Along with the hydroethoxycarbonylation of cyclohexene in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ with $AlCl_3$ in its composition as a promoter, there can also be a "hydride" mechanism, reminiscent of the carbonylation process, which occurs in the presence of strong hydrogen acids (p-TsOH, etc.).

The mechanism of the reaction of hydroethoxycarbonylation of cyclohexene can proceed in the same way as the mechanism of hydroethoxycarbonylation of octene-1 in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ [7].

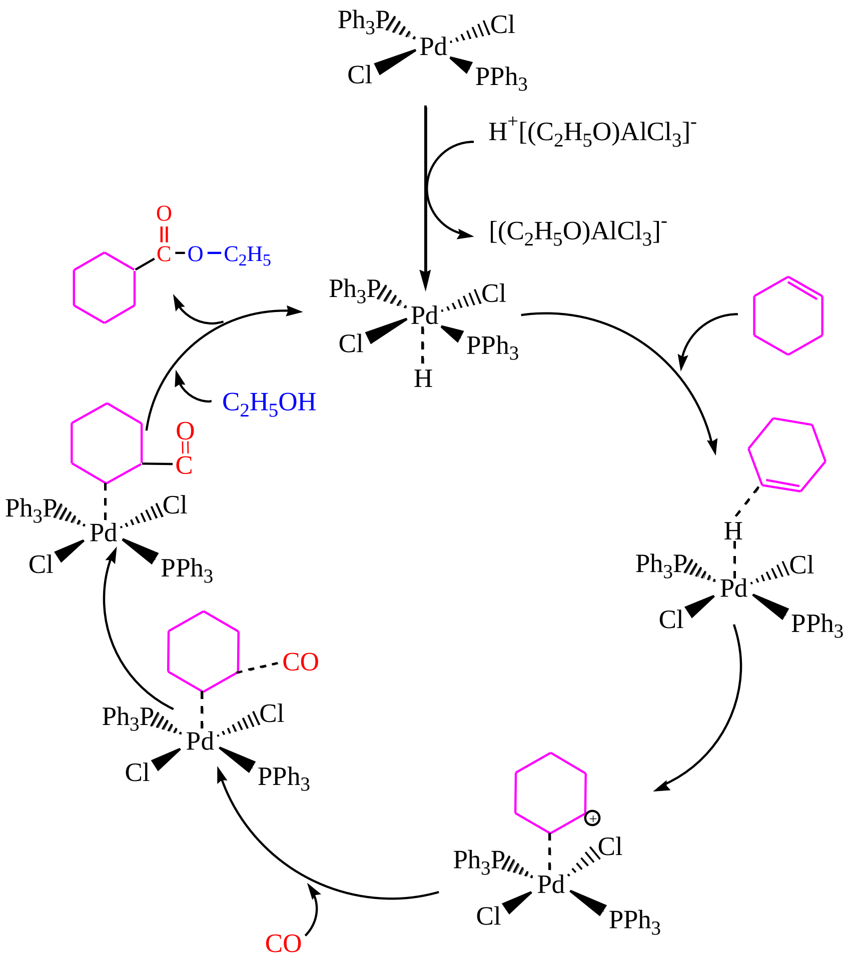

Figure 2. "Hydride" mechanism of cyclohexene hydroesterification reaction

The mechanism of cyclohexene hydroesterification in the presence of three-component $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalyst system is shown in Figure 2. The stage of HPd hydride complex formation is the main stage of the process. This complex gives the possibility of further catalytic cycle. When ethanol interacts with aluminum (III) chloride, which is a strong Lewis acid, it is possible to get the formation of $H^+[C_2H_5OAlCl_3]^-$ proton and $[C_2H_5OAlCl_3]^-$ of weakly coordinating anions complexes. The polarization of O-H bonds in alcohol under the action of strong Lewis acids allows the process to take place according to the hydride mechanism.

Conclusions

The activity of the three-component catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ with $AlCl_3$ in its composition as a promoter in the carbonylation reaction of cyclohexene with carbon monoxide and ethanol was investigated. A high catalytic activity of this catalytic system was found. The effect of process conditions, such as components of catalyst system ratio and primary reagents mole ratio, temperature, CO pressure, reaction time on the result of the hydroethoxycarbonylation reaction of cyclohexene in the presence of the catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ at low carbon monoxide pressure was studied. Optimal parameters were identified: $[C_6H_{10}]:[C_2H_5OH]:[Pd]:[PPh_3]:[AlCl_3] = 435:435:1:6:9$, $P_{CO} = 2.5$ MPa, T = 120 °C, $\tau = 5$ h. The possibility of cyclohexanecarboxylic acid ethyl ester synthesizing at these parameters with a yield of 80.7 %