

REACTION INTERMEDIATES IN PALLADIUM-CATALYZED CARBONYLATION OF OLEFINS

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Addition of carbon monoxide to organic molecules is an important industrial process, because CO is a convenient one-carbon feedstock and the resulting metal acyl complexes can be easily functionalized. Palladium catalyzed carbonylation of terminal olefins can generally lead to three different products: β -alkoxy esters **1**, succinate derivatives **2** and α,β -unsaturated esters **3** (Figure 1).¹ The first two routes have been extensively investigated, including mechanistic analysis.² In a previous work of one of us, the conditions were optimized for obtaining the ester in a selective way (Figure 1).³ However, the reaction mechanism for the formation of **3** is not clear. Therefore, we investigated the mechanism using electrospray ionization mass Spectrometry (ESI-MS) and searched for key intermediates.

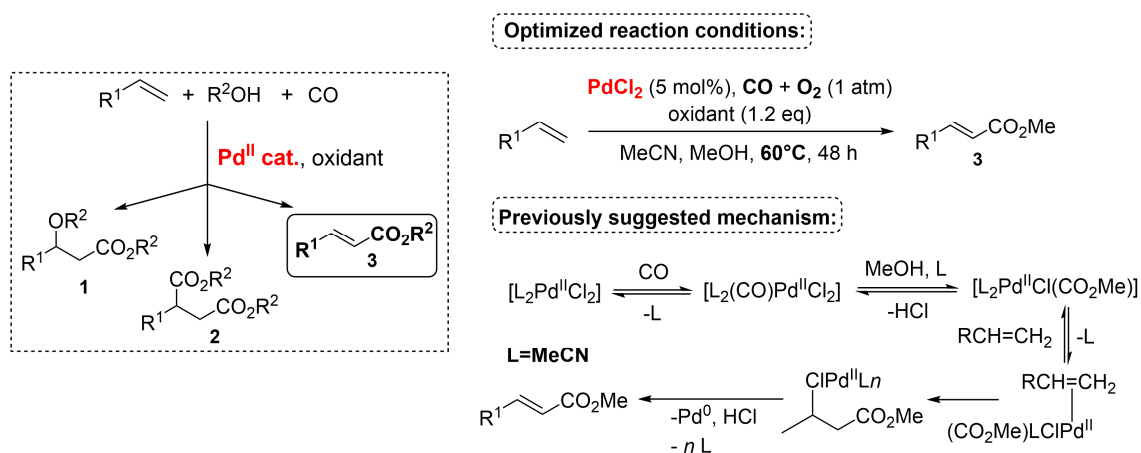


Figure 1.

Using ESI-MS under the reaction conditions for the selective formation of **3**, we detected three key intermediates: $[PdCl_3(CO)]^-$, $[PdCl_2H(\text{styrene})]^-$ and $[PdCl_2H(\text{styrene})(CO)]^-$. The isotope labelling showed that the H ligand originates either from the OH group of methanol or from styrene. Bond dissociation energy (BDE) of CO in $[PdCl_3CO]^-$ is 2.1 eV. Complex $[PdCl_2H(\text{styrene})]^-$ first eliminates HCl and only afterward the styrene ligand. The energy demand for HCl elimination is 1.5 eV. Finally, $[PdCl_2H(\text{styrene})(CO)]^-$ loses CO first with BDE of 1.6 eV. This is followed by elimination of HCl and styrene. This sequence, together with exploratory DFT calculations, allowed us to suggest a catalytic cycle.

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[1] Wu X.-F., Neumann H. and Beller M., *ChemSusChem*, 2013, 6, 229.

[2] Heck R. F., *J. Amer. Chem. Soc.*, 1968, 90, 5518.

[3] Malkov A.V., Derrien N., Barlóg M. and Kočovský P., *Chem. Eur. J.*, 2014, 20, 4542.