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Rhenium-catalyzed insertion of terminal alkenes into a C(sp^2)–H bond and successive transfer hydrogenation

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ABSTRACT

Treatment of aromatic aldimines with terminal alkenes in the presence of a rhenium catalyst, $[HRe(CO)_4]_n$, gives 2-alkenylbenzylamines in good to excellent yields. This reaction proceeds via the insertion of the alkene into a C–H bond at the *ortho*-position of the imino group of the aromatic aldimine followed by sequential β-hydride elimination from the formed alkyl rhenium intermediate and then by hydrogenation of the imino group of the aldimine.

1. Introduction

C–H functionalization is one of the most efficient and direct methods in synthetic organic chemistry. There have, therefore, recently been many efforts to develop new transformations via C–H bond activation [1]. In such transformations, insertion of unsaturated molecules into a C–H bond is well known, and the reactions usually stop at the insertion step. Our group has also reported on transformations via C–H bond activation using rhenium complexes as catalysts [2]. In some of these reactions, intramolecular nucleophilic cyclization occurs after the insertion of unsaturated molecules into a formed C(sp^2)–Re bond [2]. During investigations of rhenium-catalyzed C–H transformations, we discovered the alkenylation reaction of aromatic compounds.

There have been several reports of alkenylation reactions of aromatic C–H bonds. The first approach involves the cross coupling reaction between aromatic compounds and alkenyl halides (Fig. 1(a)) [3], and the second strategy is based on the insertion of alkynes into a C–H bond of aromatic compounds (Fig. 1(b)) [4]. The third process is oxidative–dehydrogenative alkenylation of C–H bonds using a stoichiometric amount of an oxidant (Fig. 1(c)) [5]. The fourth route, which we also report herein, is the insertion of alkenes into a C–H bond of aromatic compounds followed by dehydrogenation of the formed alkylated aromatic compounds (Fig. 1(d)) [6].

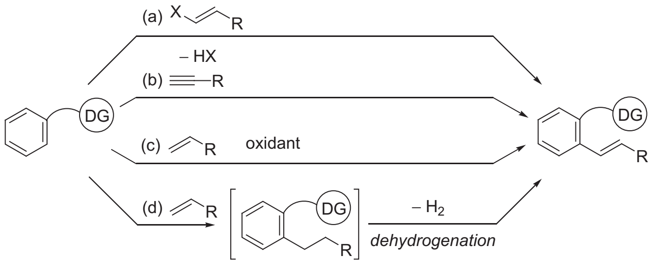

Fig. 1. Four methods for alkenylation of aromatic C–H bonds.

2. Results and discussion

First, we investigated the reaction between aromatic aldimine **1a** and styrene (**2a**) using the rhenium complex, $[ReBr(CO)_3(thf)]_2$, as the catalyst. Quinoline derivative **3** was formed in 31% yield (Eq. (1)) [7]. In this reaction, the rhenium complex worked as a Lewis acid and promoted a regioselective aza-Diels–Alder reaction [8]. *N*-Benzylaniline was also formed as a side product. This result indicated that aldimine **1a** also worked as a hydrogen acceptor to produce quinoline **3** from tetrahydroquinoline, which is part of

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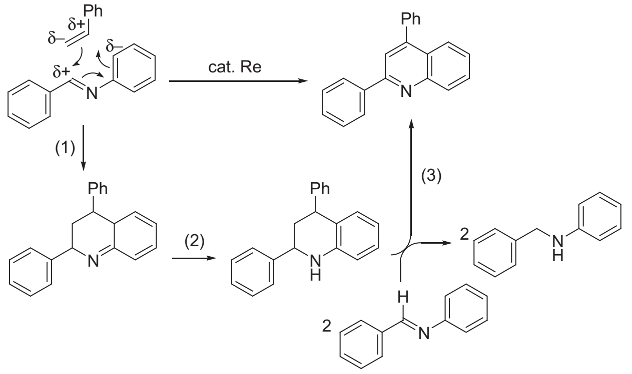
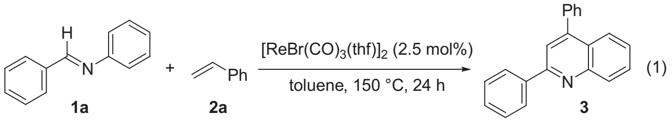


Scheme 1. Proposed mechanism for the formation of quinoline derivative **3**.

an aza-Diels–Alder adduct between **1a** and **2a**. Therefore, by increasing the amount of **1a** (3.0 equiv), the yield of **3** was improved to 66% (Eq. (1)).



Equiv of **1a**	Yield (%)
1.0	31
3.0	66

The possible mechanism for the formation of a quinoline derivative is shown in Scheme 1: (1) Aza-Diels–Alder reaction between an *N*-arylaldimine and styrene; (2) tautomerization; (3) transfer dehydrogenation of the formed tetrahydroquinoline with 2 equiv of *N*-arylaldimine. In this mechanism, the regioselectivity must be determined by electron densities of *N*-arylaldimine and styrene.

By changing the rhenium catalyst, $[ReBr(CO)_3(thf)]_2$, to $[HRe(CO)_4]_n$, the product of the reaction between aromatic aldimine **1a** and styrene (**2a**) changed dramatically. Treatment of **1a** with **2a** in the presence of a catalytic amount of the rhenium-hydride complex, $[HRe(CO)_4]_n$, gave *N*-(2-styrylbenzyl)benzenamine (**4a**) in 80% yield (Eq. (2)) [9–12]. The catalytic activity for the formation of **4a** is much higher than that of other rhenium complexes that we have previously reported as being effective in C–H bond transformations [13]. In addition, a rhenium complex, $[HRe(CO)_4]_n$, has a lower Lewis acidity than $[ReBr(CO)_3(thf)]_2$, $[HRe(CO)_4]_n$ did not promote aza-Diels–Alder reaction. There have been several reports of the transition metal-catalyzed insertion of styrene (or other alkenes) into an aromatic C–H bond; however, transfer of dihydrogen did not occur after the insertion step [14]. In this reaction, the loss of the imino group **1a** may be disadvantage. However, it must be valuable to synthesize 2-alkenylbenzylamines from aldimines and alkenes because the synthesis can be achieved without addition of any oxidant or hydrogen acceptor [15].

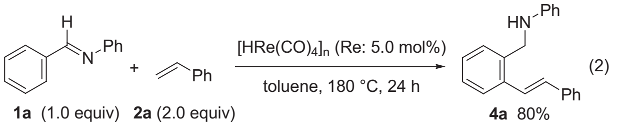
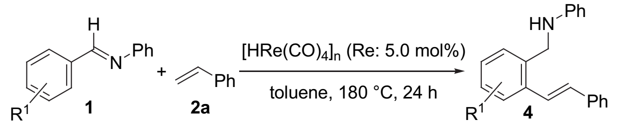
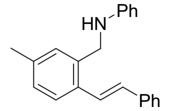
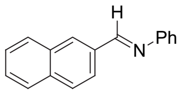
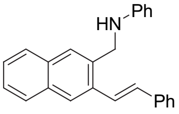


Table 1
Reactions of aldimines **1** with styrene (**2a**).[a]



Entry	R^1	Yield (%)[b]
1[c]	4-MeO **1b**	**4b** 70 (73)
2	4-Me **1c**	**4c** 76 (78)
3	4-CF_3 **1d**	**4d** 82 (87)
4	3-Me **1e**	 **4e** 75 (79)
5[c]	2-Me **1f**	**4f** 80 (84)
6[d]	 **1g**	 **4g** 78 (79)

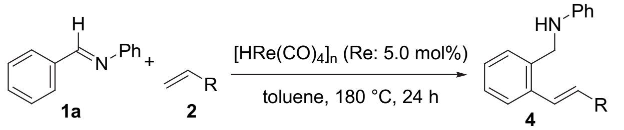
[a] **2a** (2.0 equiv).
[b] Isolated yield. Yield determined by ^1H NMR is reported in parentheses.
[c] 30 h.
[d] After 24 h, $[HRe(CO)_4]_n$ (Re: 5.0 mol%) and **2a** (2.0 equiv) were added, and the reaction mixture was stirred at 180 °C for 24 h.

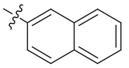
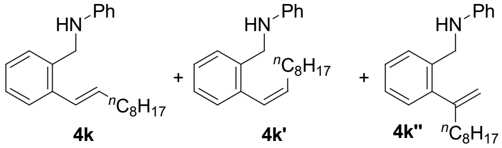
We next investigated the scope and limitations of the reaction, specifically evaluating the imines that are suitable for the transformation (Table 1). Aromatic aldimines with an electron-donating group, **1b** and **1c**, produced 2-alkenylbenzylamines **4b** and **4c** in 70% and 76% yields, respectively (entries 1 and 2). The corresponding 2-alkenylbenzylamine **4d** was generated in 82% yield when aromatic aldimine bearing an electron-withdrawing group, **1d**, was employed (entry 3). In the case of aromatic aldimine with a methyl group at the *meta*-position, **1e**, only one isomer **4e** was formed regioselectively in 75% yield (entry 4). Furthermore, the reaction was not inhibited by steric hindrance at the *ortho*-position; the corresponding 2-alkenylbenzylamine **4f** was produced in 80% yield when aromatic aldimine **1f** with a methyl group at the *ortho*-position was employed (entry 5). Only one product **4g** was obtained with (*E*)-*N*-((naphthalen-2-yl)methylene)benzenamine (**1g**), which has two possible reaction points (entry 6). However, reaction between the aromatic ketimine *N*-(1-phenylethylidene)benzenamine and styrene (**2a**) did not provide the corresponding alkenylated product, but produced alkylated aromatic ketimine [(*E*)-*N*-(1-(2-phenethylphenyl)ethylidene)benzenamine] in 7% yield.

Next, we investigated the reactivity of several alkenes (Table 2). Styrene with an electron-donating group, **2b**, gave 2-alkenylbenzylamine **4h** in 90% yield (entry 1). The corresponding 2-alkenylbenzylamine **4i** was obtained using styrene bearing a fluorine atom at the *para*-position, **2c** (entry 2). 2-Vinylnaphthalene (**2d**) also afforded 2-alkenylbenzylamine **4j** in 63% yield (entry 3). A mixture of 2-alkenylbenzylamines **4k**, **4k′** and **4k″** was formed in 85% total yield when aliphatic alkene **2e** was used as an olefinic substrate (entry 4) [16]. By investigating the ratios between **4k** (*trans*-form) and **4k′** (*cis*-form) during the reaction, it was clarified that **4k′** should be formed from **4k** by isomerization [17].

The proposed mechanism for reaction is as follows (Scheme 2): (1) oxidative addition of an aromatic aldimine to a rhenium center (C–H bond activation) [2]; (2) insertion of an alkene into the formed rhenium–carbon bond; (3) β-hydride elimination [6]; (4) insertion of a carbon–nitrogen double bond of the imino group into a rhenium–hydrogen bond [18]; (5) and reductive elimination to give 2-alkenylbenzylamines **4** and regenerate the rhenium catalyst. It is interesting to note that β-elimination from **5** proceeds preferentially instead of intramolecular nucleophilic cyclization, which

Table 2
Reactions of aldimine **1a** with alkenes **2**.[a]



Entry	R	Yield (%)[b]
1[c]	4-MeC_6H_4 **2b**	**4h** 90 (91)
2	4-FC_6H_4 **2c**	**4i** 66 (76)
3	 **2d**	**4j** 63 (66)
4[d]	$^nC_8H_{17}$ **2e**	
	 **4k** **4k'** **4k"**	**4k**+**4k′**+**4k″** 85 (86) [77:11:12][e]

[a] **2** (2.0 equiv).

[b] Isolated yield. Yield determined by ^{1}H NMR is reported in parentheses.

[c] **2** (4.0 equiv).

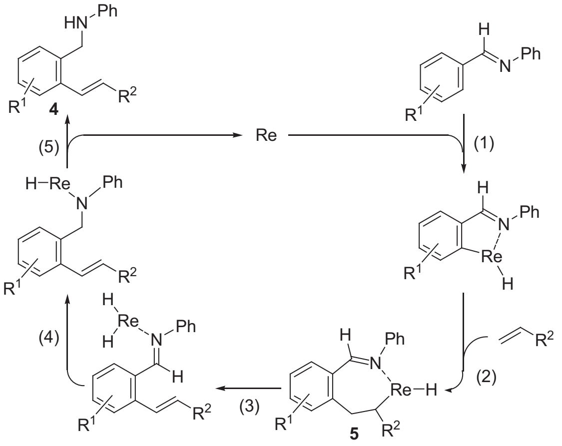
[d] After 24 h, $[HRe(CO)_4]_n$ (Re: 5.0 mol%) and **2a** (2.0 equiv) were added, and the reaction mixture was stirred at 180 °C for 24 h.

[e] The ratios between **4k**, **4k′** and **4k″** are reported in square brackets.

occurs in previously reported rhenium-catalyzed C—H transformations [2].

3. Summary

We have succeeded in developing the rhenium complex $[HRe(CO)_4]_n$, which catalyzes the synthesis of 2-alkenylbenzylamines from aromatic aldimines and alkenes. This reaction proceeds via aromatic C—H bond activation, insertion of the alkene into a C—H bond of the aromatic compound, β-hydride elimination and hydrogenation of the imino group of the aromatic aldimine. The β-hydride elimination and hydrogenation steps are rare examples in transformations that proceed via aromatic C—H bond activation. By changing the rhenium catalyst to $[ReBr(CO)_3(thf)]_2$, a quinoline derivative was produced from an aromatic aldimine and styrene via an aza-Diels—Alder reaction.



Scheme 2. Proposed mechanism for the formation of 2-alkenylbenzylamines **4**.

Acknowledgment

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.09.064.

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(b) Y. Guari, S. Sabo-Etienne, B. Chaudret, Eur. J. Inorg. Chem. (1999) 1047;
(c) G. Dyker, Angew. Chem. Int. Ed. 38 (1999) 1698;
(d) F. Kakiuchi, T. Kochi, Synthesis (2008) 3013.

[2] We have already reported several rhenium-catalyzed transformations that occur via C—H bond activation. See: (a) Y. Kuninobu, Y. Tokunaga, A. Kawata, K. Takai, J. Am. Chem. Soc. 128 (2006) 202;
(b) Y. Kuninobu, Y. Nishina, M. Shouho, K. Takai, Angew. Chem. Int. Ed. 45 (2006) 2766;
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(d) Y. Kuninobu, Y. Tokunaga, K. Takai, Chem. Lett. 36 (2007) 872;
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(b) Y. Nakao, K.S. Kanyva, S. Oda, T. Hiyama, J. Am. Chem. Soc. 128 (2006) 8146;
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[6] There have been a few reports of β-hydride elimination following the insertion of an alkene into an aromatic C—H bond. See: (a) P. Hong, H. Yamazaki, Chem. Lett. (1979) 1335;
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[7] Investigation of several rhenium catalysts and temperatures: $Re_2(CO)_{10}$ at 180 °C, 0%; $ReBr(CO)_5$ at 150 °C, 28% and at 180 °C, 30%; $[ReBr(CO)_3(thf)]_2$ at 150 °C, 31% and at 180 °C, 28%; $[HRe(CO)_4]_n$ at 150 °C, 0% and at 180 °C, 0%.

[8] Iron-promoted and rhodium-catalyzed synthesis of quinoline derivatives via an aza-Diels—Alder reaction between *N*-aryl aldimines and styrenes has been reported. See: (a) R. Leardini, D. Nanni, A. Tundo, G. Zanardi, F. Ruggieri, J. Org. Chem. 57 (1992) 1842;
(b) M. Beller, O.R. Thiel, H. Trauthwein, C.G. Hartung, Chem. Eur. J. 6 (2000) 2513.

[9] The reaction did not proceed using the following transition metal complexes: $Mn_2(CO)_{10}$, $MnBr(CO)_5$, $RuH_2(CO)(PPh_3)_3$, $Ru_3(CO)_{12}$, $RhCl(PPh_3)_3$ and $Ir_4(CO)_{12}$.

[10] Investigation of catalytic amounts: 0.50 mol%, 7%; 1.0 mol%, 9%; 2.5 mol%, 22%.

[11] Investigation of several solvents: neat, 7%; octane, trace; toluene, 80%; 1,2-dichloroethane, trace; *n*-hexanenitrile, 10%.

[12] Following the reviewer's suggestion, we have examined the reactions between aldimine **1a** and styrene (**2a**) using 5.0 equiv of a hydrogen acceptor, such as norbornene or 3,3-dimethyl-1-butene, under the reaction conditions shown in Eq. (2). As a result, alkenylated product **4a** was obtained in 4% and 64% yields, respectively.

[13] The reaction did not proceed using $Re_2(CO)_{10}$, $ReBr(CO)_5$ or $[ReBr(CO)_3(thf)]_2$.

[14] (a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, Nature 366 (1993) 529;
(b) F. Kakiuchi, M. Sonoda, T. Tsujimoto, N. Chatani, S. Murai, Chem. Lett. (1999) 1083;
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(d) R.K. Thalji, K.A. Ahrendt, R.G. Bergman, J.A. Ellman, J. Am. Chem. Soc. 123 (2001) 9692.

[15] There has been a report on palladium-catalyzed oxidative *ortho*-olefination of *N*-substituted benzylamines using alkenes in the presence of a stoichiometric amount of an oxidant. See: G. Cai, Y. Fu, Y. Li, X. Wan, Z. Shi, J. Am. Chem. Soc. 129 (2007) 7666.

[16] One possible reason for the formation of **4k**′ (*cis*-form) is that **4k** (*trans*-form) is isomerized to **4k**′ under the reaction conditions. In fact, the ratios between **4k** and **4k**′ changed during the reaction. That is, at the beginning of the reaction, the ratio of **4k** is high; however, the ratio of **4k** decreased and that of **4k**′ increased as the reaction proceeded.

[17] Yields of **4k** and **4k**′ (the ratios between **4k** and **4k**′): 1 h, 3%, 0% (100:0); 3 h, 16%, trace (>99:1); 8 h, 32%, 4% (89:11); 24 h, 63%, 10% (86:14).

[18] For an example of the insertion of a carbon–nitrogen double bond into a rhenium–hydrogen bond, see: X.-Y. Liu, K. Venkatesan, H.W. Schmalle, H. Berke, Organometallics 23 (2004) 3153.