

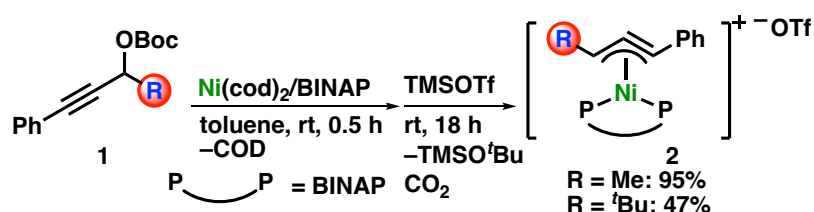
Isolation and reactivity of allenynickel complexes in Ni-catalyzed propargylic substitution reactions

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The catalytic propargylic substitution reaction has been realized as an efficient method for the synthesis of alkyne- or allene-containing organic molecules.¹ In particular, the palladium catalysis is one of the most powerful synthetic tools, in which allenylpalladium complexes are involved as key intermediates.² Recently, Tsuji, Kawatsura, and co-workers reported the nickel-catalyzed asymmetric propargylic amination of propargylic carbonates, which allowed access to the corresponding chiral propargylic amines in high yields with excellent enantioselectivity.³ However, allenynickel congeners, plausible key intermediates in nickel-catalyzed system, have not been isolated thus far. We herein disclosed the first example of the synthesis and reactivity of a series of allenynickel complexes having BINAP ligand.

Treatment of alkyne complexes, which were prepared by the reaction of propargylic *tert*-butyl carbonate (**1**) with an equimolar amount of Ni(cod)₂/BINAP, with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dry toluene at room temperature for 18 h gave the corresponding cationic η^3 -allenynickel complexes (**2-Me** and **2-^tBu**) in 95% and 47% yield, respectively. These molecular structures of **2-Me** and **2-^tBu** were unambiguously determined by X-ray diffraction analysis. The reaction of (**R**)-**2-Me** with *N*-methylaniline gave the propargylic amine in high enantioselectivity, which is comparable to that observed in the Ni-catalyzed asymmetric propargylic amination, albeit low yield.



1. a) J. A. Marshall, M. A. Wolf, *J. Org. Chem.* **1996**, *61*, 3238. b) X. Huang, S. Wu, W. Wu, P. Li, C. Fu, S. Ma, *Nat. Commun.* **2016**, *7*, 12382.
2. a) P. J. Stang, C. M. Crittall, A. M. Arif, *Organometallics* **1993**, *12*, 4799. b) J. M. A. Wouters, R. A. Klein, C. J. Elsevier, *Organometallics* **1994**, *13*, 4586. c) K. Tsutsumi, T. Kawase, K. Kakiuchi, S. Ogoshi, Y. Okada, H. Kurosawa, *Bull. Chem. Soc. Jpn.* **1992**, *72*, 2687. d) S. Ogoshi, T. Nishida, T. Shinagawa, H. Kurosawa, *J. Am. Chem. Soc.* **2001**, *123*, 7164.
3. K. Watanabe, Y. Miyazaki, M. Okubo, B. Zhou, H. Tsuji, M. Kawatsura, *Org. Lett.* **2018**, *20*, 5448.