Research Article

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Lewis acids as co-catalysts in Pd-based catalyzed systems of the octene-1 hydroethoxycarbonylation reaction

Abstract: In this work, in order to develop new, efficient, and environmentally friendly methods for the preparation of practically valuable esters of carboxylic acids, the hydroalkoxycarbonylation reaction of octene-1 with various alcohols in the presence of metal–complex catalysts based on palladium phosphine complexes has been studied. Three-component systems based on $PdCl_2(PPh_3)_2$ containing different ligands as stabilizers and Lewis acids as promoters were studied as catalysts. It is shown that the three-component system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ has the highest catalytic activity in the reactions studied. It was found that the reaction of hydroalkoxycarbonylation of octene-1 proceeds with the formation of a mixture of linear (ethyl ester of pelargonic acid) and branched (ethyl ester of 2-methylcaprylic acid) products. The influence of the ratio of initial reagents (different olefins and alcohols) and components of catalytic systems (different Pd complexes, ligands, and promoters) on the course of the process has been investigated, in which the conversion of octene-1 reached 88.5%. The optimal parameters of the reactions studied were determined.

Keywords: carbonylation, Reppe synthesis, octene-1, Lewis acids, Pd-complex catalysts

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1 Introduction

Currently, the progress in catalytic synthesis indicates that the direction of industrial organic synthesis in the future will greatly depend on the effective advancement of homogeneous catalysis. More specifically, it will rely on the innovation of novel homogeneous metal–complex catalysts, which hold significant promise for addressing critical challenges related to conserving raw materials and reducing energy expenses in large-scale organic synthesis processes [1–5]. The advantage of homogeneous metal–complex catalysts over heterogeneous ones is their high regio-, enantio-, and diastereoselectivity, while they operate under mild conditions, i.e., at low temperatures and pressures with high yields of target products [6–11].
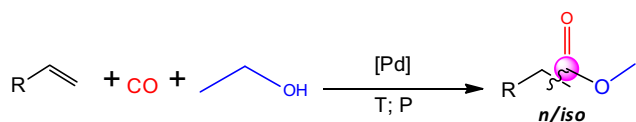
The hydroalkoxycarbonylation process presents an appealing and practical approach to the functionalization of olefins. It offers advantages such as cost-effectiveness, resource efficiency, and the ready availability of starting materials (refer to Scheme 1) [12–14]. This method is already employed in industrial settings to manufacture methyl propionate by the process known as the alpha process. In the hydroalkoxycarbonylation of olefins, which involves carbon monoxide (CO) and different alcohols (ROH), the effectiveness and specificity of homogeneous metal–complex catalysts can be enhanced by adjusting various factors. These factors include altering the ligands, introducing promoters, adjusting the ratios of components within catalytic systems and starting materials, as well as controlling the reaction pressure, temperature, and reaction duration [15–18]. The resulting products, particularly esters, have wide-ranging industrial applications and serve as valuable reagents. They have practical applications in manufacturing solvents, scents, aromas, cleaning agents, and surface-active agents [19,20].

Catalysts derived from transition metal complexes within the VIII group of the periodic table exhibit the highest level of catalytic effectiveness in the hydroalkoxycarbonylation reaction of olefins. The selectivity, endurance, and

Scheme 1: General scheme of the hydroalkoxycarbonylation of terminal olefins.

catalytic activity of these metal-based catalysts within this group depend on several factors. These variables depend on the particular chelating agent used, the makeup of the coordination sphere, process operational parameters, and the incorporation of external stabilizers and promoters. At present, among the most encouraging catalysts are those composed of palladium phosphine complexes, as they exhibit a favorable blend of donor and acceptor characteristics in both zero- and divalent states [15,16]. Within catalytic systems relying on Pd-based phosphine complexes, triphenylphosphine serves as a stabilizing agent. Its ability to provide stability is linked to its role in preserving the integrity of the core complex, thereby preventing the possible deactivation of active complexes during the catalytic reaction cycle caused by ligand exchange reactions. Additionally, different Bronsted acids are frequently used as external enhancers. These promoters assist in promoting the formation of intermediate palladium hydride complexes, which have a central role in the catalytic cycle of the process [21–23].

Recently, there has been an increasing focus on investigating Lewis acids in addition to Bronsted acids as catalyst promoters [24–29]. Huang and colleagues, for instance, employed cost-effective trivalent iron salts such as Lewis acids in the carbonylation reaction of various aromatic and aliphatic olefins. This approach resulted in the production of carboxylic acids with exceptional regioselectivity and impressive product yields of up to 96% [25]. In a different research investigation, Amezquita-Valencia highlighted the importance of employing a Lewis acid, such as $SnCl_2$ or $Ti(OiPr)_4$, along with a monodentate ligand like CYTOP 292 or P(*p*-anisyl)$_3$ to improve regioselectivity. This approach led to regioselectivity levels between 70 and 96% for linear isomers [26]. Furthermore, Ferreira and colleagues described the use of borosalicylic acid as an appealing acidic promoter catalyzed with palladium on the ethylene ethoxycarbonylation reaction, employing triphenylphosphine as a ligand [27]. Yang and Yuan also demonstrated that incorporating a Lewis acid with acidity levels similar to *p*-TsOH significantly enhanced both the rate and yield of the styrene hydroesterification reaction. This approach also led to a substantial reduction in the consumption of phosphine ligands within the catalytic system [28].

In this study, the hydroalkoxycarbonylation reaction of octene-1 was investigated using three-component Pd-

catalyzed systems. These systems featured Pd complexes with different ligands for stabilization and Lewis acids as promoters.

2 Materials and methods

2.1 Initial materials and research methods

As initial reagents in the work, (dichlorbis(triphenylphosphine) palladium, dichlorbis(triorthotolyl-phosphine) palladium, dichlorbis(trimetatolylphosphine) palladium, dichlorbis-(triparatolylphosphine) palladium, dichlorbis (triorthomethoxyphenylphosphine) palladium, dichlorbis (tricyclohexylphosphine) palladium, dixlorbis-(triparafluorophenylphosphine) palladium, dibrombis(triphenylphosphine) palladium, diiodbis(triphenylphosphine) palladium, Pd/Amberlyst IRC50, Pd/C 5%, triphenylphosphine, triorthotolylphosphine, trimetatolylphosphine, tripartolylphosphine, triorthomethoxyphenylphosphine, tricyclohexylphosphine, triparfluorophenylphosphine, hexene-1, octene-1, decene-1, cyclohexene, aluminum trichloride, tin dichloride, iron trichloride, indium trichloride, ytterbium triphthalate, lanthanum trichloride heptahydrate, praseodymium trichloride hexahydrate, ytterbium trichloride hexahydrate, samarium trichloride hexahydrate), absolute alcohols (methanol, ethanol, *n*-propanol, *n*-butanol), and CO were used without special purification (SIGMA-ALDRISH company).

The experiment procedures were conducted in a stainless steel laboratory apparatus of autoclave type, and no solvents were employed during the process. The olefin conversion and the ratio of isomeric ester products (linear and branched) were carried out by chromatography with an Agilent 7890A/5975C (USA) gas chromatography-mass spectrometer system. The chromatographic conditions were as follows: a gas chromatograph 7890A equipped with a mass-selective detector 5975C from Agilent; the carrier gas used was helium; the evaporator temperature was set at 300°C, with a flow split ratio of 1,000:1; the initial column thermostat temperature was 40°C for 1 min, followed by a temperature ramp of 50°C per min until reaching 250°C, held for 1 min, resulting in a total analysis time of 44 min; and the mass detector was operated in the electron impact ionization mode. A capillary chromatographic column, HP-FFAP, was used with a length of 30 m and an inner diameter of 0.25 mm; the stationary phase consisted of nitroterephthalic acid modified with polyethylene glycol.

The substances generated were subjected to analysis by both infrared (IR) and nuclear magnetic resonance

(NMR) spectroscopy methods. For IR spectra, a Nicolet 5700 single-beam infrared spectrometer manufactured by Thermo Electron Corporation (USA) was employed, covering the range from 400 to 4,000 cm^{-1}. For ^1H NMR spectra, a Bruker DPX 400 instrument operating at 300 MHz was utilized.

2.2 Carbonylation experiments

Hydroethoxycarbonylation of octene-1. A 100 mL steel autoclave (Figure 1), equipped with a stirrer and CO injection apparatus, was loaded with the following components: 1 mL (0.715 g, 6.37 mmol) of octene-1, 9 mL (7.1 g, 154.4 mmol) of ethanol, 0.008 g (0.0114 mmol) of $PdCl_2(PPh_3)_2$, 0.036 g (0.1367 mmol) of PPh_3, and 0.152 g (1.14 mmol) of $AlCl_3$. The autoclave was sealed and was subjected to three cycles of CO purging to eliminate any air. It was subsequently pressurized with CO to reach a pressure of 3.5 MPa, after which stirring and heating were initiated. The temperature was then gradually increased to 120°C for 1 h. The pressure was adjusted to 5.0 MPa, and under these temperature and pressure conditions, the reaction mixture was stirred for 5 h. Subsequently, stirring and heating were stopped, and the autoclave was allowed to cool to room temperature. Finally, the reaction mixture was analyzed using a gas chromatograph with a mass-selective detector. The conversion of octene-1 was 88.5%, and the ratio of branched/linear products was 1:2.35. The conversion was expressed as [(initial moles of octene-1 − final moles of octene-1)/initial moles of octene-1] × 100. The resulting reaction products (linear (ethyl ester of pelargonic acid) and branched (ethyl ester of 2-methylcaprylic acid)) were separated by fractional vacuum distillation, and experimental data of the boiling point of the products in a vacuum of 10 mmHg are 110–115°C, and literature data at a vacuum of 760 mmHg are 227–228°C.

3 Results and discussion

Our experimental data for the hydroalkoxycarbonylation reaction of octene-1 were divided into the following five sections.

The effects of the molar ratio of $AlCl_3$ on the hydroalkoxycarbonylation reaction of olefins, the nature of precursors, ligands, and promoters of various alcohols, and olefins are summarized in Tables 1–5. The catalytic system composed of $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$, with $AlCl_3$ serving as a promoter, was observed to demonstrate remarkable catalytic efficiency. The optimal process conditions and selectivity of conversion of olefins and target products were determined.

In the IR spectrum of the resulting compounds, several notable features were observed, including a prominent absorption peak at 1,737 cm^{-1} (indicating the presence of a carbonyl (C=O) group in the ester), distinct absorption bands in the 1,033–1,300 cm^{-1} range (referred to as the "ether band"), and absorption bands corresponding to CH, CH_2, and CH_3 groups at approximately 729, 1,300–1,462, and 2,800–3,000 cm^{-1}, respectively. The ^1H NMR data, recorded in deuterochloroform with tetramethylsilane as the reference, revealed that the products obtained from the
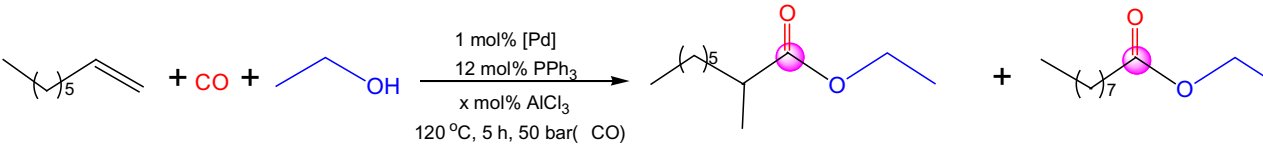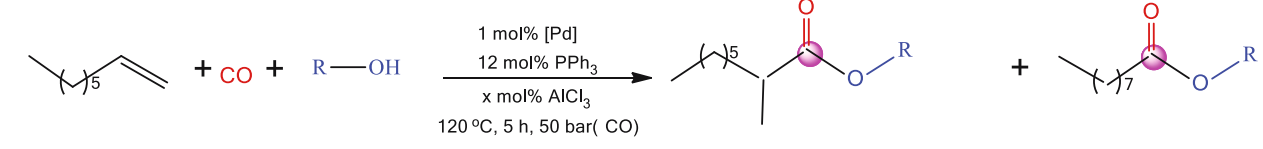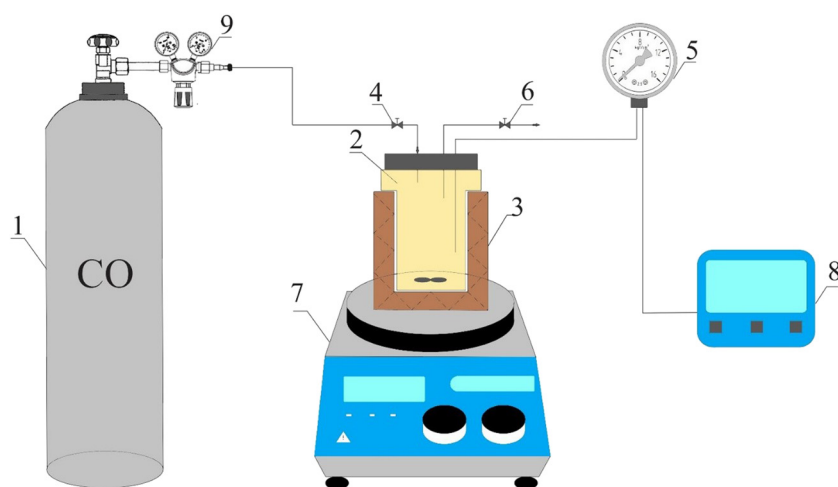

Figure 1: Schematic diagram of a laboratory autoclave unit for the olefin hydroesterification reaction. 1 – gas cylinder with CO; 2 – autoclave; 3 – electric heater; 4, 6 – microvalves for gas inlet and outlet; 5 – manometer; 7 – magnetic stirrer; 8 – gas and temperature regulator; 9 – reducer.

Table 1: Effect of the concentration of $AlCl_3$ on the hydroethoxycarbonylation of octene-1

Entry	Catalytic system ratio [PdCl₂(PPh₃)₂]/[PPh₃]/[AlCl₃] (in mmol)	Conversion of olefin (%)	Selectivity iso:*n*
1	1:12:8	46.6	1:2.5
2	1:12:16	60.5	1:2.8
3	1:12:32	70.1	1:2.7
4	1:12:100	88.5	1:2.35

Reaction conditions: The reagents [olefin]/[alcohol] and their volume, mL: [octene-1]/ [EtOH] = 1:9. T = 120°C, P_{CO} = 5.0 MPa, and τ = 5 h.

Table 2: Effect of the nature of alcohols on the hydroalkoxycarbonylation of octene-1

Entry	Reagents [octene-1]/[alcohol] = 1:9 (in volume, mL)	Catalytic system ratio [PdCl₂(PPh₃)₂]/[PPh₃]/ [promoter] = 1:12:100 (in mmol)	Conversion of olefin (%)	Selectivity iso:*n*
1	MeOH	AlCl₃	45.1	1:1.6
2	EtOH	AlCl₃	88.5	1:2.35
3	*n*-PrOH	AlCl₃	78.6	1.7:1
4	*n*-BuOH	AlCl₃	96.2	1:11.15
5	*n*-BuOH	*p*-PsOH·H₂O	84.6	1:9.1

Reaction conditions: T = 120°C, P_{CO} = 5.0 MPa, and τ = 5 h.

hydroethoxycarbonylation of octene-1 consisted of both the primary linear product and a mixture with a branched product. The NMR spectra provided specific information about proton shifts and coupling constants (J values). The methylene group protons of the ethyl radical within the alcohol component appeared at a chemical shift of 4.12 ppm as a quartet (J = 7.3 Hz). Protons from the adjacent methyl group resonated at around 1.25 ppm as a triplet with a J value of 7.3 Hz. Methyl group protons within the acid part of the molecule, with a chemical shift of 0.88 ppm, displayed a triplet with a J value of 5.3 Hz, located in the strongest field of the spectrum. Methylene group protons neighboring the

Table 3: Hydroethoxycarbonylation of other olefins under the same conditions of octene-1

Entry	Reagents [olefin]/[alcohol] (in volume, mL)	Conversion of olefin (%)	Selectivity iso:*n*
1	[Hexene-1]/[EtOH] = 0.8:9.2	41.8	1.46:1
2	[Octene-1]/[EtOH] = 1:9	88.5	1:2.35
3	[Decene-1]/[EtOH] = 1.2:8.8	84.4	1:2.48
4	[Cyclohexene]/[EtOH] = 0.65:9.35	21.1	—

Reaction conditions: T = 120°C, P_{CO} = 5.0 MPa, and τ = 5 h. Catalytic system ratio (in mmol): [PdCl₂(PPh₃)₂]/[PPh₃]/[AlCl₃] = 1:12:100.

Table 4: Effects of different catalyst complexes (**C1–C11**) and ligands (**L1–L8**) on the hydroethoxycarbonylation of octene-1

Pd/Amberlyst IRC50/ 5% - **C10**   Pd/C 5% - **C11**
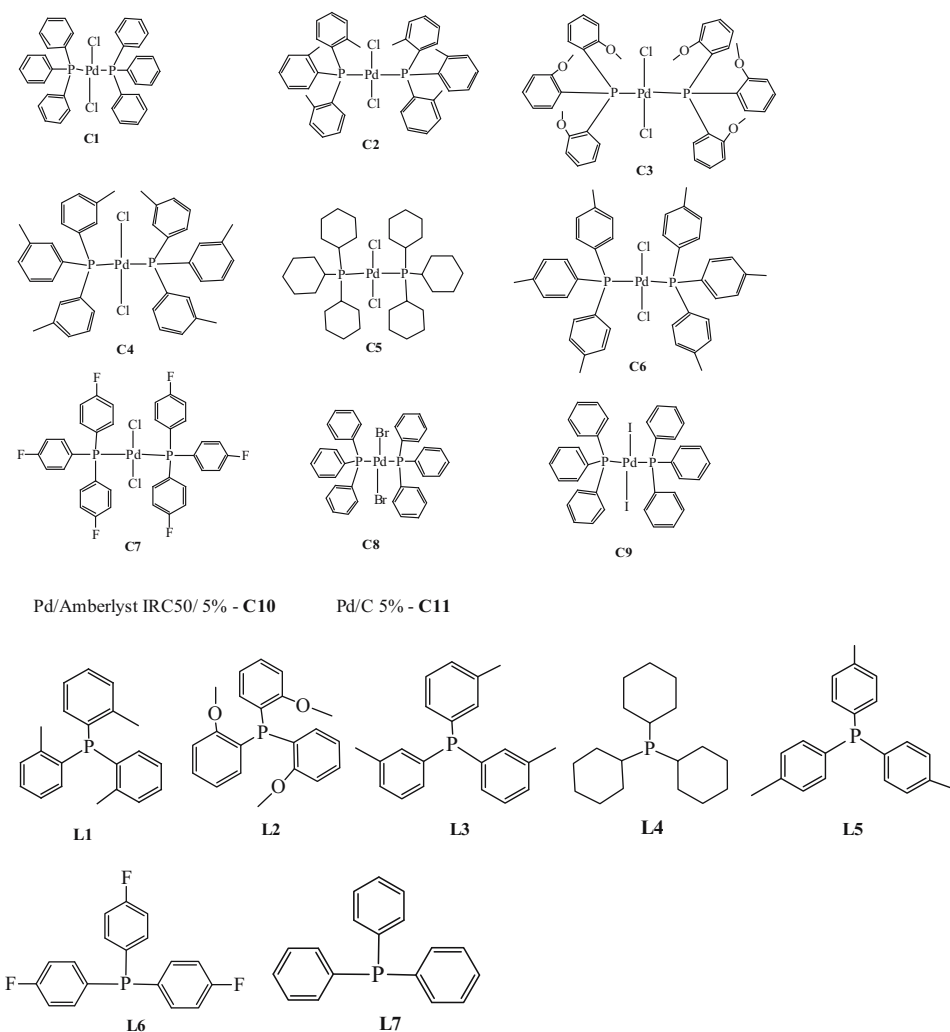
Entry	Catalytic system ratio [Pd]/[ligand]/[AlCl₃] = 1:12:100 (in mmol)	Conversion of olefin (%)	Selectivity iso:n
1	[C1]:[L1]	75.5	1.34:1
2	[C2]:[L1]	26.4	3.2:1
3	[C1]:[L2]	66.8	1:1.1
4	[C3]:[L2]	21.5	1.25:1
5	[C1]:[L3]	86.8	1:2.15
6	[C4]:[L3]	70.5	1:2.45
7	[C1]:[L4]	75.0	1.37:1
8	[C5]:[L4]	25.5	1.32:1
9	[C1]:[L5]	82.5	1:1.88
10	[C6]:[L5]	82.8	1:1.56
11	[C1]:[L6]	78.8	1:2.57
12	[C7]:[L6]	77.0	1:2.28
13	[C8]:[L7]	87.1	1:2.4
14	[C9]:[L7]	83.1	1:2.05
15	[C10]:[L7]	53.4	1:2.45
16	[C11]:[L7]	79.8	1:2.37

Reaction conditions: T = 120°C, P_{CO} = 5.0 MPa, and τ = 5 h. Reagent: [octene-1]/[EtOH] = 1:9 (in volume, mL).

carbonyl group (–CH$_2$–C(O)–O–) were observed as a triplet at 2.28 ppm (J = 7.3 Hz). A multiplet peak at 1.62 ppm was attributed to methylene protons of the carbon atom C$_5$. The remaining methylene protons of carbon atoms C$_2$, C$_3$, and C$_4$ were detected as a multiplet centered at 1.29 ppm. Additionally, the presence of an impurity, specifically the isomeric branched product (ethyl ester of 2-methylcaprylic acid), was identified by distinctive NMR signals, including a doublet signal for methylene protons of carbon atom C$_5$ at 1.13 ppm (J = 6.8 Hz) and a multiplet signal for the methyl proton of the C$_5$ carbon atom at 2.4 ppm (J = 8 Hz). The signals corresponding to other protons of the ethyl ester of 2-methylcaprylic acid were observed along with signals from the corresponding protons of the primary linear product (ethyl ester of pelargonic acid).

3.1 Effect of the [Pd]/[AlCl$_3$] concentration ratio on the hydroethoxycarbonylation of octene-1

The influence of the molar ratio of the promoter (AlCl$_3$) in the component of the catalytic system in the octene-1 hydroethoxycarbonylation reaction at low pressure of CO on the conversion of the initial octene-1 was investigated (Table 1). The ratio [PdCl$_2$(PPh$_3$)$_2$]/[PPh$_3$]/[AlCl$_3$] = 1:12:100 was proved to be the most optimal. Accordingly, the conversion of octene-1 was 88.5%. The ratio of branched/linear products was 1:2.35.

3.2 Influence of the nature of different alcohols on the hydroalkoxycarbonylation reaction of octene-1

In the reaction of hydroalkoxycarbonylation of olefins, we studied how the nature of different aliphatic alcohols affects the conversion of olefins (Table 2). The reaction with methyl alcohol proceeded very intensively. Palladium niello was observed in the reaction product, indicating the possibility of deactivation of the catalytic system. Accordingly, the conversion of octene-1 was low at 45.1%. The ratio of branched/linear products is 1:1.6 (Table 2, e1). Thus, it is established that the reaction of hydroalkoxycarbonylation of octene-1 with n-propanol in the presence of PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ system yields a mixture of products (linear and branched), with the selectivity of the branched product prevailing (Table 2, e3). The hydroalkoxycarbonylation of octene-1 with n-butanol in the presence of

Table 5: Effect of various co-catalysts on the hydroethoxycarbonylation of octene-1

Entry	Co-catalysts	Conversion olefin (%)	Selectivity iso:n
1	SnCl$_2$	20.2	1:4.35
2	Yb(OTf$_3$)	22.4	1:5.1
3	FeCl$_3$	73.5	1:2.06
4	InCl$_3$	23.3	1:2.2
5	LaCl$_3$·7H$_2$O	57.8	1:3.1
6	PrCl$_3$·6H$_2$O	76.6	1:2.85
7	YbCl$_3$·6H$_2$O	61.3	1:3.01
8	SmCl$_3$·6H$_2$O	73.4	1:2.74

Reaction conditions: T = 120°C, P_{CO} = 5.0 MPa, and τ = 5 h. Reagent: [octene-1]/[EtOH] = 1:9 (in volume, mL). Catalytic system ratio: [PdCl$_2$(PPh$_3$)$_2$]/[PPh$_3$]/[promoter] = 1:12:100 (in mmol).

PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ also proceeds with the formation of a mixture of linear and branched products, with the selectivity of the linear product predominating (Table 2, e4), and in the case of using p-PsOH·H$_2$O as a promoter, a decrease in the yield of the branched product is observed (Table 2, e5).

3.3 Hydroethoxycarbonylation of hexene-1, decene-1, and cyclohexene similar to the reaction conditions using octene-1

The hydroethoxycarbonylation of hexene-1, decene-1, and cyclohexene with the PdCl$_2$(PPh$_3$)$_2$–PPh$_3$–AlCl$_3$ system was studied in order to determine the influence of the radical size of α-olefins on the conversion of the initial olefins and regioselectivity: [PdCl$_2$(PPh$_3$)$_2$]/[PPh$_3$]/[AlCl$_3$] = 1:12:100, CO pressure 5.0 MPa, temperature 120°C, and duration 5 h. The experimental results obtained are summarized in Table 3. The reaction process also results in the creation of both linear and branched products.

As indicated by the information presented in Table 3, with an increase in the value of the radical of the initial olefin, an increase in the conversion is observed (from 41.8% for hexene-1 to 84.4% for decene-1), and in the case of cyclohexene, an insignificant conversion is observed (21.1%).

3.4 Hydroethoxycarbonylation of octene-1 using various catalytic systems with AlCl$_3$ as a promoter

The optimal properties of palladium in its role as a complex-forming agent are linked to its ability to exhibit a

beneficial blend of donor and acceptor characteristics in both its zero-valent and divalent states. Due to this, the palladium center can form relatively stable intermediates with reagents included in its coordination sphere (alkenes, CO), which at the same time have sufficient reactivity for subsequent interactions. Phosphine complexes of palladium (mainly triphenylphosphine complexes of palladium) and systems based on the latter are especially effective as a catalyst for the reaction of hydroalkoxycarbonylation of olefins.

The comparative catalytic activity of a number of phosphine complexes of Pd and free ligands in three-component systems of the reaction of hydroethoxycarbonylation of octene-1 under the optimal conditions ($T = 120°C$, $P_{CO} = 5.0$ MPa, $\tau = 5$ h) of the process in the presence of the system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ was determined. The experimental results obtained are summarized in Table 4. As can be seen from the data in Table 4, the systems $PdCl_2(PPh_3)_2$–P(m-tolyl)$_3$–$AlCl_3$, $PdCl_2(PPh_3)_2$–P(p-tolyl)$_3$–$AlCl_3$, and $PdCl_2$(P(p-tolyl)$_3)_2$–P(p-tolyl)$_3$–$AlCl_3$ show high catalytic activity, with $PdBr_2(PPh_3)_2$–PPh_3–$AlCl_3$, $PdI_2(PPh_3)_2$–PPh_3–$AlCl_3$ conversion of initial octene-1 exhibiting above 80%, and other catalytic systems showed moderate catalytic activity. At the same time, the catalytic systems are stable and palladium niello release was not observed. The following heterogeneous applied palladium catalysts were used for comparative analysis: Pd/Amberlyst IRC50/5% (C10) and Pd/C 5% (C11) [30].

3.5 Effect of different promoters on the hydroethoxycarbonylation reaction of octene-1

In order to determine the effect of Lewis acids as promoters in the reaction of hydroethoxycarbonylation of octene-1 in the initial catalytic system $PdCl_2(PPh_3)_2$–PPh_3-promoter, the following promoters were used in the initial catalytic system $PdCl_2(PPh_3)_2$–PPh_3-promoter under the optimal conditions: $SnCl_2$, Yb(OTf)$_3$, $FeCl_3$, $InCl_3$, $LaCl_3 \cdot 7H_2O$, $PrCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, and $SmCl_3 \cdot 6H_2O$ (Table 5). As can be seen from the data in Table 5, of all the Lewis acids tested, the catalytic systems using $FeCl_3$, $PrCl_3 \cdot 6H_2O$ and $SmCl_3 \cdot 6H_2O$ as promoters showed the highest catalytic activity. It was found that $SnCl_2$, Yb(OTf)$_3$, and $InCl_3$ are less efficient than $AlCl_3$. In particular, 100 mol of $AlCl_3$ is required for the efficient formation of active Pd–H forms. This result is superior to all Lewis acids tested (e.g. $FeCl_3$) in both conversion and regioselectivity. The effect of the critical anion on regioselectivity

was elucidated using $PdCl_2(PPh_3)_2$ as the metal complex. In particular, chloride anions can affect regioselectivity by promoting the formation of iso- and n-isomers, respectively.

In the hydroalkoxycarbonylation reaction of olefins using a palladium-based catalytic system, Lewis acids play a crucial role in promoting the formation of palladium hydride intermediate complexes. This reaction is a fundamental process in organic synthesis for the conversion of olefins into carbonyl compounds (aldehydes or ketones) by incorporating both an alkoxyl and a C=O group into the olefin substrate. Lewis acids, by definition, are electron-pair acceptors, while Brønsted acids are proton (H+) donors. In the hydroalkoxycarbonylation reaction, Lewis acids can coordinate with both the olefin substrate and palladium catalyst, facilitating the necessary interactions for the catalytic cycle. This coordination chemistry allows Lewis acids to activate and stabilize various intermediates and transition states during the reaction. Lewis acids can be more versatile in terms of substrate scope. They can be applied to a wide range of olefins and reaction partners, offering greater flexibility in designing and optimizing catalytic systems for various hydroalkoxycarbonylation reactions.

4 Conclusions

Thus, when using different Lewis acids as promoters in the composition of the catalytic system in the reaction of hydroalkoxycarbonylation of octene-1, the three-component system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ showed the highest catalytic activity.

Thus, in the context of the hydroalkoxycarbonylation reaction of octene-1, the inclusion of various Lewis acids as promoters within the catalytic system revealed that the three-component system combination of $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ showed the highest catalytic activity. The conversion of octene-1 was 88.5% and the ratio of branched and linear products was 1:2.35. When economical and easily obtainable Lewis acid salts are incorporated into the catalytic system, numerous olefins are transformed into the targeted carboxylic acid esters with substantial conversions and medium to excellent regioselectivity. The influence of the critical anion on the regioselectivity was elucidated using $PdCl_2(PPh_3)_2$ as a metal complex. In particular, the chloride anions can affect the regioselectivity by promoting the formation of linear and branched isomers, respectively.

For the first time, the comparative catalytic activity of a number of phosphine complexes of Pd and free ligands in three-component systems of the reaction of hydroethoxycarbonylation of octene-1 was carried out under the optimal

conditions (T = 120°C, P_{CO} = 5.0 MPa, τ = 5 h) for carrying out the process by using the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ system.

Author contributions: K.Sh. and N.K. – conceptualization; K.Sh. and A.V. – methodology; G.Zh. and F.K. – software; M.Z. and F.K. – validation; G.Zh. and N.K. – formal analysis; K.Sh., G.Zh., and N.K. – investigation; N.K. – data curation; K.Sh., A.V., and N.K. – writing – original draft preparation; K.Sh., A.V., and N.K. – writing – review and editing; K.Sh., M.Z., and N.K. – visualization; K.Sh. – supervision; N.Zh. – project administration. All authors have read and agreed to the published version of the manuscript.

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Informed consent statement: Not applicable.

Ethical approval: The conducted research is not related to either human or animal use.

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