ERRATA

**Erratum: “Regioselectivity of Styrene Carbonylation
in the Presence of Palladium(II) Complexes”
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Unfortunately the online version of the original paper is incomplete:
page 789, in part, and pages 790 and 791, altogether. The complete pages should appear as follows:

Fig. 2. Geometric structure of four-center transition states [TS₁] and [TS₂].

smaller than 100°. The lengths of terminal carbon atom bonds with the migrating hydrogen atom are slightly larger than the C–H bond length in alkanes.

A characteristic feature of “classic” electrophilic addition reactions is the formation of the palladium cation as the limiting stage. Table 2 contains the total energies E_{tot} of the complexes considered (in atomic units) and the differences of energies (in kJ/mol). Table 3 contains the energies of formation of [Pd⁺]₁ and [Pd⁺]₂ complexes from I (with various ligands) and the differences of the energies of formation $E([\text{Pd}^+]_1 - E[\text{Pd}^+]_2)$ and $E(\text{IIa}) - E(\text{IIb})$ in kJ/mol.

It follows from the presented data that the migration insertion of styrene at the Pd–H bond with the formation of [Pd⁺]₁ and [Pd⁺]₂ palladium cations is also the slowest stage. As follows from Table 3, palladium hydride π -complexes with styrene are much more stable than the [Pd⁺]₂ complexes considered irrespective of the type of ligands. In complexes with CO, we, however, observed a strong influence of the halogen atom on the stability of the [Pd⁺]₂ complex. Chlorine substantially decreases the stability of [Pd⁺]₂ compared with the bromide complex. These data explain the strong influence of the anion of the ionic liquid observed by the authors: the chloride anion increases the selectivity of styrene carbonylation with respect to acid **1** in the absence of PPh₃.

To summarize, we studied the stage of the migration insertion of styrene at the Pd–H bond and determined intermediate complexes of the formation of alkyl complexes IIa and IIb. The mechanism of this stage was treated as a variety of electrophilic addition,

Table 2. Total energies E_{tot} of complexes of I, IIa, IIb, [TS₁], [TS₂], [Pd⁺]₁, and [Pd⁺]₂ with various ligands and numbers of negative Hesse matrix eigenvalues λ

Complex	X = Cl	X = Br	λ
I	1010.5983008	3122.0050920	0
I*	1929.0385829	4040.4517548	0
IIa	1123.9505598	3235.3587996	0
IIa*	2042.3979151	4153.8088437	0
IIb	1123.9473676	3235.3566935	0
IIb*	2042.3951463	4153.8101118	0
[TS ₁]	1010.5929597	3121.9996543	1
[TS ₂]	1010.5901078	3121.9980748	1
[Pd ⁺] ₁	1010.6043528	3122.0120191	0
[Pd ⁺] ₁ *	1929.0434232	4040.4562044	0
[Pd ⁺] ₂	1010.5961679	3122.0047413	0
[Pd ⁺] ₂ *	1929.0352651	4040.4493034	0
[η^3 -Pd]	1010.6203621	3122.0284969	0

Note: Complexes with triphenylphosphine are labeled by asterisks.

Table 3. Energies of formation of [Pd⁺]₁ and [Pd⁺]₂ complexes from I with various ligands (E_1 and E_2), differences of the energies of formation $\Delta = E_1 - E_2$, and differences of the total energies of IIa and IIb (Δ')

L	$-E_1$	$-E_2$	$-\Delta$	$-\Delta'$
X = Cl				
CO	15.889	5.599	21.489	8.381
PPh ₃	12.708	−8.710	21.419	7.269
X = Br				
CO	18.187	−0.920	19.107	5.529
PPh ₃	11.682	−6.436	18.118	−3.329

Fig. 3. Geometric structure of complexes of (a) $[\text{Pd}^+]_1$ and (b) $[\text{Pd}^+]_2$ with the CO and PPh_3 ligands.

and the characteristic features of the reaction were stressed. We analyzed the influence of the nature of the ionic liquid anion participating in complex formation. Calculation results explain the experimental data on the influence of anions on the regioselectivity of styrene carbonylation.

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