## Journal Pre-proofs

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## **Graphical Abstract**





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# First Cp\*Co(III)-Catalyzed Mizoroki-Heck Coupling Reactions of Alkenes and Aryl bromide/Iodide

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#### ARTICLE INFO

#### ABSTRACT

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Keywords: Mizoroki-Heck coupling C-C bond formation Co(III) Metal carbonyl A Cp\*Co(CO)I<sub>2</sub> catalyzed Mizoroki-Heck coupling of alkenes and aryl halide is established at feasible reaction conditions. The Cp\*Co(III) catalyst excellently work to couple the aryl iodide and alkene, and produce up to 94% yield of the coupling product. In case of the coupling of aryl bromide and alkene, slightly reduced activity of the catalyst was observed, and moderate to good yield of the product was obtained. Apart from functionally different styrene, the catalyst was also able to activate the acrylates, which seems difficult to be activated by other reported metal complexes. The coupling proposed herein is tolerant a wide variety of aryl halides, stryenes, and acrylates enable to form C-C bond using inexpensive metal in catalysis. Hence, the present catalyst is highly economical, consists a non-endangered metal and is highly efficient for Heck coupling reaction. Moreover, the cobalt metal in high oxidation state (+3) is not much explored for the C-C cross-coupling reactions.

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The Heck coupling is a profoundly noteworthy reaction methodology for the formation of new C-C bonds, since, it is one of the most common methods which allows coupling of chlorides, bromides, and iodides with alkyl and aryl-substituted olefins.<sup>1-2</sup> This reaction has diversified applications which includes the synthesis of biologically active molecules,<sup>3</sup> natural products,<sup>4-6</sup> fine chemicals, active pharmaceutical ingredients (APIs)7-9 and various novel polymeric materials.<sup>10</sup> The catalysts designed and widely used for Heck reaction mostly consist of Nheterocyclic carbenes,<sup>11-15</sup> phosphines<sup>16-17</sup> and palladacycle<sup>18-19</sup> systems. Heck reaction has significant applications in organic and materials synthesis.<sup>20</sup> However, even in present scenario most of the reaction methodologies rely on palladium<sup>21-24</sup> or nickelbased catalytic systems.<sup>25</sup> Significant drawbacks such as toxicity, expensiveness, sensitivity for air and moisture of best known catalysts restrict their application in scalable synthesis. Hence there is a huge demand to address all these issues and replace the noble metals with stable, economical and non-endangered metal based complexes.

In the last decade, various 3d transition metals have been reported in the literature as potential catalysts for Heck reaction. The Fe(II) and Fe(III) complexes<sup>26, 27</sup> were identified as active catalysts for the Heck reactions as shown in Scheme 1. In 2015, Mankad and coworker used Na[FeCp(CO)<sub>2</sub>] complex as a photocatalyst for Heck reaction.<sup>28</sup> In 2017, Thomas and coworkers reported the use of FeCl<sub>2</sub> with Na<sub>2</sub>CO<sub>3</sub> for Heck coupling reaction.<sup>29</sup> Hajipour and coworkers have also reported a reusable FeCl<sub>3</sub> based heterogeneous catalyst for the Heck reaction.<sup>30</sup>



#### Scheme 1. Iron Catalyzed Heck Coupling Reactions

Apart from Fe metal, Ni complexes were also found to be active for Heck coupling as shown in Scheme 2. In this context, Inamoto and coworkers have reported an *in situ* complexation and catalysis by Ni(acac)<sub>2</sub> and NHC ligand.<sup>31,32</sup> Further, Ni(OAc)<sub>2</sub> with PPh<sub>3</sub> ligand is used by Zhao and coworkers.<sup>33</sup> Norrby and coworkers have also reported Ni(COD)<sub>2</sub> catalyst for similar transformation reactions.<sup>34</sup> Moreover, in 2009, Ni nanoparticles were used as catalysts for the Heck coupling reaction.<sup>35</sup>



#### Scheme 2. Nickel-Catalyzed Heck Coupling Reactions

Recently, cobalt-catalyzed organic transformations have attracted adequate attention, due to the easy availability, environmental benignity, non-toxicity, inexpensiveness and stability of the catalysts at room temperature. Thus, cobalt complexes are one of the possible alternates to 4d and 5d transition metals, which have the ability to fulfil the immediate demand for coupling reactions (Scheme 3). In this context, Oshima and coworkers have reported a  $CoCl_2(DPPh)$  complex with TMSCH<sub>2</sub>MgCl for Heck coupling.<sup>36</sup> In 2007, Bao and coworkers have reported Co nanoparticles for the similar reaction under ligand-free conditions.<sup>37</sup> Shao and coworkers used a flower like Co nano structure in presence of K<sub>2</sub>CO<sub>3</sub> for the Heck reaction.<sup>38</sup> Carriera and coworkers have reported a Co(III)

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reactions were performed under blue LED light source.<sup>39</sup> Two more reports, i.e. one in 2012 by Li and coworkers, and other in 2015 by Hajipour and coworkers, have used Co-B alloy and multi-walled carbon nanotubes (MWCNT) supported Co-NHC complex as a catalyst for Heck reactions.<sup>40,41</sup>



Scheme 3. Cobalt Catalyzed Heck Coupling Reactions

The metal carbonyls have high catalytic potential and several organic transformations has been reported with various metal carbonyls in recent past.<sup>42-47</sup> Matsunaga and Kanai have reported the Cp\*Co(CO)I<sub>2</sub> catalyst for C–H bond activation and gained significant attention due to the unique selectivity and reactivity of this carbonyl complex.<sup>48</sup> To the best of our knowledge, Cp\*Co(CO)I<sub>2</sub> complex is not yet explored for coupling reactions. After having some preliminary success on the Cp\*Co(III) complex for Heck reaction, it is worthy to explore the detail investigation. Herein, we report first Cp\*Co(CO)I<sub>2</sub> catalyzed coupling reaction of styrene with aryl halides in the presence of base K<sub>3</sub>PO<sub>4</sub> and TBAB as oxidant (Scheme 4).



Scheme 4. Cp\*Co(CO)I2 catalyzed Heck coupling reaction

The selection of catalyst is a necessary prerequisite for the catalysis. Relevant primary optimization indicates that Cp\*Co(III) complex works well for the Heck coupling of alkene and aryl halides (Table 1). Various derivatives of aryl halides and acrylates were examined in the presence of Cp\*Co(CO)I<sub>2</sub>, base oxidant TBAB. Almost nil conversion was  $(K_3PO_4)$  and observed in the absence of base; hence, base is found to be an essential requisite for the studied Heck coupling reaction. For the base optimizations, various bases including Na<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH, KOH were used (Table 1, entry 6-10), and K<sub>3</sub>PO<sub>4</sub> was found to be the suitable base for the present transformation reaction. However, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> also bring a satisfactory vield in comparison to NaOH and KOH but did not match the efficiency of K<sub>3</sub>PO<sub>4</sub>. Here, 2 equivalents of K<sub>3</sub>PO<sub>4</sub> was found to be highly suitable for optimum transformation. The amount of base directly affects the rate of transformations as well as the yield of the coupling product. By decreasing the amount of base from 2 equivalents, corresponding decrease in the rate of reaction as well as the yield of coupling product was observed. While increasing the amount of base does not affect the reaction productivity. Among several solvents ranging from non-polar toluene, para-xylene to polar N, N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and 1,4-Dioxane, DMF was found to be highly suitable for the present reaction (Table 1, Entry 11-14). The presence of TBAB was also found to be an essential requisite for the faster and better conversion. Trace amount of product was obtained at 50 °C, and by gradually increasing the temperature up to 120 °C, significantly increased yield of the product was obtained (Table 1, Entry 2-6). Most of the optimizations were performed at 120 °C temperature and the catalyst Cp\*Co(CO)I<sub>2</sub> was found to be highly stable. The performance of the catalyst at such a high temperature reflects its robustness. Here 20 mol % of catalyst was found to be suitable

mol% of the catalyst used was reduced (Table 1, Entry 17-19)

Table 1. Optimizations of various reaction parameters

Entry	Catalyst	Base	Temp (°C)	Cat. mol %	Solvent	% Yield <sup>a</sup>
1.	Cp*Co(CO)I <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	RT	20	DMF	Trace
2.	$Cp*Co(CO)I_2$	$K_3PO_4$	50	20	DMF	14
3.	$Cp*Co(CO)I_2$	$K_3PO_4$	80	20	DMF	35
4.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	90	20	DMF	48
5.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	100	20	DMF	65
6.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	120	20	DMF	90
7.	Cp*Co(CO)I <sub>2</sub>	$K_2CO_3$	120	20	DMF	68
8.	Cp*Co(CO)I <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	120	20	DMF	64
9.	Cp*Co(CO)I <sub>2</sub>	КОН	120	20	DMF	45
10.	Cp*Co(CO)I <sub>2</sub>	NaOH	120	20	DMF	42
11.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	120	20	ACN	50
12.	Cp*Co(CO)I <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	120	20	NMP	65
13.	Cp*Co(CO)I <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	120	20	Dioxane	46
14.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	120	20	Toluene	42
15.	CoBr <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	120	20	DMF	Trace
16.	CoCl <sub>2</sub>	$K_3PO_4$	120	20	DMF	12
17.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	120	15	DMF	72
18.	Cp*Co(CO)I <sub>2</sub>	$K_3PO_4$	120	10	DMF	58
19.	Cp*Co(CO)I <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	120	5	DMF	22

<sup>a</sup>Isolated Yields, Styrene (1.5 Equiv), Iodobenzene (1 Equiv)

The yield of product with respect to time is presented in figure 1, which shows an immediate increase in the yield of the product in first 18h, which gradually approaches saturation in 24h. However, no further improvement in the yield of product was observed till 30h.



Figure 1. Optimization of reaction time

After the optimized reaction condition, we embark the substrate scope and found that the product yield strictly depends on the type of halides used. Iodo-, bromo- and chloro- arylhalides were used for the reaction. With iodobenzene, the reaction produces exceptional results, while reactions with bromobenzene produced low to average yield. Moreover, the catalyst was found inactive to activate the chlorobenzene for the present Heck reaction. Hence, Iodo- and bromo- benzenes were further explored for Heck coupling with various styrenes (Table 2 and 3).





<sup>a</sup>Isolated Yield, Catalyst (20 mol%), Solvent (DMF), Temp (120 °C), Base (K<sub>3</sub>PO<sub>4</sub>), 24h.

It was observed that the presence of functional groups influences the yield of corresponding product. The electrondonating or withdrawing groups attached on either side (styrene or bromobenzene) affects the product yield to a certain extent. The reaction of bromobenzene with *para*-methyl styrene (Table 2, Entry 2) produces an average yield of 40%, the yield of coupling product was further reduced when para-chloro- and para-flouro styrene were used (Table 2, entry 3-4). Improved yield of 50% of the coupling product was obtained with bulky napthylstyrene (Table 2, entry 5). The aliphatic alkene, i.e. nbutyl acrylate was also explored with bromobenzene, and the average yield of 28% was observed (Table 2, entry 6). The functionalized bromobenzene, i.e. the para-nitro and paramethyl bromobenzene were also tested with styrene to widen the substrate scope, and 30-32% yield of product was obtained (Table 2, entry 7-8). Coupling of para-methyl chlorobenzene and styrene was failed to give significant yield of product. However, trace amount of the coupling product was obtained (Table 2, Entry 9).

The reaction was further explored for different derivatives of iodobenzene and various functionally substituted styrenes, and outstanding yield of 90% of the corresponding coupling product was obtained in the presence of Cp\*Co(III) catalyst (Table 3, entry 1). Using functionalized (*para*-methyl and -methoxy) styrenes, a slightly reduced yield of 80-85% was obtained (Table 3, entry 2-3). Furthermore, a slightly reduced yield of 78% and 75% was obtained for *para*-chloro and -fluoro styrenes, respectively (Table 3, entry 4-5). An excellent yield was recorded with naphthyl styrene (Table 3, entry 6). Moreover, attractive results were obtained when aryl halides and acrylates were taken

and n-butyl acrylate produced a sizeable yield of 82% and 84%, respectively (Table 3, entry 7-8). The reaction of *para*-nitro and *para*-methyl iodobenzene with styrene produced a substantial yield of 76% and 80%, respectively (Table 3, entry 9-10). Further reaction of *para*-nitro iodobenzene with *para*-methyl styrene produced a significant yield of 78% (Table 3, entry11), while with *para*-chloro styrene produced comparatively lower yield of 67% (Table 3, entry 12). A significant yield of 72% was obtained for the reaction of *para*-methyl iodobenzene with para-chlorostyrene (Table 3, Entry 13).

 Table 3.
 Substrate Scope for functionalized styrene with iodobenzene





Entry	Halide	Product	% Yieldª
9	O <sub>2</sub> N-	O <sub>2</sub> N	76%
10	H <sub>3</sub> C-	H <sub>3</sub> C	80%
11	O <sub>2</sub> N-	O <sub>2</sub> N-CH <sub>3</sub>	78%
12	O <sub>2</sub> N-		67%
13	H <sub>3</sub> C-	H <sub>3</sub> C-CI	72%

<sup>a</sup>Isolated Yield, Catalyst (20 mol%), Solvent (DMF), Temp (120 °C), Base (K<sub>3</sub>PO<sub>4</sub>), 24h.

A plausible reaction mechanism for Cp\*Co(CO)I<sub>2</sub> catalyzed Heck coupling reaction is proposed and depicted in Figure 2. Here, the reaction is initiated, when the iodine of the complex was abstracted by the base  $K_3PO_4$ .<sup>49-51</sup> This lead to the reduction of Co(III) to (a) Co(I). Further, the activated Cobalt complex undergoes an oxidative addition of halo benzene to form an intermediate (b). Then, the intermediate (b) undergo insertion of alkene via a concerted step to form an intermediate (c) and subsequently gets converted into an intermediate (d). The intermediate (d) reductively eliminated the desired product



**Figure 2.** A plausible mechanism of Co(III) catalyzed Heck coupling reaction

#### Conclusion

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In conclusion, we have developed a facile method to convert a wide range of styrene/acrylates and aryl halides to their corresponding diphenylethene and cinnamates. These compounds are obtained through a well known Mizoroki-Heck reaction catalyzed by a high valent Cp\*Co(III) carbonyl complex. The complex is robust, inexpensive, highly efficient, easy to synthesize, extremely stable under aerobic conditions and work for wide range of functionalized alkene and aryl halides. Moreover, this is the first report of Cp\*Co(CO)I<sub>2</sub> as a catalyst for the Heck coupling reaction.

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#### References

- 1. Mizoroki, T.; Mori, K.; Ozaki, A. Bull. Chem. Soc. Jpn. 1971, 44, 581.
- 2. Heck, R. F.; Nolley, J. P., J. Org. Chem. 1972, 37, 2320.
- 3. S. Tarnowicz-Ligus, A. M. Trzeciak, *Molecules* 2018, 23, 2227
- 4. Gaudin, J. M. Tetrahedron Lett. 1991, 32, 6113.
- Overman, L. E.; Ricca, D. J.; Tran, V. D. J. Am. Chem. Soc. 1993, 115, 2042.
- 6. Tietze, L. F.; Buhr, W. Angew. Chem., Int. Ed. Engl. 1995, 34, 1366.
- 7. Bader, R. R.; Baumeister, P.; Blaser, H. U. *Chimia* **1996**, 50, 99.
- 8. Wu, T. C. US Pat. 5536870, 1996.

- Herkes, Marcel Dekker, New York, **1998**.
  - 10. Sun, L.; Zou, Y.; Liang, Z.; Yu, J.; Xu, R. Polym. Chem. 2014, 5, 471.
  - 11. Herrmann, W. A. Angew. Chem., Int. Ed. 2002, 41, 1290.
  - 12. Bedford, R. B.; Cazin, C. S. J.; Holder, D. Coord. Chem. Rev. 2004, 248, 2283.
  - Nielsen, D. J.; Cavell, K. J.; K. J. Skelton, K. J.; White, A. H. Inorg. Chim. Acta 2006, 359, 1855.
  - 14. Tubaro, C.; Biffis, A.; Gonzato, C.; Zecca, M.; Basato, M. *J. Mol. Catal. A: General* **2006**, 248, 93.
  - Wang, R.; Twamley, B.; Shreeve, J. M. J. Org. Chem. 2006, 71, 426.
  - Affo, W.; Ohmiya, H.; Fujioka, T.; Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K.; Imamura, Y. Mizuta, T.; Miyosh, K. *J. Am. Chem. Soc.* **2006**, 128, 8068.
  - 17. Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K. J. Am. Chem. Soc. 2002, 124, 6514.
  - Dupont, J.; Pfeffer, M.; Spencer, J. Eur. J. Inorg. Chem. 2001, 1917.
  - 19. Bedford, R. B. Chem. Commun. 2003, 1787.
  - 20. Oestreich, M. The Mizoroki-Heck Reaction 2009, John Wiley & Sons, Ltd
  - Calo, V.; Nacci, A.; Monopoli, A.; Detomaso, A.; Iliade, P. Organometallics 2003, 22, 4193.
  - 22. Meier, M. A. R.; Filali, M.; Gohy J. F.; Schubert, U. S. J. Mater. Chem. 2006, 16, 3001.
  - 23. Yeung, L. K.; Crooks, R. M. Nano Lett. 2001, 1, 14.
  - Gopidas, K. R.; Whitesell, J. K.; Fox, M. A. Nano Lett. 2003, 3, 1757.
  - 25. Kwiatkowski, M. R.; Alexanian, E. J. Angew. Chem., Int. Ed. Engl. 2018, 57, 16857
  - Mako, T. L.; Byers, J. A. Inorg. Chem. Front. 2016, 3, 766-790.
  - Loska, R.; Volla, C. M. R.; Vogel, P. Adv. Synth. Catal. 2008, 350, 2859.
  - Waldhart, G. W.; Mankad, N. P. J. Organomet. Chem. 2015, 793, 171.
  - Zhu, K.; Dunne, J.; Shaver, M. P.; Thomas, S. P. ACS Catal. 2017, 7, 2353.
  - Hajipour, A. R.; Abolfathi, P.; Rizi, Z. T. Appl Organometal Chem. 2018, 4353.
  - Inamoto, K.; Kuroda, J.; Danjo, T.; Sakamoto, T. SYNLETT 2005, 10, 1624.
  - Inamoto, K.; Kuroda, J.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T. Organometallics 2006, 25, 3095.
  - Maa, S.; Wang, H.; Gaoc, K.; Zhao, F. J. Mol Catal A: Chemical 2006, 248, 17.
  - Gøgsig, T. M.; Kleimark, J.; Lill, S. O. N.; Korsager, S.; Lindhardt, A. T.; Norrby, P.; Skrydstrup, T. *J. Am. Chem. Soc.* 2012, 134, 443.
  - Zhang, W.; Qi, H.; Li, L.; Wang, X.; Chen, J.; Peng, K.; Wang, Z. *Green Chem.* 2009, 11, 1194.
  - 36. Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K. J. Am. Chem. Soc. 2002, 124, 6514.
  - Zhou, P.; Li, Y.; Sun, P.; Zhou, J.; Bao J. Chem. Commun. 2007, 1418.
  - Qi, H.; Zhang, W.; Wang, X.; Li, H. Chen, J.; Peng, K.; Shao, M. Catal. Commun. 2009, 10, 1178.
  - 39. Weiss, M. E.; Kreis, L. M.; Lauber, A.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2011**, 50, 11125.
  - Zhu, Z.; Ma, J.; Xu, L.; Xu, L.; Li, H.; Li, H. ACS Catal. 2012, 2, 2119.
  - 41. Hajipour, A. R.; Khorsandi, Z. Catal. Commun. 2016, 77, 1.
  - 42. Joshi, R. K.; Satrawala, N.; *Tetrahedron Lett.* 2017, 58, 2931.

- M. *J. Organomet. Chem.* **2010**, 695, 2687. 44. Mathur, P.; Joshi, R. K.; Rai, D. K.; Jha, B.; Mobin, S. M.
- *Dalton Trans.* 2012, 41, 5045.
- 45. Mathur, P.; Rai, D. K.; Joshi R. K.; Jha, B.; Mobin, S. M. Organometallics **2014**, 33, 3857.
- Mathur, P.; Jha, B.; Raghuvanshi, R.; Joshi, R. K.; Mobin. S. M. J. Organomet. Chem. 2012, 7, 712.
- 47. Jha, B. N.; Raghuvanshi, R.; Joshi R. K.; Mobin, S. M.; Mathur, P. Appl Organometal Chem. 2017; e3805.
- Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. Chem. Eur. J. 2013, 19, 9142.
- 49. Wang, S.; Chen, S.; Yu, X. Chem. Commun. 2017, 53, 3165.
- 50. Yoshinoa, T.; Matsunaga, S. Adv. Synth. Catal. 2017, 359, 1245.
- 51. Lerchen, A.; Knecht, T.; Daniliuc, C. G.; Glorius, F. *Angew. Chem. Int. Ed.* **2016**, 55, 15166.

### Highlights

- 1. First report of  $Cp*Co(CO)I_2$  catalyzed Mizoroki-Heck coupling reaction.
- 2. Catalyst works for wide range of functionally substituted styrene/acrylates.
- 3. Arylbromide and aryliodide both found active for the heck coupling reaction.
- 4. Methodology enables to achieve efficient results via a cost effective catalysis.

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