ISSN 0012-5008, Doklady Chemistry, 2010, Vol. 434, Part 1, pp. 226–232. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © N.V. Zvyagintsev, O.L. Eliseev, L.T. Kondrat'ev, A.L. Lapidus, 2010, published in Doklady Akademii Nauk, 2010, Vol. 434, No. 2, pp. 189–195.

Effect of the Ligand Nature on the Regioselectivity of the Styrene Carbonylation in the Presence of Palladium(II) Complexes

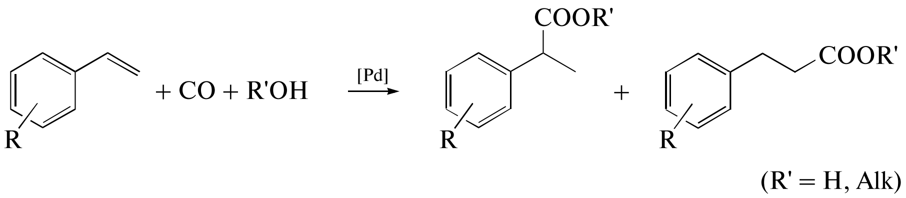
N. V. Zvyagintsev[b], O. L. Eliseev[a], L. T. Kondrat'ev[b],
and Corresponding Member of the RAS A. L. Lapidus[a]

Received March 30, 2010

DOI: 10.1134/S0012500810090053

This study dealt with the influence of halide ligands on the regioselectivity of the styrene carbonylation reaction in ionic liquids without phosphine ligands. The stage of migration insertion of styrene into the Pd–H bond in the hydride π complex [HPdX(styrene)L] (**II**; X = Cl, Br) was modeled. The energies of the most important reaction states were considered, and the effect of the acidity of hydride palladium π complexes with styrene on the yield of complexes was examined.

Studying the mechanism of the styrene carbonylation reaction



is of considerable interest for the development of theory of metal complex catalysis, as well as in the context of the practical use of this reaction in synthesis of pharmaceutical preparations.

The reaction yields 1- and 2-arylpropionic acids, and the regioselectivity of this reaction depends on temperature, the medium, pressure, and the presence of a certain acidic promoter in the system [1–8].

The fact that an acidic promoter should be present in the system for the reaction to occur [9–11] is evidence in favor of the hydride mechanism of carbonylation, which is consistent with the literature data [5]. This mechanism implies the formation of hydride palladium π complexes with styrene. The influence of pressure on the regioselectivity of the reaction indicates that catalytically active complexes are hydride palladium π complexes with styrene also liganded by the CO molecule and halide anion. The regioselectivity of the entire reaction is determined at the stage of migration insertion of styrene into the Pd–H bond in the π complex to produce branched and linear Alk–Pd complexes.

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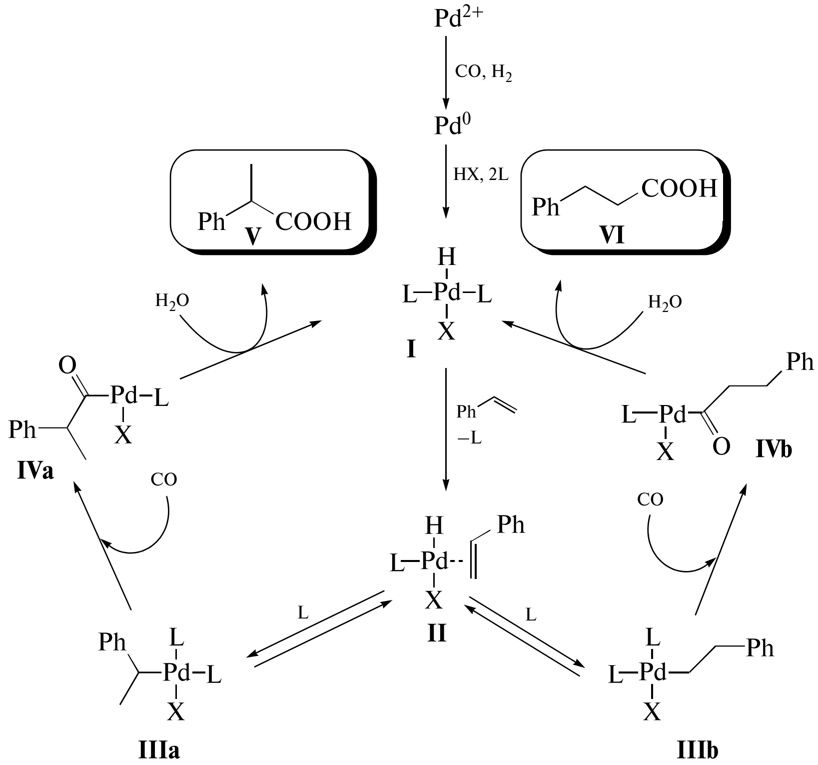
[a] *Zelinsky Institute of Organic Chemistry,
Russian Academy of Sciences, Leninskii pr. 47, Moscow, 119991 Russia*

[b] *Russian State University of Tourism and Service,
ul. Glavnaya 99, Cherkizovo, Pushkino region,
Moscow oblast, 141221 Russia*



(X = Cl, Br; L = PPh_3, CO)

Scheme 1.

As shown in Scheme 1, the addition of the CO molecule to complexes **IIIa** and **IIIb** leads to acyl complexes **IVa** and **IVb**, which are hydrolyzed to give corresponding phenylpropionic acids with the closure of the catalytic cycle on the initial Pd–H complex **I**.

The available experimental data demonstrate that the regioselectivity of the reaction is considerably dependent on the halogen incorporated in the nascent palladium complex. We theoretically studied the transformations of hydride π complex **II** to Alk–Pd complexes **IIIa** and **IIIb** (X = Cl, Br; L = CO) with the aim of elucidating the role of halide ligands in the course of the stage of migration insertion of styrene into the Pd–H bond. In this paper, we report the

Table 1. Selected geometrical parameters of complexes **II**, $\mathbf{S_1}$, and $\mathbf{S_2}$ (X = Cl, Br) (bond lengths are in picometers, bond angles are in degrees)

Parameter	X = Cl			X = Br		
	II	S_1	S_2	**II**	S_1	S_2
Pd–C(α)	230.2	215.0	205.5	230.7	215.4	205.8
Pd–C(β)	241.6	239.2	240.6	240.7	238.2	240.4
C(α)–C(β)	137.6	141.4	148.8	137.6	141.4	149.0
Pd–H	155.3	160.3	187.6	155.3	159.8	188.3
Pd–X	243.8	240.1	236.1	255.2	251.0	247.7
Pd–CO	192.1	215.0	201.6	191.9	195.5	201.0
C–O	113.9	114.0	114.0	114.0	114.0	114.0
C(β)–C	146.8	141.4	148.8	108.7	148.8	151.2
PdC(α)C(β)	77.6	81.5	83.9	77.1	80.9	836.9
CPdC(O)	162.9	175.8	174.0	161.7	174.9	172.7
OCPd	179.0	177.2	175.0	179.4	178.4	176.5
HPdX	178.9	169.9	158.2	178.5	169.7	156.2
$XPdC^1C^2$	–68.6	–7.6	–3.7	–66.7	–10.3	–6.3
HPdC(α)C(β)	112.5	172.1	176.7	114.7	169.3	172.1

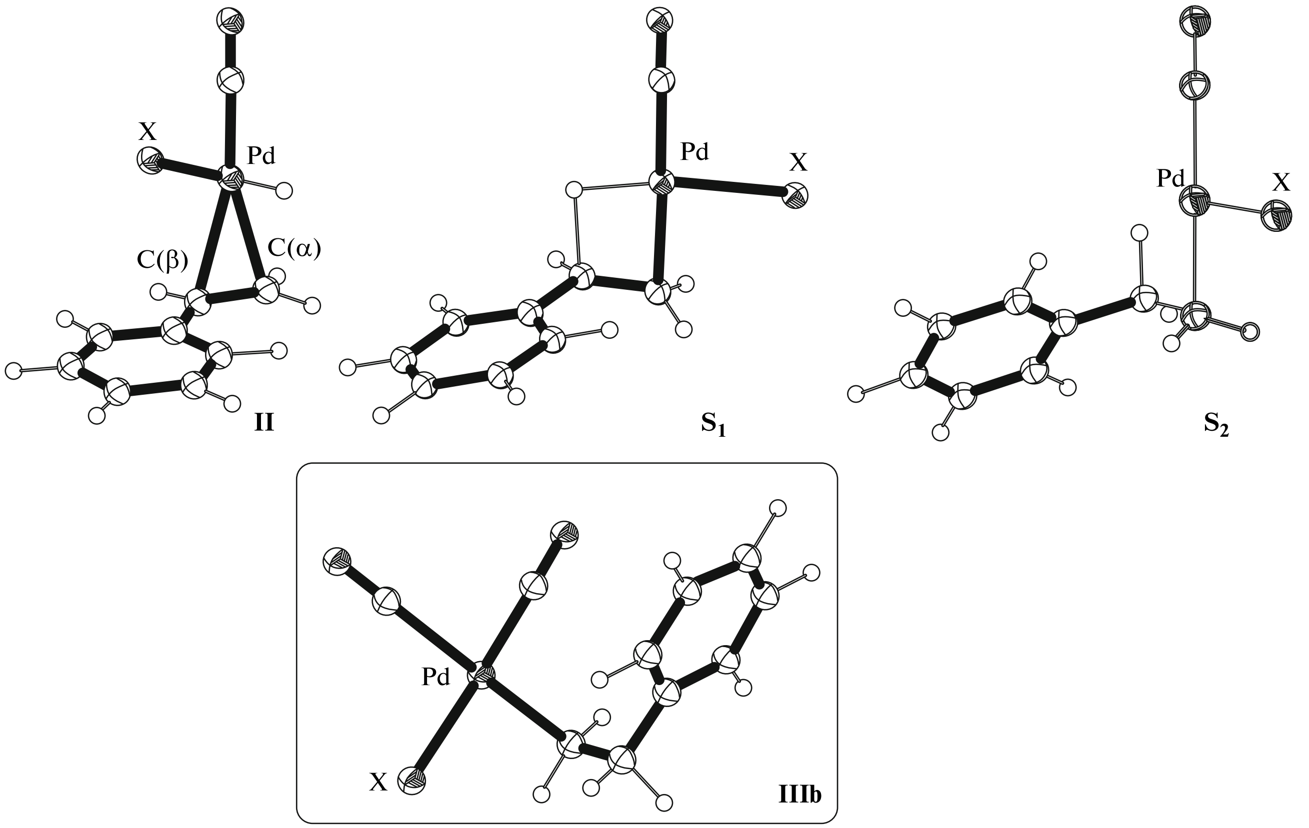


Fig. 1. Geometric structures of complexes **II**, **IIIb**, S_1, and S_2 (X = Cl, Br; L = CO).

results of studying the structures of complexes **II**, **IIIa**, and **IIIb** and intermediate complexes that form at this stage of the reaction, as well as the calculated energies of all transformations under consideration.

Calculations were performed by the B3LYP method with the combined LANL2TZ + TZV + 6-31Gdp basis set in which the LANL2TZ ECP basis set (with pseudopotential) was used for the palladium atom, the DZV basis set was used for the halogen atoms, and the 6-31G(d, p) basis set was used for the remaining atoms. All calculations were performed with the PC GAMESS/Firefly 7.1 program package [13, 14]. The geometric structures of the complexes were studied with full geometry optimization, and Hessians were calculated for all the structures.

Figure 1 shows the spatial structures of hydride π complex **II**, Alk–Pd complex **IIIb** (X = Cl, Br), and intermediate complexes $\mathbf{S_1}$ and $\mathbf{S_2}$, which form at this stage of the reaction.

The vinyl carbon atom of styrene not bonded to the phenyl ring is denoted as C(α), and the carbon atom bonded to the phenyl ring is denoted as C(β) (Fig. 1). We found that hydride π complex **II**, through the rotation of the Pd–H and Pd–X bonds in the course of reaction, transforms to intermediate complex $\mathbf{S_1}$ (which is a transition state and has one negative eigenvalue of the Hessian). Then, the Pd–H bond in complex $\mathbf{S_1}$ is broken, and the hydrogen atom forms a chemical bond to the C(β) atom, which gives complex $\mathbf{S_2}$. In the next step, complex $\mathbf{S_2}$ directly interacts with the CO molecule to give complex **IIIb**. Selected geometric parameters (bond lengths, interatomic distances, bond and torsion angles) of complexes **II**, $\mathbf{S_1}$, and $\mathbf{S_2}$ (X = Cl, Br), reflecting the change in their geometries in the course of reaction, are presented in Table 1. The data were obtained by the B3LYP/LANL2TZ + TZV + 6-31Gdp method.

According to Table 1, for any type of halogen in the complexes, the geometric parameters change only slightly. The Pd–X bond length mainly changes.

The formation of branched complex **IIIa** from **II** also proceeds in several intermediate steps. The structures of complexes **IIIa** and intermediate complexes $\mathbf{S_3}$, $\mathbf{S_4}$, and $\mathbf{S_5}$ (X = Cl, Br) are shown in Fig. 2.

In the course of reaction in hydride π complex **II**, the hydrogen atom is shifted to the α-carbon atom and the X ligand is rotated about the Pd–CO bond, which results in complex $\mathbf{S_3}$ (with one negative eigenvalue in the Hessian). Further transformations of transition state $\mathbf{S_3}$ leads to complex $\mathbf{S_4}$, which is accompanied by an increase in the Pd–H bond length. The arrangement of the substituents about the C(α) and C(β) atoms becomes typical of the sp^3 hybrid state of the

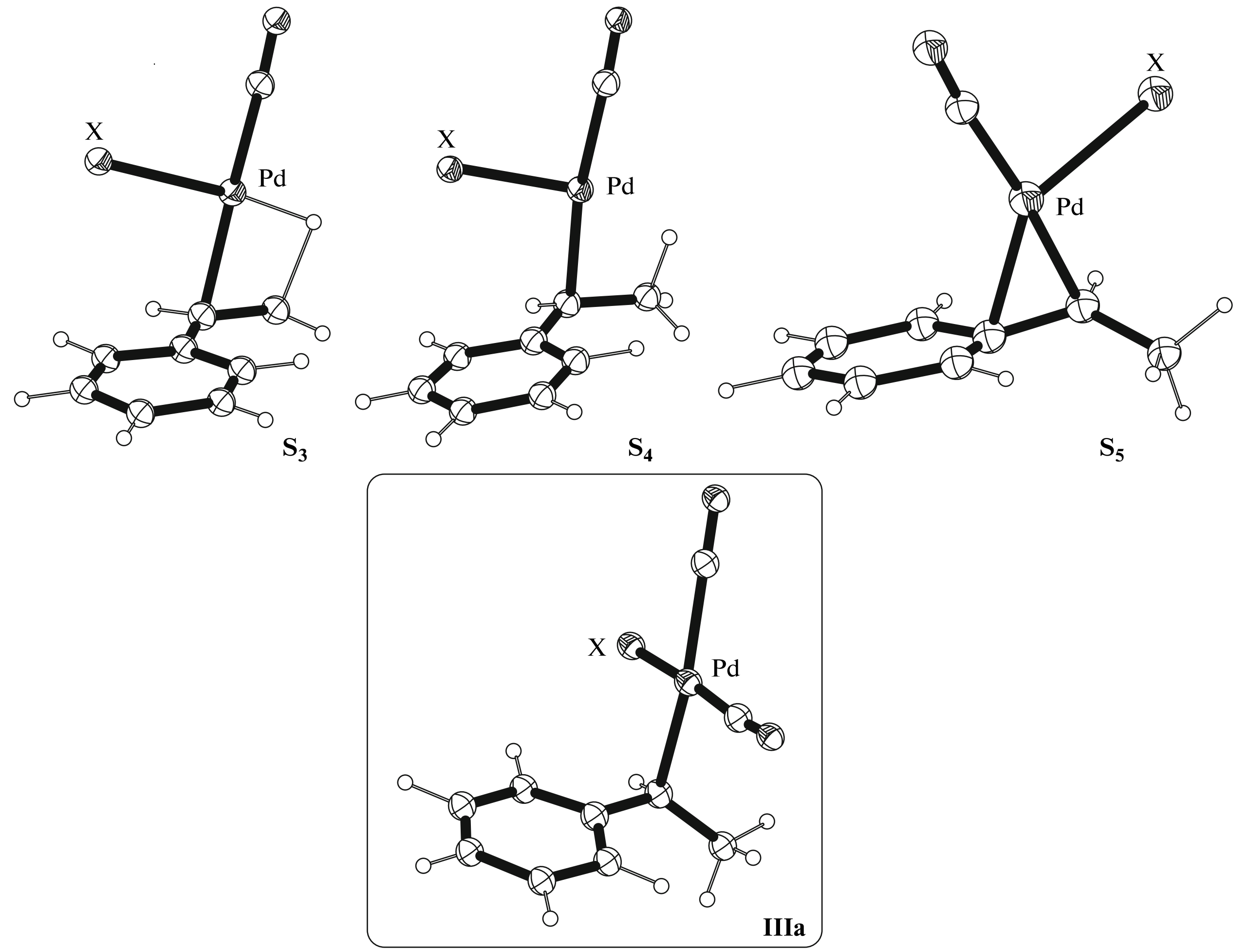


Fig. 2. Structure of complex **IIIa** and intermediate complexes $\mathbf{S_3}$, $\mathbf{S_4}$, and $\mathbf{S_5}$ (X = Cl, Br; L = CO).

carbon atom. Further study of the reaction path showed that complex $\mathbf{S_4}$ either interacts with the CO molecule to form complex **IIIa** or forms η^3-benzyl complex $\mathbf{S_5}$. The existence of η^3-benzyl complex $\mathbf{S_5}$ was experimentally proved, and its influence on the regioselectivity of the styrene carbonylation has been discussed in the literature (see, e.g., [6]). Table 2 compares the geometric parameters of complexes **II**, $\mathbf{S_3}$, and $\mathbf{S_4}$ (X = Cl, Br) most significant for studying the reaction path. The data were obtained by the B3LYP/LANL2TZ + TZV + 6-31Gdp method.

To study the influence of the halide ligands on the regioselectivity of the reaction, we compared the energies of all transformations. Table 3 summarizes the total energies E_{tot} of complexes **II**, **IIIa**, **IIIb**, $\mathbf{S_1}$, $\mathbf{S_2}$, $\mathbf{S_3}$(X), $\mathbf{S_4}$(X), and $\mathbf{S_5}$(X) (X = Cl, Br) calculated by the B3LYP/LANL2TZ + TZV + 6-31Gdp method.

From the results obtained, we calculated the energy effects (ΔE) of the transformations that occur at this stage. The ΔE values most significant for studying the regioselectivity of the reaction are listed in Table 4.

As follows from Table 4, the type of halogen has a considerable effect on the energies of formation of complexes $\mathbf{S_2}$ and $\mathbf{S_4}$, which directly interact with the CO molecule. When the catalytic complex is liganded by the chloride anion, the formation of complex $\mathbf{S_2}$ requires an energy input of ~3.16 kJ/mol, whereas the presence of the bromide anion in the reactive complex leads to the release of ~–1.72 kJ/mol. At the same time, the formation of complex $\mathbf{S_4}$ when the catalyst contains the chloride anion is more favorable than in the presence of the bromide anion. Thus, the chloride anion favors the formation of complex $\mathbf{S_4}$ to a greater extent than the bromide anion. This is supported by the experimental data on the yield of hydratropic acid (**V**) and hydrocinnamic acid (**VI**) formed in the styrene carbonylation reaction in ionic liquids, such as tetrabutylammonium chloride (TBAC) and tetrabutylammonium bromide (TBAB).

Table 5 summarizes the data on the styrene conversion and the overall yield and the ratio between the branched (**V**) and linear (**VI**) acids (b : l) in the final product obtained with the use of the $Pd(OAc)_2$ and

Table 2. Selected geometrical parameters of the transition states of complexes **II**, $\mathbf{S_3}$, and $\mathbf{S_4}$ (X = Cl, Br) (bond lengths are in picometers, bond angles are in degrees)

Parameter	X = Cl			X = Br		
	II	S_3	S_4	**II**	S_3	S_4
Pd–C(α)	230.2	224.8	243.5	230.7	225.6	243.6
Pd–C(β)	241.6	231.9	210.6	240.7	231.7	210.8
C(α)–C(β)	137.6	140.4	149.4	137.6	140.4	149.6
Pd–H	155.3	158.4	197.6	155.3	157.8	198.2
Pd–X	243.8	242.4	239.1	255.2	253.4	250.6
Pd–C(O)	192.1	194.7	200.1	191.9	194.5	199.5
C–O	113.9	114.0	114.0	114.0	114.0	114.0
C(β)–C	146.8	147.3	146.8	108.7	147.3	146.7
PdC(α)C(β)	77.6	69.3	59.2	77.1	69.8	59.2
C(α)PdC(O)	162.9	177.4	174.0	161.7	177.4	172.8
OCPd	179.0	177.3	174.1	179.4	178.3	175.2
HPdX	178.9	171.6	152.5	178.5	172.9	151.6
$XPdC^1C^2$	–68.6	–20.2	–25.5	–66.7	–18.7	–25.4
HPdC(α)C(β)	112.5	163.0	166.4	114.7	164.3	165.9

$Pd(PPh_3)_2$ salts in ionic liquids. *p*-Toluenesulfonic acid and hydrochloric acid were used as the acid promoter. The reaction conditions were as follows: 4 mmol of styrene, 20 mmol of water, 0.02 mmol of [Pd], 0.8 mmol of *p*-toluenesulfonic acid, 2 g of TBAC or TBAB, 5 mL of heptane [13].

Information on the influence of the ligands on the acidity of the hydride palladium π complexes with styrene is of special interest for studying the regioselectivity of the styrene carbonylation reaction. For comparison of the acidities of the complexes, we considered also the hydride palladium π complexes with styrene, triphenylphosphine, and halide anions $[HPdX(styrene)PPh_3]$ (X = Cl, Br) (Fig. 3).

Table 6 lists the partial charges calculated by the B3LYP/DZVP + TZV + 6-31Gdp method (for the palladium atom, the DZVP basis set was used; for the carbon and hydrogen atoms of the triphenylphosphine molecule, the 3-21G basis set was used).

As follows from Table 6, the substitution of the bromide anion for the chloride anion has almost no effect on the partial atom on the carbon, palladium, and hydrogen atoms; therefore, the type of halogen slightly affects the acidity of the hydride π complex. In the case

Table 3. Total energies E_{tot} (au) of complexes **II**, **IIIa**, **IIIb**, $\mathbf{S_1}$, $\mathbf{S_2}$, $\mathbf{S_3}$, $\mathbf{S_4}$, and $\mathbf{S_5}$ (X = Cl, Br)

Parameter	X = Cl	X = Br
II	–1010.58155	–3121.987988
IIIa	–1123.934372	–3235.341757
IIIb	–1123.930109	–3235.3384
$\mathbf{S_1}$	–1010.573002	–3121.980589
$\mathbf{S_2}$	–1010.580346	–3121.988641
$\mathbf{S_3}$	–1010.576171	–3121.982466
$\mathbf{S_4}$	–1010.594355	–3121.997039
$\mathbf{S_5}$	–1010.60458	–3122.01238

Table 4. Influence of the halogen on the energy effects (kJ/mol) of intermediate transformations of the stage of migration insertion of styrene into the Pd–H bond

ΔE	X = Cl	X = Br
$E_{tot}(\mathbf{S_1}) - E_{tot}(\mathbf{II})$	22.4446	19.4261
$E_{tot}(\mathbf{S_2}) - E_{tot}(\mathbf{II})$	3.16294	–1.715239
$E_{tot}(\mathbf{S_1}) - E_{tot}(\mathbf{S_2})$	19.28167	21.14131
$E_{tot}(\mathbf{S_3}) - E_{tot}(\mathbf{II})$	14.1239	14.4977
$E_{tot}(\mathbf{S_4}) - E_{tot}(\mathbf{II})$	–33.61952	–23.76497
$E_{tot}(\mathbf{S_3}) - E_{tot}(\mathbf{S_4})$	47.7434	38.26272
$E_{tot}(\mathbf{S_2}) - E_{tot}(\mathbf{S_4})$	36.7825	22.0497
$E_{tot}(\mathbf{IIIa}) - E_{tot}(\mathbf{IIIb})$	–11.1917	-8.81275

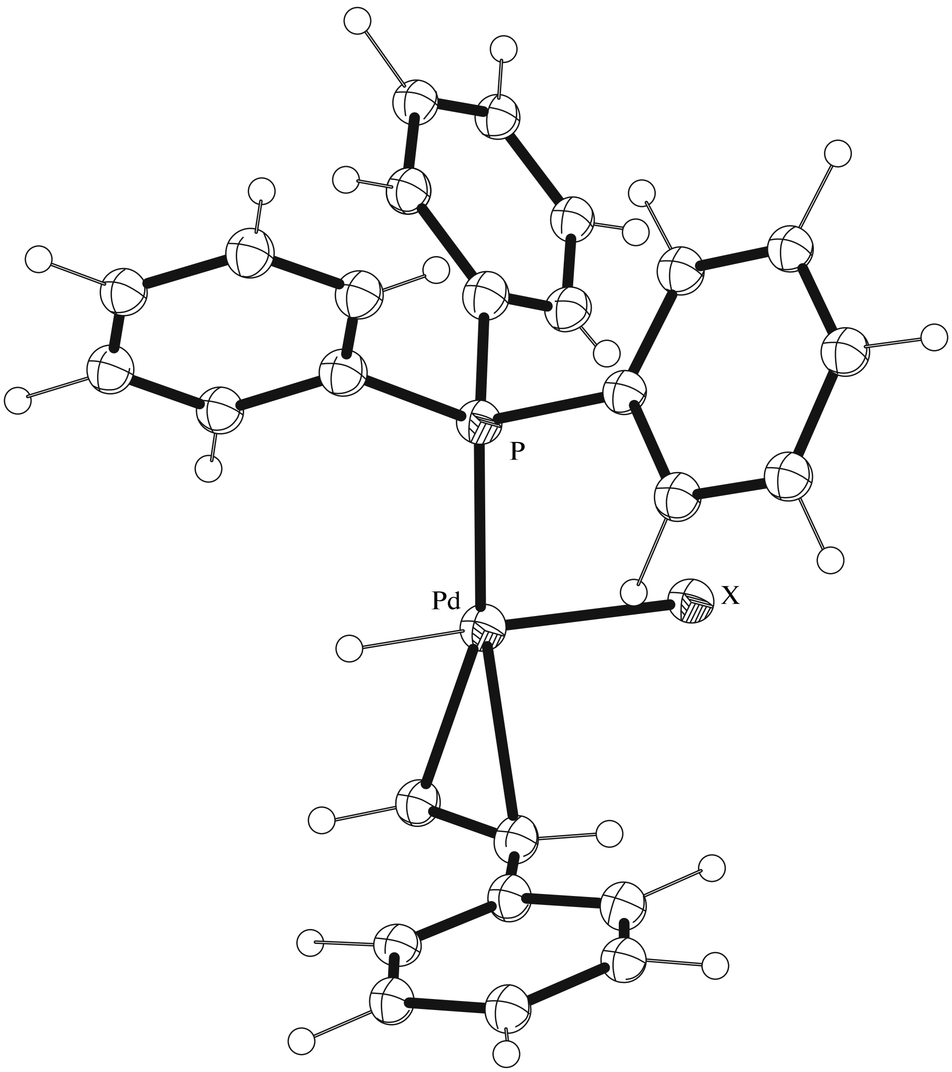


Fig. 3. Structure of the hydride π complex [HPdX(styrene)PPh_3] (X = Cl, Br; L = PPh_3).

of the complexes with triphenylphosphine [HPdX(styrene)PPh_3] (X = Cl, Br), the charge on the hydrogen atoms changes considerably. The data on the partial charges show that the complexes with the CO molecule have a higher acidity than the complexes with triphenylphosphine.

Thus, we comprehensively studied the mechanism of the migration insertion of styrene into the Pd–H bond in complex **II.** The geometries of complexes **II**, **IIIa**, **IIIb**, and all intermediate complexes were considered. The calculation results showed that halogens have a significant effect on the energy of the migration insertion of styrene into the Pd–H bond in complex **II**. The chloride anion promotes the transformation of hydride π complex **II** into complex $\mathbf{S_4}$. Inasmuch as this stage determines the regioselectivity of the entire reaction, the presence of the chloride anion in the catalytic complex is favorable for the formation of a branched acid, which is confirmed by experimental data. We demonstrated that, in the hydride complexes with halide anions and CO, the nature of the halogen (chlorine or bromine) has no effect on the acidity of

Table 5. Experimental data on the styrene conversion and the yield and ration of hydratropic and hydrocinnamic acids (b : l)

Catalyst	IL	Conversion, %	Acid yield, %	b : l
$Pd(OAc)_2$	TBAB*	97.1	87.2	0.8
	TBAB**	93.5	83.0	1.0
	TBAC*	22.2	16.0	6.3
$Pd(PPh_3)_2$	TBAB*	33.1	29.2	1.0
	TBAB**	76.1	69.2	1.4
	TBAC*	100	89.5	7.2

Note: IL stands for ionic liquids. Promoters are *—p-$CH_3C_6H_4SO_3H$ and **—HCl.

Table 6. Mulliken charges on the atoms of the hydride palladium π complexes with styrene and different ligands

π Complex	Atomic charge, au				
	H	Pd	X	C(α)	C(β)
[HPdClCO(styrene)]	0.008470	0.033833	–0.406539	–0.279935	–0.131644
	0.009072	0.005932	–0.322479	–0.274910	–0.129654
[HPdCl(styrene)PPh_3]	–0.01233	0.057556	–0.478243	–0.278868	–0.168963
	–0.01714	0.005751	–0.419937	–0.273290	–0.170327

the entire complex. The substitution of the triphenylphosphine molecule for the CO molecule considerably acidifies the hydride complex.

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