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C–H Bond Functionalization

# Oxidative Olefination of Anilides with Unactivated Alkenes Catalyzed by an (Electron-Deficient $\eta^5$-Cyclopentadienyl)Rhodium(III) Complex Under Ambient Conditions

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**Abstract:** The oxidative olefination of sp$^2$ C–H bonds of anilides with both activated and unactivated alkenes using an (electron-deficient $\eta^5$-cyclopentadienyl)rhodium(III) complex is reported. In contrast to reactions using this electron-deficient rhodium(III) catalyst, [Cp*RhCl$_2$]$_2$ showed no activity against olefination with unactivated alkenes. In addition, the deuterium kinetic isotope effect (DKIE) study revealed that the C–H bond cleavage step is thought to be the turnover-limiting step.

Transition-metal-catalyzed oxidative sp$^2$ C–H bond olefination reactions of arenes with alkenes are efficient and atom-economical methods for the synthesis of vinylarene derivatives.[1] Following the pioneering work by Fujiwara–Moritani,[2] a number of reliable methods have been reported to date.[3–5] However, applicable alkenes were limited to “activated” ones (e.g., acrylates and styrenes).[6–9] Recently, “unactivated” aliphatic alkenes have been successfully employed in the Pd$^{II}$-catalyzed olefination of dialkoxybenzene[10] and *N*-(8-quinolinyl)-phenylacetamide,[11] the Ir$^{I}$-catalyzed olefination of furans,[12] and the Rh$^{III}$-catalyzed olefination of aryl oximes,[13] *N*-(1-naphthyl)sulfonamides,[14] and isoquinolones.[15] However, these examples required stoichiometric external oxidants (or hydrogen acceptors) and/or elevated temperature. Consequently the development of the transition-metal-catalyzed oxidative sp$^2$ C–H bond olefination of arenes with unactivated alkenes that proceeds under ambient conditions (at room temperature using air as a terminal oxidant) remains a challenge.[16]

On the other hand, our research group established that the use of ethoxycarbonyl-substituted cyclopentadienyl-Rh$^{III}$ complex **1**, [{Cp$^E$RhCl$_2$}$_2$],[17a] in place of [{Cp*RhCl$_2$}$_2$] as a precatalyst enables the C–H bond functionalization of electron-rich arenes under ambient conditions with the broad substrate scope presumably due to electron-deficient nature of **1**.[17–20] For example, in the oxidative annulation of anilides with internal alkynes, although the use of the [{Cp*RhCl$_2$}$_2$] precatalyst required elevated temperature as well as a stoichiometric Cu$^{II}$ oxidant (or oxygen atmosphere) and afforded a product from an aliphatic alkyne in moderate yield,[21] the use of **1** instead of [{Cp*RhCl$_2$}$_2$] allowed the reactions to proceed under ambient conditions and afforded products from aliphatic alkynes in high yields.[17a,b] Similarly, in the oxidative olefination of anilides with alkenes using the [{Cp*RhCl$_2$}$_2$] precatalyst, elevated temperature as well as the stoichiometric Cu$^{II}$ oxidant were required and available alkenes were limited to activated ones.[4e] Herein we report the oxidative olefination of anilides with both activated and unactivated alkenes using **1** as the precatalyst under ambient conditions.

We first examined the reaction of acetanilide (**2a**) with 1-octene (**3a**, 1.1 equiv) in the presence of a cationic Rh$^{III}$/Cp$^E$ catalyst, generated in situ from **1**, AgSbF$_6$, and [Cu(OAc)$_2$] at room temperature under air. Pleasingly, the desired oxidative olefination proceeded to give mono-olefinated acetanilides (linear isomer **4aa** and branched isomers **5aa**/**6aa**) in 41% yield along with diolefinated product **7aa** in 9% yield (Table 1, entry 1). Importantly, no reaction was observed when using [{Cp*RhCl$_2$}$_2$] instead of **1** (entry 2). Screening of solvents (entries 3–6) revealed that the use of *t*AmylOH (entry 3) improves the yield of **4**–**7aa**. In order to avoid the formation of the diolefinated acetanilide **7aa**, we tested the reactions of **2a** (2 equiv) and **3a** in acetone and *t*AmylOH (entries 7 and 8). As a result, the use of operationally more convenient acetone solvent afforded **4**–**6aa** in the highest yield (entry 7).

The scope of alkenes and anilides is shown in Scheme 1. Primary and secondary alkyl-substituted alkenes **3a**–**c** smoothly reacted with **2a** to give olefinated acetanilides in good yields. Under the optimized reaction conditions, only a trace amount of olefinated acetanilides were generated when using [{Cp*RhCl$_2$}$_2$] instead of **1**. Increasing the steric bulk of alkyl groups improved linear/branch selectivity (**4**/**5**+**6**). On the other hand, the reaction of vinyltrimethylsilane (**3d**) and **2a** proceeded with moderate linear/branch selectivity (**4ad**/**5ad**).

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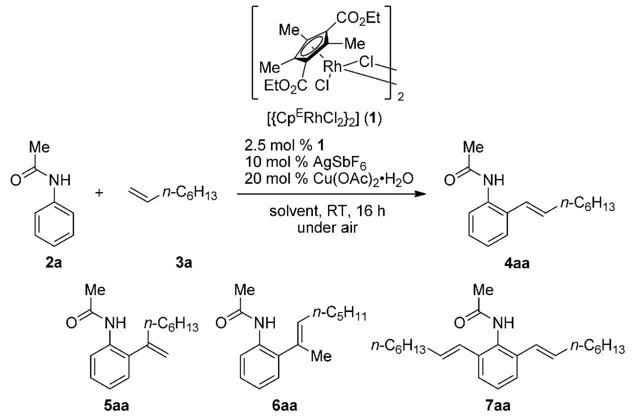
**Table 1.** Optimization of reaction conditions for rhodium-catalyzed oxidative olefination of acetanilide (**2a**) with 1-octene (**3a**).[a]



| Entry | Solvent | **2a**/**3a** | Yield [%][b] (**4aa**/**5aa**/**6aa**) | **7aa** |
|---|---|---|---|---|
| 1 | acetone | 1:1.1 | 41 (72:19:9) | 9 |
| 2[c] | acetone | 1:1.1 | 0 | 0 |
| 3 | *t*AmylOH | 1:1.1 | 55 (68:19:13) | 8 |
| 4 | $(CF_3)_2CHOH$ | 1:1.1 | $<5$ | 0 |
| 5 | $CH_3CN$ | 1:1.1 | 0 | 0 |
| 6 | DMF | 1:1.1 | 0 | 0 |
| 7[d] | acetone | 2:1 | 80 (76:16:8) | 2 |
| 8[d] | *t*AmylOH | 2:1 | 76 (75:15:10) | 2 |

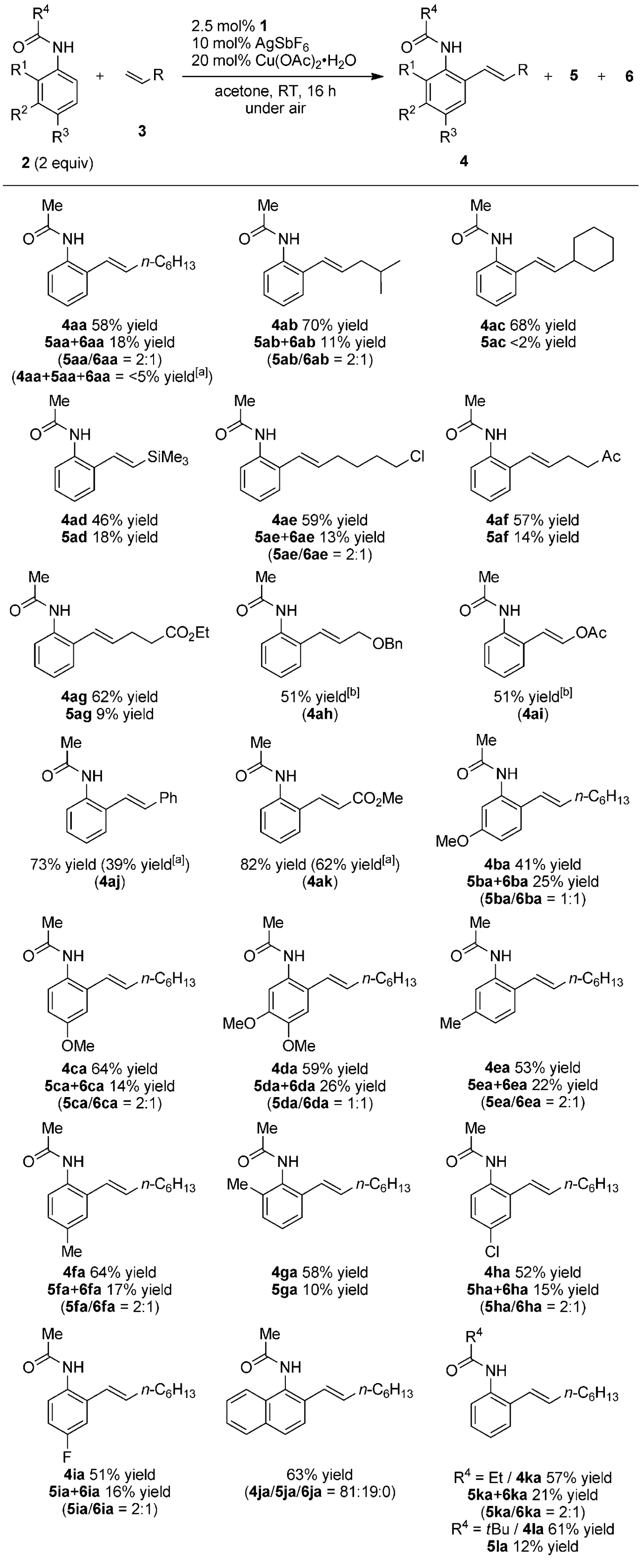
[a] **1** (0.0050 mmol), $AgSbF_6$ (0.020 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.040 mmol), **2a** (0.20 mmol), **3a** (0.22 mmol), and solvent (1.0 mL) were used. [b] Determined by $^1H$ NMR spectroscopy. [c] $[\{Cp^*RhCl_2\}_2]$ was used instead of **1**. [d] **1** (0.010 mmol), $AgSbF_6$ (0.040 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.080 mmol), **2a** (0.40 mmol), **3a** (0.20 mmol), and solvent (1.0 mL) were used.

Functionalized alkenes **3e**–**g** could also be employed, and allylbenzyl ether (**3h**) and vinyl acetate (**3i**)[22] reacted with **2a** to give linear products **4ah** and **4ai**. Importantly, activated alkenes **3j** and **3k** were also able to react with **2a** to give linear products **4aj** and **4ak** in higher yields than the use of the $[\{Cp^*RhCl_2\}_2]$ precatalyst. With respect to anilides, a variety of methoxy- and methyl-substituted acetanilides **2b**–**g** reacted with **3a** to give olefinated acetanilides in good yields. It is worth mentioning that 2-methylacetanilide (**2g**), which showed poor reactivity in the $Cp^*Rh^{III}$-catalyzed oxidative olefination with **3j**,[4e] reacted with **3a** in good yield. 4-Haloacetanilides **2h**,**i** and 1-acetamidenaphthalene (**2j**) were also able to react with **3a** in good yields. Not only acetanilides but also propioanilide (**2k**) and pivaloanilide (**2l**) could equally be employed. The major linear isomers **4** could be isolated in pure forms, although **4ja** and **5ja** were isolated as a mixture.

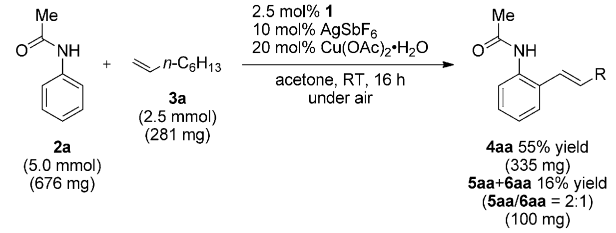
The large-scale reaction of **2a** with **3a** proceeded under the same conditions without significant yield loss as shown in Scheme 2.

Chemoselectivity between an alkyne vs. an alkene was examined as shown in Scheme 3. The reaction of **2a** with enyne **3l** gave the corresponding indole **8** exclusively without formation of olefinated product **4al**.

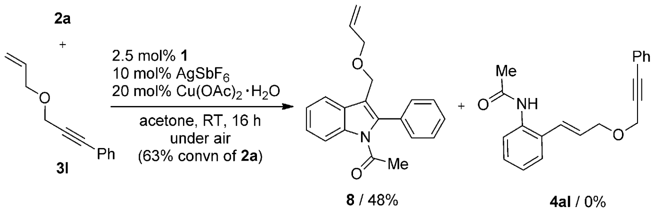
Unsymmetrically diolefinated anilides could be synthesized by the sequential olefination as shown in Scheme 4. The reactions of mono-olefinated anilide **4aa** with alkenes **3c**, **3j**, and



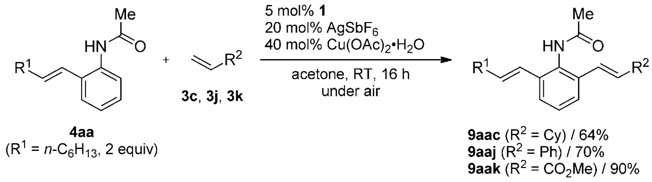
**Scheme 1.** Scope of anilides **2** and alkenes **3**. Reactions were conducted using **1** (0.0050 mmol), $AgSbF_6$ (0.020 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.040 mmol), **2** (0.40 mmol), **3** (0.20 mmol), and acetone (1.0 mL). The cited yields are of the isolated products. [a] $[\{Cp^*RhCl_2\}_2]$ was used instead of **1**. [b] Trace amounts of **5** were detected in the crude mixture by $^1H$ NMR.



**Scheme 2.** Large-scale reaction of **2a** with **3a**.



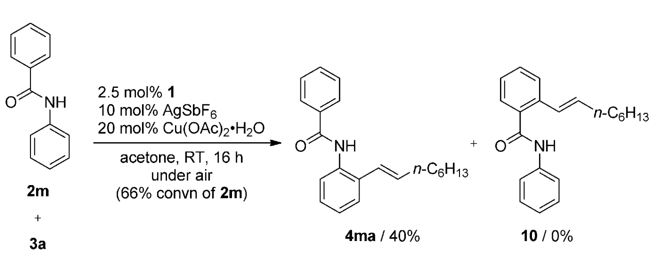
**Scheme 3.** Chemoselectivity between alkyne vs. alkene.



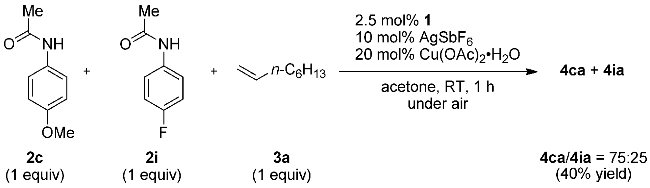
**Scheme 4.** Synthesis of unsymmetrically diolefinated anilides **9aac**, **9aaj**, and **9aak** by olefination of **4aa** with alkenes **3c,j,k**.

**3k** proceeded to give unsymmetrically diolefinated anilides **9aac**, **9aaj**, and **9aak**, respectively, in good to high yields.

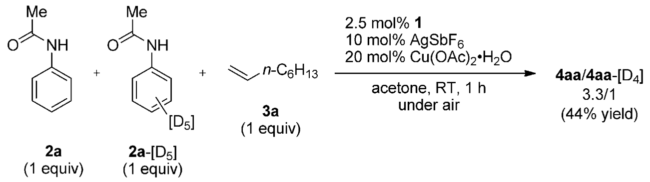
It was speculated that highly electrophilic nature of the electron-deficient complex **1** would facilitate the C–H bond functionalization of not electron-poor arenes but electron-rich arenes. Indeed, not the benzamide C–H bond, but the anilide C–H bond of **2m** was olefinated with **3a** to give **4ma** without formation of **10** (Scheme 5). Similarly, the competition experiment between electron-rich anilide **2c** and electron-deficient anilide **2i** revealed the preference for olefination across **2c** over **2i** (Scheme 6).



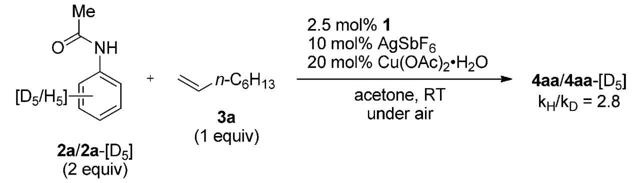
**Scheme 5.** Competition experiment between benzamide and anilide C–H bonds.



**Scheme 6.** Competition experiment between electron-rich and electron-deficient anilides.



**Scheme 7.** Intermolecular competition experiment between **2a** and **2a**-[D$_5$].



**Scheme 8.** Deuterium kinetic isotope effect obtained from individual reactions of **2a** and **2a**-[D$_5$].

In order to gain mechanistic insights into the C–H bond activation step using the electron-deficient complex **1**, a deuterium kinetic isotope effect (DKIE) of olefination of **2a** with **3a** was measured.[23] The intermolecular competition experiment between **2a** and **2a**-[D$_5$] in the presence of **3a** revealed a DKIE value of 3.3 (Scheme 7), which is the almost the same value as that of our previously reported oxidative annulation of **1a** with diphenylacetylene (DKIE value = 3.5).[17b] A DKIE value, measured by comparing the initial rates obtained from individual reactions of **2a** and **2a**-[D$_5$] with **3a**, was 2.8 (Scheme 8). Importantly, as almost no loss of deuterium from both **1a**-[D$_5$] and **3aa**-[D$_5$] was observed, the metalation of the anilide was found to be irreversible using **1** as the precatalyst. These results indicate that the C–H bond cleavage step is thought to be the turnover-limiting step.[24]

In conclusion, we have established that a dinuclear (electron-deficient $\eta^5$-cyclopentadienyl)Rh$^{\text{III}}$ complex is a highly active precatalyst for the oxidative sp$^2$ C–H bond olefination of anilides with both activated and unactivated alkenes under ambient conditions (at room temperature under air). In contrast, a commonly employed Rh$^{\text{III}}$ precatalyst, [{Cp*RhCl$_2$}$_2$], showed no activity against olefination with unactivated alkenes. Competition experiments ensured highly electrophilic nature of complex **1** toward aromatic C–H bond functionalization. The study of deuterium kinetic isotope effects indicated that the C–H bond cleavage step is thought to be the turnover-limiting step. This paper clearly demonstrated that the use of the electron-deficient Rh$^{\text{III}}$ catalyst [Cp$^{\text{E}}$Rh$^{\text{III}}$] realizes not only mild reaction conditions but also significant expansion of the substrate scope.

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**Keywords:** alkenes · anilides · C–H bond functionalization · olefination · rhodium

[1] For recent reviews involving oxidative C–H bond olefination, see: a) S. De Sarkar, W. Liu, S. I. Kozhushkov, L. Ackermann, *Adv. Synth. Catal.* **2014**, *356*, 1461; b) S. I. Kozhushkov, L. Ackermann, *Chem. Sci.* **2013**, *4*, 886; c) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; d) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879; e) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740; f) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; g) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; h) J. Le Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170; i) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; j) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212.

[2] a) I. Moritani, Y. Fujiwara, *Tetrahedron Lett.* **1967**, *8*, 1119; b) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, S. Teranishi, *J. Am. Chem. Soc.* **1969**, *91*, 7166.

[3] For selected examples of oxidative C–H bond olefination using activated alkenes catalyzed by Pd, see: a) M. Miura, T. Tsuda, T. Satoh, M. Nomura, *Chem. Lett.* **1997**, *26*, 1103; b) M. D. K. Boele, G. P. F. van Strijdonck, A. H. M. de Vries, P. C. J. Kamer, J. G. de Vries, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2002**, *124*, 1586; c) T. Yokota, M. Tani, S. Sakaguchi, Y. Ishii, *J. Am. Chem. Soc.* **2003**, *125*, 1476; d) M. Tani, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **2004**, *69*, 1221; e) N. P. Grimster, C. Gauntlett, C. R. A. Godfrey, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2005**, *44*, 3125; *Angew. Chem.* **2005**, *117*, 3185; f) G. Cai, Y. Fu, Y. Li, X. Wan, Z. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7666; g) A. Maehara, H. Tsurugi, T. Satoh, M. Miura, *Org. Lett.* **2008**, *10*, 1159; h) J.-J. Li, T.-S. Mei, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2008**, *47*, 6452; *Angew. Chem.* **2008**, *120*, 6552; i) Y.-H. Zhang, B.-F. Shi, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 5072; j) J. Wu, X. Cui, L. Chen, G. Jiang, Y. Wu, *J. Am. Chem. Soc.* **2009**, *131*, 13888; k) D.-H. Wang, K. M. Engle, B.-F. Shi, J.-Q. Yu, *Science* **2010**, *327*, 315; l) B.-F. Shi, Y.-H. Zhang, J. K. Lam, D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 460; m) K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2010**, *49*, 6169; *Angew. Chem.* **2010**, *122*, 6305; n) K. M. Engle, D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 14137; o) M. Ye, G.-L. Gao, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 6964; p) D. Leow, G. Li, T.-S. Mei, J.-Q. Yu, *Nature* **2012**, *486*, 518; q) G. Li, D. Leow, L. Wan, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2013**, *52*, 1245; *Angew. Chem.* **2013**, *125*, 1283.

[4] For selected examples of oxidative C–H bond olefination using activated alkenes catalyzed by Rh, see: a) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407; b) N. Umeda, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2009**, *74*, 7094; c) F. Wang, G.-Y. Song, X.-W. Li, *Org. Lett.* **2010**, *12*, 5430; d) S. Mochida, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 5776; e) F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9982; f) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 3024; g) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 1064; *Angew. Chem.* **2011**, *123*, 1096; h) S. H. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372; i) J. Willwacher, S. Rakshitb, F. Glorius, *Org. Biomol. Chem.* **2011**, *9*, 4736; j) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; k) C. Wang, H. Chen, Z. Wang, J. Chen, Y. Huang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7242; *Angew. Chem.* **2012**, *124*, 7354; l) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 468; m) D. Zhao, C. Nimphius, M. Lindale, F. Glorius, *Org. Lett.* **2013**, *15*, 4504; n) B. Li, J. Ma, W. Xie, H. Song, S. Xu, B. Wang, *Chem. Eur. J.* **2013**, *19*, 11863.

[5] For selected examples of oxidative C–H bond olefination using activated alkenes catalyzed by Ru, see: a) K.-H. Kwon, D. W. Lee, C. S. Yi, *Organometallics* **2010**, *29*, 5748; b) T. Ueyama, S. Mochida, T. Fukutani, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2011**, *13*, 706; c) Y. Hashimoto, T. Ueyama, T. Fukutani, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2011**, *40*, 1165; d) L. Ackermann, L. Wang, R. Wolfram, A. V. Lygin, *Org. Lett.* **2012**, *14*, 728; e) B. Li, J. Ma, N. Wang, H. Feng, S. Xu, B. Wang, *Org. Lett.* **2012**, *14*, 736.

[6] Several reports include a few examples of the oxidative olefination with unactivated aliphatic alkenes, while the substrate scope was limited (e.g. *t*BuCH=CH$_2$) and/or elevated temperature was required. See: a) S. H. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254; b) A. García-Rubia, R. G. Arrayas, J. C. Carretero, *Angew. Chem. Int. Ed.* **2009**, *48*, 6511; *Angew. Chem.* **2009**, *121*, 6633; c) X. Zhang, S. Fan, C.-Y. He, X. Wan, Q.-Q. Min, J. Yang, Z.-X. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 4506; d) Y. Lu, D.-H. Wang, K. M. Engle, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 5916; e) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350; f) L. Zheng, J. Wang, *Chem. Eur. J.* **2012**, *18*, 9699; g) Y. Donga, G. Liu, *Chem. Commun.* **2013**, *49*, 8066; h) W. Liu, X. Yu, C. Kuang, *Org. Lett.* **2014**, *16*, 1798; i) L. Yang, G. Zhang, H. Huang, *Adv. Synth. Catal.* **2014**, *356*, 1509; j) Y. Lu, H.-W. Wang, J. E. Spangler, K. Chen, P.-P. Cui, Y. Zhao, W.-Y. Sun, J.-Q. Yu, *Chem. Sci.* **2015**, *6*, 1923.

[7] Oxidative allylation with unactivated aliphatic alkenes has been reported, while the yields were low; see references [3k,m,n,4l,n].

[8] Oxidative olefination with cyclic aliphatic alkenes has been reported; see references [3e,4j,5a,e].

[9] For oxidative olefination with allyl esters, see: a) Y. Zhang, Z. Li, Z.-Q. Liu, *Org. Lett.* **2012**, *14*, 226; b) N. Gigant, J.-E. Bäckvall, *Org. Lett.* **2014**, *16*, 1664; for that with *N*-allylphthalimide, see: c) C.-Z. Wu, C.-Y. He, Y. Huang, X. Zhang, *Org. Lett.* **2013**, *15*, 5266.

[10] N. Gigant, J.-E. Bäckvall, *Org. Lett.* **2014**, *16*, 4432.

[11] A. Deb, S. Bag, R. Kancherla, D. Maiti, *J. Am. Chem. Soc.* **2014**, *136*, 13602.

[12] C. S. Sevov, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 10625.

[13] A. S. Tsai, M. Brasse, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2011**, *13*, 540.

[14] X. Li, X. Gong, M. Zhao, G. Song, J. Deng, X. Li, *Org. Lett.* **2011**, *13*, 5808.

[15] P. Zhao, R. Niu, F. Wang, K. Han, X. Li, *Org. Lett.* **2012**, *14*, 4166.

[16] Very recently, Cp*Rh$^{III}$-catalyzed room temperature annulation of aryldiazenecarboxylates with alkenes involving aliphatic ones has been reported; see: D. Zhao, S. Vásquez-Céspedes, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 1657; *Angew. Chem.* **2015**, *127*, 1677.

[17] a) Y. Shibata, K. Tanaka, *Angew. Chem. Int. Ed.* **2011**, *50*, 10917; *Angew. Chem.* **2011**, *123*, 11109; b) Y. Hoshino, Y. Shibata, K. Tanaka, *Adv. Synth. Catal.* **2014**, *356*, 1577.

[18] The intramolecular oxidative annulation of anilides with alkynes also proceeds at room temperature under O$_2$ using **1**; see: B. Zhou, Y. Yang, H. Tang, J. Du, H. Feng, Y. Li, *Org. Lett.* **2014**, *16*, 3900.

[19] The oxidative annulation of benzylalcohols with alkynes also proceeds under ambient conditions using **1**; see: M. Fukui, Y. Hoshino, T. Satoh, M. Miura, K. Tanaka, *Adv. Synth. Catal.* **2014**, *356*, 1638.

[20] The Cp$^{E}$Rh$^{III}$-catalyzed intramolecular oxidative C–H/C–H coupling reactions of diarylmethane derivatives have been reported; see: a) K. Morimoto, M. Itoh, K. Hirano, T. Satoh, Y. Shibata, K. Tanaka, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 5359; *Angew. Chem.* **2012**, *124*, 5455; b) M. Itoh, K. Hirano, T. Satoh, Y. Shibata, K. Tanaka, M. Miura, *J. Org. Chem.* **2013**, *78*, 1365; c) H. Baars, Y. Unoh, T. Okada, K. Hirano, T. Satoh, K. Tanaka, C. Bolm, M. Miura, *Chem. Lett.* **2014**, *43*, 1782.

[21] a) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 16474; b) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326.

[22] Very recently, Cp*Rh$^{III}$-catalyzed vinylation of phenylpyridines and benzamides with vinyl acetate has been reported; see: K. D. Otley, J. A. Ellman, *Org. Lett.* **2015**, *17*, 1332.

[23] See the Supporting Information for details.

[24] E. M. Simmons, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2012**, *51*, 3066; *Angew. Chem.* **2012**, *124*, 3120.

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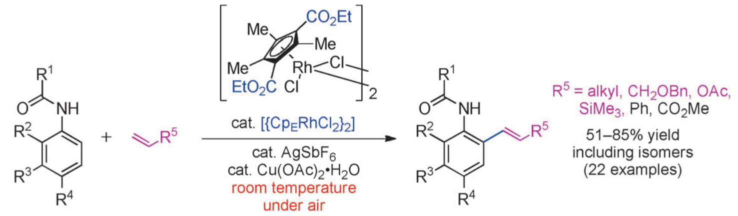
# COMMUNICATION



**It takes two**: It has been established that a dinuclear (electron-deficient $\eta^5$-cyclopentadienyl)Rh$^{III}$ complex is a highly active precatalyst for the oxidative sp$^2$ C–H bond olefination of anilides with both activated and unactivated alkenes under ambient conditions (at room temperature under air; see scheme). In contrast, a commonly employed Rh$^{III}$ precatalyst, [{Cp*RhCl$_2$}$_2$], showed no activity against olefination with unactivated alkenes.

**C–H Bond Functionalization**

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■■–■■

**Oxidative Olefination of Anilides with Unactivated Alkenes Catalyzed by an (Electron-Deficient $\eta^5$-Cyclopentadienyl)Rhodium(III) Complex Under Ambient Conditions**