EurJIC
European Journal of Inorganic Chemistry

Chemistry Europe
European Chemical Societies Publishing

Accepted Article

Title: Half-Sandwich (η6-Benzene)Ru(II) Complex of Picolyl Functionalized N-Heterocyclic Carbene as an Efficient Catalyst for Thioether Directed C-H Alkenylation of Arenes

Authors: Sangeeta Kumari, Charu Sharma, Avinash K Srivastava, Naveen Satrawala, Kamal N Sharma, and Raj Kumar Joshi

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.202100501

Link to VoR: https://doi.org/10.1002/ejic.202100501

WILEY-VCH

COMMUNICATION WILEY-VCH

Half-Sandwich (η^6-Benzene)Ru(II) Complex of Picolyl Functionalized *N*-Heterocyclic Carbene as an Efficient Catalyst for Thioether Directed C-H Alkenylation of Arenes

Sangeeta Kumari,[+] Charu Sharma, Avinash K. Srivastava, Naveen Satrawala, Kamal N. Sharma,[+] Raj K. Joshi*

This manuscript is dedicated to Prof. Christian Bruneau, Institut des Sciences Chimiques - ISCR, Université de Rennes, France for his contribution to catalysis.

Department of Chemistry, Malaviya National Institute of Technology, Jaipur – 302017, Rajasthan, INDIA. E-mail: rkjoshi.chy@mnit.ac.in
+ equal contribution

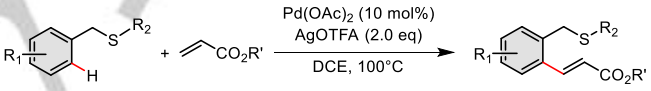
Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

Abstract: In this report, a half-sandwich (η^6-benzene)Ru(II) complex of picolyl functionalized H-heterocyclic carbene was synthesized and efficiently used for the alkenylation arenes through thioether directed C-H bond activation. The thioether functionality of the substrate directed a selective *ortho*-vinylation through C-H bond activation. Moreover, reaction significantly works under mild reaction conditions than the previously reported ones which use the precious noble metal catalyst including the Pd(II), Rh(III), and Ir(III). Broad substrate scope using several benzyl thioethers and vinyl were found to be well tolerated for the present catalytic reaction to produces moderate to good yields of the desired products. Moreover, it is the first report where a Ru-based catalyst was used for the alkenylation of thioethers.

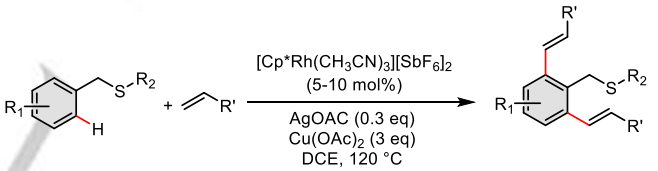
Introduction

C-H bond functionalization is a cost-effective and efficient method for constructing complex molecules like natural or pharmaceutical products, [1] which has attracted much attention in recent years.[2-4] Implementation of a directing group on the substrate is an effective and robust approach for enhancing the efficiency and regulating the selectivity of C-H activations.[5] Literature indicates that Nitrogen[6-8], Oxygen[9-11], and Phosphorous based ortho directing groups are quite common and frequently used, but, the sulfur base directing group has received very less attention, despite the fact that sulfur-containing moieties are building blocks for a large number of drug compounds those are frequently used for pharmaceutical or agrochemical applications.[12-13] As per a recent revelation, thioethers are an effective directing group for C-H alkenylation, however, the use of thioether as a directing group is challenging due to the tendency of poisoning of the transition metals. Nevertheless, it is worthy to use thioether as a directing group, as under reductive conditions these groups can be easily removed.[14] Furthermore, thioether could go through a variety of useful transformations[15-17], sulphur is also found in various useful molecules including functional material, organocatalyst[18-21], and water reduction catalyst.[22-23] Zhang and co-workers reported a Pd catalyzed C-H bond alkenylation of thioethers in 2012 (Scheme 1).[24] Furthermore, Shi reported an Rh catalyst for C-H olefination of benzyl thioether (Scheme 2) in 2013.[25]

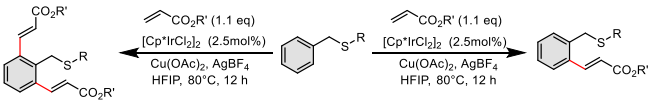
Recently in 2019, Wang *et. al*. reported Ir catalyzed thioether-directed mono and di-alkenylation of arene C-H bonds (Scheme 3) [26].



Scheme 1. Pd catalyzed *o*-vinylation via C-H activation by Zhang *et.al* (2012)



Scheme 2. Rh catalyzed ortho-vinylation via C-H activation by Shi *et.al* (2013)

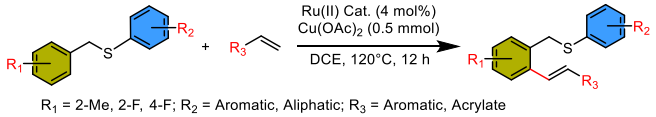


Scheme 3. Ir catalyzed mono and di-vinylation via C-H activation by Wang *et.al* (2019)

These reports include the utilization of precious noble metal and expensive additives, hence, a method that consists of much economical metal catalyst and works under mild reaction conditions for a range of substrates is strongly desired for the functionalization of thioethers. Knowing the high catalytic potential of Ru complexes[27], and in the mindset to search a feasible methodology, a half-sandwich Ru(II) complex of picolyl-functionalized *N*-heterocyclic carbene was synthesized and catalytically explored for the thioether directed C-H alkenylation of arenes (Scheme 4). The Ru-catalyst along with copper acetate (co-catalyst) is efficiently working at the mild conditions for broad varieties of substrates. To the best of our knowledge, the use of relatively inexpensive Ru(II) complexes for the C-H alkenylation of arenes with benzyl thioethers using sulfur as a directing group has not been reported so far. As a result, the

ultimate focus of the present research is to make our approach more effective for late-stage activation while keeping it more economical.

Present Work

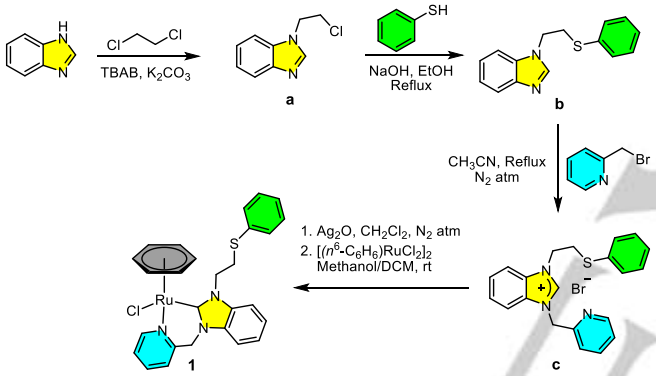


Scheme 4. Ru-catalyzed thioether directed C-H vinylation of arenes.

Results and Discussion

Design, synthesis, and characterization of a Half-Sandwich (η^6-Benzene)Ru(II) Complex of Picolyl-Functionalized N-Heterocyclic Carbene (1):

The methodology used for the synthesis of the Ru-complex (**1**) is depicted in Scheme 5. 1-(2-Chloroethyl)-1*H*-benzimidazole (**a**) and 1-(2-(phenylthio)ethyl)-1*H*-benzimidazole (**b**) were synthesized by using a previously reported procedure.[27]



Scheme 5. Synthesis of picolyl/thioether functionalized benzimidazolium bromide salt (**c**) and half-sandwich (η^6-benzene)Ru(II) complex (**1**)

In the next step, the atom economy reaction of (2-bromomethyl)pyridine with 1-(2-(phenylthio)ethyl)-1H-benzimidazole resulted in *N*-(1-thiophenyl-2-ethyl)-N'-(pyridine-2-ylmethyl)benzimidazolium bromide (c). Thereafter, the Ru(II) complex was synthesized by employing a silver carbene transfer reaction in which **c** was first treated in CH_2Cl_2 with Ag_2O in a N_2 atmosphere at room temperature (in dark), followed by the addition of a methanol suspension of $[\eta^6(C_6H_6)RuCl(\mu\text{-}Cl)]_2$. The orange solid **1** was found to be stable and thermally robust. A singlet observed at 11.02 ppm in the ^{1}H NMR of **c** is related to the highly deshielded proton of precarbene carbon. The absence of this signal in the ^{1}H NMR spectrum of **1** suggests deprotonation of carbene carbon due to the coordination with Ru(II). Furthermore, in comparison to the free ligand (**c**-HBr), the coordination of ligand with Ru(II) produces deshielded NMR signals. The two protons of each methylene group (C-8 and C-9) are not equivalent (anisochronous), even they are not part of a chelate ring, therefore, appeared as four multiplets in ^{1}H NMR. Due to the diastereotopic nature of C-16 methylene protons which are part of the six-membered chelate ring, appeared as two doublets in the proton NMR of **1**. In the ^{13}C NMR, C-16, and the carbons of pyridine and benzimidazole rings have been appeared deshielded as compare to the other carbon atoms of the complex, which further confirm the complexation of the ligand with Ru(II). The presence of Ru in the proximity induces a high magnitude shift in the deshielded region in both ^{1}H and ^{13}C NMR.

Crystallographic analysis of Complex (1).

Complex **1** was found to be soluble in CH_3CN, DMF, and DMSO while sparingly soluble in CH_2Cl_2, CH_3Cl, and CH_3OH and insoluble in diethyl ether and *n*-hexane. The single crystal suitable for X-ray crystallographic analysis were grown in CH_3CN: CH_3OH (3:1) solution under ambient conditions. The analysis of crystallographic data resulted in the following molecular structures of complex **1** (Figure 1). The bidentate coordination mode of the ligand through carbene and nitrogen of the pyridine resulted in a six-membered chelate ring with Ru(II) metal center. The complex form a pseudo-octahedral half-sandwich "piano stool" geometry at Ru center. The Ru−N bond distance was observed at 2.119(4) Å, which is in close agreement to the reported Ru(II) complex of picolyl functionalized NHC.[28] Key crystallographic distances and bond angles are mentioned in Figure 1 and the summary of crystallographic data and structural refinements are outlined in Table S1 (supporting information).

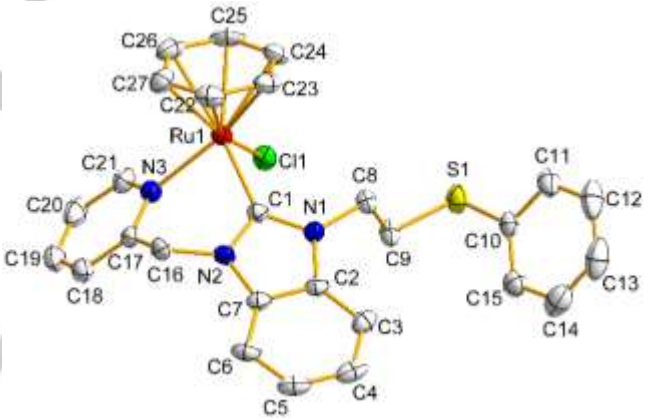


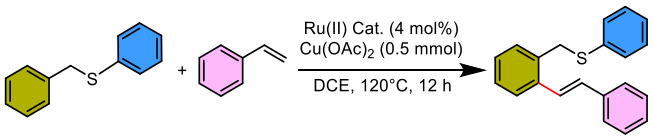
Figure 1. Molecular structure diagram (thermal ellipsoids at 30% probability level) of half-sandwich (η^6-benzene)Ru(II) complex (1); Hexafluorophosphate anion and hydrogen atoms are not shown for the sake of clarity; Key crystallographic distances [Å]: Ru(1)−C(1)$_{NHC}$ 2.034(5), Ru(1)−N(3) 2.119(4), Ru(1)−Cl(1) 2.4309(12); Bond angles [°] N(3)−Ru(1)−Cl(1) 85.72(12), C(1)−Ru(1)−Cl(1) 88.73(13), C(1)−Ru(1)−N(3) 84.24(18), N(1)−C(1)−Ru(1) 132.4(3), N(2)−C(1)−Ru(1) 121.7(3), N(1)−C(1)−N(2) 105.8(4).[CCDC 2085434]

Catalytic investigation of complex 1 for thiol directed C-H alkenylation of arenes:

The study started with the reaction of benzyl phenyl sulfane and styrene in presence of $RuCl_3$ or Ru_3CO_{12} (Table 1, Entry 1,2) in dichloroethane at 120°C, but no transformation was obtained. The desired *o*-vinylation was observed when synthesized Ru(II) complex (**1**) was used as a catalyst with $Cu(OAc)_2$ as an oxidant (Table 1, Entry 3-6). Other oxidants including the $AgSbF_6$, TBHP, TFA, AcOH were also screened in search of better productivity, but none of them works for the reaction. The $Cu(OAc)_2$ was found to be an essential requisite for the reaction, as the reaction under the complete absence of $Cu(OAc)_2$ failed to

produce the desired product. Moreover, 0.5 mmol of the $Cu(OAc)_2$ which bring 59% transformation was found to be an ideal amount for the reaction, and increasing the quantity of $Cu(OAc)_2$ to 1 mmol and 1.5 mmol reduces yields to 49%, and 38%, respectively (Table 1, Entry 7-9). During the Ru-catalyst (**1**) optimization, it was observed that a blank reaction does not form the desired product (Table 1, entry 10), which indicates the role of the Ru-catalyst in facilitating the present transformation. During the optimizations of catalyst amount, it was noted that increasing the amount of catalyst from 2 to 4 mol%, the yield of desire product significantly increased from 23 to 59% respectively, while marginal progress in yield (62% yield) was observed with 6 mol% of catalyst (Table 1, entry 7 and 11-12). Moving further to solvent optimization, below to average yield (28%) was obtained in absence of solvent, but, surprising to us, it decreased to 18% when toluene was used as a solvent. Other solvents such as ethyl acetate, hexane, 1,4- dioxane, and water were also failed to mimic the transformations (Entry 13-18).

Table 1. Optimization Table



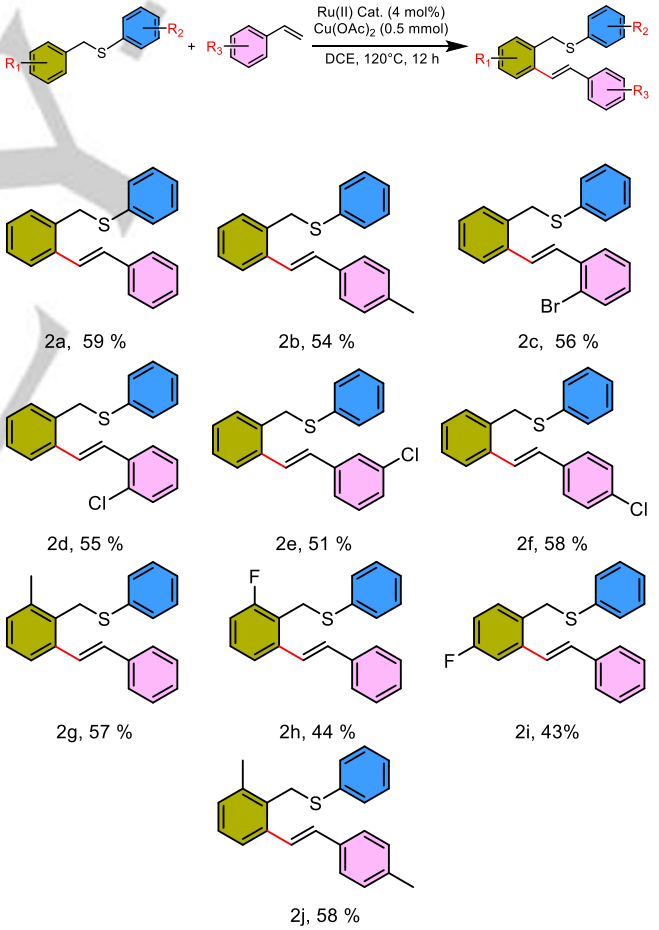
S. No.	Ru(II) Cat. (mol%)	$Cu(OAc)_2$ (mmol)	Solvent	Temp (°C)	Time (h)	Yield[a] (%)
1.	$RuCl_3$ (4)	0.5	DCE	120	24	--
2.	Ru_3CO_{12} (4)	0.5	DCE	120	24	--
3.	4	$AgSbF_6$ (0.5)	DCE	120	24	--
4.	4	TBHP (0.5)	DCE	120	24	--
5.	4	Acetic acid (0.5)	DCE	120	24	--
6.	4	TFA (0.5)	DCE	120	24	--
7.	4	0.5	DCE	120	12	59
8.	4	1	DCE	120	24	48
9.	4	1.5	DCE	120	24	39
10.	--	0.5	DCE	120	24	--
11.	2	0.5	DCE	120	12	23
12.	6	0.5	DCE	120	12	62
13.	4	0.5	--	120	12	28
14.	4	0.5	Toluene	120	12	18
15.	4	0.5	EtOAc	120	12	--
16.	4	0.5	Hexane	120	12	--
17.	4	0.5	Water	120	12	--
18.	4	0.5	Dioxane	120	12	trace
19.	4	0.5	DCE	80	12	29
20.	4	0.5	DCE	100	12	40
21.	4	0.5	DCE	120	24	61

[a]Isolated Yields, *Condition*. Benzylsulfane (0.5 Equiv), Styrene (1 Equiv)

The dichloroethane was the only solvent that shows a 59% transformation with 4 mol% catalysts loading. Temperature optimizations concluded that product formation was started at 80°C and the yield of the product was continues increases until the reaction temperature reaches 120°C (Entry 19-20). The product formation was observed in the initial 6h, but it takes another 6 h to reach the maximum and no further significant changes in the yield were obtained beyond 24h (Table 1, Entry 21).

Substrate Scope. After having the best-optimized reaction conditions, the general scope of *o*-vinylation of arenes was investigated (Table 2). The reaction of benzyl(phenyl)sulfane and styrene produces the desired product in a good amount (2a, 59%). Whereas, a slight variation in the transformation was observed when the electronic nature of the functional group attached with styrene was varied. In the case of the electron-donating group (*p*-methylstyrene) yield was slightly reduced compared to the styrene containing an electron-withdrawing group (2-bromostyrene) [2b and 2c].

Table 2. Substrate scope with respective isolated yields of derivative of benzyl (phenyl) sulfane with various styrene's.



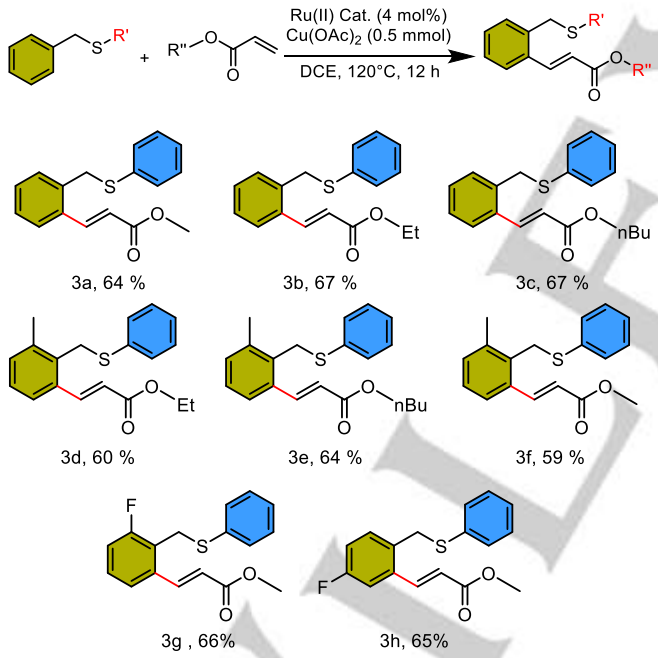
*Isolated yields, Condition. sulfane (0.5 Equiv), Styrene (1 Equiv), $Cu(OAc)_2$ (0.5 mmol) , Ru Catalyst (4 mol%), Solvent: DCE, Temp 120^{0}C, 12h

Furthermore, a slight variation in the transformation was also experienced when the position of the functional group switched from *ortho*- to *meta*- or *para*- position. In the case of chloro substituted styrene, the highest 58% transformation was

obtained with *p*-chlorostyrene, and it reduced to 55% and 51% with changing the substitution to *meta*- and *ortho*- position respectively [2d-2f]. Functional groups present on benzyl group also alter the rate of transformation and a good yield of 57% was obtained for methyl substitution (2g), while 44% yield was obtained for fluoro substitution (2h), and quite similar trends of reactivity were noted for *m*-fluoro benzyl(phenyl) sulfane [2i]. A significant coupling product (2j) was recorded by the reaction of *o*-methylbenzyl(phenyl)sulfane and *p*-methylstyrene.

The substrate scope of the present alkenylation reaction was further explored for acrylates and good yield of desire product obtained with various benzyl(phenyl)sulfane and acrylates (Table 3). A 64 % transformation was recorded by the reaction of benzyl(phenyl)sulfane and methyl acrylate, and it increased to 67% with increasing the chain length of acrylates (3a-3c). All three acrylates were found to be well-tolerated, and provide fairly good yields, however, a slightly reduced transformation was recorded for *o*-methylbenzyl(phenyl)sulfane [3d-3f]. While examining the effect of *o*-flourobenzyl(phenyl)sulfane and *m*-flourobenzyl(phenyl)sulfane with methyl acrylate, almost similar transformations were obtained [3g and 3h]. Here, we found that acrylate is a much compatible coupling partner for alkenylation in comparison to styrene.

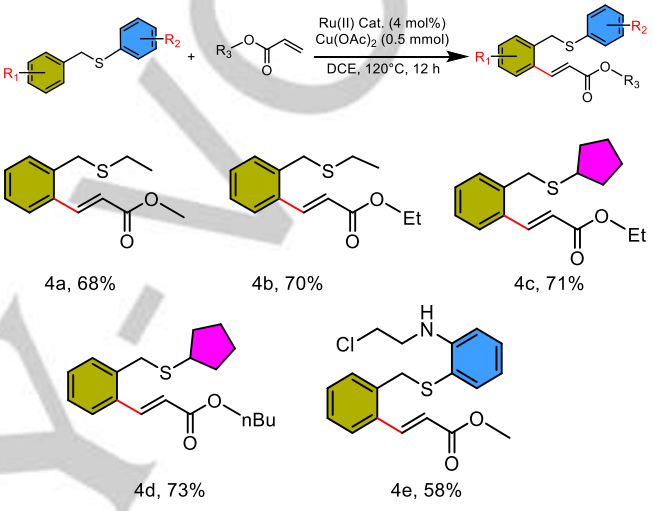
Table 3. Substrate scope of benzyl(phenyl)sulfane with acrylate's



*Isolated Yields, Condition. sulfane (0.5 Equiv), Acrylates (1 Equiv), $Cu(OAc)_2$ (0.5 mmol) , Ru Catalyst (4 mol%), Solvent: DCE, Temp 120^0C, 12h

The general scope of the reaction was further extended and some new benzylsulfanes consisting of the aliphatic and substituted arenes were synthesized by the reaction of benzyl bromide with and thiol derivatives (Table 4). The benzyl(ethyl)sulfane and methyl/s produced fairly good yields of 68% and 70% (4a and 4b). Moreover, benzyl(cyclopentyl)sulfane was also found to be well tolerated with methyl/butylacrylates and shows highly significant transformations of 71% and 73% (4c and 4d) respectively. A highly rigid chloroalkyl functionalized 2-(benzylthio)aniline was also investigated and it was found significantly reactive with methylacrylate to form a good amount of desired alkenylated product (58%, 4e). Here, the formation of 4e is quite unprecedented due to dual transformation in a single step, the C-H activations followed by C-N coupling or vice versa could be the possible steps. Here, solvent dichloromethane participated in the reaction to form the CN bond by the loss of a Cl^- while interacting with NH_2.

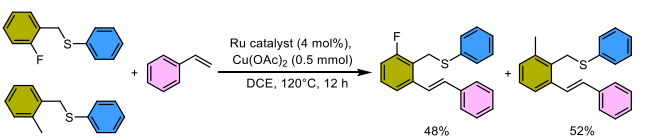
Table 4. Substrate scope of various thioethers with various acrylate's



*Isolated Yields, Condition. sulfane (0.5 Equiv), Acrylates (1 Equiv), $Cu(OAc)_2$ (0.5 mmol) , Ru Catalyst (4 mol%), Solvent: DCE, Temp 120^0C, 12h

Control Experiments.

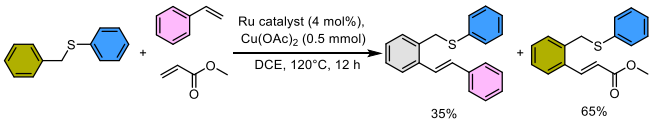
Intramolecular competitive experiments were carried out to evaluate the selectivity towards various alkenes and benzyl thioethers. In this sequence, the very first experiment was performed with a mixture of 2-flourobenzyl(phenyl)sulfane and 2-methylbenzyl(phenyl)sulfane, however, both the sulfane formed the desired product in almost equal amount, but a little more selectivity was shown by 2- methylbenzyl(phenyl)sulfane (Scheme 6). Furthermore, the selectivity trends were retained when investigating the reactivity of aromatic/aliphatic substituted sulfane towards the styrene (Scheme 7).



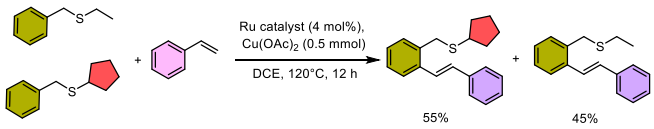
Scheme 6. Selectivity between 2-flouro/2-methylbenzyl(phenyl)sulfane with styrene

Scheme 7. Selectivity between benzyl(phenyl)sulfane and benzyl(ethyl)sulfane with styrene

A significant change in the reactivity was experienced when different alkenes were investigated with benzyl(phenyl)sulfane, and a reasonably good selectivity was obtained for methylacrylate (Scheme 8). Furthermore, the mixture of benzyl(cyclopentyl)sulfane and benzyl(ethyl)sulfane, and styrene shows slightly better selectivity towards benzyl(cyclopentyl) sulfane (Scheme 9).

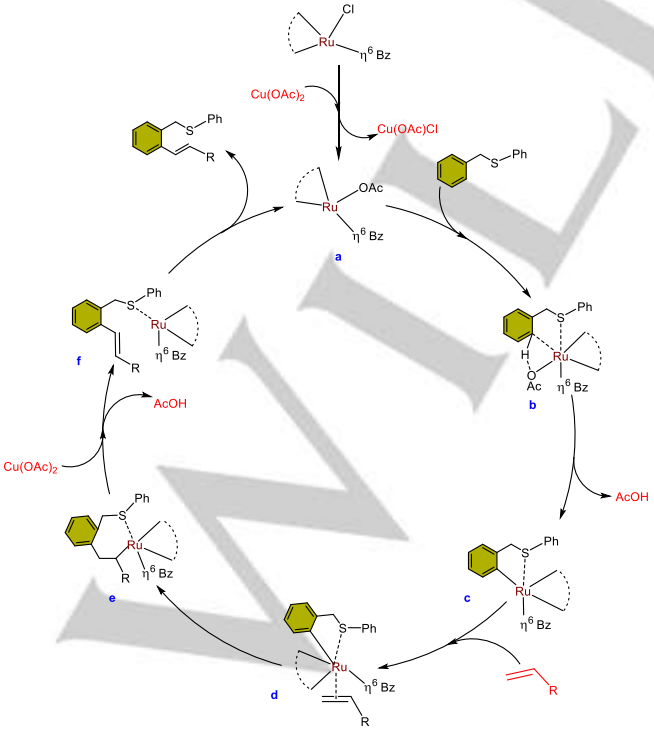


Scheme 8. Selectivity between acrylate and styrene



Scheme 9. Selectivity between benzyl(cyclopentyl)sulfane and benzyl(ethyl)sulfane

Plausible Mechanism. A plausible mechanism (Scheme 10) has been formulated on the basis of available literature.[26,29-32] The catalytic process may be initiate by the loss of Cl from Ru-complex (1) to forms an active catalytic species (**a**). Thioether chelated with (**a**) and undergoes ortho- metalation–deprotonation at the benzyl ring and resulted in a five-membered ruthenacycle intermediate (**c**). The coordinative insertion of an olefin into Ru-C metallacycle (**d**) forms an intermediate (**e**). Finally, the β-hydride elimination in presence of $Cu(OAc)_2$ resulted in the desire *o*-vinylated product and regenerates the active ruthenium species for the next catalytic cycle.



Scheme 10. Plausible Mechanism for ortho-vinylatation of arene

Conclusion

In summary, we had designed, synthesized, and characterized a Ru(II)-NHC half pincer complex and explored the catalytic efficiency of this complex for alkenylations of arenes. Here, Ru complex and $Cu(OAc)_2$ enable the ortho-vinylation of thiol-directed functionalized arenes. The Ru and Cu show excellent functional group tolerance on either of the reactants and show significant S-directed ortho-vinylation via C-H activations of activated styrenes and acrylates. Good selectivity was obtained for acrylates and benzyl(cyclopentyl)sulfane.

Supporting information

Experimental details, spectral data, all NMR spectrams and crystal and refinement data along with CIF of complex 1 (CCDC 2085434), are provided as supporting information.

Acknowledgments

RKJ thanks CSIR for research funding [01(2996)/19/EMR-II]. SK and CS thank MNIT for the research fellowships. Authors acknowledge MNIT-MRC for characterization facilities.

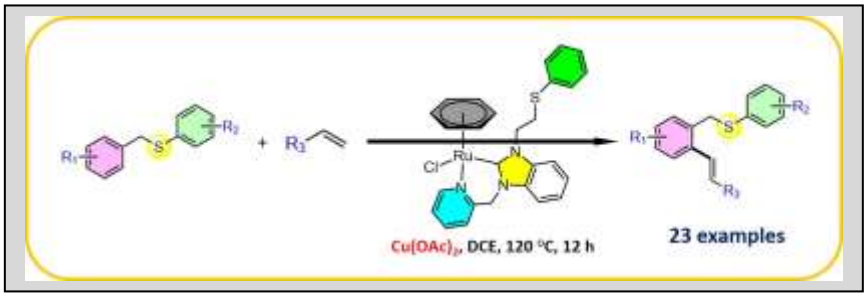
Keywords: C-H Activation, O-alkenylation, Picolyl NHC Thioether Ligand, Ru(II) Half Pincer Complex, S-Directing Alkenylation

1. J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960-9009.
2. B. Song, B. Xu, *Chem. Soc. Rev.* **2017**, *46*, 1103-1123.
3. G. Yin, X. Mu, G. Liu, *Acc. Chem. Res*. **2016**, *49*, 2413-2423.
4. C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. A. Hor, X. Liu, *Chem. Soc. Rev*. **2015**, *44*, 291-314.
5. Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu, Y. Zhang, *Org. Chem. Front*. **2015**, *2*, 1107-1295.
6. D. -S Kim, J. -W. Park, C. -W. Jun, *Adv. Synth. Catal*. **2013**, *355*, 2667-2669.
7. N. Guimond, K. Fagnou, *J. Am. Chem. Soc*. **2009**, *131*, 12050-12051.
8. X. Wei, M. Zhao, Z. Du, X. Li, *Org. Lett.* **2011**, *13*, 4636-4639.
9. M. Miura, T. Tsuda, T. Satoh, S. Pivsa-Art, M. Nomura, *J. Org. Chem.* **1998**, *63*, 5211-5215.
10. H. -X. Dai, G. Li, X. -G Zhang, A. F. Stepan, J. -Q. Yu, *J. Am. Chem. Soc*. **2013**, *135*, 7567-7571.
11. L. Ackermann, J. Pospech, K. Graczyk, K. Rauch, *Org. Lett*. **2012**, *14*, 930-933.
12. E. A. Ilardi, E. Vitaku, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 2832-2842.
13. M. D. McReynolds, J. M. Dougherty, P. R. Hanson, *Chem. Rev.* **2004**, *104*, 2239-2258.
14. N. Barbero, R. Martin, *Org. Lett*. **2012**, *14*, 796-799.
15. A. Senthilmurugan, I. S. Aidhen, *Eur. J. Org. Chem*. **2010**, *2010*, 555-564.
16. H. M. Ko, D. G. Lee, M. A. Kim, H. J. Kim, J. Park, M. S. Lah, E. Lee, *Org. Lett*. **2007**, *9*, 141-144.
17. J. F. Hooper, A. B. Chaplin, C. Gonzalez-Rodriguez, A. L. Thompson, A. S. Weller, M. C. Willis, *J. Am. Chem. Soc.* **2012**, *134*, 2906-2909.
18. C. Sharma, A. K. Srivastava, K. N. Sharma, R. K. Joshi, *Org. Bio. Chem*. **2020**, *18*, 3599-3606.
19. K. N. Sharma, M. Ali, A. K. Srivastava, R. K. Joshi, *J. Organomet. Chem*. **2019**, *879*, 69-77.
20. K. N. Sharma, N. Satrawala, R. K. Joshi, *Eur. J. Inorg. Chem*. **2018**, *16*, 1743-1751.
21. C. Sharma, A. K. Srivastava, A. Soni, S. Kumari, *RSC Advance*, **2020**, *10*, 32516-32521.
22. F. Wang, W. -G. Wang, X. -J. Wang, H. -Y. Wang, C. -H. Tung, L. -Z. Wu, Wu, *Angew. Chem. Int. Ed.* **2011**, *50*, 3193-3197.

23. R. Cammack, *Nature*,**1999**, *397*, 214-215.
24. J. Yao, M. Yu, Y. Zhang, *Adv. Synth. Catal*., **2012**, *354*, 3205-3210.
25. J. Yao, X. -S. Zhang, Q. -L. Zhu, Y. -F. Zhang, Y. -B. Li, Z. -J. Shi, *Chem. Eur. J*., **2013**, *19*, 11898-11903.
26. C. Li, X. Chen, R. Bao, D. Li, K. Zhang, D. Wang, *RSC Adv*., **2019**, *9*, 30134-30138.
27. (a) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev*. **2012**, *112*, 11, 5879–5918; (b) G. Rouquet, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 2–20 (c) P. Kumar, R. K. Gupta, D. S. Pandey, *Chem. Soc. Rev.* **2014**,*43*, 707-733; (d) C. Shan, L. Zhu, L. -B. Qu, R. Bai, Y. Lan, *Chem. Soc. Rev.* **2018**, *47*, 7552-7576; (e) W. Zhu, T. B. Gunnoe, *J. Am. Chem. Soc.* **2021**, *143*, 6746–6766.
28. C. del Pozo, M. Iglesias, F. Sánchez, *Organometallics*, **2011**, *30*, 2180–2188.
29. K. N. Sharma, N. Satrawala. R. K. Joshi, *Eur. J. Inorg. Chem,* **2018**, *16*, 1743-1751.
30. M. Selvaraju, Y. Wang, C. Sun, *Org. Chem. Front*., **2017**, *4*, 1358-1362.
31. N. Satrawala, C. Williams, A. K. Srivastava, K. N. Sharma, G. S. Smith, R. K. Joshi, *Catal. Commun.*, **2019**, *129*, 105727.
32. K. Padala, M. Jeganmohan, *Org. Lett*. **2011**, *13*, 6144-6147.

10.1002/ejic.202100501

Entry for the Table of Contents



Picolyl Functionalized *N*-Heterocyclic Carbene Thioether ligand-based Novel Half sandwich pincer (η^6-Benzene)Ru(II) Complex was synthesized. The prepared Ru(II) complex in presence of $Cu(OAc)_2$ *was* identified as an excellent catalyst for O-Alkenylation via CH activation through the S-directing group. Transformations under Mild reaction condition and tolerance for a wide range of functional groups was observed.