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A New Combined Source of "CN" from N,N-Dimethylformamide and Ammonia in the Palladium-Catalyzed Cyanation of Aryl C-H Bonds

Jiho Choi¹, Jinho Kim², Sukbok Chang*

Korea Advanced Institute of Science of Technology (KAIST)

Aromatic nitriles possess versatile utilities and are indispensible not only in organic synthesis but also in chemical industry. In fact, the nitrile group is an important precursor for various functional groups such as aldehydes, amines, amidines, tetrazoles, amides, and their carboxyl derivatives. Representative methods for the preparation of organonitriles with cyanide-containing reagents are the Sandmeyer and Rosenmund-von Braun reactions. Recently, a catalytic route to aryl nitriles has been reported on the basis of the chelation-assisted C-H bond activation or metal-catalyzed cyanation of haloarenes. In those cyanation protocols, the "CN" unit is provided from metal-bound precursors of MCN (M=Cu, K, Na, Zn), TMSCN, or K3Fe(CN)6. Additionally, it can be generated in situ from nitromethane or acetone cyanohydrin. Herein, we report the first example of generating "CN" from two different, readily available precursors, ammonia and N,N-dimethylformamide (DMF). In addition, its synthetic utility is demonstrated through the Pd-catalyzed cyanation of arene C-H bonds.

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