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Nickel-Catalyzed Heck Reaction

Pragya Gahlot[a]
Kavita Mittal[*b]

[a] Sri Venkateswara College, University of Delhi, Benito Juarez Marg, New Delhi 110021, India
pgahlot@svc.ac.in
[b] Acharya Narendra Dev College, University of Delhi, Govindpuri, New Delhi 110019, India
kavitamittal@andc.du.ac.in

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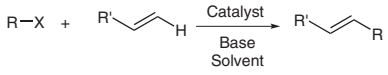
The Heck reaction is a chemical reaction for creating C–C bonds between alkenes and aryl halides in the presence of a suitable catalyst.[1] It is widely used in various conversions, synthesis of intermediates, natural products, and biologically active compounds. Traditionally, a suitable catalyst in the presence of base is required for Heck[1] coupling reaction as shown in Scheme 1. The steps[2] 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 complexes[6] along with Ni bimetallic systems,[7] alloys, and Ni nanoparticles[8] 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 elimination step of Heck reaction, recent developments[10] 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.

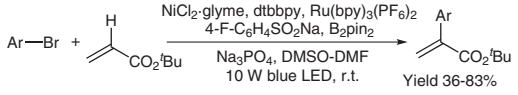
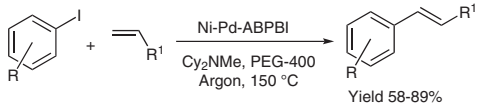
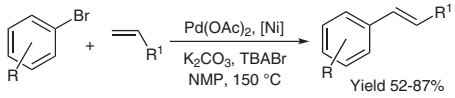
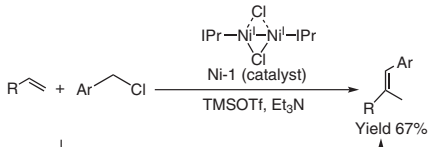
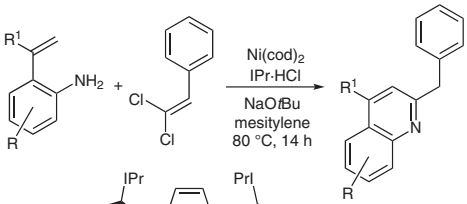
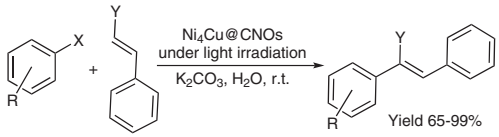
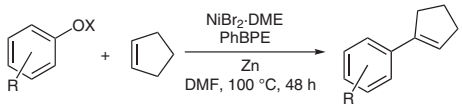
Kavita Mittal completed PhD (2008) from the University of Delhi, India. She is currently teaching as assistant professor at Acharya Narendra Dev College, University of Delhi. She has 14 years of teaching experience at undergraduate level. Her research interest includes green synthesis of heterocyclic compounds and exploring different catalysts.

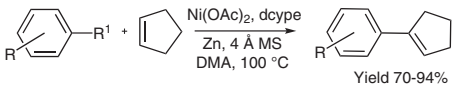
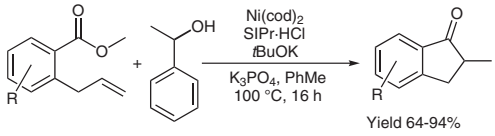
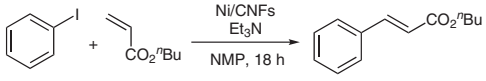
Pragya Gahlot holds a PhD in chemistry from University of Delhi, which she earned in 2009 for her research on protein–ligand interactions study. She is working as an assistant professor at Sri Venkateswara College (University of Delhi) for 15 years teaching physical chemistry at undergraduate level. Her research interests include docking, drug designing, and QSAR.



Scheme 1 General Heck coupling reaction

Table 1 Nickel-Catalyzed Heck Coupling Reactions

(A) Liu *et al.*[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.	
(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. Cy_2NMe was proved as the base of choice in comparison to K_2CO_3 and NaOAc in terms of yields using PEG-400 as solvent.[11]	 R = H, 4-CH_3O, 4-CF_3O, 4-F, 4-Cl, 2-CH_3, 2,4-F R^1 = $COOC_2H_5$, C_6H_5
(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]	 R = H, 4-CH_3O, 4-CH_3, 4-Cl, 4-OH, 1-Nap, 4-C_6H_5 R^1 = $COOC_2H_5$, C_6H_5
(D) Zhao *et al.*[13] developed a new catalyst with bulky N-heterocyclic carbene and Ni^I (Ni-1) and utilized it successfully under basic conditions to furnish trisubstituted C=C bonds by reaction of styrenes with benzyl chlorides. The authors claimed the reaction to show significant regio- and *trans*-selectivities.	 R = $B(OR)_2$, Ar, NAr
(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 NaO*t*-Bu as the best base in terms of product yields, mesitylene proved to be a good solvent.	 R = H, 5-CH_3, 4-CH_3, 3,5-$(CH_3)_2$ R^1 = C_6H_5, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 3-$CH_3OC_6H_4$, 3-FC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 3-thiophenyl, CH_3
(F) Considering the exceptional properties of bimetallic nanostructures, the Metkazini group[15] developed and used Ni_4Cu@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.	 R = H, 4-OCH_3, 4-NO_2, 3-CN, 3-NO_2, X = I, Cl, Br Y = H, $COOCH_3$
(G) Zeng and co-workers[16] 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.	 X = Boc, $SO_2N(CH_3)_2$

(H) Zhou *et al.*[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.	 R = H, CH_3, C_2H_5, 3,5-$(CH_3)_2$, 2,5-$(CH_3)_2$, C_6H_5, 3-$CH_3OC_6H_4$, 2-$CH_3OC_6H_4$, 3-*t*Bu, 4-*t*Bu, 3-F, 4-F, 3-CF_3, 4-CF_3, 4-$COOC_2H_5$, 4-CN, 2-$COOCH_3$, 3-OC_6H_5 R^1 = OTs, OMs, OTf
(I) Variably substituted methyl *ortho*-allyl benzoate has been analyzed as effective electrophile with 1-phenylethanol to synthesize cyclic products. Zheng *et al.*[18] have devised mild reaction conditions to carry out such transformation taking Ni catalyst and K_3PO_4 as base through Heck reaction.	 R = H, 4-CH_3, 5-CH_3, 6-CH_3, 3-F, 4-F, 4,5-$(F)_2$, 4-CH_3O, 5-CH_3, 4,5-$(CH_3O)_2$, 5-CF_3
(J) Bai research group[19] constructed three dimensional Ni carbon nanofibers (Ni/CNFs) and explored it as heterogeneous catalyst for Heck coupling reaction. Iodobenzene and *n*-butyl acrylate reacted successfully taking small amount of catalyst Ni/CNFs and Et_3N as base in *N*-methylpyrrolidone solvent to furnish butyl cinnamate with good product selectivity.	

Conflict of Interest

The authors declare no conflict of interest.

References

(1) Heck, R. F. *Org. React.* **1982**, *27*, 345.
(2) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.
(3) Alisha, M.; Philip, R. M.; Anilkumar, G. *Eur. J. Org. Chem.* **2022**, e202101384.
(4) Bhakta, S.; Ghosh, T. *Adv. Synth. Catal.* **2020**, *362*, 5257.
(5) Liu, K.; Leifert, D.; Studer, A. *Nat. Synth.* **2022**, *1*, 565.
(6) Lin, C.; Chen, S.; Wang, Y.; Gao, F.; Shen, L. *Org. Chem. Front.* **2022**, *9*, 608.
(7) Zhou, L.; Wang, R. B. *React. Kinet., Mech. Catal.* **2022**, *135*, 3243.
(8) Bhakta, S.; Ghosh, T. *ChemCatChem* **2021**, *13*, 828.
(9) Lv, H.; Kang, H.; Zhou, B.; Xue, X.; Engle, K. M.; Zhao, D. *Nat. Commun.* **2019**, *10*, 5025.
(10) Huang, X.; Teng, S.; Chi, Y. R.; Xu, W.; Pu, M.; Wu, Y. D.; Zhou, J. S. *Angew. Chem. Int. Ed.* **2021**, *60*, 2828.
(11) Patil, V. P.; Kashid, A. A.; Solanki, B. S.; Kharul, U. K.; Iyer, S. *J. Chem. Sci.* **2021**, *133*, 8.
(12) Kashid, A. A.; Patil, D. J.; Mali, R. D.; Patil, V. P.; Neethu, T. V.; Meroliya, H. K.; Waghmode, S. A.; Iyer, S. *Catal. Lett.* **2021**, *151*, 353.
(13) Zhao, Y.; Liu, C. F.; Lin, L. Q. H.; Chan, A. S. C.; Koh, M. J. *Angew. Chem. Int. Ed.* **2022**, *61*, e–202202674.
(14) Lin, J.; Wu, C.; Tian, X. *Org. Lett.* **2022**, *24*, 4855.
(15) Mohammadi Metkazini, S. F.; Khorsandi, Z.; Heydari, A.; Varma, R. S. *ACS Sustain. Chem. Eng.* **2021**, *9*, 14061.
(16) Zeng, X.; Zhang, Q.; Wu, X.; Zhang, J.; Zhang, X.; Huang, X. *Chin. J. Org. Chem.* **2022**, *42*, 2981.
(17) Zhou, J. S.; Huang, X.; Teng, S.; Chi, Y. R. *Chem. Commun.* **2021**, *57*, 3933.
(18) Zheng, Y.; Newman, S. G. *Angew. Chem.* **2019**, *131*, 18327.
(19) Wang, W.; Bai, J.; Wang, J.; Li, C. *Appl. Surf. Sci.* **2019**, *465*, 82.