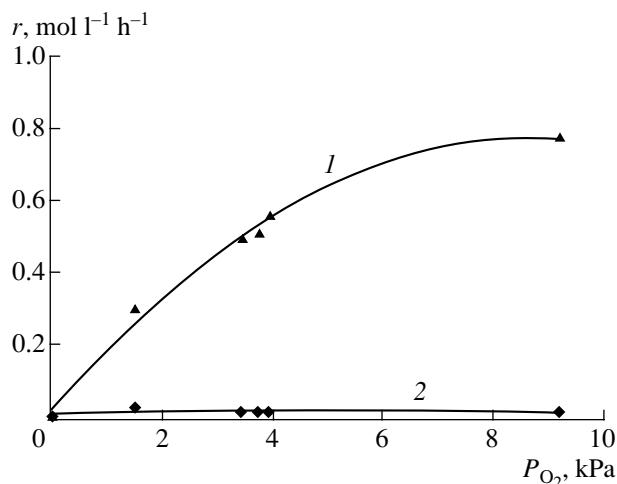


Fig. 3. Plots of the rate constants (r) of (1) MA and (2) SA syntheses vs. P_{O_2} in the $PdBr_2$ – $LiBr$ – $PcCo$ – CH_3CN system at $40^\circ C$ [89].

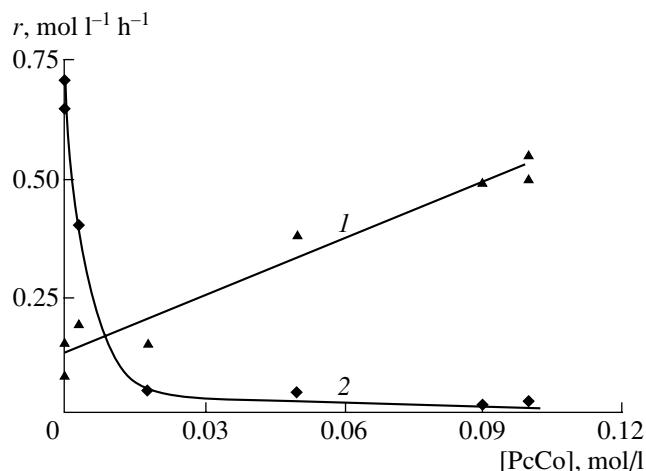


Fig. 4. Plots of the rates of (1) MA and (2) SA formation vs. $[PcCo]$ at $40^\circ C$ in the $PdBr_2$ – $LiBr$ – $PcCo$ – CH_3CN system at $P_{O_2} = 0.1$ atm [89].

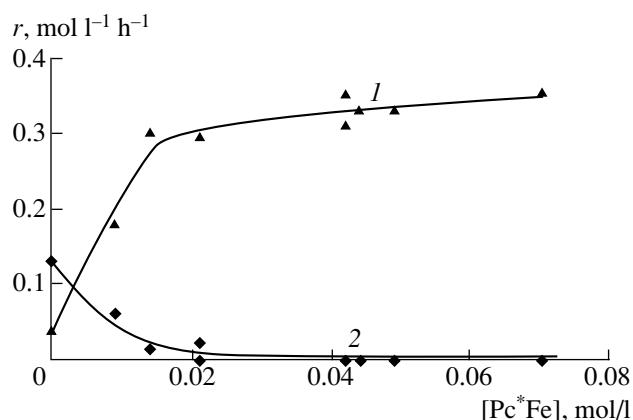
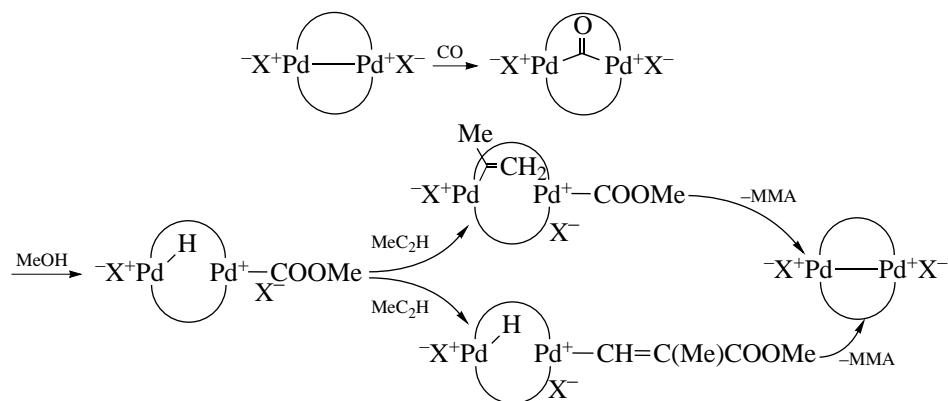


Fig. 5. Plots of the rates of (1) MA and (2) SA formation vs. $[Pc^*Fe]$ in the $PdBr_2$ – $LiBr$ – Pc^*Fe –adipodinitrile system at $40^\circ C$, $P_{O_2} = 0.1$ atm [89].



Scheme 7.

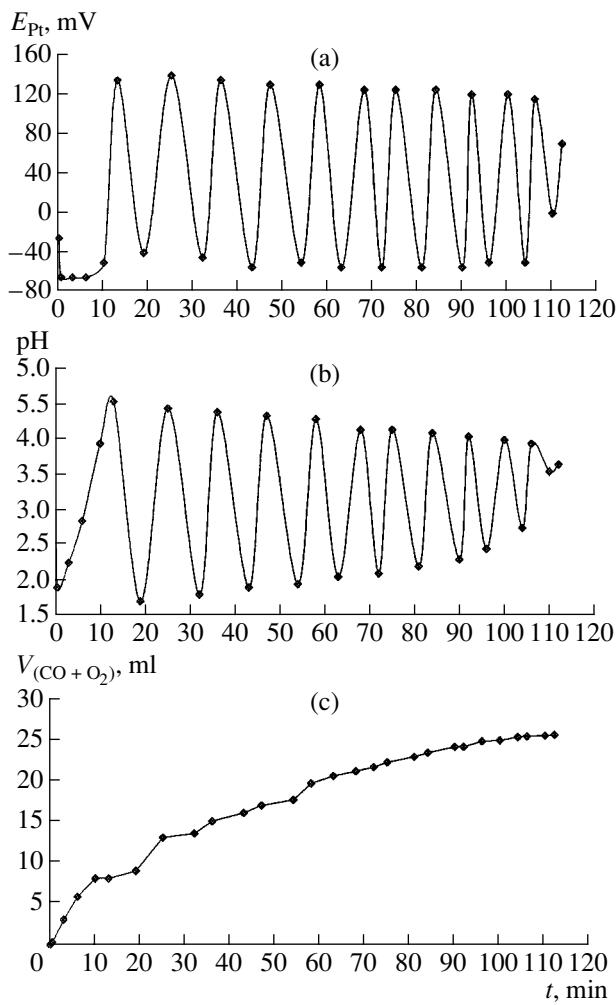


Fig. 6. Changes in time of (a) E_{Pt} , (b) pH, and (c) volume of absorbed gases V during the oxidative carbonylation of phenylacetylene ($[\text{KI}]_0 = 0.4 \text{ mol/l}$, $[\text{PdI}_2]_0 = 0.01 \text{ mol/l}$, $[\text{PhC}_2\text{H}]_0 = 0.1 \text{ mol/l}$; $[\text{CO}]_0 : [\text{O}_2]_0 = 1.5$; 40°C [47]).

In the framework of this scheme, the intermediate with the XPdC(O)PdX fragment (first step of hypothesis no. 3) reacts with alcohol to transform into the Pd(II) methoxycarbonyl and hydride complexes, which react with alkyne according to dogma no. 2 or no. 1 to transform into the product of alkyne hydrocarbalkoxylation (hybrid mechanism). In connection to this, it is interesting that the reaction of the $\text{Pd}_2(2\text{-PyPPh}_2)_2(\text{OAc})_2$ complex with CO in methanol affords the methoxycarbonyl complex $\text{Pd}_2(2\text{-PyPPh}_2)_2(\text{COOMe})\text{OAc}$ in which the pyridylphosphine ligand is monodentate with phosphorus as a contact atom [97]. The probable route for the formation of this compound is the decomposition of the $\text{Pd}_2(2\text{-PyPPh}_2)_2(\text{H})(\text{COOMe})(\text{OAc})_2$ complex by the reaction $\text{Pd}_2(2\text{-PyPPh}_2)_2(\text{H})(\text{COOMe})(\text{OAc})_2 \rightarrow \text{Pd}(2\text{-PyPPh}_2)_2(\text{COOMe})(\text{OAc}) + \text{Pd}(0) + \text{HOAc}$.

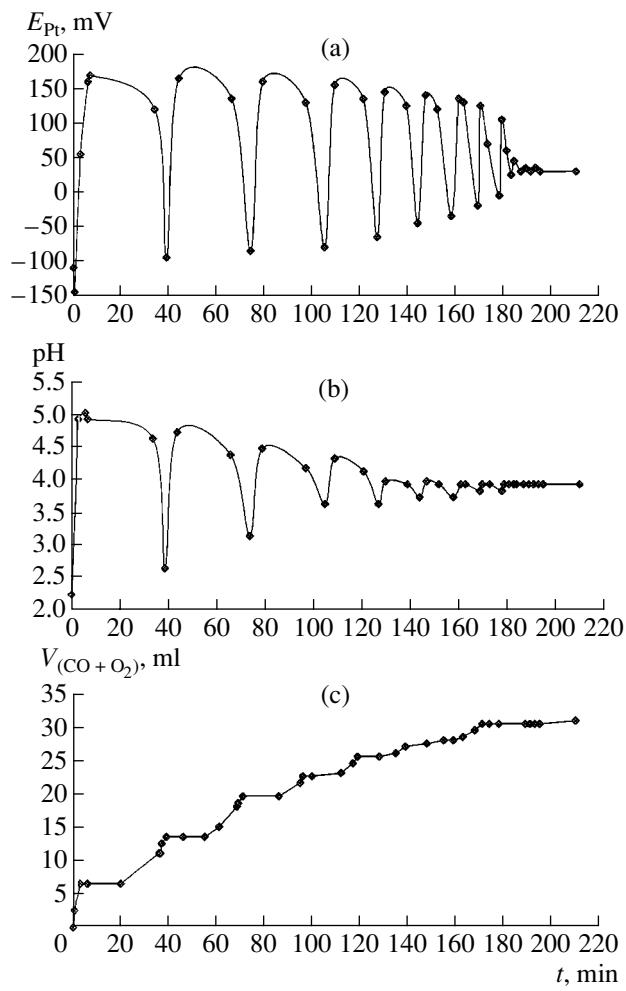


Fig. 7. Changes in time of (a) E_{Pt} , (b) pH, and (c) volume of absorbed gases V during the oxidative carbonylation of dimethyl ethynyl carbinol (DMEC) ($[\text{KI}]_0 = 0.4 \text{ mol/l}$, $[\text{PdI}_2]_0 = 0.01 \text{ mol/l}$, $[\text{DMEC}]_0 = 0.1 \text{ mol/l}$; $[\text{CO}]_0 : [\text{O}_2]_0 = 1.5$; 40°C [47]).

OXIDATIVE CARBOXYLATION OF ALKYNES IN THE SELF-OSCILLATION REGIME

The study of the oxidative carbonylation of phenylacetylene (PAc) to Z,E -diesters of dicarboxylic acids in system 1.9 revealed that self-oscillations of the platinum electrode potentials E_{Pt} ($[\text{Pd(II)}]^2/[\text{Pd}_2(\text{I})]$), pH, and rate of gas absorption $V_{\text{CO} + \text{O}_2}$ were observed at certain concentrations of the reactants, PdI_2 , and KI and pH values [46, 47] (Figs. 6, 7). The study [47] of this system using Pd(I) compounds synthesized confirmed that Pd(I) complexes were active species leading to the formation of diesters. The observed hydrogen peroxide and the previously studied mechanism of maleic anhydride synthesis (Scheme 5) suggest the transformation of Pd_2I_2 into 2HPdI in the course of carbonylation. The oxidation of HPdI by oxygen results in the formation of H_2O_2 , which oxidizes Pd(I) to Pd(II) terminating the synthesis. The preliminary scheme of the mechanism

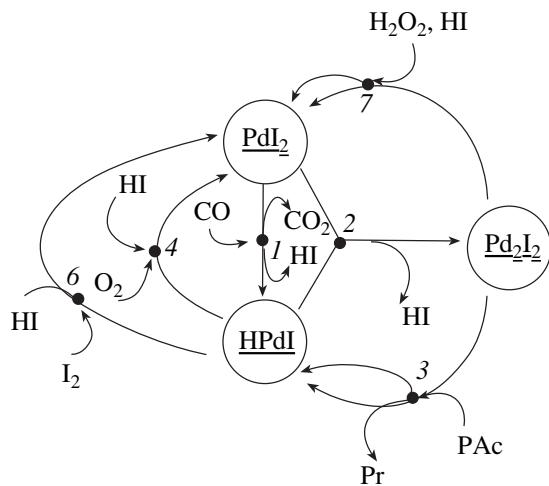
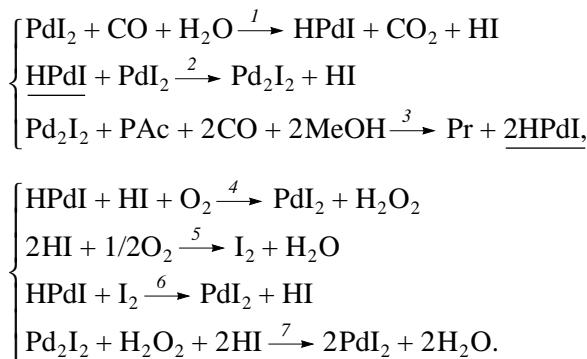


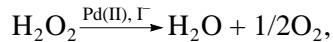
Fig. 8. Bipartite graph of the mechanism of the self-oscillation process including palladium-containing intermediates (underlined) and (1, 4, and 6) linear and (2, 3, and 7) nonlinear with respect to [Pd] steps of the process (●).

includes seven steps of HPdI and Pd_2I_2 synthesis and the decay of active species (oxidation of HPdI and Pd_2I_2 to PdI_2) (Scheme 8).

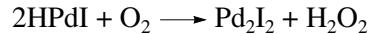


Scheme 8.

The steps of transformation of various palladium complexes are presented in the bipartite graph of the mechanism (Fig. 8), which reflects the involvement of PdI_2 , HPdI, and Pd_2I_2 in the multichannel process. Since HI, I_2 , and H_2O_2 are intermediates, five direct steps of the mechanism are nonlinear with autocatalysis by HPdI (steps 2 and 3). Thus, the nonlinear steps of generation and decay of active species involved in the catalytic cycle of product formation (Pd_2I_2 , HPdI, and PdI_2) result in the fast transformation of a considerable portion of palladium into one of the following forms: Pd(I) (active state) or Pd(II) (inactive state). Therefore, unlike stable stationary processes catalyzed by the Pd(II), Pd(I), or Pd(0) complexes, all (three) active species play an important role in the mechanism of appearance of oscillations but at different time moments. Steps 2, 3, and 4 (Scheme 8) supplemented by the decomposition of H_2O_2 ,



form the catalytic cycle with the resulting equation of oxidative carbonylation (system 1.9), which also involves PdI_2 , HPdI, and Pd_2I_2 . A possible pathway to Pd_2I_2 from HPdI (in addition to steps 4 and 2, Scheme 8) is the reaction



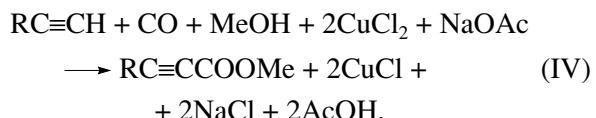
in combination with the decomposition of H_2O_2 . In addition to phenylacetylene, other alkynes (methylacetylene, propargyl alcohol, dimethyl ethynyl carbinol) are also transformed in the self-oscillation regime in system 1.9 (in methanol and *n*-butanol).

OXIDATIVE CARBONYLATION OF TERMINAL ALKYNES AT THE $\equiv\text{C}-\text{H}$ BOND

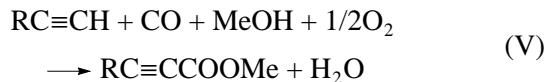
Three catalytic systems of oxidative carbonylation of alkynes with the formation of esters of alkynylcarboxylic acids are known [43]. In the Tsuji system [98],

2.3. $\text{PdCl}_2-\text{NaOAc}-\text{CuCl}_2-\text{MeOH}$,

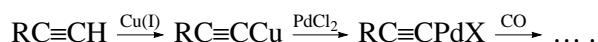
the following reaction occurs:



in which Pd(II) is the catalyst. The studies showed that the reaction was autocatalytic and its rate depended on $[\text{CuCl}_2]$. Thus, the system is polyfunctional and contains two catalysts, PdCl_2 and CuCl_2 [99, 100]. Under certain conditions, the reaction can occur without NaOAc according to the equation



and, thus, CuCl_2 also becomes a component of the catalytic system [99]. The kinetic studies showed that the reaction occurred through the successive formation of organic σ -copper and palladium intermediates [100]

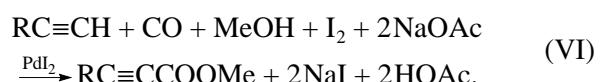


The mechanism of the reaction in this system can be attributed to hypothesis (dogma) no. 1 because the M–C bond (Cu(I) , Pd(II)) is formed from the organic substrate before the formation of the C–C and C–O bonds in the intermediate. In this case, the RPdX intermediate is formed from Pd(II).

Diiodine can be used as an oxidant in the system

2.4. $\text{PdI}_2-\text{NaOAc}-\text{I}_2-\text{MeOH}$ [32].

The following reaction occurs in this system:



The catalysts are Pd(0) (or Pd(I)) complexes formed from PdI_2 , and the intermediate is $\text{RC}\equiv\text{CI}$, whose con-

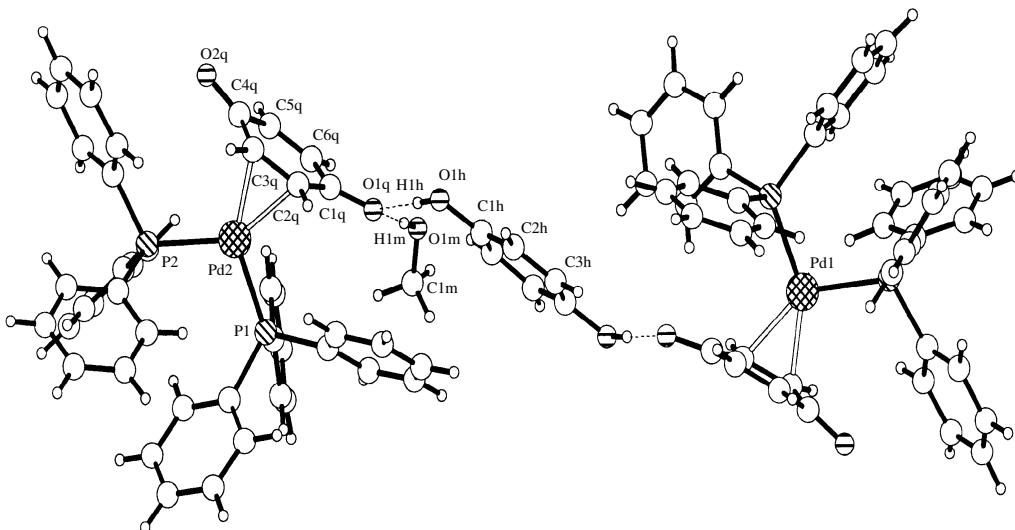
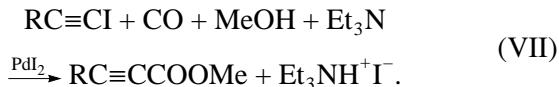


Fig. 9. Structure of the $\text{Pd}(\eta^2\text{-Q})(\text{PPh}_3)_2\text{QH}_2 \cdot \text{MeOH}$ complex (VI) [44].

centration passes through a maximum during the reaction [43, 101]. Reaction (VII) also occurs with ~50% yield but in the presence of Et_3N

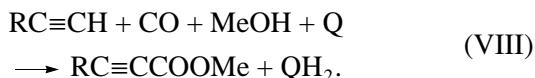


Assuming that the intermediate $\text{RC}\equiv\text{CI}$ forms, reaction (VI) also occurs in the framework of dogma no. 1 (formation of the $\text{RC}\equiv\text{CPdI}$ intermediate).

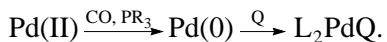
In the third system 2.5 developed by Tsuji [98] and improved by the introduction of PPh_3 [43], *para*-benzoquinone (Q) is the oxidant and the Pd(0) complexes are the acting catalyst.

2.5. $\text{Pd}(\text{OAc})_2\text{-PPh}_3\text{-Q-MeOH}$.

The following reaction occurs in this system:

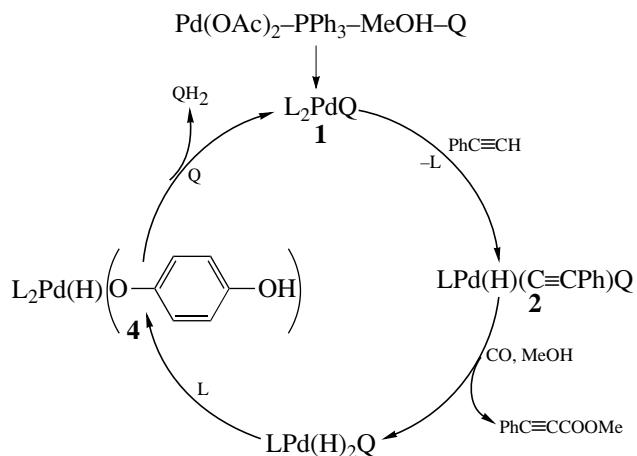


The studies of the mechanism of active species formation showed that Q was the ligand involved in the formation of the catalytically active complex [44]



The Q complexes with Pd(0) are known for several ligands (Bipy, Phen, cod, and others). However, the structural studies were only carried out for nitrogen-containing ligands (see [44]). We synthesized and studied two new Pd(0) complexes with Q and PPh_3 by X-ray diffraction analysis [44]. The structure of the $[\text{Pd}(\eta^2\text{-Q})(\text{PPh}_3)_2]_2\text{QH}_2 \cdot \text{MeOH}$ complex (VI) is presented in Fig. 9, and that of $\text{Pd}_2(\mu\text{-}\eta^2, \eta^2\text{-Q})_2(\text{PPh}_3)_2 \cdot \text{MeOH}$ (VII) is shown in Fig. 10. The Pd–Pd distance in VII is 2.975(1) Å.

Complexes VI and VII, as well as the PdL_4 and $\text{Pd}(\text{dba})_2 + 2\text{PPh}_3$ complexes, are active in reaction (VIII) [44]. The ^{31}P , ^{13}C , and ^1H NMR data, kinetic studies, an almost complete absence of acids (H^+), and the rate independent of the pH (5.9–7.7) in the systems with the Pd(0) complex suggest the scheme of the mechanism of this reaction (Scheme 9).



Scheme 9.

It is also possible that the cleavage of the C–H bond in alkyne is accompanied by the formation of complex 5 followed by its transformation into 4



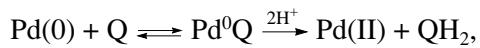
The possibility of oxidation of the palladium hydride complexes by quinone (and oxygen) is of no doubt. However, in the case of sterically hindered ligands (for example, $1,2\text{-}(\text{CH}_2\text{PBu}_2')_2\text{C}_6\text{H}_4$), the cationic hydride

complexes do not interact with Q and oxygen to a noticeable extent [25].

ON THE FUNCTIONS OF *para*-BENZOQUINONE IN REACTIONS OF ORGANOMETALLIC COMPOUNDS AND IN CATALYSIS

The results and published data considered in this article make it possible to draw some conclusions on the known functions of *para*-benzoquinones in reactions involving the Pd(II, I, 0) complexes and in various mechanisms of electron transfer through palladium to Q.

(1) Oxidation of the Pd(0) or HPdX complexes to Pd(II) [2, 3, 6, 7, 9]



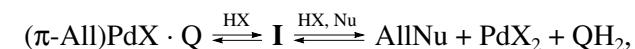
For this mechanism of electron transfer to the oxidant, the reaction rate of Pd(II) reduction is independent of [Q] and the concentrations of other oxidants.

(2) Oxidation of the intermediate Pd(I) complexes in olefin oxidation and termination of the Pd(I)-catalyzed process of positional isomerization of olefins [62, 65, 66]

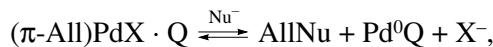


In this case, Q performs functions of a stop-reagent. The same function of Q appears in the Pd(I)-catalyzed carbonylation of alkynes [75].

(3) Elimination of thermodynamic restrictions (formation of Pd_{sol}^0 , $\text{PdCl}_{\text{sol}}^-$, or $\text{Pd}(\text{OAc})_{\text{sol}}^-$) during the redox decomposition of the organic σ -palladium compounds due to the electron transfer to protonated Q in the RPdX · Q complex [102, 103] (I is an intermediate)

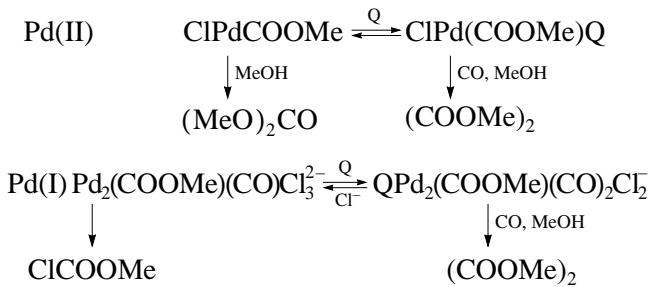


or due to the stabilization of Pd(0) evolved as a result of the formation of a complex with Q



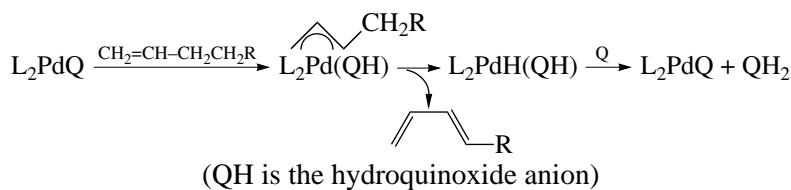
followed by the proton and electron transfer from Pd(0) to Q [104, 105]. In these cases, Q acts both as a ligand and an oxidant.

(4) Change in the selectivity of the reactions due to complex formation with Q [31, 72, 73]

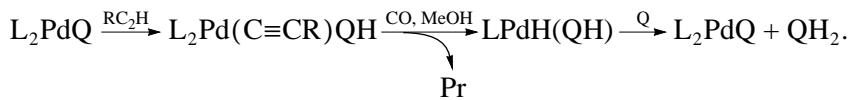


Here, in addition to the function of a ligand, which changes the direction of transformations of the intermediate, and an oxidant, Q decreases probable thermodynamic restrictions related to the formation of Pd(0) or Pd₂(0). In the case of the Pd(I) complexes, Pd(I) is not oxidized to Pd(II) by quinone due to a low concentration of HX. The selectivity of oxidation reactions changes also at high concentrations of such an oxidant as CuCl₂ [6].

(5) Formation of the catalytically active Pd(0)–L₂PdQ complexes [44, 106]. Benzoquinone performs a function of the key ligand and oxidant, which oxidizes the hydride H⁻ ligand without participation of acid from a solution. For example, in the oxidative dehydrogenation of olefins (or allylation of quinones) [106]



and in the oxidative carbonylation of alkynes [44]



In the L₂PdH(QH) complex, quinone is already reduced and Pd(II) is reduced to Pd(0) due to the reductive elimination of QH₂. The transfer of a hydrogen atom from the C–H bond to Q probably occurs through HPd~.

Thus, the electron or proton transfer to *para*-benzoquinone can occur through Pd(0), HPdX, or HPdX · Q and HPdR · Q complexes followed by the transfer of H⁻

to Q, as well as through Pd(II) to protonated Q in the RPdX · (QH)⁺ complex.

(6) Formation of the LPdQ complexes catalyzing nonoxidative reactions. The Pd(0) complexes with stable carbenes (imidazol-2-ylidene) and quinones (*para*-benzoquinone, naphthoquinone) have recently been shown to be active catalysts of the Heck reaction (with aryl chlorides and aryl diazonium salts) and Suzuki

reaction (with arylboron acids) [107, 108]. The stabilization of the Pd(0) state by quinones toward decomposition to Pd(sol) is assumed.

CONCLUSIONS

Analysis carried out in this work demonstrated that the carbonylation of alkenes, alkynes, and alcohols catalyzed by the Pd(II), Pd(I), and Pd(0) complexes can proceed through different mechanisms, including the occurrence of the oxidation reactions in the self-oscillation regime.

Possible mechanisms of electron transfer to *para*-benzoquinone (Q) as an oxidant examined in this work allow one to judge the functions of Q in oxidation. The possibility of catalysis by Pd(I) complexes in the presence of quinones and oxygen and the recently found oxidation of alkynes catalyzed by Pd(0) complexes with the formation of active catalysts (L_2PdQ complexes) are worth mentioning.

It is useful to compare the oxidation states of palladium in active complexes and different hypotheses discussed above.

Depending on the ligand surrounding and the nature of the reaction medium (reductive, oxidative, acidic, or basic), the starting palladium complexes can be in the Pd(II), Pd(I), or Pd(0) states. In a strongly oxidative medium (Cl_2 , Br_2) or in the presence of CH_3I or ArI , Pd(II) can transform into Pd(IV) [41, 42, 109, 110]. However, the chemistry of Pd(IV) complexes is not yet developed to such an extent as the coordination and catalytic chemistries of Pd(I), and hypotheses involving intermediate Pd(IV) compounds are very rare.

Different oxidation states of palladium are responsible for the occurrence of predominantly one of the possible mechanisms of carbonylation or oxidative carbonylation of organic compounds.

Pd(II) complexes. The electrophilicity of the Pd(II) complexes (π -, n -acceptor properties) favors hypothesis no. 2: the formation of the key intermediate $XPdCOY$ (Y is Hal, OR, NR_2 , and others) followed by its transformation under the action of a nucleophile or due to the nucleophilic addition of the COY fragment to the coordinated π -ligand. Cross-coupling reactions of

the COY fragments to form the C–C bond are also within the framework of dogma no. 2 ($L_2Pd(COOR)_2$).

Pd(0) complexes. The most characteristic reaction of the Pd(0) complexes is the oxidative addition of HX (HCl, HOAc, CF_3SO_3H , HBF_4 , and others) [25, 111] and RX [107, 108, 110] to form HPdX or RPdX (see Scheme 1). The studies of the oxidative carbonylation of alkynes at the $\equiv C–H$ bond suggest [44] that the Pd(0) π -quinone complexes are capable of oxidative addition of alkynes to the C–H bond to form RPdH (or RPdQH), which undoubtedly extends the area of application of dogma no. 1. This hypothesis also includes the formation of the $RC\equiv CPdX$ ethynyl complexes by transmetallation



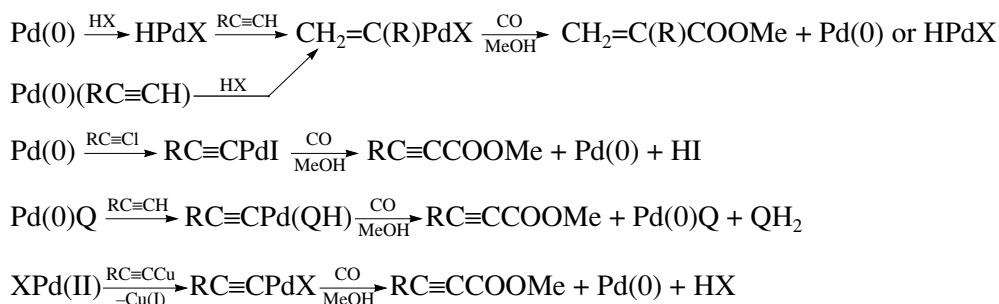
Thus, the appearance of the key intermediate in dogma no. 1 (RPdX) can involve Pd(II). The formation of intermediates $XPdCOOR$ in this case (dogma no. 2) is not confirmed by the kinetic isotope effects when CD_3OD is used ($k_H/k_D \approx 1$ [100]). Therefore, the hydride mechanism (participation of HPdX) is only one of the variants of hypothesis no. 1. The general scheme of RPdX formation can be presented by Scheme 10 using alkyne carbonylation as an example.

Pd(I) complexes. The ability of these complexes to exhibit the electrophilic properties (good π , n -acceptors) and to serve as electron donors in the oxidative addition of different molecules with the Pd–Pd bond cleavage [36] allows them to be involved in hypothesis nos. 2 and 3 and diverse hybrid variants.

The body of experimental data on the oxidative carbonylation of methanol to dimethyl oxalate in the presence of Q argues in favor of hypothesis no. 2. Although the alcoholysis of the Pd_2X_2 complex



should be less efficient than the alcoholysis of Pd(II) complexes, the presence of Q in the complex probably facilitates this reaction. In addition, the nucleophilic attack of the bridging carbonyl in the $Pd_2(\mu-CO)_2Cl_4^{2-}$



Scheme 10.

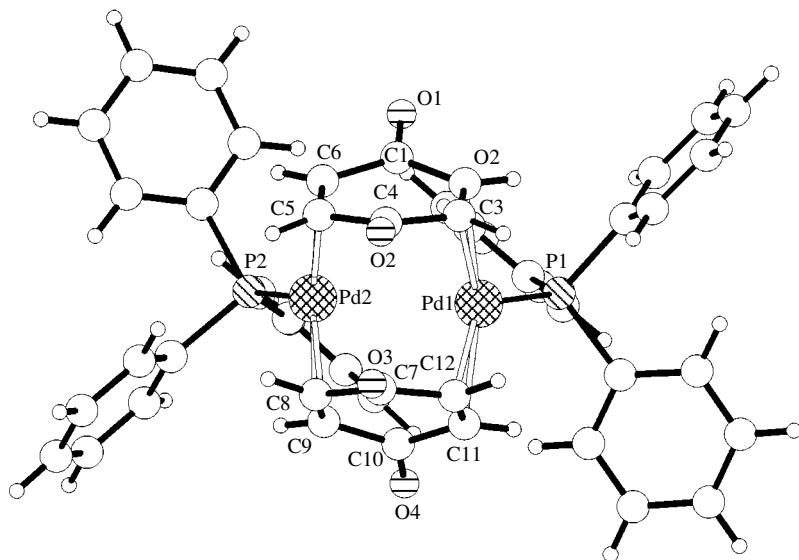


Fig. 10. Structure of the $\text{Pd}_2(\mu-\eta^2, \eta^2-\text{Q})_2(\text{PPh}_3)_2 \cdot \text{MeOH}$ complex (VII) [44].

complex by an alcohol can be more efficient than the insertion of CO into the $\text{ClPd}-\text{OR}$ bond.

Probably, the most characteristic scheme of the mechanism involving the Pd(I) complexes is hypothesis no. 3 leading to σ -organometallic intermediates to form the C–C bond between the substrates. In the case of alkynes,



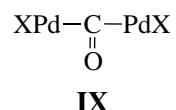
VIII

The transformations of complex **VIII** in reactions with the nucleophile, HX or CO , via different “hybrid” mechanisms can result in all observed products (Scheme 11).

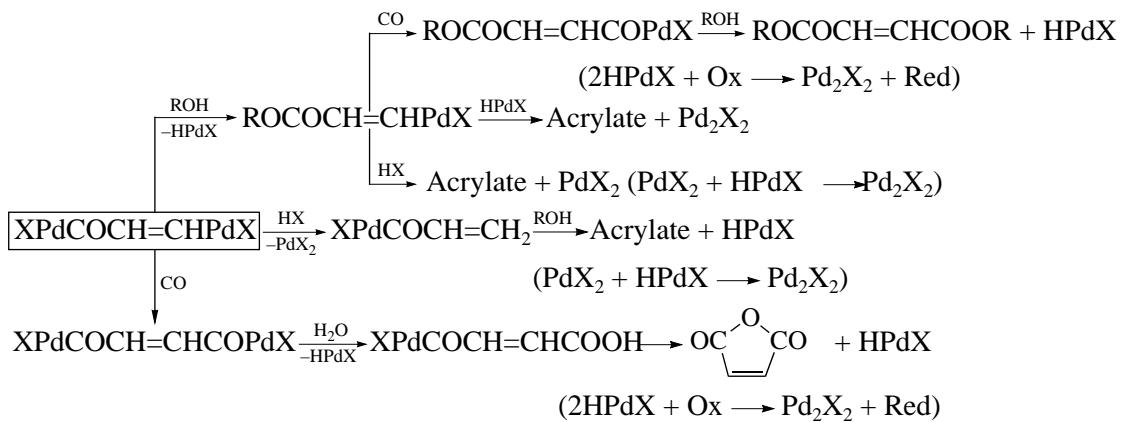
The oxidation of the hydride anion in HPdX by oxidants that are present in the system can result in the formation of PdX_2 , and then the process should include

additional steps of formation of catalytically active Pd(I) complexes (Scheme 8).

If the primary product is a complex with the fragment



(Scheme 7), its interaction with the nucleophile in oxidative addition can afford two species, HPdX and XPdCOOR , whose transformations in the framework of hypothesis nos. 2 and 1 and hybrid schemes (Scheme 7) give the products of oxidative and nonoxidative (additive) carbonylation of unsaturated substrates. Further studies of processes catalyzed by Pd(I) complexes will allow one to reject some of the considered hypotheses.



Scheme 11.

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