Mechanistic Studies in Palladium Catalysis: The Role of Anionic Arylpalladium Halide Intermediates in the Mizoroki-Heck Reaction

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Much work has been directed towards the development of ligands for cross-coupling reactions, yet many reactions, such as the Mizoroki-Heck reaction under "Jeffery conditions", are conducted with ligandless palladium (palladium without added dative ligand). Ligandless systems are attractive alternatives to common cross-coupling methods due to their simplicity and low cost. However, little is known about the reactivity of intermediates in these ligand-free processes. We have recently isolated and characterized several anionic arylpalladium complexes possessing the general structure $[Pd(Ar)(Br)(\mu\text{-}Br)]_2^{2-}$. These anionic complexes were found to be active for insertion of a variety of olefins at room temperature. Kinetic data support the intermediacy of these complexes in catalytic Mizoroki-Heck reactions under ligand-free conditions. Additional studies also indicate these anionic complexes are potential intermediates in reactions conducted with catalysts containing bulky electron-rich phosphines (e.g. P^tBu_3).