

SYNLETT Spotlight 116

Nickel(0) Catalysts in Organic Synthesis

Compiled by Ze Zhang



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Ze Zhang was born in Anhui (China) in 1976. He achieved his Bachelor degree from Anhui University in China. He is currently in the fifth year of his Master-PhD through-train studies in the Department of Chemistry, University of Science and Technology of China (USTC), where he is working on solid-state organic synthesis using mechanical milling techniques, under the supervision of Professor G.-W. Wang.

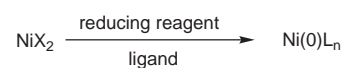
C/O Prof. G.-W. Wang, Laboratory of Fullerene Chemistry and Green Organic Synthesis, Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China
E-mail: zhangze@mail.ustc.edu.cn

Introduction

With the rapid expansion of the utility of palladium catalysts in organic synthesis, nickel catalysts, including nickel(0) catalysts, have been arousing great attention and efforts in recent years. A great deal of work has demonstrated that the Ni(0)-catalyzed carbon–carbon bond forming reaction is an extremely powerful tool in organic synthesis.¹ Using Ni(0) catalysts, it is often possible to invoke reactivity with substrates that are not activated by palladium analogues, or to perform reactions using less forcing conditions. In addition, nickel is a significantly cheaper alternative to palladium. In recent years, they

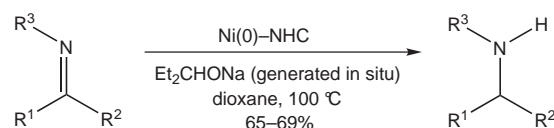
have been applied in a wide range of organic transformations. Even though the use of Ni(0) catalyst in organic synthesis is still in its early stages compared to the widespread utility of Pd catalysts, it is certain that future work from various research groups will greatly expand the use of this chemistry both in industry and academia.

Due to their high air sensitivity, Ni(0) catalysts are most commonly generated in situ first by the reduction of stable Ni(II) complexes with strong reducing reagents and then by association with bulky ligands.

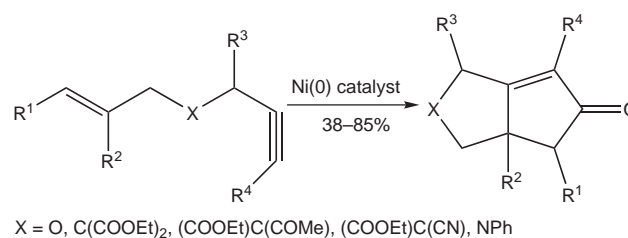


Abstracts

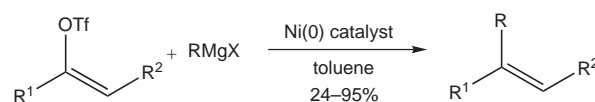
(A) Transfer hydrogenation of imines to the corresponding amines was efficiently catalyzed by a Ni(0)–NHC (N-heterocyclic carbene) complex. Using this catalyst, a variety of aldimines and ketimines were reduced in good to excellent yields under mild conditions.²



(B) Buchwald and Zhang³ reported a Ni(0)-catalyzed process for the transformation of enynes to bicyclic cyclopentenones. This method is tolerant of a variety of functional groups including esters, ketones, nitriles, ethers, and amines. It is also more effective with more highly substituted olefins than is the corresponding titanium procedure.



(C) The Ni(0)-catalyzed cross-coupling of vinyl triflates with alkyl Grignard reagents have been achieved in good to excellent yield by Busacca and co-workers. The effects of triflate substitution, solvent and especially ligands have been investigated.⁴



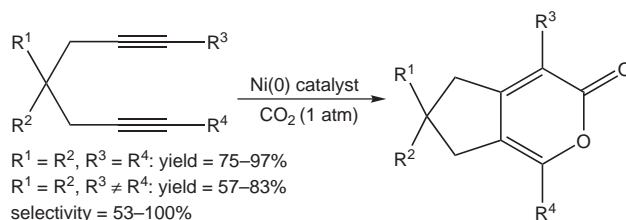
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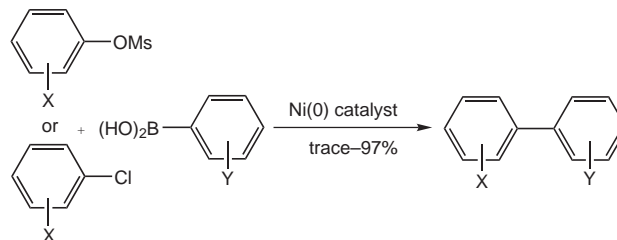
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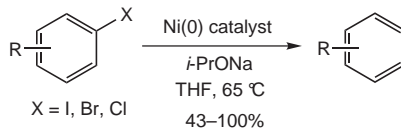
(D) Louie and co-workers used Ni(0)–imidazolylidene complexes to catalyze the coupling reactions of various symmetrical diynes with CO₂ under mild conditions to produce pyrones.^{5a} They later reported the Ni(0)-catalyzed cycloaddition of CO₂ with various asymmetrical diynes to afford regioisomeric mixtures of pyrones.^{5b}



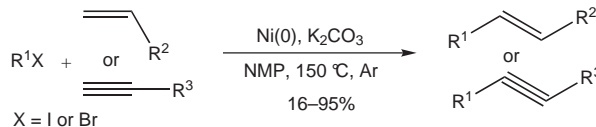
(E) The cross-coupling reaction of aryl mesylates or chloroarenes with arylboronic acids proceeded efficiently in the presence of a Ni(0) catalyst and K₃PO₄, and various biaryls were synthesized in high yields.⁶



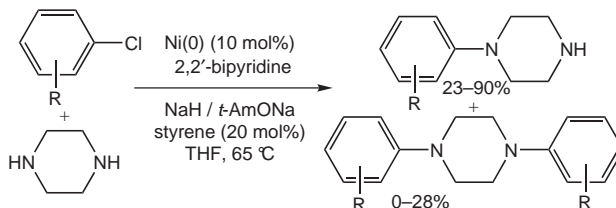
(F) Dehalogenation of aryl halides was efficiently performed in refluxing THF using a catalytic combination composed of Ni(0)–NHC–β-hydrogen-containing alkoxide. A Ni(0)–IMes–HCl–(*i*-Pr)ONa combination proved to be efficient for the dehalogenation of aryl chlorides, bromides, and iodides in short reaction times and under mild conditions.⁷



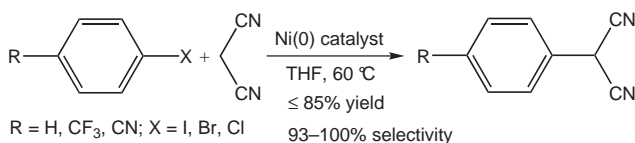
(G) Some stable Ni(0) catalysts, such as Ni[P(OPh)₃]₄ and Ni[P(OEt)₃]₄, were employed to efficiently promote the Heck reactions of aryl and vinyl halides with olefins and alkynes.⁸



(H) The selective synthesis of *N*-aryl- or *N,N'*-diarylpiperazines and trimethylene (bis)piperidines from the corresponding diamines and aryl chlorides was achieved using a catalyst combination of Ni(0) associated to 2,2'-bipyridine. The Ni(0)/2,2'-bipyridine catalyst is also effective for the sequential arylation of piperazine.⁹



(I) A Ni(0) catalyst was used for the direct arylation of malononitrile, a b-difunctionalized compound, from halogenated aromatic substrates. The catalytic system is quite simple: Ni(PPh₃)₃, generated in situ from NiBr₂(PPh₃)₂, PPh₃ and zinc. Good yields and excellent selectivities have been obtained in *α*-arylmalononitriles from iodobenzene, but also from bromo- or chloro-aromatic substrates.¹⁰



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