

Oxidative Addition Step in Reactions Involving Palladium Activation of Carbon–Halogen and Carbon–Oxygen Bonds

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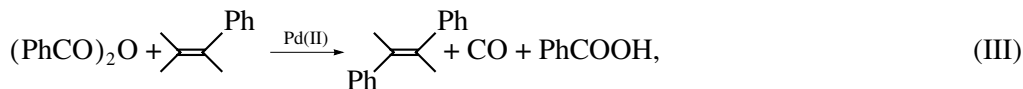
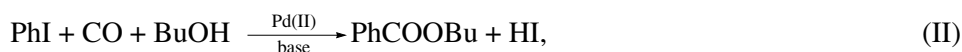
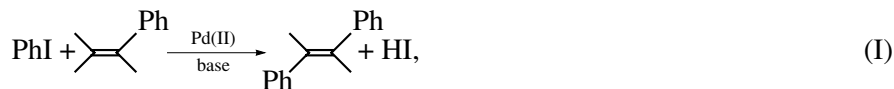
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Abstract—Different modifications of the Heck reaction involving the activation of carbon–halogen and carbon–oxygen bonds by palladium (styrene phenylation with iodobenzene or benzoic anhydride and iodobenzene carbonylation, reductive coupling, and reduction) are studied by *in situ* ^{31}P NMR spectroscopy. The catalytic cycles of the reactions include oxidative addition to Pd(0) formed *in situ*. The product composition in this step depends strongly on the composition of the reaction mixture, which is related to PhX conversion in the main catalytic process and with the nature of the catalyst precursor. A new hypothesis as to the mechanism of the catalytic cycle in alkene arylation in the presence of phosphine ligands is suggested. This hypothesis is consistent with NMR monitoring data and with the value of the kinetic isotope effect.

In this work, we present the results of NMR studies of different modifications of the Heck reaction involv-

ing the activation of carbon–halogen and carbon–oxygen bonds by palladium,



For all of these processes, the oxidative addition of a PhX molecule to the Pd(0) complex is postulated to be the first step of their catalytic cycles:



where X is the leaving group. Depending on the reaction, this group may be a halogen atom or part of the anhydride molecule (–OCOR). In essence, the presence of the step of oxidative addition of an aryl halide to the Pd(0) complex in the catalytic cycles of reactions (II)–(IV) is only inferred from the general coordination chemistry of palladium. Not long ago, the same could be said about reaction (I), the most thoroughly studied, classical Heck reaction, because the first experimental evidence for this step was published only 25 years after the discovery of this reaction [1–4]. However, more than two parts tertiary phosphine to one part palladium were used in those studies. In such systems, phosphine reduces the original palladium(II) complex. Strictly

speaking, the experiments reported in [1–4] were conducted under conditions very different from real catalysis conditions. Most of the NMR measurements were made in the absence of certain components that are necessary for the reaction to occur in the catalytic regime. Even when catalytic conditions were formally established, low substrate-to-catalyst ratios were used. In this work, we present the results of NMR monitoring of real catalytic reactions, by which we mean reactions conducted at temperatures and component concentrations most typical for reactions (I)–(IV). This approach enabled us to find principal distinctions between the oxidative addition step that occurs during the catalytic process and its stoichiometric analogue. There are two main causes of these distinctions: first, the Pd(0) complexes are formed *in situ*, directly in the reaction mixture; second, in the case of real catalysis, the reaction mixture contains anions of leaving groups. We examined catalytic systems containing two phosphine equiv-

alents per palladium equivalent. In these systems, the Pd(II) salt rapidly forms a stable $\text{Pd}(\text{PR}_3)_2\text{A}_2$ complex (where A is an acido ligand), which does not undergo reduction in the absence of additional reducing agents. These systems are often used in practice, because they exhibit a high catalytic activity. They can also serve as models of catalytic systems containing ligands other than phosphines. First of all we studied PPh_3 , which is often used in reactions (I)–(IV) as an admixture.

We preliminarily obtained complexes that can be formed in the reaction mixture (Scheme 1), according to the postulated mechanisms of reactions (I)–(IV). Chemical shifts were determined for all complexes in *N,N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP), and the reactivity of the complexes was studied. The complexes were synthesized either from Pd(II) compounds or from Pd(0) complexes by a standard procedure [3, 5, 6] (Scheme 1).

EXPERIMENTAL

Catalytic reactions (I)–(V) and the syntheses of the palladium phosphine complexes were carried out under anaerobic conditions (the solvents and reagents were thoroughly degassed and stored under argon). ^{31}P NMR spectra were recorded on Bruker WP-200SY (200 MHz) and Varian VXR-500S (500 MHz) instruments. The spectrometer was stabilized by locking on the deuterium signal from CDCl_3 (external reference). Chemical shifts were referenced to the signal of 85% H_3PO_4 . Catalytic reactions (I)–(IV) were kinetically monitored by GLC on an HP-4890 chromatograph (HP-5 capillary column 15 m in length (Hewlett-Packard), 100–200°C, flame-ionization detector, and naphthalene as the internal standard). Substances were purified according to standard procedures.

Catalytic Reactions (I)–(IV)

For the classical Heck reaction (I), styrene (10 mmol), PhI (10 mmol), and NBu_3 (13 mmol) were dissolved in DMF (10 ml). The solution was added to a mixture of PdCl_2 and PPh_3 or to preliminarily prepared $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.16 mmol) in a flask fitted with a magnetic stirrer and thermostated at 80°C.

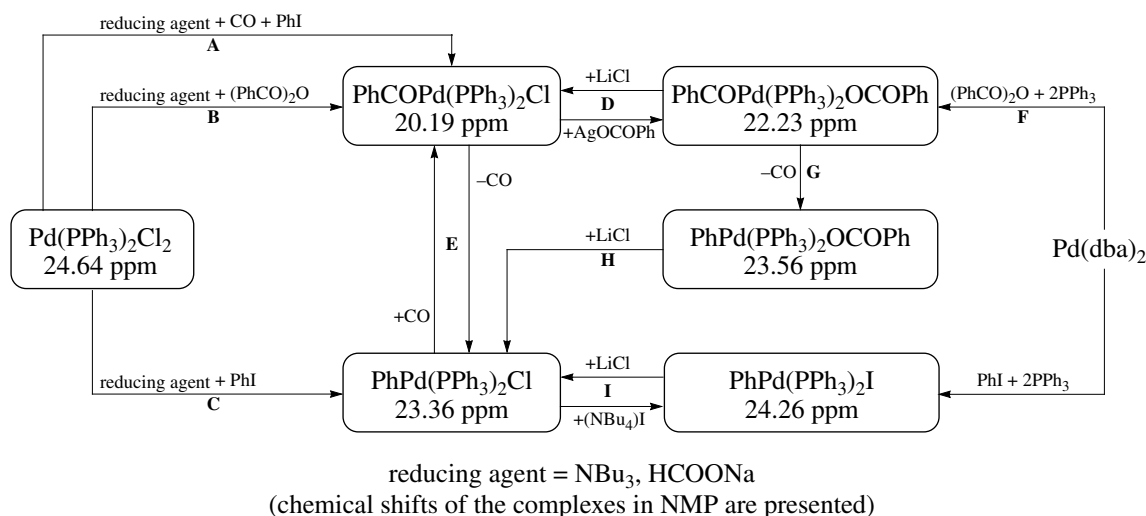
For carbonylation reaction (II), PhI (10 mmol), BuOH (10 mmol), and NBu_3 (13 mmol) were dissolved in DMF (10 ml). The solution was added to $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.16 ml) in a flask preliminarily purged with CO, fitted with a magnetic stirrer, and thermostated at 80°C. The reaction was performed until the products stopped building up under 1 atm CO. CO absorption was detected using a burette.

In reaction (III), iodobenzene (which was used in reactions (I) and (II)) was replaced with the same amount of benzoic anhydride and NMP was used instead of DMF. The reaction was carried out at 140°C.

Reactions (IV) were similar to the classical Heck reaction (I), but styrene was excluded from the system.

Synthesis of $\text{PhCOPd}(\text{PPh}_3)_2\text{X}$ and $\text{PhPd}(\text{PPh}_3)_2\text{X}$ from Pd(II) Complexes

To obtain $\text{PhCOPd}(\text{PPh}_3)_2\text{Cl}$, $(\text{PhCO})_2\text{O}$ (10 mmol) and a reducing agent (NBu_3 or HCOONa , 0.32 mmol) were added to an NMP solution (10 ml) containing $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.16 mmol). The reaction mixture was stirred at 100°C until the NMR signal from the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ complex disappeared completely (~40 min) and a signal at 20.19 ppm appeared (presumably, from $\text{PhCOPd}(\text{PPh}_3)_2\text{Cl}$). Under similar conditions, the same signal was observed for the reaction of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ with PhI and a reducing agent in a CO atmosphere. The chloride ligand was exchanged for benzoate by reacting the resulting complex with an equivalent amount of AgOCOPh at room temperature. The AgCl precipitate



Scheme 1.

was separated by decantation. The complex was decarbonylated at 100°C in flowing argon (≈ 120 min).

$\text{PhPd}(\text{PPh}_3)_2\text{Cl}$ was prepared under similar conditions by the addition of PhI (10 mmol) and a reducing agent (0.32 mmol) to a solution of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$. The process was continued until the starting complex was completely converted and a signal at 23.36 ppm appeared. The chloride ligand in the resulting complex was exchanged for iodide using a 20-fold excess of $(\text{NBu}_4)\text{I}$ at room temperature. The complex was carbonylated in a CO atmosphere at room temperature (≈ 30 min).

Synthesis of $\text{PhCOPd}(\text{PPh}_3)_2\text{X}$ and $\text{PhPd}(\text{PPh}_3)_2\text{X}$ from $\text{Pd}(0)$ Complexes

$\text{PhCOPd}(\text{PPh}_3)_2\text{OCOPh}$ (22.23 ppm) and $\text{PhPd}(\text{PPh}_3)_2\text{I}$ (24.26 ppm) were synthesized according to known procedures [5, 7] by the oxidative addition of $\text{Pd}(\text{dba})_2$ ($\text{dba} = \text{trans,trans-dibenzylideneacetone}$) (0.16 mmol) to $(\text{PhCO})_2\text{O}$ (10 mmol) and PhI (10 mmol), respectively, in the presence of PPh_3 (0.32 mmol). The reagent ratios and decarbonylation and ligand exchange conditions were identical to those described above.

RESULTS AND DISCUSSION

Phenyl iodide in the presence of CO (1 atm), $(\text{PhCO})_2\text{O}$, or PhI began to react with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ only if the system contained a reducing agent (Scheme 1, **A**, **B**, **C**), such as HCOONa or NBu_3 (twofold excess). The ability of NBu_3 to efficiently reduce $\text{Pd}(\text{II})$ complexes was demonstrated in [8], and sodium formate is among the compounds conventionally used in palladium reduction, including the Heck reaction [9–11]. The reactions resulted in the quantitative formation of a σ -benzoyl ($\text{PhCOPd}(\text{PPh}_3)_2\text{Cl}$) or a σ -phenyl ($\text{PhPd}(\text{PPh}_3)_2\text{Cl}$) complex.

The ^{31}P NMR spectra of these complexes consist of one singlet, which is evidence of the *trans* conformation of the phosphine ligands. The presence of a chlorine atom and a benzoyl fragment in $\text{PhCOPd}(\text{PPh}_3)_2\text{Cl}$ is confirmed by reversible ligand exchange in the presence of AgOCOPh and LiCl (Scheme 1, **D**), by CO elimination (at 100°C in flowing Ar) yielding $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$, and by the carbonylation of this complex (Scheme 1, **E**). These transformations are characteristic of $\text{ArCOPd}(\text{PR}_3)_2\text{X}$ complexes [3, 6]. Note that decarbonylation requires an elevated temperature and proceeds much more slowly than carbonylation.

Classical Heck Reaction (I)

Adding iodobenzene to a solution of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in DMF or NMP and holding the mixture at 80°C for several hours (the reactant concentrations and temperatures were the same as in the catalytic experiments) did not change the ^{31}P NMR spectrum of the mixture. The spectrum contained only a singlet due to the starting

complex $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$. Addition of one or two equivalents of NBu_3 or HCOONa (per palladium equivalent) to a solution of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and PhI at 80°C resulted immediately in the appearance of a singlet from the σ -phenyl complex. However, instead of the iodo complex $\text{PhPd}(\text{PPh}_3)_2\text{I}$ (which would be anticipated from the classical mechanism of the Heck reaction), we detected its chlorine-containing analogue $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$ (Scheme 1, **C**). The appearance of the oxidative addition product after the addition of a reducing agent to a mixture containing the $\text{Pd}(\text{II})$ complex and PhI indicates that this step can take place during catalysis. The formation of a chloro complex instead of the expected iodo complex was also observed in [3]. The formation of the chloro complex was explained by the fact that a $\text{Pd}(0)$ chloro complex was taken as a reactant and the reaction involved a pentacoordinated anionic transition state [3]. In our opinion, the formation of the chloro complex at our experimental temperature can be due to this complex being thermodynamically more stable than the iodo complex. This explanation is consistent with the possibility of the reversible exchange of acido ligands with sources of another anion (Scheme 1, **I**). The same is indicated by earlier stability constant data for several σ -phenyl complexes containing different acido ligands [3]. Note that, according to these data, the chloride complexes in DMF are much more stable than the iodide complexes.

Direct NMR monitoring of styrene phenylation with iodobenzene in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and NBu_3 (80°C) showed that the signal from the starting complex disappeared immediately after the reaction began, and only a signal from $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$ was detected in the spectrum at the initial stage (including the induction period and the reaction period up to $\sim 10\%$ PhI conversion). This fact is unambiguous evidence of the Heck reaction including an oxidative addition step. After the 10% conversion was achieved, a signal from $\text{PhPd}(\text{PPh}_3)_2\text{I}$, whose intensity increased in time, appeared in the spectrum of the solution. The intensity of the signal from $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$ decreased simultaneously. Thus, the increase in PhI conversion and, hence, an increase in the concentration of iodide ions were accompanied by an increase in the concentration of the iodide complex. These facts are consistent with the earlier hypothesis that the acido ligands are exchanged at a high rate and the formation of the complexes is thermodynamically controlled by their stability constants.

The authors of the few existing kinetic studies of the Heck reaction [12–14] assume that the step of alkene insertion into the Pd-Ph bond is markedly retarded by phosphines because it requires the dissociation of at least one of the phosphine ligands. If this is the case, this insertion will be the rate-determining step. The results of NMR monitoring might seem to confirm this hypothesis. Indeed, coordinately saturated complexes of the $\text{PhPd}(\text{PPh}_3)_2\text{X}$ type, which formed in the presence of two phosphine equivalents per palladium equiv-

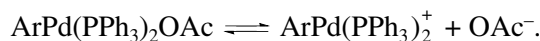
alent and were postulated to be intermediates in the catalytic cycle, were the most stable under the Heck reaction conditions. According to NMR data, even at 140°C, most of the palladium charged into the reactor is in the form of these complexes during the catalytic process. However, it turned out that these facts cannot be viewed as unambiguous evidence for the slow rate of the alkene insertion step because they contradict the kinetic isotope effect data. The absolute values of the rate of reaction (I) were substantially lower in the presence of phosphine than in the absence of phosphine [15]. However, irrespective of whether phosphine is present, the phenylation rate of an equimolar mixture of styrene and styrene- d_8 is half as high as the reaction rate of styrene alone. According to an earlier developed approach [15], this indicates a kinetic isotope effect of $k_H/k_D \approx 3$ in the step that determines the reaction rate and includes C–H bond dissociation. According to the conventional mechanism of the Heck reaction, this step is the β -elimination of palladium hydride. Note that this inference is valid only for reactions involving reactive arylating agents such as iodobenzene (for details, see [15]). The existence of isotope effects and the finding that they have nearly equal values (close to 3) for the phosphine-containing and phosphine-free catalytic systems suggest that the palladium complexes involved in the rate-determining steps of these processes are similar in nature.

Our kinetic isotope effect and NMR monitoring data for the reaction in the presence of a phosphine can be interpreted in terms of the following reaction mechanism.

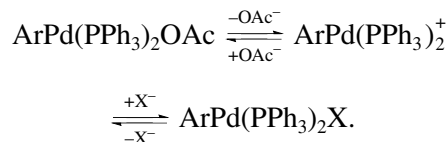
The main distinction of our hypothesis as to the catalytic cycle of the Heck reaction from the mechanism suggested in the literature is that the coordinately saturated σ -alkyl palladium complexes with two phosphine ligands (Scheme 2, complexes **A**, **B**, **C**) are postulated to be catalytically inactive and it is assumed that complexes **B** and **C** cannot be intermediates of the catalytic cycle. They are outside the cycle, and their formation is actually catalyst deactivation. This is not true for the oxidative addition product $\text{ArPd}(\text{PPh}_3)_2\text{X}$ (Scheme 2, complex **A**), which contains most of the palladium, according to NMR data, and can be formed directly from the coordinately unsaturated 14-electron complex $\text{Pd}(0)\text{L}_2$ [16]. However, the much higher rate of the Heck reaction in the absence of phosphines indicates that “ligand-free” $\text{Pd}(0)$ can also participate in this step. The phosphine complexes (Scheme 2, complexes **A**, **B**, and **C**) become a source (“reservoir”) of active intermediates with coordination vacancies due to the reversibility of complex formation. Due to most of the palladium existing as stable coordinately saturated complexes, the catalytic activity of the phosphine-containing catalytic systems is markedly lower than that of their phosphine-free counterparts. However, the addition of phosphine does not change the nature or, accordingly, reactivity of those intermediates of the catalytic cycle that make the main contribution to the catalytic reaction. Due to this

fact, the kinetic isotope effects in the presence and absence of phosphine ligands are equal.

Furthermore, our data cast doubts upon the Heck reaction mechanism [2] according to which the use of palladium acetate as the starting complex and tertiary amines as bases leads the Heck reaction only via intermediates that contain acetate ligands and are equilibrated with cationic σ -aryl complexes:



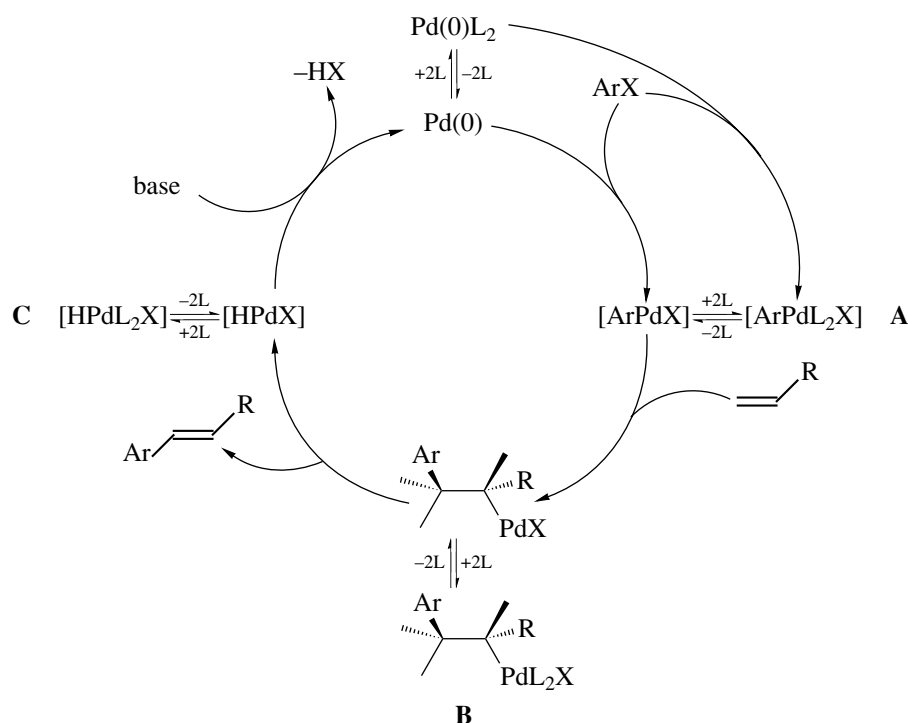
As already mentioned, these data were obtained for model systems in which the reaction could not be catalytic. The results of monitoring of the real catalytic process using $\text{Pd}(\text{PPh}_3)_2(\text{OAc})_2$ as the catalyst precursor demonstrate that the reaction system contains an iodo complex $(\text{PhPd}(\text{PPh}_3)_2\text{I})$ along with the acetato complex $\text{PhPd}(\text{PPh}_3)_2\text{OAc}$ once 10% conversion is achieved. The intensity of the signal from the iodine-containing complex increases parallel to the accumulation of iodide anions in the solution due to the equilibrium shift in the system



Starting at a conversion of 80%, only the signal from $\text{PhPd}(\text{PPh}_3)_2\text{I}$ is observed in the spectrum. Moreover, even in the catalytic system using NaOAc instead of amine ($[\text{Pd}] : [\text{NaOAc}] = 1 : 130$), in which a domination of the acetate complexes would be natural, the amounts of the acetate and iodide complexes at the end of the reaction are approximately equal.

Oxidative Addition Step in the Iodobenzene Carbonylation Reaction (II)

The oxidative addition step of the carbonylation reaction (II), like that of the arylation reaction (I), has important specific features. It has already been mentioned that these reactions do not occur in a solution of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and PhI under catalysis-like conditions. According to NMR data, nothing takes place in this solution as it is held in a CO atmosphere even after the addition of BuOH , which is the last component necessary for the formation of products of carbonylation (II). At the same time, addition of tributylamine, which is necessary as a base in this reaction and can simultaneously act as a reducing agent for $\text{Pd}(\text{II})$ [8], or of HCOONa (Scheme 1, **A**), which is also used as a reducing agent [9, 10], to the $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ – PhI – CO system results in the rapid formation of a benzoyl complex. This complex, like the complex observed in the system without CO, contains a chlorine atom as the acido ligand ($\text{PhCOPd}(\text{PPh}_3)_2\text{Cl}$). We found that this product forms rapidly if a solution of preliminarily obtained $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$ is placed in a CO atmosphere (Sche-



Scheme 2. Mechanism of alkene phenylation in the presence of phosphine ligands (L).

me 1, **E**). Thus, it cannot be doubted that carbonylation (II), as well as the arylation reaction, includes an oxidative addition step followed by the insertion of a CO molecule into the Pd–Ph bond.

The NMR monitoring of catalytic iodobenzene carbonylation in the presence of BuOH (as a nucleophile) and $\text{Pd(PPh}_3)_2\text{Cl}_2$ gave qualitatively the same results as in the case of arylation. The fundamental difference is that, according to ^{31}P NMR data, most of the palladium is concentrated in benzoyl complexes of the $\text{PhPd(PPh}_3)_2\text{X}$ rather than in $\text{PhCOPd(PPh}_3)_2\text{X}$ complexes. This finding is rather to be expected in view of the fact that the reaction is conducted in CO, which is inserted rapidly into the Pd–Ph bond. Again, the chloride anion acts as an acido ligand at the early stages of the reaction. The proportion of the iodo complex gradually increases with increasing conversion and iodide anion concentration, as in the case of arylation.

NMR monitoring data apparently indicate that the substitution of the nucleophile present in the system for the halide ligand is the rate-determining step. However, it should be kept in mind that the main contribution to catalysis may be from palladium complexes containing no phosphine ligands in their coordination sphere, as in the case of the conventional Heck reaction. If this is the case, the $\text{PhCOPd(PPh}_3)_2\text{X}$ complexes observed by ^{31}P NMR may serve only as a “reservoir” of true catalytically active compounds, as in the Heck reaction, and another step of the catalytic cycle can be rate-determining.

ing. Kinetic studies are required to determine the rate-determining step.

Oxidative Addition Step in Alkene Arylation with Benzoic Anhydride (Reaction (III))

Detailed data for alkene arylation with anhydrides of aromatic acids (reaction (III)), which was discovered by Dutch researchers [17], were presented in our earlier works [18, 19]. A mechanism including the oxidative addition of an anhydride molecule to the Pd(0) complex was postulated for this reaction. Japanese researchers [5] demonstrated the principal possibility of this step. However, we found that the oxidative addition step occurring under conditions of *in situ* Pd(0) formation affords not palladium benzoate complexes but rather their chlorine-containing analogues (Scheme 1, **B**). The same was indicated by the analysis of samples taken during the catalytic process (III). NMR data unambiguously indicate that complexes containing benzoate ligands are absent from the reaction mixture in all steps of the process.

The mechanism and kinetics of the oxidative addition of $(\text{PhCO})_2\text{O}$ to $\text{Pd(PPh}_3)_4$ were studied by NMR in [20]. The results of that study are similar to our data, but it was concluded that benzoate complexes play the key role in the real catalytic reaction (III). This conclusion followed from the fact that the model reaction considered in that study involved only a Pd(0) complex as the starting compound, while, in the real catalytic pro-

cess, palladium is initially in the oxidized state, in the form of PdCl_2 , and the formation of catalytically active $\text{Pd}(0)$ is required. Bringing the model process closer to the real catalytic reaction, which may seem insignificant at first glance, and directly monitoring the reaction led us to more correct conclusions as to the mechanism of the process. In particular, we established the absence of palladium benzoato complexes.

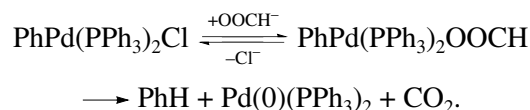
Oxidative Addition Step in the Reductive Coupling and Reduction of Iodobenzene (Reactions (IV))

We are interested in reactions (IV) not only because they provide promising and widely used methods of organic synthesis (including industrial ones) but also for the following reasons. The reductive homocoupling and reduction of aryl halides (IV) do not require any reagents except aryl halides and stoichiometric amounts of a reducing agent, the latter being necessary for these reactions to be catalytic. In view of this, reactions (IV) are the main side processes in (I)–(III). The reduction reactions (IV) can affect the yield of the main products in reactions (I)–(III) and determine, to a considerable extent, the catalytic activity of palladium. Indeed, the absence of efficient reducing agents in all of these three reactions can lead to the complete loss of catalytic activity because of palladium oxidation in reactions (IV).

The complete conversion of iodobenzene in reactions (IV) is possible only in the presence of stoichiometric amounts of tributylamine or sodium formate. The main difference between these two reducing agents is in the diphenyl-to-benzene yield ratio. In the case of sodium formate, most of the iodobenzene is converted into PhH , while the use of amine favors diphenyl formation (up to 70% yield in the absence of phosphine). According to ^{31}P NMR data, the $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$ σ -aryl complex forms in the PdCl_2 – 2PPh_3 –reducing agent– PhI system. As in previous cases, the monitoring of reactions (IV) indicated the gradual transformation of this complex into the iodo complex ($\text{PhPd}(\text{PPh}_3)_2\text{I}$).

An interesting feature of the Heck reaction (I) in the presence of sodium formate as a reducing agent is the fairly high rate of side iodobenzene reduction to benzene at the initial stage of the reaction (over ~15 min). The corresponding portion of the accumulation curve of stilbene (a product of reaction (I)) exhibits a distinct induction period, and the NMR spectrum of the reaction mixture contains a signal from $\text{PhPd}(\text{PPh}_3)_2\text{Cl}$. Based on these data, we can assume that benzene formation, unlike the Heck reaction (I) and reductive coupling, does not require the dissociation of the phosphine ligand and proceeds via the substitution of the chloride anion by the formate anion followed by

intramolecular transformations affording benzene and reduced palladium:



As for reducing coupling, the most probable mechanism of diphenyl formation is the interaction of two palladium-containing species:



Considering that the Heck reaction under similar conditions has a higher rate, the rate-determining step of diphenyl formation cannot be oxidative addition (V). Under the assumption that reaction (VI) is the slowest in the diphenyl formation pathway, the effective reaction order with respect to catalyst must be close to 2. This reaction order is in agreement with experimental data obtained with tributylamine as the reducing agent or, in other words, under conditions of predominant diphenyl formation.

Thus, NMR data for reactions (I)–(IV) indicate that their catalytic cycles include oxidative addition to $\text{Pd}(0)$ formed *in situ*. However, the product of this step is determined, to a great extent, by the reaction mixture composition, whose changes affect the conversion of PhX in the main catalytic process.

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