

Catalysis with Ammonia through Terminal Amido Complexes: Studies on Selectivity and New Catalytic Transformations

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In the presence of a (Josiphos)PdCl₂ catalyst and base, aryl halides couple with ammonia to produce mono- and diarylamines with selectivities as high as 50:1 favoring the monoarylamine. Herein, mechanistic studies of these transformations with an emphasis on the factors that control selectivity (i.e. electronics, sterics) will be presented. First, a set of Josiphos-palladium arylamido and arylanilido complexes with various aryl groups were generated *in situ*, and the equilibria between the two palladium amido species were determined. Additionally, the rates of reductive elimination of the respective anilines were measured. Parent amido complexes appear more stable in solution than the anilido counterparts, but reductive elimination from the anilido complexes is much faster. Further studies are necessary to fully explain the observed selectivity. The applicability of the amido complexes as intermediates in new aminocarbonylation reactions will be discussed. The first aminocarbonylation of aryl halides and triflates with ammonia and carbon monoxide employing the highly active Pd[P(o-tol)₃]₂/Josiphos precatalyst, as well as initial investigations on the scope and limitations of this reaction, are presented.