Mechanism of the Nickel-Catalyzed Electrosynthesis of Ketones by Heterocoupling of Acyl and Benzyl Halides

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Summary. The mechanism of the nickel-catalyzed electrosynthesis of ketones by heterocoupling of phenacyl chloride and benzyl bromide has been investigated by fast scan rate cyclic voltammetry with [Ni(bpy)2]+(BF4) as the catalytic precursor (bpy = 2, 2’-bipyridine). The key step is an oxidative addition of Ni0(bpy) (electrogenerated by reduction of the Ni(II) precursor) to PhCH2Br whose rate constant is found to be 10 times higher than that of PhCH2COCl. The complex PhCH2NiIIBr(bpy) formed in the oxidative addition is reduced at the potential of the NiII/Ni0 reduction by a two-electron process which affords an anionic complex PhCH2NiI(bpy)− able to react with PhCH2COCl to generate eventually the homocoupling product PhCH2COCH2Ph. The formation of the homocoupling product PhCH2COCH2Ph is prevented because of the too slow oxidative addition of Ni0(bpy) to PhCH2COCl compared to PhCH2Br. The formation of the homocoupling product PhCH2COCH2Ph is also prevented because PhCH2NiI(bpy)− does not react with PhCH2Br. This explains why the electrosynthesis of the ketone can be performed selectively in a one-pot procedure, starting from an equal mixture of PhCH2COCl and PhCH2Br and a nickel catalyst ligated by the bpy ligand.

Keywords. Electron transfer; Heterocoupling; Kinetics; Mechanism; Nickel.

Introduction

The synthesis of symmetrical biaryls by homocoupling of aryl halides [1] or triflates [2] requires a nickel or palladium catalyst and a reducing agent: a metallic powder or the electrons delivered by a cathode (Eq. (1)).

\[ 2\text{ArX} + 2\text{e}^- \xrightleftharpoons{\text{Ni or Pd}} \xrightarrow{\text{Ni or Pd}} \text{ArAr} + 2\text{X}^- \] (1)

The detailed mechanism of such reactions has been established under catalytic conditions [3] for a nickel catalyst ligated by a bidentate phosphine (dppe = 1,2-bis-(diphenylphosphino)-ethane) in which mono-electronic transfers are involved (Scheme 1) [4a,b] and for a palladium catalyst ligated by a monodenate phosphine (PPh3) in which the reaction proceeds via bielectronic transfers (Scheme 2) [5]. When the

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nickel catalyst is ligated by PPh$_3$ [4c] or by 2,2'-bipyridine (bpy) [4d], the mechanism is similar to that reported in Scheme 1.

In both mechanisms, two sequential oxidative additions are involved: between ArX and an $M^0$ complex (steps 1 in Schemes 1 and 2) and between ArX and an Ar-$M^0$ complex (step 3 in Scheme 1) or an Ar-$M^0^-$ complex (step 3 in Scheme 2). Those