

Nickel-Catalyzed Reductive and Borylative Cleavage of Aromatic Carbon–Nitrogen Bonds in *N*-Aryl Amides and Carbamates

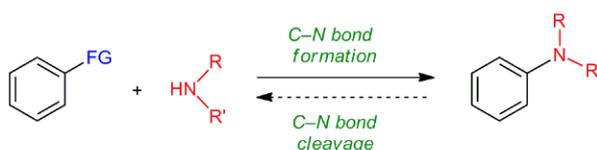
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■ Although substantial progress has been made in the development of catalytic C(aryl)–N bond-formation reactions for the construction of aryl amine derivatives, reports pertaining to the reverse process, namely the catalytic cleavage of C(aryl)–N bonds, remain scarce. C(aryl)–N bond cleavage of aniline derivatives normally requires the use of highly reactive cationic intermediates, such as diazonium and ammonium salts, in which the elimination of electronically neutral dinitrogen and amine moieties facilitates the C–N bond-cleavage process. A notable exception to this is the ruthenium-catalyzed C–N bond activation of electronically neutral aniline derivatives, although applicable substrates are limited to compounds that contain ortho-directing groups. Recently, the group of Professor Naoto Chatani and Associate Professor Mamoru Tobisu at Osaka University (Japan) reported on a

catalytic method for cleavage of C(aryl)–N bonds of electronically neutral, simple aryl amine derivatives, including amides and carbamates. The process involves the nickel-catalyzed conversion of inert C(aryl)–N bonds into C(aryl)–H and C(aryl)–B bonds.

Professor Chatani said: “Our research group has focused on the development of new catalytic methods that can be used for the direct transformation of strong σ -bonds, including C–H, C–C and C–O bonds. In this context, we previously reported a series of nickel-catalyzed cross-coupling reactions using anisole derivatives as aryl halide surrogates (for a review, see: *Top. Organomet. Chem.* **2013**, *44*, 35). We wondered whether the low-valent nickel species could be used for the transformation of even stronger σ -bonds.” After selecting C(aryl)–N bonds as the target for cleavage by nickel

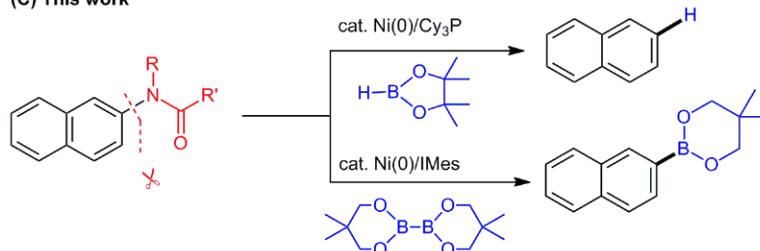
(A) C–N bond cleavage: A challenging task

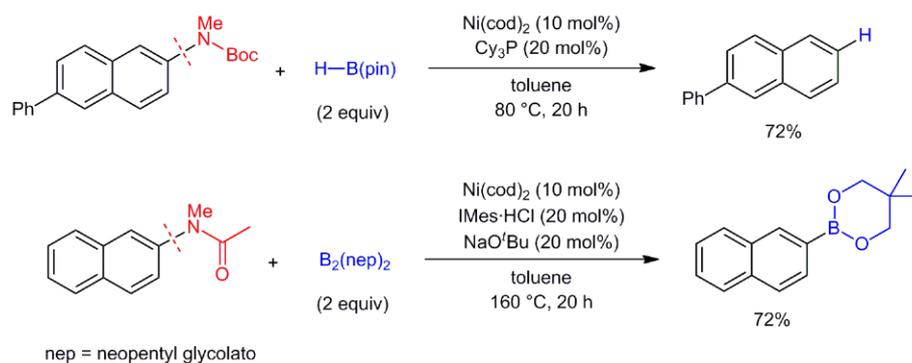


(B) Chatani's previous work: C–OMe activation using Ni(0)



(C) This work

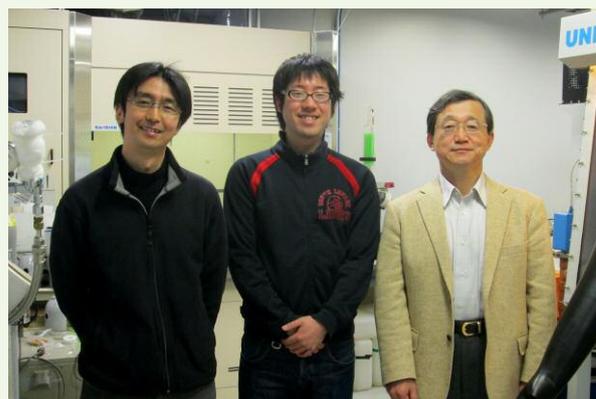




catalysis, the Osaka-based researchers examined a series of reagents, ligands and reaction conditions. “The first promising result was obtained just after Keisuke Nakamura joined the group as an undergraduate researcher,” revealed Associate Professor Tobisu. “He examined the nickel-catalyzed reaction of 1-(naphthalen-2-yl)pyrrolidin-2-one with hydrosilane and found that naphthalene, a C–N bond-cleavage product, was formed in 7% yield. He dedicated his master’s degree studies to further developing this intriguing C–N bond-cleavage reaction.” After considerable study, the reductive cleavage of C–N bonds was revealed to proceed in synthetically useful yield when hydroborane was used as the reducing agent. Professor Chatani concluded: “What excited us even more was that substitution of an amide group by a boryl group was also possible when a diboron reagent was used. Although the mechanism responsible for this new C–N activation process is unclear at present, we conclude that the C(aryl)–N bond cleavage reaction can now be considered to be a viable methodology for enabling a nonconventional synthetic strategy.”

Matteo Zanda

About the authors



From left to right: Prof. M. Tobisu, K. Nakamura, Prof. N. Chatani

Mamoru Tobisu received his PhD from Osaka University (Japan) in 2001 under the direction of Professor Shinji Murai. During the course of his PhD studies, he also worked with Professor Gregory C. Fu at the Massachusetts Institute of Technology (USA) as a visiting scientist (1999). Following a period of employment with the Takeda Pharmaceutical Company, Japan (2001–2005), he began his academic career at Osaka University in 2005 as an Assistant Professor. He then moved to the Frontier Research Base for Global Young Researchers at Osaka University as a lecturer in 2006 and was appointed as an Associate Professor at the Center for Atomic and Molecular Technologies at Osaka University in 2011.

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Keisuke Nakamura graduated from Osaka University (Japan) in 2011 and obtained his MSc from the same university in 2013. He is currently pursuing his PhD under the supervision of Professors Chatani and Tobisu at Osaka University.

Naoto Chatani received his PhD in 1984 under the guidance of Professors Noboru Sonoda and Shinji Murai. In 1984 he joined the Institute of Scientific and Industrial Research at Osaka University (Japan) and was involved in research in the laboratory of Professor Terukiyo Hanafusa. After postdoctoral studies (1988–1989 under Professor Scott E. Denmark at the University of Illinois, Urbana-Champaign, USA), he moved back to Osaka University and was promoted to Associate Professor in 1992 and to Full Professor in 2003.