The role of phosphine ligands in the catalytic systems of the Heck reaction with aromatic carboxylic anhydrides*

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The results of a comparative study of phosphine-containing and phosphine-free catalytic systems of the Heck reaction using aromatic carboxylic anhydrides as arylating agents are presented. It was demonstrated that the patterns of differential selectivity of the reaction under competition of two aromatic anhydrides or two alkenes are independent of the presence of a tertiary phosphine additive in the system. It was established that palladium complexes with no phosphine ligands in their coordination sphere are catalytically active at the step of activation of aromatic carboxylic anhydride and alkene. The patterns of differential selectivity for regioisomers of arylated products provide the evidence of the participation of phosphine-containing anionic palladium complexes in the regioselectivity-determining step of the catalytic cycle. The data obtained are in agreement with the phosphine involvement in the catalyst transformations proceeding outside the main catalytic cycle.

Key words: the Heck reaction, palladium, catalysis, kinetics, mechanism, differential selectivity.

Palladium-catalyzed alkene arylation with aromatic anhydrides represents a modification of the well-established Heck reaction. This reaction offers a promising trend of the fine organic synthesis, which has found application in production of various pharmaceuticals and agrochemicals as well as semi-products for tailor-made polymers.[1] Despite the numerous studies of the mechanism of this catalytic process using various substrates,[2—4] many aspects of the main catalytic cycle and related processes are still unclear. The majority of homogeneous catalytic systems reported for the Heck reaction contain various organic ligands (primarily, phosphines).[5] At the same time, the ligand role in the functioning of catalytic systems still remains an open question. Thus, it is usually believed[6] that there is at least one phosphorus-containing ligand in the coordination sphere of palladium complexes directly involved in a catalytic cycle which results in formation of the reaction product. However, the concepts of the ligand role usually rest on the data of the model experiments performed either without some or other components of the real catalytic system, or with a low substrate/catalyst ratio.[7,8] Such deviations from actual catalytic conditions can cause errors when these conclusions are extended to real catalytic systems. In this context, convincing evidence has been accumulated favoring the idea that it is just phosphine-free Pd(2+) complexes that are catalytically active in the Heck reaction with aryl bromides using phosphine-containing catalytic systems.[9] To justify this conclusion, the results of model experiments under stoichiometric conditions were also invoked. Moreover, the above conclusion concerning the role of phosphine ligands in the Heck reaction was drawn for a "classic" variant in which aryl halides are used as arylating agents. Up to now, the mechanism of functioning of phosphine-containing catalytic reaction systems for the reaction with aromatic carboxylic anhydrides was reported only in two studies. Thus, the model reaction of oxidative addition of an aromatic anhydride to palladium using $Pd(PPh_3)_4$ phosphine precursor in a ratio close to that used in catalytic experiments was examined. The formation of neutral and cationic benzoyl palladium complexes $[(PhCO)Pd(OCOPh)(PPh_3)_2]$ and $[(PhCO)Pd(solv)(PPh_3)_2]^+$ was established in the absence of other components of the catalytic reaction.[10] Using NMR spectroscopy technique under conditions of real catalytic process, it was shown that the most part of palladium (catalyst resting state) in the reaction with benzoic anhydride existed[11] in the form of phosphine-containing complex $[(PhCO)PdX(PPh_3)_2]$. In the latter complex, halide ions introduced into the catalytic system to improve its catalytic activity acted as counterion X. Nevertheless, the experimentally detected presence of phosphine-containing palladium compounds cannot

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provide any information on the role of such compounds in functioning of the catalytic system.[12,13]

Obviously, the question of involvement of phosphine ligands in catalytically active species can be only elucidated when studying reactions proceeding under real catalytic conditions. Studies of patterns of differential selectivity of catalytic systems can become the most important tool in such investigations. In contrast to the value of catalytic activity, which is generally measured in kinetic studies, the value of differential selectivity is related exclusively to the nature of catalytically active compounds. Therefore, assessing this parameter upon controlled change under the process conditions (particularly, on adding phosphine ligands to the catalytic system) will help to get an unambiguous answer to the question whether the ligand addition results in changing the nature of an active catalyst.

Experimental

Samples of the reaction mixture were analyzed on a Chromatech-Crystal 5000 gas-liquid chromatograph (Chromatech, Russia) (FID, column HP-5 15 m) and Shimadzu GC-MS QP-2010 Ultra gas chromatograph-mass spectrometer (Shimadzu, Japan) with electron-impact ionization (ionization energy 70 eV, column GsBP-5MS 0.25 μm×0.25 mm×30 m, helium as carrier gas) and programmed heating from 100 to 250 °C. Mass spectra obtained were compared to the library ones (Wiley, NIST, and NIST05 mass spectral libraries). Quantitative sample compositions were determined using the internal standard (naphthalene) method with calibration on authentic samples.

UV spectra of the solutions under investigation were recorded on a SF-2000 spectrophotometer (EDO «Spektr», Russia) in the wavelength range of 190—600 nm in quartz cells with 0.01 cm optical path length. Concentrations of complex $Pd(PPh_3)_2Cl_2$ were measured using the absorption intensity at 350 nm. A calibration curve for this wavelength was pre-constructed based on the spectra of reference solutions of $Pd(PPh_3)_2Cl_2$ in *N*-methylpyrrolidone (NMP). Herewith, also through plotting the calibration curves, the absorbance maximum at 350 nm from stilbene, 4-methoxystilbene, *n*-butyl cinnamate, and chalcone formed in the process was used with quantitites of the said substances being determined using chromatography-mass spectrometry technique.

Catalytic experiments. All experiments reported herein were run in inert atmosphere (argon). Reagents and solvents in use were preliminary degassed and stored under argon. Experiments on arylating alkenes with aromatic anhydrides were performed by mixing a pair of competing anhydrides or alkenes (2.5 mmol each), a common reagent (styrene or benzoic anhydride respectively, 5 mmol), a halide salt additive (0.5 mmol), and naphthalene (0.5 mmol) as an internal standard, in 5 mL of NMP. The resulting solution was purged with argon and transferred into a glass reactor, pre-evacuated and filled with argon, fitted with a rubber membrane and a magnetic stirrer. The reactor with pre-added $PdCl_2$ (0.08 mmol) and in some cases PPh_3 (0.16 mmol), was then placed in an oil bath thermostatized at 140 °C. The experiments were run at constant stirring. Each experiment was carried out in triplicate for a reproducibility check.

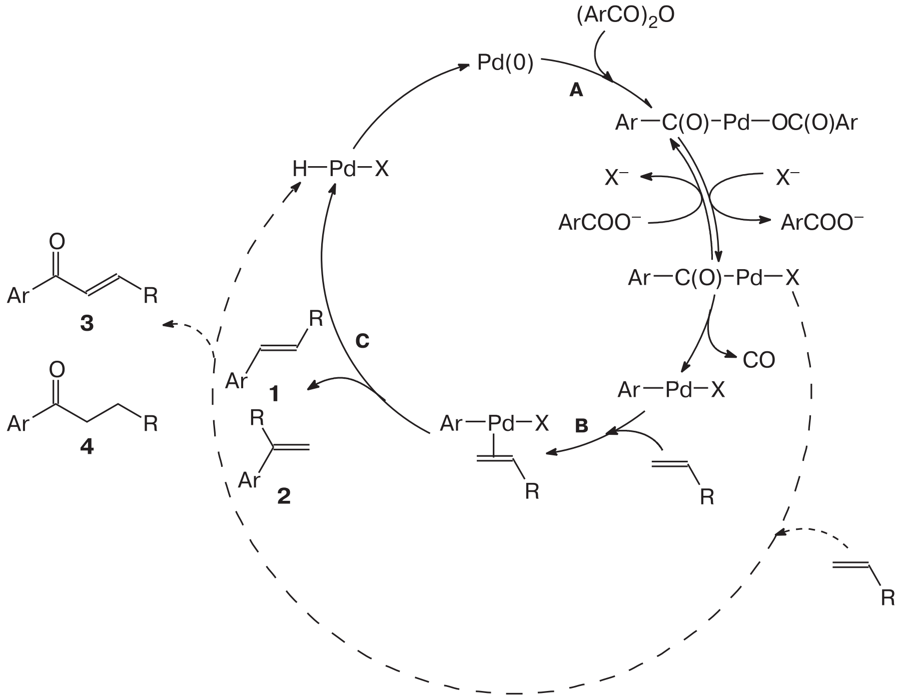
Results and Discussion

Earlier, we proposed a method of qualitative and quantitative assessment of the reaction differential selectivity under conditions of competition between two similar substrates by using the so-called phase trajectories representing the dependencies between the yields of the products obtained from the competing substrates.[14,15] In this case a slope to any point of the phase trajectory is a ratio of accumulation rates of the products of competing reactions, which is related unambiguously to the value of the differential selectivity.[15] Therefore, a change in phase trajectories obtained on varying the reaction conditions, such as ligand addition, is an unequivocal evidence for a change of the differential selectivity value of the catalytic system, and consequently, for a change in the nature of the active catalyst. In turn, a coincidence of phase trajectories can be considered as a proof of invariability of the catalytically active species. This requires, however, an additional experimental verification with a wider set of variable parameters because of possible lower sensitivity of the selectivity to a change in variable parameters.

In most studies, selectivity is assessed based on the target and side reaction products formed from the same substrate. At the same time, an approach based on analysis of differential selectivity using two equitype competing substrates, enables one to recognize the case wherein competing reactions proceed on the catalytically active species of the same type. This enhances the validity of an interpretation of the observed regularities in the differential selectivity changes. Moreover, using pairs of various competing reagents (*e.g.*, a pair of anhydrides or a pair of alkenes in the Heck reaction) makes it possible to elucidate the nature of active catalyst directly in the steps of the catalytic cycles, in which the given reagents operate. The conventional mechanism of the catalytic cycle of the Heck reaction, that includes aromatic anhydrides (ligands attached to the palladium atom are omitted) is illustrated in Scheme 1. In Scheme 2 the mechanism for the Heck reaction with two aromatic anhydrides (*a*) or two alkenes (*b*) competing is shown. Scheme 3 represents catalytically active complexes the nature of which governs the value of differential selectivity when a pair of aromatic anhydrides (*a*) or a pair of alkenes (*b*) are involved in competition. The value of differential regioselectivity (*c*) is also dependent of the complexes.

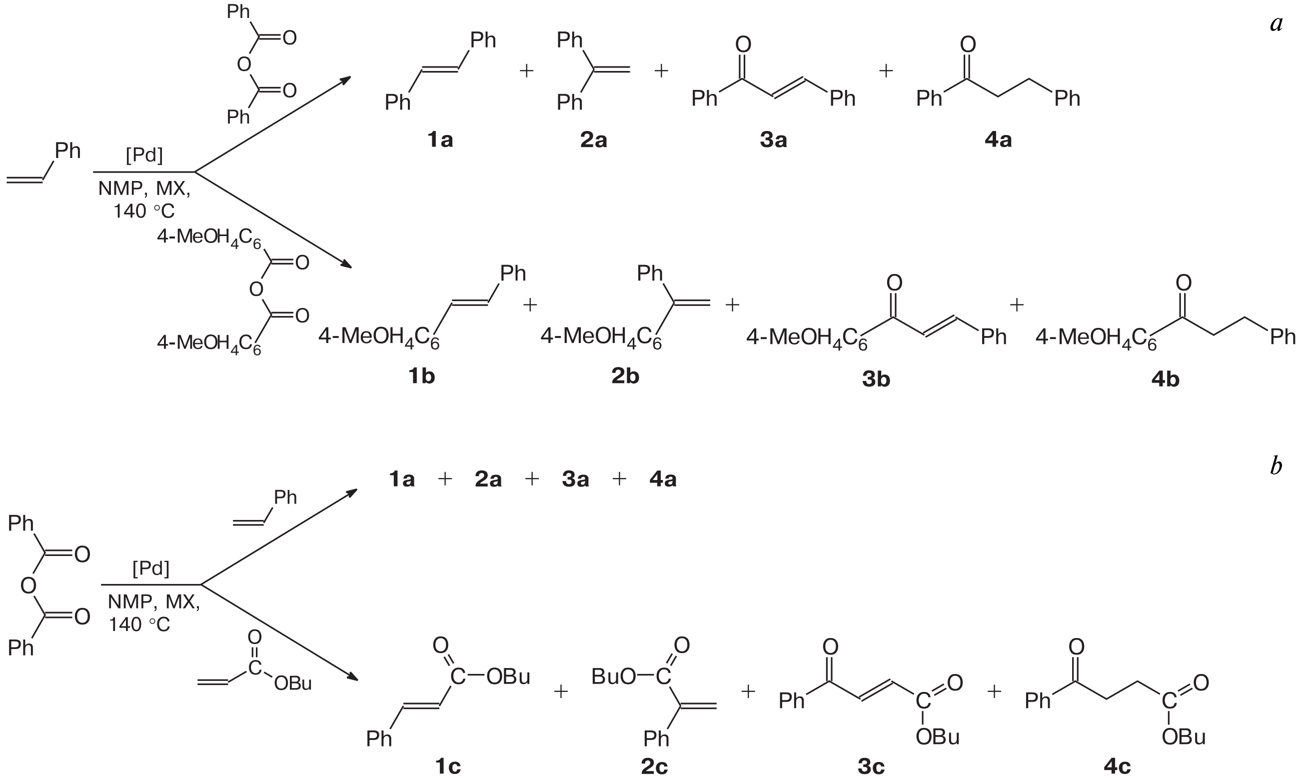
According to the generally accepted concepts, an aromatic anhydride is activatied in a catalytic cycle of the Heck reaction at the step of its oxidative addition to Pd(0) complexes[10] (see Scheme 1, **A**). Therefore, evaluation of differential selectivity patterns based on the products of alkene arylation with two aromatic anhydrides competing (see Scheme 2, *a*) enables one to get insight into the nature of Pd(0) complexes (see Scheme 3, *a*) involved in the oxidative addition step. Experiments with competing al-

Scheme 1



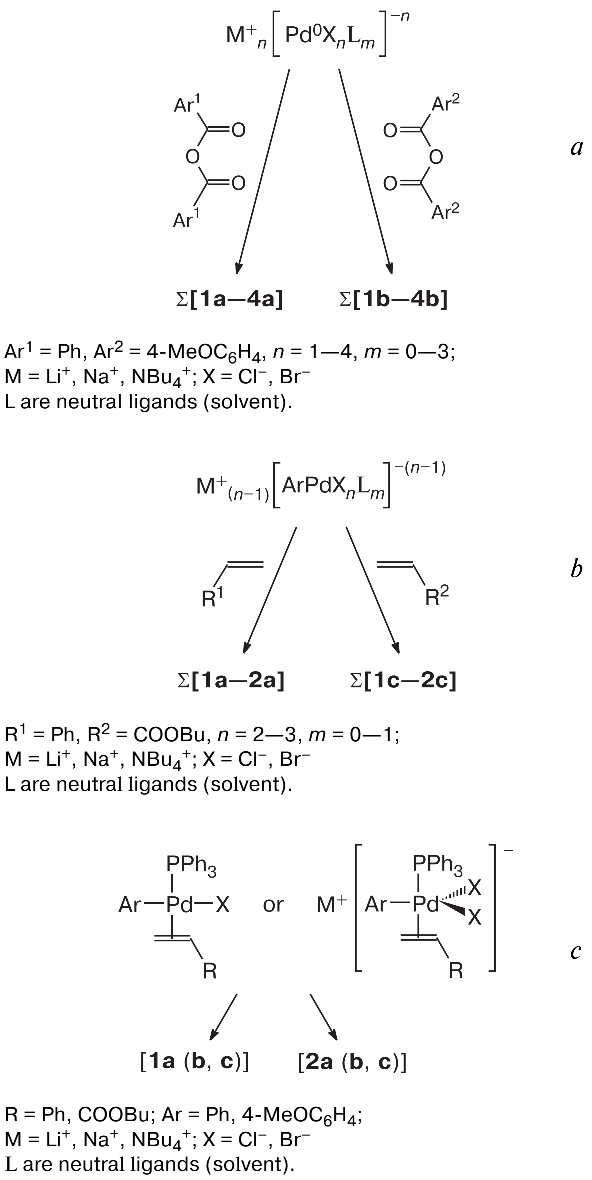
R = Ar, C(O)OAlk

Scheme 2



[Pd] = PdCl$_2$, PdCl$_2$ + 2 PPh$_3$
MX = LiCl, LiBr, NaBr, NaCl, NBu$_4$Br

Scheme 3



Ar^1 = Ph, Ar^2 = 4-$MeOC_6H_4$, *n* = 1—4, *m* = 0—3;
M = Li^+, Na^+, NBu_4^+; X = Cl^-, Br^-
L are neutral ligands (solvent).

R^1 = Ph, R^2 = COOBu, *n* = 2—3, *m* = 0—1;
M = Li^+, Na^+, NBu_4^+; X = Cl^-, Br^-
L are neutral ligands (solvent).

R = Ph, COOBu; Ar = Ph, 4-$MeOC_6H_4$;
M = Li^+, Na^+, NBu_4^+; X = Cl^-, Br^-
L are neutral ligands (solvent).

kenes (see Scheme 2, *b*) provide knowledge about the step of the catalytic cycle involving alkenes (see Scheme 1, **B**), wherein alkenes react with Pd^{II} σ-aryl complex according to the generally accepted mechanism (see Scheme 3, *b*).

Carrying out the competing arylation of styrene with benzoic and 4-methoxybenzoic anhydrides (see Scheme 2, *a*) it was found that apart from "Heck's" products of arylation at α- and β-positions of alkenes **1** and **2**, the formation of chalcones **3** and dihydrochalcones **4** was observed. Phase trajectories constructed from the sums of all products **1—4** obtained from each competing anhydride using phosphine-free catalytic system and a system with triphenylphosphine additive, were identical (Fig. 1). On phosphine addition, the phase trajectories remained identical not only in the presence of LiCl and NaBr (see Fig. 1), but also in the presence of LiBr and NBu_4Br. It is assumed that formation of all products **1—4** requires activation of an anhydride at the oxidative addition step (see Scheme 1, **A**). In this case, coincidence of phase trajectories constructed from the sums of the products obtained with and without phosphine, suggests the similar nature of formed catalytically active compounds reacting with the anhydride. In terms of the generally accepted concepts of the reaction mechanism (see Scheme 1, **A** and Scheme 3, *a*) these should be Pd(0) complexes having no phosphine ligands in their coordination sphere.

On going from phosphine-free to the phosphine-containing catalytic systems, the value of catalytical activity decreased significantly. The initial consumption rate of a reagent (styrene) common for competing aromatic anhydrides showed a 2—2.5-fold decrease. Nevertheless, on using these two types of catalytic systems, the value of differential selectivity remained the same thus unequivo-

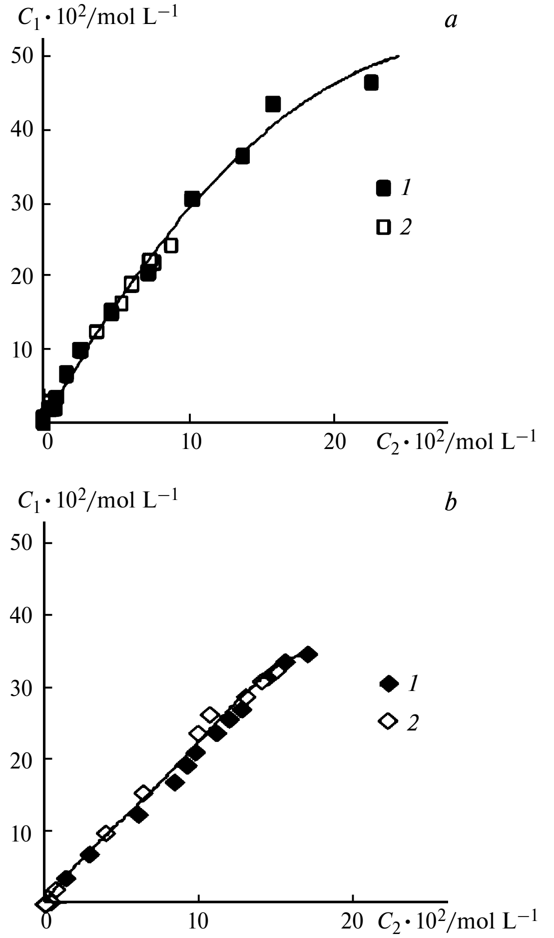


Fig. 1. Phase trajectories of competing arylation of styrene with benzoic and 4-methoxybenzoic anhydrides using catalytic systems: $PdCl_2$ + LiCl (*1*) and $PdCl_2$ + LiCl+PPh_3 (*2*) (*a*); $PdCl_2$ + NaBr (*1*) and $PdCl_2$ + NaBr + PPh_3 (*2*) (*b*); $C_1 = C_{(\mathbf{1a+2a+3a+4a})}$, $C_2 = C_{(\mathbf{1b+2b+3b+4b})}$.

cally suggesting the similar nature of the catalytically active species. This result demonstrates that studies of the differential selectivity patterns can provide more reliable conclusions than evaluation of the catalytical activity. In fact, the activity value depends not only on the type of an active catalyst but also on variations in its amount that can occur even when the nature of the catalytically active species remains unchanged.

Earlier, we have demonstrated that Pd(0) complexes, active at the oxidative addition step in arylation of alkenes with aromatic anhydrides using phosphine-free catalytic systems, have an anionic nature.[16] In this case, the value of differential selectivity is governed by the nature of both an anion and a cation of the salt applied as an additive to the catalytic system. As evident from our data (Fig. 2), the value of differential selectivity on competing aromatic anhydrides in the presence of phosphine-containing catalytic system also depends on the nature of both an anion and a cation of the salt additive. An obvious example provide phase trajectories shown in Fig. 2 constructed using LiCl and LiBr or NBu_4Br and NaBr respectively. Effect of the nature of the salt anion on selectivity is explained by its incorporation in the coordination sphere of Pd(0) catalytically active species. A possibility of formation of Pd(0) anionic complexes under cross-coupling conditions was demonstrated using both *ex situ* and *in situ* studies under stoichiometric[6,17] and catalytic[18,19] conditions. When an alkaline cation is unable to form a coordinate bond with the palladium atom its effect on the selectivity is most likely accounted for by the formation of close ion pairs with catalytically active anionic palladium species.[16]

For the Heck reaction with aromatic anhydrides, another type of competing experiments is also possible wherein two alkenes, rather than an anhydride, will compete for the common catalyst (see Scheme 2, *b*). In this case differential selectivity patterns based on the sums of the yields of the arylation products **1** and **2** makes it possible to examine the nature of the catalytic species involved in the activation of alkenes that results in the formation of these products (see Scheme 3, *b*). According to the accepted concepts of the mechanism of the Heck reaction catalytic cycle, activation of alkene takes place during the step of its coordination to ArPdX complexes (where X is halide or benzoate anion) (see Scheme 1, **B**).[6] Thus, analysis of phase trajectories of the reactions yielding the traditional arylation products **1** and **2** under competing of two alkenes, namely, styrene and *n*-butyl acrylate, can provide insight into the nature of active species of the ArPdX type (see Scheme 3, *b*).

As it follows from the data obtained in our group, differential selectivity for competing alkenes in the catalytic cycle of formation of the "Heck's" products **1** and **2**, as in the case with competing pair of aromatic anhydrides, does not depend on the presence of phosphine ligands in the catalytic system (Fig. 3). This suggests the involvement of the active σ-aryl complexes of Pd(2+) without phosphine ligands in the step of the catalytic cycle wherein competition of alkenes takes place. However, in this case the dependence of differential selectivity on the nature of a cation and an anion of the salt presenting in the catalytic system is observed. This observation is in agreement with

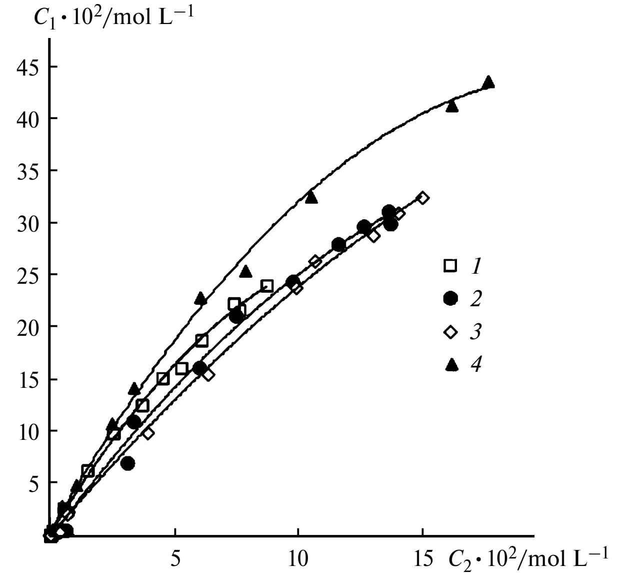


Fig. 2. Phase trajectories of competing arylation of styrene with benzoic and 4-methoxybenzoic anhydrides using catalytic systems: $PdCl_2$ + LiCl + PPh_3 (*1*), $PdCl_2$ + LiBr + PPh_3 (*2*), $PdCl_2$ + NaBr + PPh_3 (*3*), $PdCl_2$ + NBu_4Br + PPh_3 (*4*); $C_1 = C_{(1a+2a+3a+4a)}$, $C_2 = C_{(1b+2b+3b+4b)}$.

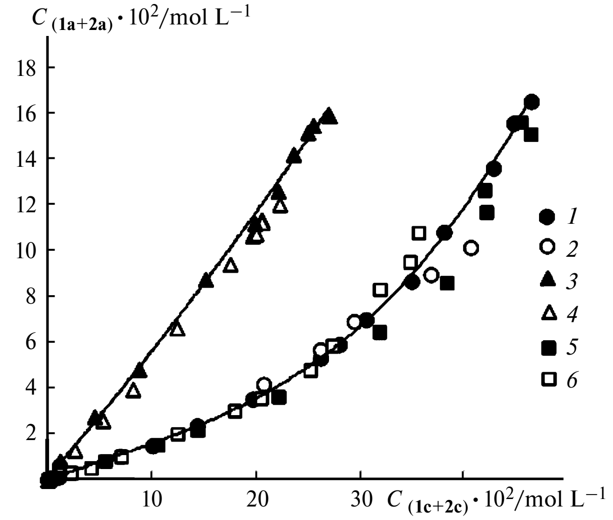


Fig. 3. Phase trajectories of competing arylation of styrene and *n*-butyl acrylate with benzoic anhydride using catalytic systems: $PdCl_2$ + LiCl (*1*), $PdCl_2$ + LiCl + PPh_3 (*2*), $PdCl_2$+NaCl (*3*), $PdCl_2$ + NaCl + PPh_3 (*4*), $PdCl_2$ + NaBr (*5*), $PdCl_2$ + NaBr + + Ph_3 (*6*).

the participation of anionic Pd(2+) species in the catalysis similar to the competition of a pair of aromatic anhydrides (analogously to a phosphine-free reaction modification).[16]

The patterns of differential selectivity outlined above present the evidence that phosphine ligands introduced into a catalytic system are not incorporated into catalytically active species on arylation of alkenes with aromatic anhydrides both at the step of activation of an anhydride molecule (see Scheme 1, **A**), and at the step of alkene activation (see Scheme 1, **B**).

Additional information concerning a possible transfer of phosphine ligands into intermediates of the Heck reaction catalytic cycle can be derived from patterns of differential selectivity of formation of products **1** and **2** from one of the competing substrates. According to the generally accepted mechanism, the step determining differential regioselectivity for such products includes an alkene insertion into the palladium—carbon bond (the step following the coordination of the alkene to ArPdX complexes) (see Scheme 1, **C**). It was established that the differential selectivity value of formation of regioisomer products **1a** and **2a** changes when passing from phosphine-free to phosphine containing catalytic systems. This change is observed when using both a pair of competing aromatic anhydrides and a pair of competing alkenes (see Scheme 2). Thus, for example, with LiCl or LiBr as additives to the catalytic system, phase trajectories in coordinates of concentrations of stilbene **1a** (β-regioisomeric product) and 1,1-diphenylethylene **2a** (α-regioisomeric product) were different (Fig. 4). Such result unequivocally suggests changing the nature of catalytically active compounds involved in the step of an alkene insertion (see Scheme 1, **C**). The change in the nature of catalytically active compounds can result from incorporation of a phosphine ligand into the active palladium species, which govern the differential selectivity of formation of regioisomer "Heck´s" products (see Scheme 3, *c*). Regioselectivity in the presence of a phosphine depends not only on the nature of an anion of the salt presenting in the system but also on its cation nature. For example, phase trajectories for phosphine systems with LiCl and NaCl additives differ significantly (Fig. 5). Similar to the previously published data,[16] this result can be explained by the presence of anionic complexes in the system forming close ionic pairs with a salt anion which is unable to adopt coordination to the palladium atom. However, taking into account the inherent ability of the palladium atom to form tetrahedrally coordinated saturated complexes, one can suggest that σ-aryl complex containing, apart from a halogen anion and an alkene, at least one phosphine ligand, should be electroneutral (see Scheme 3, *c*). Dependence of regioselectivity on concentration of phosphine and cation of the salt additive testifies that phosphines are incorporated into an active complex (see Fig. 4). This dependence also suggests the anionic nature of the active complex. All these data strengthen the suggestion that in a real catalytical system phosphine *ate*-complexes of Pd^{II} are formed (see Scheme 3, *c*) similar to those recently detected under model non-catalytic conditions.[17]

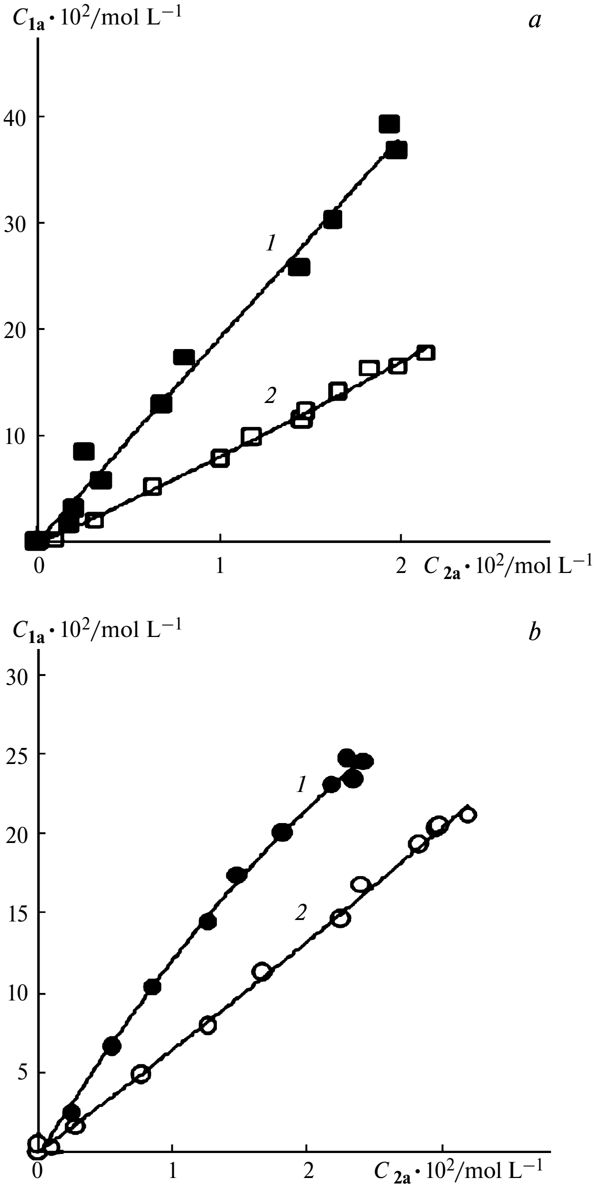


Fig. 4. Phase trajectories of accumulation of the "Heck´s" regioisomeric products **1a** and **2a** of arylation of styrene with benzoic anhydride (under conditions of competing arylation of styrene with benzoic and 4-methoxybenzoic anhydrides) using catalytic systems: $PdCl_2$ + LiCl (*1*) and $PdCl_2$ + LiCl+PPh_3 (*2*) (*a*), $PdCl_2$ + LiBr (*1*) and $PdCl_2$ + LiBr + PPh_3 (*2*) (*b*).

The data obtained in the present study clearly demonstrate the advantages offered by measurements of the differential selectivity. This method can be used primarily to solve the problem of participation of phosphine-containing complexes in the main catalytic cycle of the Heck reaction. The results thus obtained also enable one to

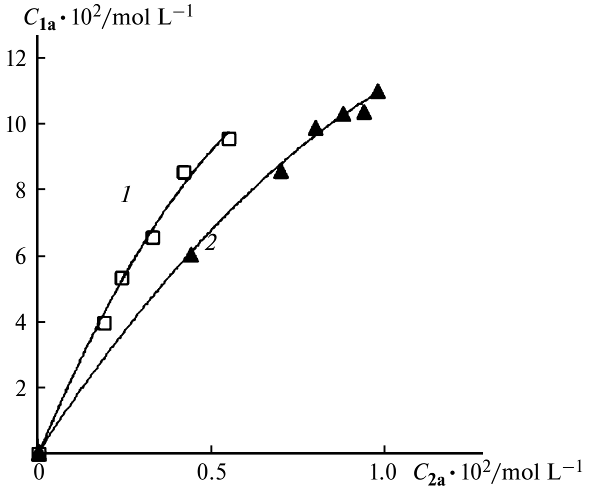


Fig. 5. Phase trajectories of accumulation of the "Heck's" regioisomeric products **1a** and **2a** of arylation of styrene with benzoic anhydride (under conditions of competing arylation of styrene and *n*-butyl acrylate with benzoic anhydride) using catalytic systems: $PdCl_2$ + LiCl + PPh_3 (*1*), $PdCl_2$ + NaCl + + PPh_3 (*2*).

elucidate the possibility for such ligands to be incorporated into active intermediates involved in certain steps of the cycle, namely, activation of anhydrides and alkenes, as well as the regioselectivity-determining step. The results obtained therefrom do not depend on a hypothetical mechanism of these steps. Various experiments performed under conditions, in which two aromatic anhydrides or two alkenes compete were directed on evaluation of differential selectivity. Investigations of alkene arylation were aimed at evaluation of differential regioselectivity of formation of traditional α- and β-products. The obtained data allows one to distinguish between situations, in which a phosphine ligand forms a part of catalytically active palladium π-complexes determining regioselectivity of the alkene insertion (see Scheme 1, **C** and Scheme 3, *c*) and those, in which catalytically active Pd(0) and Pd(2+) complexes involved in the steps of activation of an aromatic anhydride and an alkene respectively (see Scheme 1, **A** and **B**, and Scheme 3, *a* and *b*), have a phosphine-free nature.

A conclusion of the absence of phosphine ligands in the active palladium complexes participating in the oxidative anhydride addition and coordination of alkene appears to be in conflict with the known ability of tertiary phosphines to form stable complexes with palladium including the cross-coupling conditions.[6,11] Actually, we were able to detect in the UV spectra of the reaction mixtures, *e.g.*, in the presence of chlorine-containing salt additives, a considerable amount of phosphine complex $PdCl_2(PPh_3)_2$ (up to 70% of the total amount of palladium added to the system). However, according to the concepts of the reaction mechanism this complex is catalytically inactive and is outside the main catalytic cycle. This concept fits well with a decrease of the catalytic reaction rate observed in all runs with a phosphine added. Thus, phosphine ligands play dual role in arylation of alkenes with aromatic anhydrides. First, they are incorporated into Pd(2+) complexes, active at the insertion step, that govern the regioselectivity of formation of traditional products of α- and β-arylation of an alkene. Secondly, they are involved in the transformations of palladium outside the main catalytic cycle wherein the reaction products are formed. At the same time, contrary to the generally accepted concepts of the Heck reaction mechanism, catalytically active species participating in the steps of the substrate activation contain no phosphine ligands.

To summarize, differential selectivity patterns of the Heck reaction with aromatic anhydrides using phosphine-free and phosphine-containing catalytic systems were analyzed. A conclusion has been drawn that complexes of Pd(0) and Pd(2+) involved in the steps of the catalytic cycle wherein activation of an aromatic anhydride and alkene respectively takes place, have no phosphine ligands in their coordination sphere. Dependence of differential selectivity on the nature of a cation and an anion of the salt added to the catalytic system suggests that the anionic nature of active complexes is not changed in the presence of a phosphine similar to phosphine-free catalytic systems. At the same time features of differential selectivity of formation of traditional "Heck's" products indicate that the phosphine ligands are incorporated into catalytically active species and in this way determine selectivity of the regioisomeric products formation. Dependence of differential selectivity on a phosphine and a cation of a salt additive to the catalytic system makes it possible to assume the formation of anionic phosphine complexes representing probably pentacoordinated *ate*-complexes Pd(2+). Moreover, starting from the experimental data and taking into account the observed effects of the phosphine addition on the catalytic activity and UV spectroscopy data, one can make a conclusion that phosphine ligands are also involved in the transformation of a catalysts outside the main catalytic cycle wherein the reaction products are formed.

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References

1. J. P. Corbet, G. Mignani, *Chem. Rev.*, 2006, **106**, 2651.
2. J. G. De Vries, in *Selective Nanocatalysts and Nanoscience*, Eds A. Zecchina, S. Bordiga, E. Groppo, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2011, p. 73.
3. D. B. Eremin, V. P. Ananikov, *Coord. Chem. Rev.,* 2017, **346**, 2.
4. A. Biffis, P. Centomo, A. Del Zotto, M. Zecca, *Chem. Rev.*, 2018, **118**, 2249.

5. I. P. Beletskaya, A. V. Cheprakov, in *The Mizoroki—Heck reaction*, Ed. M. Oestreich, John Wiley and Sons Ltd., Munster, 2009, p. 51.
6. A. Jutand, in *The Mizoroki—Heck reaction*, Ed. M. Oestreich, John Wiley and Sons Ltd., Munster, 2009, p. 1.
7. C. Amatore, E. Came, A. Jutand, M. A. M´Barki, G. Meyer, *Organometallics*, 1995, **14**, 5605.
8. C. Amatore, B. Godin, A. Jutand, F. Lemaitre, *Chem. Eur. J.*, 2007, **13**, 2002.
9. B. P. Carrow, J. F. Hartwig, *J. Am. Chem. Soc.*, 2010, **132**, 79.
10. A. Jutand, S. Negri, J. G. de Vries, *Eur. J. Inorg. Chem.* 2002, **7**, 1711.
11. A. F. Shmidt, V. V. Smirnov, *Kinet. Catal.*, 2002, **43**, 195.
12. A. F. Schmidt, A. A. Kurokhtina, *Kinet. Catal.*, 2012, **53**, 714.
13. A. F. Schmidt, A. A. Kurokhtina, E. V. Larina, *Mendeleev Commun.*, 2017, **27**, 213.
14. A. F. Schmidt, A. A. Kurokhtina, E. V. Larina, *Kinet. Catal.*, 2012, **53**, 84.
15. A. F. Schmidt, A. A. Kurokhtina, E. V. Larina, *Cat. Sci. Technol.*, 2014**, 4**, 3439.
16. A. F. Schmidt, A. A. Kurokhtina, E. V. Larina, E. V. Yarosh, N. A. Lagoda, *Organometallics*, 2017, **36**, 3382.
17. M. Kolter, K. Boeck, K. Karaghiosoff, K. Koszinowski, *Angew. Chem.*, *Int. Ed.,* 2017, **56**, 13244.
18. F. Schroeter, J. Soellner, T. Strassner, *ACS Catal.*, 2017, **7**, 3004.
19. F. Schroeter, T. Strassner, *Inorg. Chem.,* 2018, **57**, 5159.

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