

Nickel-Catalyzed Heck Reaction

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Received: 30.12.2022

Accepted after revision: 21.02.2023

Published online: 13.03.2023 (Version of Record)

DOI: 10.1055/s-0042-1751432; Art ID: SO-2022-12-0086-SPOT



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Key words alkenes, aryl halides, coupling, Heck reaction, nickel

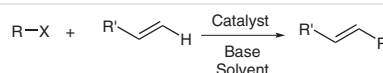
The Heck reaction is a chemical reaction for creating C–C bonds between alkenes and aryl halides in the presence of a suitable catalyst.¹ It is widely used in various conversions, synthesis of intermediates, natural products, and biologically active compounds. Traditionally, a suitable catalyst in the presence of base is required for Heck¹ coupling reaction as shown in Scheme 1. The steps² involved in the plausible mechanism initiates with the activation of catalyst. The electrophilic moiety undergoes oxidative addition to produce an intermediate, which further go through olefin addition. This step is followed by migratory insertion, β -hydride elimination, and regeneration of the catalyst.³ Apart from the decisive use of palladium catalysts for this reaction, propitious results are also being revealed by researchers for the newly customized nickel-based catalysts from last few years.⁴ Switching the metal from Pd to Ni has shown improved and distinctive selectivity in certain cases. This owes to the unique behavior of nickel as a transition metal to entwine with other systems.⁵ Nickel metal salts, its complexes⁶ along with Ni bimetallic systems,⁷ alloys, and Ni nanoparticles⁸ lead to extensive catalytic applicability. Nickel catalysts along with phosphine-based ligands were also extensively used by researchers for Heck reaction.⁹

Various methods for the preparation of the catalysts can be accessed from the indicated references. New protocols designed with nickel catalysis show tolerability with different terminal alkenes and aryl halides. Although employing Nickel as catalyst showed some unacceptance in β -hydride



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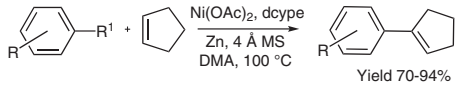
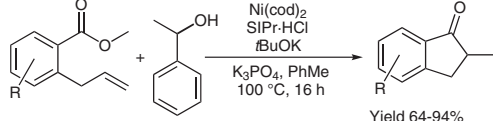
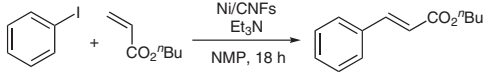
Scheme 1 General Heck coupling reaction

elimination step of Heck reaction, recent developments¹⁰ have reported the smooth behavior of Ni catalysts overcoming the difficulty. Its earth abundance, low cost, and non-toxic nature further help in promoting green methodologies. Some recent advances of this area are concisely reported in review.⁴

The interesting and diverse results reported so far for the application of Ni-based catalysts to Heck reaction have captured the interest of synthetic chemists. Table 1 presents recent protocols involving diversified forms of nickel (a non-noble metal) complexes as catalyst.

Table 1 Nickel-Catalyzed Heck Coupling Reactions

<p>(A) Liu <i>et al.</i>⁵ discovered a new synergism of three catalytic cycles involving photoredox steps, sulfinate catalysis, and various transition states of Ni. Even different aryl/heteroaryl bromides reacted well with styrenes and electron-withdrawing alkenes to afford the large series of desired products.</p>	<p>Yield 36-83%</p>
<p>(B) Ligand-free Ni and Pd nano alloy system heterogenized with polymer base (ABPBI) was designed and studied for Heck reaction. This catalytic system demonstrated enhanced properties taking varied aryl iodides, styrene, as well as ethyl acrylate. Cy₂NMe was proved as the base of choice in comparison to K₂CO₃ and NaOAc in terms of yields using PEG-400 as solvent.¹¹</p>	<p>Yield 58-89%</p> <p>R = H, 4-CH₃O, 4-CF₃O, 4-F, 4-Cl, 2-CH₃, 2,4-F R¹ = COOC₂H₅, C₆H₅</p>
<p>(C) A superior system by merging the properties of Ni and Pd was investigated by taking various ligands to acquire high yields for Heck reaction. Redox mechanism has seemingly occurred where Pd(II) reduced to Pd(0) as Ni complex transfers an electron.¹²</p>	<p>Yield 52-87%</p> <p>R = H, 4-CH₃O, 4-CH₃, 4-Cl, 4-OH, 1-Nap, 4-C₆H₅ R¹ = COOC₂H₅, C₆H₅</p>
<p>(D) Zhao <i>et al.</i>¹³ developed a new catalyst with bulky N-heterocyclic carbene and Ni^I (Ni-1) and utilized it successfully under basic conditions to furnish tri-substituted C=C bonds by reaction of styrenes with benzyl chlorides. The authors claimed the reaction to show significant regio- and <i>trans</i>-selectivities.</p>	<p>Yield 67%</p> <p>R = B(OR)₂, Ar, NAr</p> <p>branched-selective → [R-CH(Ar)-CH=CH₂] → <i>trans</i>-selective</p>
<p>(E) For the synthesis of substituted quinoline compounds, a simple method showing splendid catalytic activity of Ni(cod)₂ in the combination of IPr-HCl ligand was unveiled by Lin and co-workers.¹⁴ Employing NaOt-Bu as the best base in terms of product yields, mesitylene proved to be a good solvent.</p>	<p>Yield 40-71%</p> <p>IPr-HCl = </p> <p>R = H, 5-CH₃, 4-CH₃, 3,5-(CH₃)₂ R¹ = C₆H₅, 3-CH₃C₆H₄, 4-CH₃C₆H₄, 3-CH₃OC₆H₄, 3-FC₆H₄, 4-FC₆H₄, 4-ClC₆H₄, 3-thiophenyl, CH₃</p>
<p>(F) Considering the exceptional properties of bimetallic nanostructures, the Metkazini group¹⁵ developed and used Ni₄Cu@CNOs for the Heck reaction. Synergic effects of Ni nanoparticles with mercury lamp irradiation endowed excellent results at room temperature taking water as solvent. Even without the requirement of any hazardous ligand, the catalyst showed high recyclability with reduced reaction time and energy.</p>	<p>Yield 65-99%</p> <p>R = H, 4-OCH₃, 4-NO₂, 3-CN, 3-NO₂, X = I, Cl, Br Y = H, COOCH₃</p>
<p>(G) Zeng and co-workers¹⁶ have explored the use of a series of carbonates and sulfamates in Heck reaction which has been effectively accelerated by Ni catalyst taking PhBPE as ligand and Zn as reductive metal.</p>	<p>Yield 48-99%</p> <p>X = Boc, SO₂N(CH₃)₂</p>

<p>(H) Zhou <i>et al.</i>¹⁷ developed nickel complexes with highly donating ligands like dcype, and PhBPE as distinctly effective catalysts for the Heck reaction. Cycloalkene along with the use of strongly reactive aryl/heteroaryl triflates, aryl mesylates, and tosylates found to be well adapted to the reaction conditions.</p>	 <p>Yield 70-94%</p> <p>R = H, CH₃, C₂H₅, 3,5-(CH₃)₂, 2,5-(CH₃)₂, C₆H₅, 3-CH₃OC₆H₄, 2-CH₃OC₆H₄, 3-<i>t</i>Bu, 4-<i>t</i>Bu, 3-F, 4-F, 3-CF₃, 4-CF₃, 4-COOC₂H₅, 4-CN, 2-COOCH₃, 3-OC₆H₅ R¹ = OTs, OMs, OTf</p>
<p>(I) Variably substituted methyl <i>ortho</i>-allyl benzoate has been analyzed as effective electrophile with 1-phenylethanol to synthesize cyclic products. Zheng <i>et al.</i>¹⁸ have devised mild reaction conditions to carry out such transformation taking Ni catalyst and K₃PO₄ as base through Heck reaction.</p>	 <p>Yield 64-94%</p> <p>R = H, 4-CH₃, 5-CH₃, 6-CH₃, 3-F, 4-F, 4,5-(F)₂, 4-CH₃O, 5-CH₃, 4,5-(CH₃O)₂, 5-CF₃</p>
<p>(J) Bai research group¹⁹ constructed three dimensional Ni carbon nanofibers (Ni/CNFs) and explored it as heterogeneous catalyst for Heck coupling reaction. Iodobenzene and <i>n</i>-butyl acrylate reacted successfully taking small amount of catalyst Ni/CNFs and Et₃N as base in <i>N</i>-methylpyrrolidone solvent to furnish butyl cinnamate with good product selectivity.</p>	

Conflict of Interest

The authors declare no conflict of interest.

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