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Asymmetric Alkenylation of Enones and Imines Enabled by Highly Efficient Aryl to Vinyl 1,4-Rhodium Migration**

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Enantioselective rhodium-catalyzed addition of organoboron reagents to electron-deficient double bonds has proven to be a powerful and reliable method for asymmetric carbon-carbon bond construction.[1] Compared to the wide application of arylboronates, vinylboronates are far less studied, and quite limited with easily accessible ones bearing a di-substituted double bond.[2] When vinylboronates with more substitutions on the double bond are needed, one of the challenges aroused is to control the olefin stereochemistry. Although several methods to effectively prepare these vinylboronates have been released,[3] new and even more ingenious strategies to address this issue are always desirable.

In rhodium catalysis, new reactivity of the original organoboronates sometimes can be pursued by rhodium migration approach, and achieve synthetic transformations that are inaccessible by conventional methods. In 2012, Hayashi and co-workers reported a vinyl to aryl 1,4-rhodium migration starting from a vinylboronic acid, which provided a novel method to add an *ortho*-vinyl substituted phenyl ring to enones (Scheme 1a).[4] In 2014, Lam and co-workers described an allyl to allyl 1,4-rhodium migration and realized a complicated allylation of cyclic imines with simple allylic boronates (Scheme 1b).[5] We envisioned that an aryl to vinyl rhodium migration could occur for the corresponding arylboronates, providing a new method to attach multi-substituted vinyl moiety with controllable stereochemistry of the double bond (Scheme 1c).

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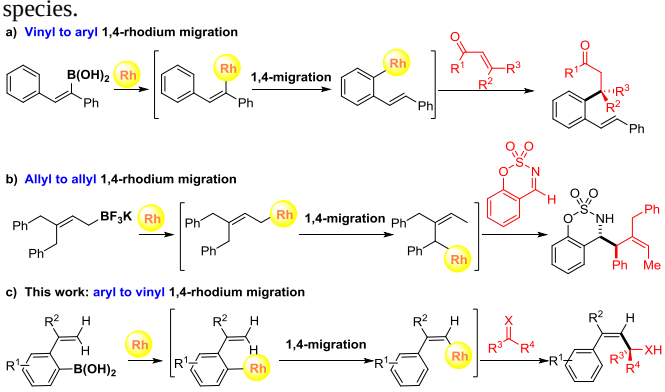
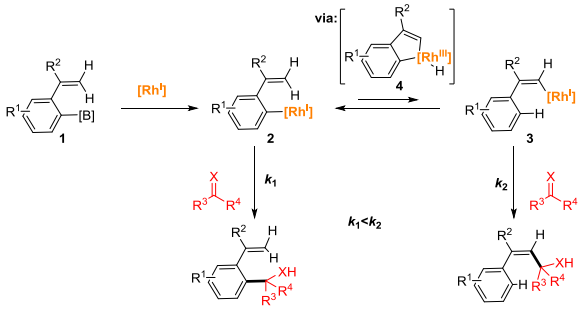
Since the pioneering work of Miura,[6] rhodium migration has been extensively explored.[7-12] Vinyl to aryl 1,4-rhodium migration is one of the most studied migration mode in this field, and has been applied in many novel organic transformations.[8] In contrast, the reverse approach, application of aryl to vinyl 1,4-rhodium migration in organic synthesis, has not been reported yet,[13] probably because the aryl position is normally more thermodynamically favoured. Recently, we discovered an aryl to vinyl 1,4-palladium migration and applied in the stereoselective synthesis of vinylboronates and 1,3-dienes.[14] We speculate that the key to success is the use of terminal olefins, and the driving force for this migration process likely comes from faster cross-coupling for less sterically hindered vinyl palladium compared to the corresponding aryl palladium species.



Scheme 1. New reactivity of organoboronates enabled by 1,4-rhodium migration



Scheme 2. Proposed strategy.

Therefore, we think that a similar strategy is also possible for enabling aryl to vinyl 1,4-rhodium migration (Scheme 2). When the arylrhodium species **2** is generated through transmetalation with the arylboronates **1**, the following direct addition to electron-deficient double bonds may be hampered by the *ortho*-vinyl substitution. In this case, an oxidative addition of the adjacent vinyl C-H bond may be triggered to form **4**, which has been well established by experimental and theoretical investigations.[15] The subsequent H-transfer of **4** leads to the completion of the 1,4-rhodium migration. Although the resulting vinyl rhodium **3** is supposed to be less stable compared to the arylrhodium, the faster and favored addition to electron-deficient double bonds would push the whole reaction toward this migration path.

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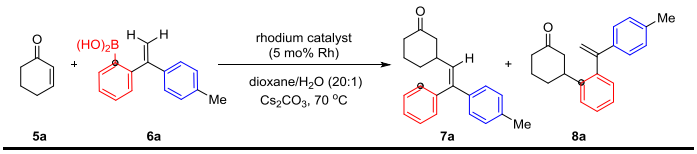
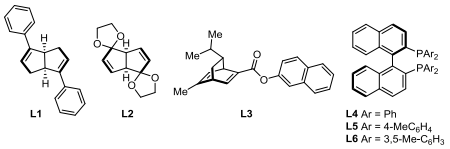
To test our hypothesis, the addition of arylboronic acid **6a** to 2-cyclohexenone **5a** was explord as a model reaction, and a number of rhodium catalysts were examined (Table 1). Delightfully, the desired 1,4-rhodium migration/addition product **7a** was produced in excellent yield by using simple $[RhCl(COD)]_2$ as catalyst (entry 1). Only trace amounts of possible undesirable addition product **8a** was detected by ^1H NMR and GC-MS analysis, and this is also the case in the following studies using chiral catalysts. The in situ prepared chiral rhodium catalyst from the reaction of $[RhCl(C_2H_4)_2]_2$ and optically pure bicycle[3.3.0] octadiene **L1**[16] gave good enantioselectivity, albeit with low yield (entry 2), which may attributed to the huge steric hindrance of diene **L1** for the attachment of a bulky vinyl moiety. Higher reactivity was achieved when dienes **L2**[17] and **L3**[18] were used, and an excellent enantioselectivity was obtained with diene **L3** (entries 3 and 4). In contrast to fact that BINAP/rhodium complex failed to promote vinyl to aryl 1,4-rhodium migration,[4] excellent performances of BINAP and its derivatives were observed in our aryl to vinyl rhodium migration process, and almost quantative yields and perfect enantioselectivities were obtained for all the tested examples (entries 5-7). Reducing the catalyst loading to 3 mol % resulted in an obvious loss in reaction yield(entry 8). It is worth mentioning that only a single *E*-isomer was obtained in this migration/addition process.

Table 1. Optimization of reaction conditions.[a]

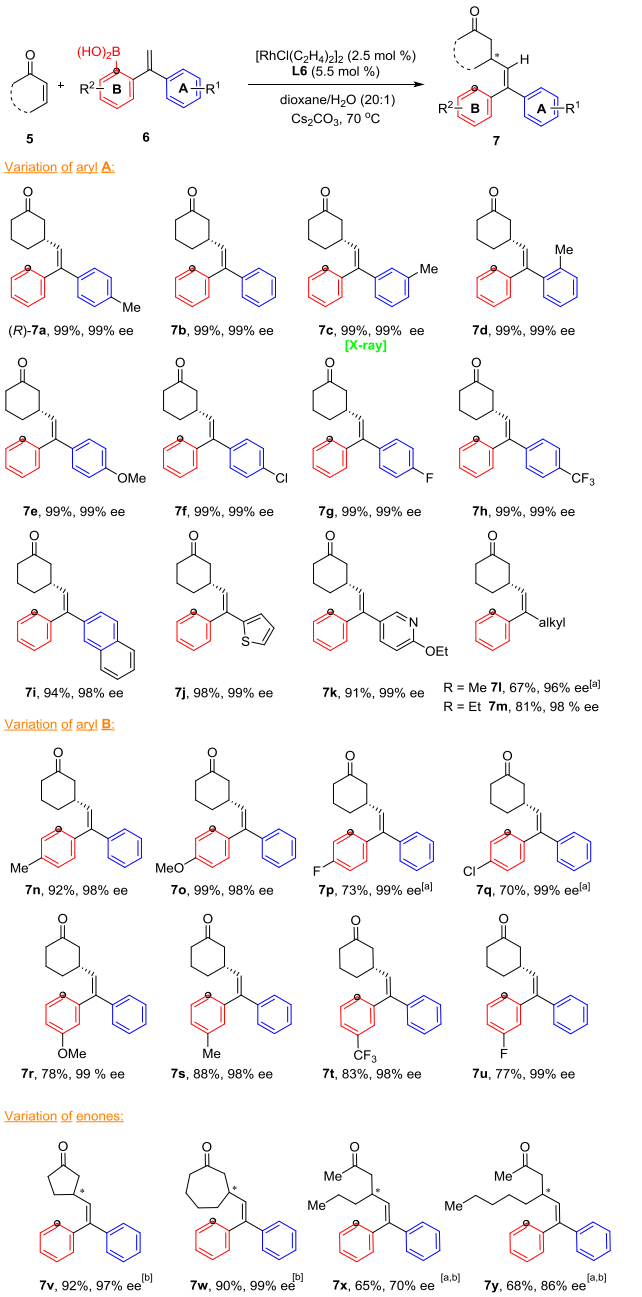


Entry	Rhodium catalyst	Yield of **7a** (%)[b]	ee of **7a** (%)[c]	**7a**/**8a**[d]
1	$[RhCl(COD)]_2$	97	--	>20/1
2	$[RhCl(C_2H_4)_2]_2$/**L1**	17	-93	>20/1
3	$[RhCl(C_2H_4)_2]_2$/**L2**	95	87	>20/1
4	$[RhCl(C_2H_4)_2]_2$/**L3**	99	97	>20/1
5	$[RhCl(C_2H_4)_2]_2$/**L4**	99	98	>20/1
6	$[RhCl(C_2H_4)_2]_2$/**L5**	99	99	>20/1
7	$[RhCl(C_2H_4)_2]_2$/**L6**	99	99	>20/1
8[e]	$[RhCl(C_2H_4)_2]_2$/**L6**	82	99	>20/1

[a] Unless otherwise noted, reactions were carried out with **5a** (0.20 mmol), **6a**(0.40 mmol), cesium carbonate (0.30 mmol), $[RhCl(COD)]_2$ (2.5 mol %) or $[RhCl(C_2H_4)_2]_2$ (2.5 mol %)/ligand (5.5 mol %) in dioxane (2 mL)/H_2O(0.1 mL) at 70 °C for 3 h. [b] Yields were determined by ^1H NMR spectroscopy analysis using CH_2Br_2 as an internal standard. [c] Ee values were determined by chiral HPLC. [d] Determined by ^1H NMR spectroscopy and GC-MS analysis [e] $[RhCl(C_2H_4)_2]_2$ (1.5 mol%)/**L6** (3.3 mol %) and a prelonged reaction time of 4 h.



Next, the generality of this rhodium migration/addition sequence was examined under the optimized reaction conditions (Table 1, entry 7). In all tested cases, the desired 1,4-rhodium migration/addition reaction proceeded smoothly (Scheme 3). Increasing steric hindrance by moving the *para*-methyl group in the phenyl ring A to the *meta* or *ortho*-position had no negative effect on both reaction yields and enantioselectivities (**7a** vs **7c** and **7d**). Excellent reaction yields and enantioselectivities were also observed no matter either electron-donating or electron-withdrawing group was introduced to *para*-position (**7e** - **7h**). The phenyl ring A could be replaced by a naphthyl (**7i**), thienyl (**7j**) or pyridyl (**7k**) group without affecting the reaction outcome. However, replacement with alkyl substitutions still offered high enantioselectivities albeit with lower reaction yields (**7l** and **7m**), which partially was attributed to the incomplete conversion of enone **5a**. In comparison, substitutions on the phenyl ring B showed significant impact on the reaction activity. Introduction of a substituent generally led to a reduced reaction yield, especially with an electron-withdrawing group (like **7p** and **7q**), however excellent enantioselectivities were maintained. The substitution on the phenyl ring B changes electronic property of C-B/C-Rh bond, which may increase the difficulty of rhodium migration, as well as accelerate the hydrolysis of the arylboronates.[19]



Scheme 3. Alkenylation of enones via aryl to 1,4-rhodium migration. Unless otherwise noted, reactions were carried out with **5** (0.20 mmol), **6** (0.40 mmol), $[RhCl(C_2H_4)_2]_2$ (2.5 mol %)/**L6** (5.5 mol %) and Cs_2CO_3 (0.30 mmol) in dioxane (2 mL)/H_2O(0.1 mL) at 70 °C for 3 h. [a] A small amount of unreacted enone **6** can be observed by ^1H NMR analysis of the crude product. [b] A prelonged reaction time of 5 h.

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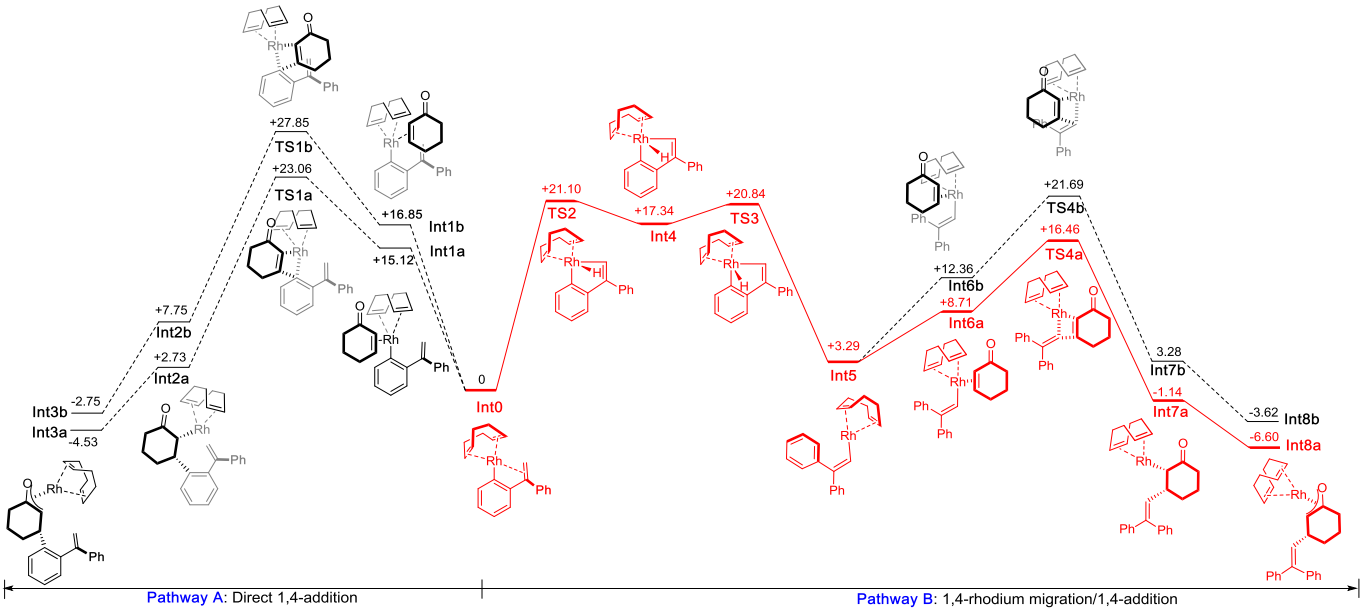


Scheme 5. Mechanistic rationale supported by DFT calculations at the B3LYP/Def2TZVP//B3LYP/B1 level (B1: SDD-6-31G(d,p)). The relative free energies are given in kcal/mol. The preferred pathway is shown in red.

While other cyclic enones (**7v** and **7w**, Scheme 3) were also qualified as excellent coupling partners, a slightly reduced efficiency was observed for less reactive but more flexible linear enones (**7x** and **7y**).

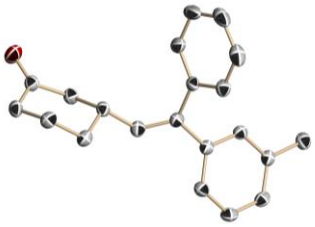
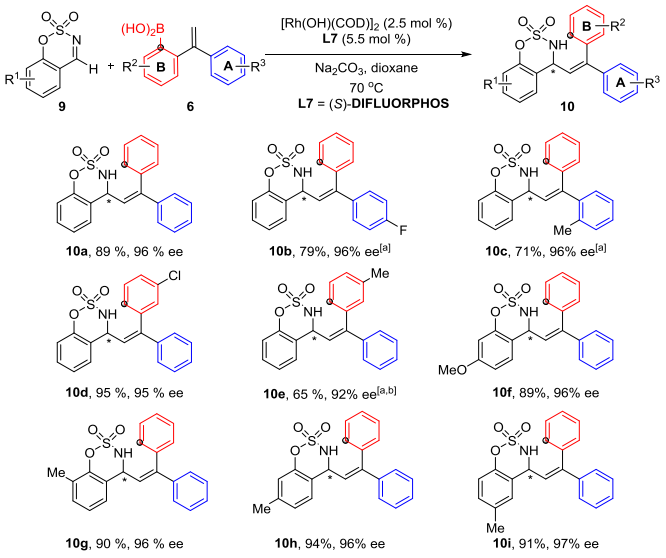


Figure 1. X-ray crystal structure of **7c** at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Scheme 4. Alkenylation of imine **9** via aryl to 1,4-rhodium migration. Reactions were carried out with **9** (0.20 mmol), **6** (0.60 mmol), $[Rh(OH)(COD)]_2$ (2.5 mol %)/**L7** (5.5 mol %), and Na_2CO_3 (0.30 mmol) in dioxane (2 mL) at 70 °C for 5.5 - 8 h. [a] Conversions were calculated by ^{1}H NMR analysis of the crude products to be 90% (**10b**), 90% (**10c**) and 78% (**10e**), respectively. [b] **6** (1.00 mmol) was used.

The absolute configuration of **7c** was unambiguously determined to be *R* by X-ray crystallography (Figure 1),[20] which is in accordance to the stereochemistry-defining model for the arylation of cyclohexenone previously proposed by Hayashi group.[21] The configurations of other cyclohexenone adducts were also assigned as *R* by assuming a similar reaction pathway.

Encouraged by the above success, the addition to less active imine was also studied (Scheme 4). In this case, $[Rh(OH)(COD)]_2$ proved to be the best precatalyst and DIFLUORPHOS (5,5'-bis(diphenylphosphanyl)-2,2,2',2'-tetrafluoro-4,4'-bi[benzo-1,3-dioxolyl]) was crucial for the reactivity. Under the newly optimized reaction conditions, several arylboronic acids were tested for the addition to cyclic imine **9**. The desired rhodium migration/addition sequence went very well for most examined examples, affording the adducts **10** in good reaction yields with excellent enantioselectivities. But the reactivity was greatly inhibited by a methyl substitution on the phenyl ring B, and 5 equivalents of boronic acid **6** were needed for a decent reaction yield.

DFT calculations were performed to gain mechanistic insights into this 1,4-rhodium migration process (Scheme 5).[22] Aided by experimental data, a model system with COD as ligand was constructed for simplification. Starting from the aryl rhodium intermediate **Int0**, which was generated by transmetalation between rhodium catalyst and arylboronic acid **6a**,[23] two different pathways **A** and **B** would afford direct 1,4-addition product **8a** and 1,4-rhodium migration/1,4-addition product **7a**, respectively. In the pathway **A**, the overall energy barrier for the direct insertion of 2-cyclohexenone to C-Rh bond is 23.1 kcal/mol. While in the pathway **B**, the 1,4-rhodium migration of **Int0** includes a C-H oxidative addition[4] and H-transfer sequence with an overall energy barrier of 21.1 kcal/mol,[4, 15] which is slightly lower than the direct addition process. The resulting vinyl rhodium **Int5** is thermodynamically less stable than the original aryl rhodium **Int0** (+3.3 kcal/mol *vs* 0 kcal/mol), which may be attributed to a stronger stabilizing effect of phenyl group as well as the additional stabilizing effect from the coordination of the vinyl group in **Int0**. Although the reverse migration (**Int5** → **Int0**) seems to be energetically favourable, the much lower energy barrier (+13.2 kcal/mol) for the subsequent addition of **Int5** to 2-cyclohexone leads to a quick conversion of **Int5** to the desired alkenylation product, in other words, this facile

1,4-addition step makes the whole reaction process move towards this direction. These results indicate that, unlike the previous thermodynamically favored vinyl to aryl 1,4-rhodium migration,[4] the current process is kinetically controlled, which is in accordance with the basic hypothesis assumed above. This mechanism also illuminates for the explanation of similar aryl to vinyl 1,4-palladium migration/cross-coupling sequences.[14]

In conclusion, we have reported an asymmetric rhodium-catalyzed alkenylation of enones and imines with arylboronic acids. A highly efficient aryl to vinyl 1,4-rhodium migration is the key to success, providing a new mode to generate stereodefined vinylrhodium species. Both diene and bis-phosphine ligands proved to be competent to promote this rhodium migration sequence, and excellent enantioselectivities were also obtained with the corresponding chiral ligands. DFT calculations revealed that the excellent migration efficiency is attributed to a kinetically favored process. Further application this unique 1,4-rhodium migration strategy in other transformations is ongoing.

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Metal Migration

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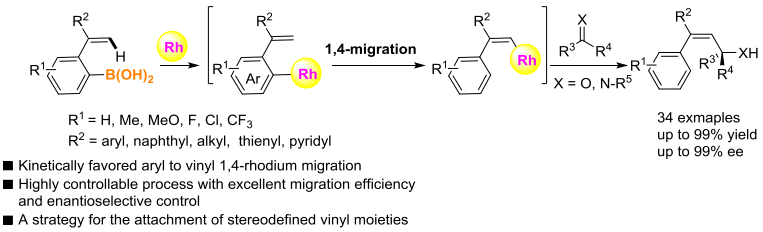
Asymmetric Alkenylation of Enones and Imines Enabled by Highly Efficient Aryl to Vinyl 1,4-Rhodium Migration



The asymmetric rhodium-catalyzed alkenylation of enones and imines with arylboronic acids has been developed. An highly controllable aryl to vinyl 1,4-rhodium migration is the key step. Stereodefined vinyl moieties were installed in excellent enantioselectivies for most examined examples. DFT calculations reveal that the driving force of this rhodium migration is a kinetically favored process.