Abstract

Palladium-catalysed cross-coupling reactions are one of the most powerful tools in synthetic organic chemistry. The understanding of reaction mechanisms is vital to the optimization of known transformations and the development of new palladium-catalysed reactions. In this research work, we studied the mechanism of palladium-catalyzed coupling of aryl halides and terminal alkynes, which has still not been definitively confirmed despite numerous efforts to solve it. Our goal was to uncover the proposed reaction mechanism by dividing it into individual steps and analysing them, mainly by using nuclear magnetic resonance (NMR) spectroscopy. In order to gain insight into each individual step of the mechanism, key intermediates – palladium alkynyl halides, palladium bisalkynyls and palladium aryl halides – had to be prepared. The synthesis of the latter was already reported, however, palladium alkynyl halides and bisalkynyls are less known. The former were prepared from corresponding terminal alkynes in two synthetic steps, and the latter were prepared in three. We have also developed a new synthetic method for preparation of symmetrical palladium bisalkynyls in one synthetic step.

The prepared palladium organometallic compounds were used to investigate the effect of substituents on the rate of transmetallation, the crucial step of the proposed reaction mechanism. The analysis of the reaction kinetics revealed that the halide in palladium aryl halide has the greatest influence on the transmetallation rate. This discovery was used to accelerate the catalytic reaction between phenylacetylene and 4-iodotoluene, catalysed by a simple palladium precatalyst ($Pd(PPh_3)_2I_2$). We have also evaluated the effect of other substances, i.e. ligand (triphenylphosphine) and organic base (pyrrolidine), on the separate steps of the proposed reaction mechanism. These new insights allowed us to better understand the palladium-catalysed reactions of terminal alkynes and aryl iodides.

The described method was used to predict and confirm the success of new catalytic reactions.

Keywords: palladium, mechanism, cooperative catalysis, palladium bisalkynyls, kinetics.