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.

Using ESI-MS under the reaction conditions for the selective formation of 3, we detected three key intermediates: [PdCl₃(CO)]⁻, [PdCl₂H(styrene)]⁻ and [PdCl₂H(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 [PdCl₃CO]⁻ is 2.1 eV. Complex [PdCl₂H(styrene)]⁻ first eliminates HCl and only afterward the styrene ligand. The energy demand for HCl elimination is 1.5 eV. Finally, [PdCl₂H(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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