Organic LETTERS

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Heteroarene-Directed Oxidative sp^2 C−H Bond Allylation with Aliphatic Alkenes Catalyzed by an (Electron-Deficient η^5-Cyclopentadienyl)rhodium(III) Complex

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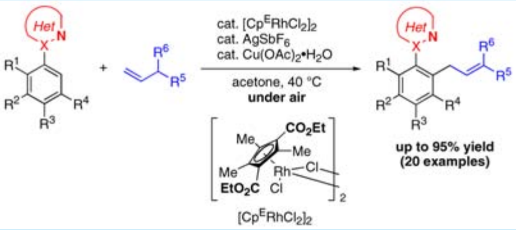
Supporting Information

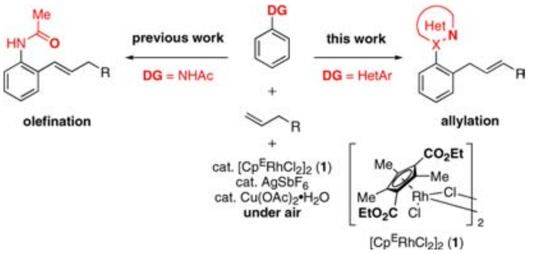
ABSTRACT: It has been established that the oxidative sp^2 C−H bond allylation with aliphatic alkenes proceeds under mild conditions by using heteroarenes as directing groups and an (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex, $[Cp^ERhCl_2]_2$, as a precatalyst. In sharp contrast, the use of $[Cp^*RhCl_2]_2$ instead of $[Cp^ERhCl_2]_2$ led to a complex mixture of products under the same reaction conditions.



The transition-metal-catalyzed allylation of arenes is widely employed as an important tool for the synthesis of allylarenes.[1] Specifically, the direct allylation of sp^2 C−H bonds of arenes is a highly attractive protocol from the viewpoint of atom- and step-economy.[2] A number of successful examples of the sp^2 C−H bond allylation with allylic compounds, possessing heteroatom-containing leaving groups (e.g., allyl carboxylates, allyl carbonates, and allyl halides), have been reported[3−7]) by using various late transition-metal complexes (e.g., Pd(II),[3] Rh(III),[4] Fe(III),[5] Co(III),[6] and other metal complexes[7]) as catalysts. Yet, the direct oxidative (dehydrogenative) sp^2 C−H bond allylation with aliphatic alkenes is an extremely atom- and step-economical method, since this process produces only water as a byproduct and requires no preactivation or prefunctionalization of both coupling partners. Despite the high synthetic utility of this transformation, the oxidative sp^2 C−H bond allylation with aliphatic alkenes has been succeeded in a limited number of examples[8,9] and it is awaiting the expanded substrate scope. For example, although several Pd(II)-catalyzed reactions have been reported,[8] the desired allylation products were obtained in a few examples[8a−c] as minor products[8d] or by using uncommon substrates (polyfluorobenzenes).[8e,f] The Rh(III)-catalyzed reactions have also been reported,[9] while examples have been limited to the use of a *N*-alkyl (or phenyl)-*N*-nitrosoamino directing group[9a] or strained unimolecular reactants.[9b]

On the other hand, our research group reported that several oxidative sp^2 C−H bond functionalization reactions of arenes can be catalyzed by a bis(ethoxycarbonyl)-substituted cyclopentadienyl−rhodium(III) complex, $[Cp^ERhCl_2]_2$ (**1**),[10] under mild conditions.[11,12] For example, the oxidative [3 + 2] annulation of anilides with internal alkynes using **1** as a precatalyst proceeded under ambient conditions (room temperature, under air) to give multisubstituted indoles in high yields, while elevated temperature and a stoichiometric oxidant (or oxygen atmosphere) were required in the same reactions using a widely used commercially available rhodium(III) complex, $[Cp^*RhCl_2]_2$, instead of **1**.[10,11a] In addition to the annulation with alkynes, the oxidative sp^2 C−H bond olefination of acetanilides with aliphatic alkenes also proceeded under ambient conditions by using **1** as the precatalyst to give styrene derivatives in good yields (Scheme 1, left). In sharp contrast, when using $[Cp^*RhCl_2]_2$ instead of **1** under the same reaction conditions, no reaction was observed.[11c] In this paper, we have established that not the olefination but the allylation of the aromatic sp^2 C−H bonds with aliphatic alkenes proceeds by using heteroarenes[13] in place of N−H amides as directing groups and **1** as the precatalyst (Scheme 1, right).

Scheme 1



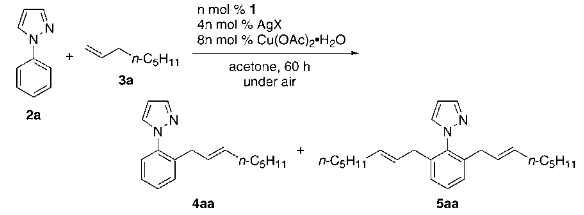
We first examined the reaction of 1-phenylpyrazole (**2a**, 2 equiv) and 1-octene (**3a**, 1 equiv) in the presence of a cationic rhodium(III)/Cp^E catalyst, generated in situ from **1**, $AgSbF_6$, and $Cu(OAc)_2 \cdot H_2O$. We were pleased to find that not the olefination but the allylation of **2a** with **3a** proceeds at room temperature under air to give monoallylated product **4aa** as a mixture of *E*/*Z*

Received: May 3, 2016
Published: May 26, 2016

DOI: 10.1021/acs.orglett.6b01288
Org. Lett. 2016, 18, 2934−2937

isomers in 56% yield along with diallylated product **5aa** in 26% yield at the 85% conversion of **3a** (Table 1, entry 1). In order to increase the conversion of **3a** and the selectivity for **4aa**, optimization of reaction conditions was conducted. Screening of silver salts (entries 1−5) revealed that $AgSbF_6$ is the most effective one (entry 1). With respect to solvents, the use of dichloroethane and 2-butanone slightly lowered the product yields (entries 6 and 7). In order to inhibit the formation of diallylated product **5aa**, the ratio of **2a** to **3a** was investigated. As expected, increasing the amount of **2a** increased the yield of **4aa** (entry 8); in contrast, decreasing the amount of **2a** decreased the conversion of **3a** (entry 9). Gratifyingly, when the amount of **1** was reduced to 2.5 mol %, the selectivity for **4aa** was improved, although the conversion of **3a** was decreased (entry 10). Finally, when the reaction was conducted at slightly elevated temperature (40 °C), **4aa** was obtained in the highest yield (entry 11). Importantly, the use of $[Cp^*RhCl_2]_2$ instead of **1** afforded only a trace amount of **4aa** (entry 12). Other than this product, an extremely complex mixture of unidentified products was generated (entry 12).

Table 1. Optimization of Reaction Conditions[a]

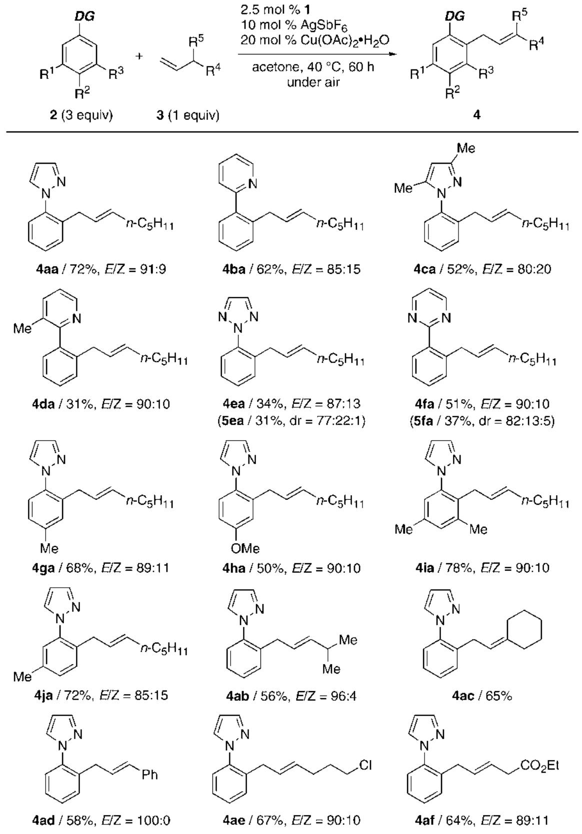


entry	n	AgX	temp	2a/3a	conv (%) of 3a[b]	yield (%)[c]	
						4aa	5aa
1	5	$AgSbF_6$	rt	2:1	85	56	26
2	5	$AgPF_6$	rt	2:1	88	51	26
3	5	$AgBF_4$	rt	2:1	86	48	30
4	5	$AgNTf_2$	rt	2:1	96	39	34
5	5	AgOTf	rt	2:1	84	53	30
6[d]	5	$AgSbF_6$	rt	2:1	88	49	15
7[e]	5	$AgSbF_6$	rt	2:1	92	51	24
8	5	$AgSbF_6$	rt	3:1	89	62	20
9	5	$AgSbF_6$	rt	1.1:1	66	28	19
10	2.5	$AgSbF_6$	rt	3:1	60	50	8
11	2.5	$AgSbF_6$	40 °C	3:1	90	73	16
12[f]	2.5	$AgSbF_6$	40 °C	3:1	>99	3	0

[a] **1** (0.0063 mmol), AgX (0.025 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.050 mmol), **2** (0.75 mmol), **3** (0.25 mmol), and acetone (1.3 mL) were used. [b] As **3a** could not be recovered after evaporation, conversions of **3a** were estimated from recovered **2a**, which was determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. [c] Determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. [d] Solvent: $(CH_2Cl)_2$. [e] Solvent: 2-butanone. [f] $[Cp^*RhCl_2]_2$ was used instead of **1**.

With the optimized reaction conditions in hand, we next focused our attention into the substrate scope (Scheme 2). A wide variety of heteroarylbenzenes could be allylated with 1-octene (**3a**), although the product yields were varied.[14] A 2-pyridyl group worked as a good directing group to give the desired monoallylated product **4ba** in good yield, which is comparable to that of **4aa**. However, sterically demanding substituted heteroarylbenzenes, 1-phenyl-3,5-dimethylpyrazole (**2c**) and 3-methyl-2-phenylpyridine (**2d**), reacted with **3a** to give monoallylated products **4ca** and **4da**, respectively, in lower yields than **4aa** and **4ba** presumably due to steric repulsion between the methyl group (red) on the heteroarene ring and the *ortho* hydrogen (blue) on the benzene ring (Figure 1), which deters the rhodacycle formation through the C−H bond activation. The reactions of heteroarylbenzenes **2e** and **2f**, possessing more than one nitrogen atom, were also investigated, which revealed that the yields of the desired monoallylated products **4ea** and **4fa** were lower than those of **4aa** and **4ba**, as a result of the formation of significant amounts of diallylated products **5ea** and **5fa**.[15,16] With respect to the substituents on the benzene ring, *para*-substituted and *meta*-disubstituted heteroarylbenzenes **2g−i** reacted with **3a** to give monoallylated products **4ga−ia** in good yields. The reaction of *meta*-substituted heteroarylbenzene **2j** with **3a** proceeded with perfect regioselectivity in the same yield as **4aa**. The scope of aliphatic alkenes was also examined. Not only 1-octene (**3a**) but also sterically demanding branched alkenes **3b** and **3c** and allylbenzene **3d** could be employed for this process. Furthermore, functionalized alkenes **3e** and **3f**, bearing chloro and ethoxycarbonyl groups,

Scheme 2[a]



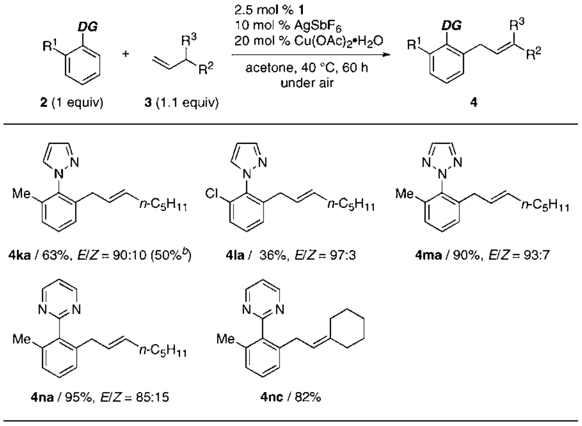
[a] **1** (0.0063 mmol), $AgSbF_6$ (0.025 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.050 mmol), **2** (0.75 mmol), **3** (0.25 mmol), and acetone (1.3 mL) were used. The cited yields are of the isolated products.

Figure 1. Steric repulsion between the methyl group (red) and the *ortho* hydrogen (blue).

were also capable of reacting with **2a** to give monoallylated products **4ae** and **4af** in good yields without affecting the functional groups. With respect to the stereochemistry of the allylation products, *E* isomers were obtained as major products.

It was anticipated that the use of 1-(2-methylphenyl)pyrazole (**2k**) would afford the corresponding monoallylated products in good yields without using excess **2k**. However, steric repulsion between the *ortho* methyl group (red) on the benzene ring and hydrogen (blue) on the heteroarene ring (Figure 1) would deter the rhodacycle formation through the C−H bond activation. As shown in Scheme 3, the reaction of **2k** and **3a** in the ratio of 3 to 1 proceeded sluggishly to give the corresponding monoallylated product **4ka** in lower yield than **4aa** as a result of the insufficient conversion of **3a**. Pleasingly, when 1.1 equiv of **3a** with respect to **2k** was used, the yield of **4ka** was increased to 63%. This yield is markedly higher than that of **4aa** under the same conditions (28%: Table 1, entry 9). Unfortunately, the reaction of 1-(2-chlorophenyl)pyrazole (**2l**) with **3a** was sluggish even using 1.1 equiv of **3a** with respect to **2l**. In contrast to the poor yields of **4ea** and **4fa** shown in Scheme 2, the use of 2-methylphenyl-substituted heteroarenes **2m** and **2n**, possessing more than one nitrogen atom, dramatically increased the yields of monoallylated products **4ma** and **4na**. Sterically demanding branched alkene **3c** also reacted with **1n** to give monoallylated product **4nc** in high yield. The formation of *E* isomers as major products is the same as the case shown in Scheme 2.

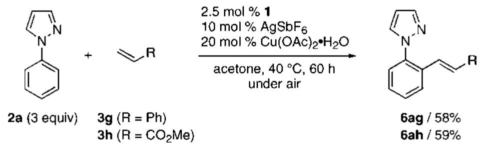
Scheme 3[a]



[a] **1** (0.0063 mmol), AgSbF$_6$ (0.025 mmol), Cu(OAc)$_2$·H$_2$O (0.050 mmol), **2** (0.25 mmol), **3** (0.275 mmol), and acetone (1.3 mL) were used. The cited yields are of the isolated products. [b] **2** (0.75 mmol) and **3** (0.25 mmol) were used.

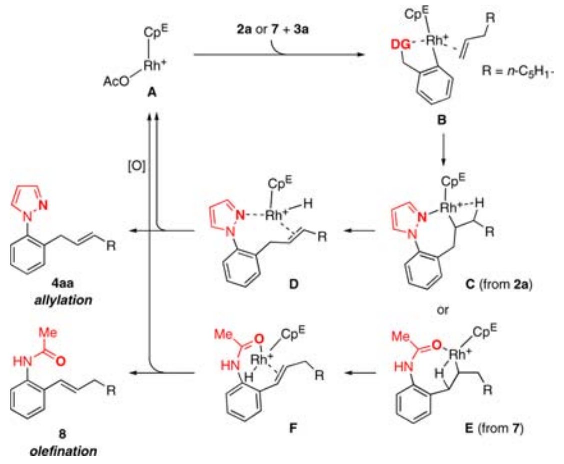
Under the optimized reaction conditions employed in Scheme 2, the oxidative coupling of **2a** with "activated" alkenes, styrene (**3g**) and methyl acrylate (**3h**), also proceeded to give the corresponding olefinated products **6ag** and **6ah** in good yields (Scheme 4).

Scheme 4



A plausible explanation for the effect of the directing groups on the reaction pathways (oxidative allylation vs olefination) is shown in Scheme 5. The cationic rhodium(III) complex **A** reacts with 1-phenylpyrazole (**2a**) and 1-octene (**3a**) to give five-membered rhodacycle **B** through sp^2 C−H bond cleavage. Next, regioselective insertion of **3a** into **B** gives seven-membered rhodacycle **C**. β-Hydride elimination away from the benzene ring[8,9,17] gives heteroarene- and olefin-coordinated intermediate **D**. Subsequent oxidative decomplexation affords allylated product **4aa** and regenerates the Rh(III) catalyst. Yet, when using acetanilide (**7**) in place of **2a**, the sp^2 C−H bond cleavage followed by insertion of **3a** gives eight-membered rhodacycle **E**. In this intermediate, β-hydride elimination adjacent to the benzene ring proceeds to give olefinated product **8** through carbonyl- and olefin-coordinated intermediate **F**. The selectivity of the β-hydride elimination might be determined by flexibility of the rhodacycles **C** and **E** induced by both the ring size (seven- or eight-membered ring) and the coordinative functional group (heteroarene or carbonyl).[18]

Scheme 5



In summary, we have established that the oxidative sp^2 C−H bond allylation with aliphatic alkenes proceeds under mild conditions by using heteroarenes as directing groups and an (electron-deficient η^5-cyclopentadienyl)rhodium(III) complex, [Cp^{E}RhCl$_2$]$_2$, as a precatalyst. In sharp contrast, the use of [Cp*RhCl$_2$]$_2$ instead of [Cp^{E}RhCl$_2$]$_2$ led to a complex mixture of products under the same reaction conditions. The selective formation of the allylated products might arise from the selective β-hydride elimination away from the benzene ring in the heteroarene-coordinated seven-membered rhodacycle.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01288.

Experimental procedures and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported partly by ACT-C from the Japan Science and Technology Agency (JST, Japan), Grants-in-Aid for Scientific Research (Nos. 26102004 and 25105714) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan), and a Grant-in-Aid for Research Activity Start-up (No. 15H06201) from Japan Society for the Promotion of Science (JSPS, Japan). We are grateful to Umicore for generous support in supplying the rhodium complex.

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(14) The reactions of 1-phenyl-1*H*-1,2,4-triazole, 4-phenylpyrimidine, and 2-phenyloxazole with **3a** were also examined under the same conditions as Scheme 2. However, unfortunately, no reactions were observed for the former two substrates and the last reaction was sluggish to give the allylation product in <10% yield.

(15) The formation of significant amounts of diallylated products **5ea** and **5fa** might arise from diminished steric repulsion between two *ortho* substituents on the heteroarene and benzene rings due to the absence of the *ortho* hydrogen in heteroarenes **2e** and **2f**.

(16) In the reactions other than **2e** and **2f**, diallylated products **5** were generated in less than 10%.

(17) For examples of the allylation by the Mizoroki−Heck type reactions involving β-hydride elimination away from the arene ring, see: (a) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896. (b) Arcadi, A.; Chiarini, M.; Marinelli, F.; Berente, Z.; Kollar, L. *Org. Lett.* **2000**, *2*, 69. (c) Rosenblum, S. B.; Huynh, T.; Afonso, A.; Davis, H. R., Jr. *Tetrahedron* **2000**, *56*, 5735. (d) Arcadi, A.; Chiarini, M.; Marinelli, F.; Berente, Z.; Kollar, L. *Eur. J. Org. Chem.* **2001**, *2001*, 3165. (e) Mino, T.; Shindo, H.; Kaneda, T.; Koizumi, T.; Kasashima, Y.; Sakamoto, M.; Fujita, T. *Tetrahedron Lett.* **2009**, *50*, 5358.

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