Nickel-Catalyzed Bromide-to-Iodide Aromatic Finkelstein Reaction

Significance: In 1978, Takagi, Hayama, and Okamoto disclosed an early example of a halogene exchange reaction using a simple nickel(II) precatalyst, with added Zn or PbBu3, and a nucleophilic source of iodide (KI). As the authors explain, at this time the most common strategy to perform an aromatic Finkelstein reaction was to use copper; however, the ability to go from a bromide to iodide was unattainable. This topic has remained of interest for the last 50 years, with notable contributions from a wide variety of groups.

Comment: The addition of Zn was crucial for the reaction to occur at lower temperatures. Moreover, it was found that the addition of a donating phosphine ligand, such as PbBu3, suppressed the formation of the reductive homocoupled side product. At elevated temperatures, only the phosphine additive was necessary for a successful reaction, without the need of the Zn reductant. The reaction did not occur when using various nickel(0) precatalysts.