Mechanism of the Palladium-Catalyzed Electrocarbonylation of Ethanol to Diethylcarbonate

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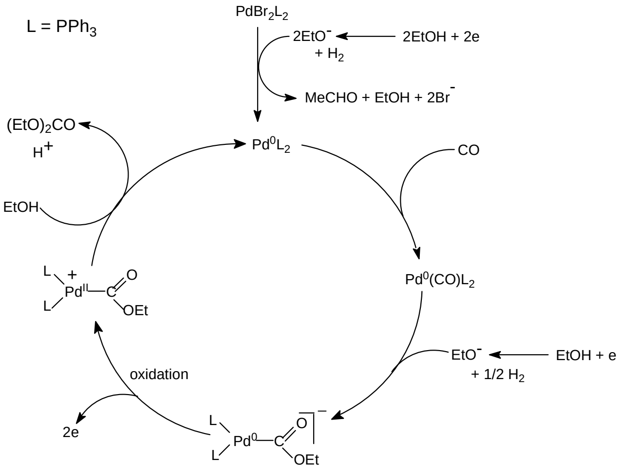
Palladium salts or complexes catalyzed the electosynthesis of dialkylcarbonates from alcohols and carbon monoxide.[1]

$$2\ ROH + CO \xrightarrow{[Pd^{II}]} (RO)_2CO + 2H^+ + 2e$$

The mechanism of the carbonylation of ethanol has been investigated by means of cyclic voltammetry associated to ^{31}P-NMR.[2]



The catalytic cycle is initiated by the chemical reduction of $PdBr_2(PPh_3)_2$ to a Pd^0 complex by the ethoxide ion electrogenerated at the cathode by the electrochemical reduction of EtOH. After coordination of the electrogenerated $Pd^0(PPh_3)_2$ complex by CO, the resulting complex undergoes a nucleophilic attack by the ethoxide ion to form an anionic Pd^0 complex. The electrochemical oxidation of the latter gives a cationic $(PPh_3)_2Pd^{II}$-CO_2Et^+ complex. A nucleophilic attack of its organic ligand by EtOH generates the diethylcarbonate and the Pd^0 catalyst.

[1] G. Filardo, A. Galia, F. Rivetti, O. Scialdone, G. Silvestri, *Electrochim. Acta,* 41, 1996, 2893-2896
[2] C. Amatore, S. Bensalem, A. Jutand, G. Silvestri, manuscript in preparation