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Heterogeneous Chiral Diene-Rh Complexes for Asymmetric Arylation of α,β -Unsaturated Carbonyl Compounds, Nitroalkenes, and Imines

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In the memory of late Professor Teruaki Mukaiyama

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Abstract. A chiral diene ligand with tertiary alkyl amine-derived secondary amide moiety was immobilized on cross-linked polystyrene (PS) by radical polymerization, which was combined with Rh to form heterogeneous chiral Rh complexes (PS-diene Rh–Cl). PS-diene Rh–Cl catalyzed asymmetric arylation reactions of α,β -unsaturated carbonyl compounds (ketones, esters, and amides), nitroalkenes, and imines afforded the desired products in high yields with excellent enantioselectivities. PS-diene Rh–Cl is stable in air, can be stored for several months, and can be reused more than 10 times without any reduction of either yield or enantioselectivity. We also developed a method of activation of PS-diene Rh–Cl to generate more active species.

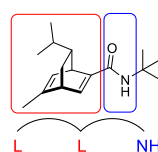
Keywords: heterogeneous catalyst; asymmetric 1,4-addition; chiral diene; Rh catalyst; flow reaction

The development of heterogeneous chiral catalysts for asymmetric C–C bond-forming reactions is among the most important subjects in modern chemistry. Here, precious chiral resources can be effectively utilized to construct chiral skeletons of target molecules.^[1–2] Not only their ease of recovery and reuse, but their potential application in continuous-flow reactions using columns packed with heterogeneous catalysts are attracting much attention as environmentally benign, safe, and efficient systems.^[3–5]

Chiral diene ligands, pioneered by Hayashi^[6] and Carreira,^[7] are well-studied class of ligands to construct chiral transition metals such as Rh and Ir catalysts, and they are utilized in many catalytic asymmetric reactions, including asymmetric arylation of electron-deficient olefins.^[8–11] In our laboratory, we have developed diene **L** with tertiary alkyl amine-derived secondary amide, which was designed as a bifunctional ligand where the diene parts could coordinate to metal and the relatively acidic secondary amide group could activate substrates through hydrogen bonding (Scheme 1). The ligand was applied

for both chiral Rh homogeneous complexes and chiral Rh heterogeneous nanoparticle systems, both of which show outstanding reactivities and enantioselectivities in asymmetric 1,4-addition and 1,2-addition reactions of a wide variety of substrates.^[12–16] Considering the value of the precious metal and the ligand, recovery and reuse of both components has a high impact in synthetic organic chemistry. There are several reports of immobilization of Rh complexes with chiral phosphine and diene ligands,^[17–22] however, phosphine ligands are prone to rapid oxidation under air, which prevents facile recovery and reuse. On the other hand, Lin et al. reported that immobilization of a diene Rh complex could be achieved on a metal-organic framework.^[21] Very recently, Uozumi et al. succeeded in the immobilization of a diene Rh complex on polystyrene–poly(ethylene glycol).^[22] However, none of the catalysts have high catalytic efficiency or display broad substrate scope with high enantioselectivities for reactions of simple α,β -unsaturated carbonyl compounds, heteroarenes, and nitroalkenes. Therefore, the development of highly active heterogeneous catalysts that show wide substrate generality for asymmetric arylation reactions is desired.

Here, we describe chiral diene ligand-immobilized heterogeneous Rh catalysts for asymmetric arylation reactions. A broad range of substrates, including α,β -unsaturated ketones, esters, amides, nitroalkenes, and imines, could be arylated in high yields with excellent enantioselectivities, and the catalyst could be reused more than 10 times without any loss of either yield or enantioselectivity.



diene **L**

L: coordination to the metal

NH: activation of substrate via H-bonding

Scheme 1. Tertiary alkyl amine-derived secondary amide substituted diene.

Considering our previous investigations, the tertiary alkyl amine moiety in diene **L** is essential to achieve outstanding activity and enantioselectivity, probably because structurally rigid nature of the amide group that restricts the rotation of the ^tBuNH group to fix the favored conformation.^[13] In the above-mentioned previous examples of immobilized dienes, the dienes were conjugated to primary amines on supports by amide condensation; however, they could not introduce a tertiary alkyl amine moiety probably because of difficulty to prepare a tertiary alkyl amine-containing support. Therefore, we designed a tertiary alkyl amine-derived chiral diene ligand with a styryl moiety to immobilize the ligand directly by polymerization. Such a strategy has never been conducted, presumably because it is concerned that an unsaturated carbonyl moiety in a ligand might induce side reactions under radical polymerization conditions.

We synthesized a chiral diene monomer bearing a styrene moiety (see the Supporting Information (SI)), and as shown in Scheme 2, the diene monomer was carefully copolymerized with styrene and divinylbenzene (DVB) in the presence of AIBN (0.8 mol%) at 80 °C, affording a chiral diene ligand supported on cross-linked polystyrene (PS-diene). PS-diene was then mixed with [Rh(C₂H₄)₂Cl]₂ in toluene to afford a yellow powder (PS-diene Rh–Cl). Successful immobilization of Rh was confirmed by ICP-OES measurements. STEM images and EDS analysis showed that Rh was well dispersed on polymer and the absence of Rh nanoparticles (see SI). Notably, PS-diene Rh–Cl was readily prepared, was stable in air, and could be stored for several months.



Scheme 2 Immobilization of diene ligand.

PS-diene Rh–Cl **A–E**, with different ratios of styrene, DVB, and the diene monomer, were tested in the asymmetric 1,4-addition of phenylboronic acid (**2a**) to cyclic enone **1a** in toluene/water biphasic co-solvent system^[23] (Table 1). The highest yield with outstanding enantioselectivity for the product **3aa** was obtained using PS-diene Rh–Cl **E** with 94:3.6:2.4

ratios of styrene, DVB, and the chiral diene monomer (entry 5).

Table 1. Optimization of reaction conditions.

entry	catalyst	x:y:z	yield (%) ^{a)}	ee (%) ^{b)}
1	A	96:2.5:1.3	75	99
2	B	95:3.6:1.3	86	99
3	C	93:6.0:1.3	74	99
4	D	96:3.6:0.7	91	99
5	E	94:3.6:2.6	98	99

^{a)} Determined by ¹H NMR analysis. ^{b)} Determined by HPLC analysis.

With PS-diene Rh–Cl **E** (0.5 mol%), several reactions of boronic acids with α,β-unsaturated carbonyl compounds were examined (Table 2). Neither electron-withdrawing nor electron-donating groups at the *para*-position of arylboronic acids (**2b** and **2c**) affected the catalytic activity, and high yields and outstanding enantioselectivities of the desired products were obtained (entries 2 and 3). *meta*-Methoxyphenylboronic acid (**2d**) was also a suitable substrate (entry 4). Arylboronic acid **2e**, with a substituent at the *ortho*-position, gave the desired product in lower yield (69%), presumably because of a steric effect, but outstanding enantioselectivity was observed (entry 5). The yield was improved to 92% by using 3 equiv. of **2e** while keeping the same enantioselectivity. As previously reported,^[12] lower reactivity was observed for acyclic α,β-unsaturated ketones than for cyclic α,β-unsaturated ketone. For example, acyclic α,β-unsaturated ketone **1b** reacted with **2a** to afford the product in only 5% yield, although the enantioselectivity was very high (entry 6). Other acyclic α,β-unsaturated ketones **1c** and **1d** showed moderate to good yields, albeit with very high enantioselectivities (entries 7 and 8). These low-yield issues were solved later (see below). When acyclic α,β-unsaturated ester **1e** was treated with **2a**, the desired product was obtained in 76% yield with 98% ee. Given that decomposition of the boronic acid was observed, 3.0 equiv. of **2a** were used and the yield was improved to 99% with the same enantioselectivity (entry 9). Other α,β-unsaturated esters, including heteroaromatics and even cyclic α,β-unsaturated esters, also worked well to afford the desired products in satisfactory yields with very high enantioselectivities (entries 10–15). Finally, α,β-unsaturated amides were tested, and it was found that this type of compounds were acceptable to this catalytic system (entries 16 and 17).

Recovery and reuse experiments of heterogeneous PS-diene Rh–Cl **E** were conducted for the reaction of **2a** with **1a** (Table 3). Even after the 10th cycle, no loss of either yield or enantioselectivity was observed. We also compared the activity of PS-diene Rh **E** with the

corresponding homogeneous Rh-diene **L** complex in the reaction of **1e** with **2a**.^[24] Although a similar high yield was observed in the presence of 0.1 mol% of the homogeneous catalyst, enough fast reaction rate and reusability of the heterogeneous catalyst are still remarkable advantages.

Table 2. Substrate scope (α,β -unsaturated carbonyl compounds).

entry	1	2	yield (%) ^{a)}	ee (%) ^{b)}	entry	1	2	yield (%) ^{a)}	ee (%) ^{b)}
1	1a	2a	98	99	9 ^{c)}	1e	2a	99	98
2	1a	2b	88	99	10 ^{c)}	1f	2d	89	98
3	1a	2c	90	99	11 ^{c)}	1g	2d	80	98
4	1a	2d	94	99	12 ^{c)}	1h	2a	93	98
5	1a	2e	69	99	13 ^{c)}	1i	2a	76	98
			(92) ^{c)}						
6	1b	2a	5	99	14 ^{c)}	1j	2a	60	96
			(87) ^{c,d)}						
7	1c	2a	25	99	15 ^{c)}	1k	2a	95	95
			(89) ^{c,d)}						
8	1d	2d	64	96	16	1l	2a	89	98
			(90) ^{e)}		17	1m	2a	96	98

a) Isolated yield. b) Determined by HPLC analysis. c) ArB(OH)₂ (3.0 equiv) was used. d) Cinnamyl alcohol (1.0 mol%) was used as an additive. e) PS-diene Rh-OH was used.

Table 3. Recovery and reuse.

cycle	yield (%) ^{a)}	ee (%) ^{b)}	cycle	yield (%) ^{a)}	ee (%) ^{b)}
1	99	99	6	97	99
2	98	99	7	98	99
3	99	99	8	99	99
4	98	99	9	98	99
5	97	99	10	98	99

a) Isolated yield. b) Determined by HPLC analysis.

We then investigated asymmetric 1,4-addition reactions of aryl boronic acids with nitroalkenes,

which are valuable because the resulting chiral nitro compounds can be converted into a range of useful compounds such as chiral amines. However, because of the strong coordination ability of the nitro group, stoichiometric to substoichiometric amounts of additives, such as KOH or KHF₂, were required to achieve an efficient catalytic turnover.^[25,26] Moreover, reported examples of heterogeneous catalysts for this asymmetric reaction have been very limited. We conducted several reactions of boronic acids with nitroalkenes using PS-diene Rh-Cl **E** (Table 4). Nitrostyrene derivatives bearing either electron-donating or electron-withdrawing substituents on the benzene ring worked well (entries 1–5). Heteroarenes-substituted nitroalkenes could react with **2a** to afford the corresponding adducts in high yields with high enantioselectivities (entries 6 and 7). Even aliphatic substrates could be utilized keeping high level of enantioselectivity (entries 8 and 9). Notably, PS-diene Rh-Cl **E** gave the same level or slightly higher enantioselectivities compared with the corresponding homogeneous Rh-diene **L** complex system.^[16]

We also examined asymmetric addition reactions of arylboronic acids with imines using PS-diene Rh-Cl. Since the first report of asymmetric addition of arylboronic acids to aryl tosylimines catalyzed by chiral Rh complexes in 2004,^[27] many efforts have been made to develop this type of reaction to provide chiral amines, which are found in many pharmaceutical skeletons.^[28] By using PS-diene Rh-Cl **E** (0.5 mol%), several imines were treated with **2a** under the optimal conditions (Table 5). Regardless of the substituents, all aromatic (entries 1–5) and heteroaromatic imines (entries 6 and 7) worked well to afford the corresponding amines in high yields with outstanding enantioselectivities. Although aliphatic imines are usually unstable in aqueous media, imine **6h** could be smoothly converted to the corresponding amine **7ha** even in a water-rich co-solvent system (entry 8). These results indicated that the immobilized catalyst maintained enough fast reaction rate to avoid hydrolysis of substrates.

Based on these studies of substrate scope, it was revealed that chiral environments around the immobilized Rh complex were not disturbed by the polymer matrix, and thus comparable enantioselectivities with the corresponding homogeneous Rh-diene **L** catalyst could be achieved for all the substrates regardless of electronically or sterically affective substituents. The same absolute configurations with the homogeneous catalyst were observed, indicating that the mechanism of enantioselection^[16,29] might not be different. Such a broad generality had never been achieved in previously-reported immobilized Rh complex catalysts.^[24]

Table 4. Substrate scope (nitroalkenes).

$$\text{R}-\text{CH}=\text{CH}-\text{NO}_2 \xrightarrow[\text{tol}/\text{H}_2\text{O} = 1:2, 100^\circ\text{C}, 16\text{ h}]{\text{PS-diene Rh-Cl } \mathbf{E} \text{ (Rh: 0.5 mol\%)} \atop \text{ArB(OH)}_2 \mathbf{2} \text{ (1.5 equiv)}} \text{R}-\text{CH}(\text{Ar})-\text{CH}_2-\text{NO}_2$$

4a-i **5ad-ia**

4a

4b

4c

4d

4e

4f

4g

4h

4i

entry	4	2	yield (%) ^{a)}	ee (%) ^{b)}	entry	4	2	yield (%) ^{a)}	ee (%) ^{b)}
1	4a	2d	88	94	6	4f	2a	93	96
2	4b	2a	91	93	7	4g	2a	93	93
3	4c	2a	95	95	8	4h	2a	90	90
4	4d	2a	92	93	9	4i	2a	94	89
5	4e	2a	94	93					

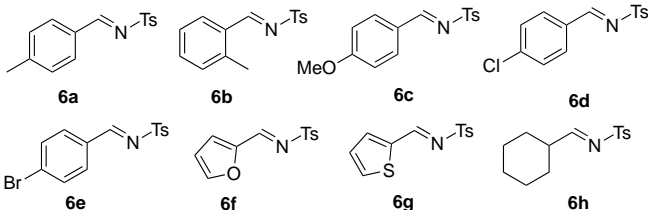
^{a)} Isolated yield. ^{b)} Determined by HPLC analysis.

^{a)} Isolated yield. ^{b)} Determined by HPLC analysis.

Table 5. Substrate scope (imines).

$$\text{R}-\text{CH}=\text{N}-\text{Ts} \xrightarrow[\text{tol/H}_2\text{O} = 1:2, 100^\circ\text{C}, 16\text{ h}]{\text{PS-diene Rh-Cl } \mathbf{E} \text{ (Rh: 0.5 mol\%)} \atop \text{PhB(OH)}_2 \mathbf{2a} \text{ (1.5 equiv)}} \text{R}-\text{CH}(\text{Ph})-\text{CH}_2-\text{N}-\text{Ts}$$

6a-h **7aa-ha**



6a **6b** **6c** **6d** **6e** **6f** **6g** **6h**

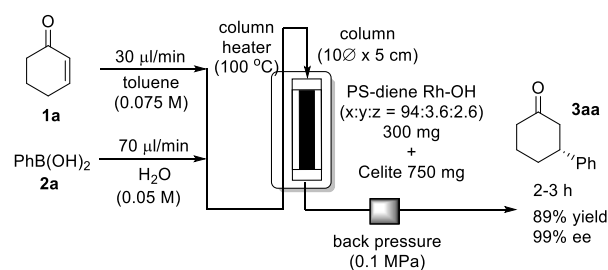
entry	6	yield (%) ^{a)}	ee (%) ^{b)}	entry	6	yield (%) ^{a)}	ee (%) ^{b)}
1	6a	95	99	5 ^{c)}	6e	89	97
2	6b	93	98	6	6f	85	99
3	6c	98	99	7	6g	90	99
4 ^{c)}	6d	98	98	8 ^{c)}	6h	78	99

^{a)} Isolated yield. ^{b)} Determined by HPLC analysis.

While various substrates in asymmetric 1,4-addition and even 1,2-addition reactions proceeded well, the lower yield associated with acyclic α,β -unsaturated ketones remained. It is known that the active species in Rh-catalyzed 1,4-addition reactions are Rh–OH complexes,^[30] and that treatment of Rh–Cl complexes with a base generates more active Rh–OH complexes.^[31] We then treated PS-diene Rh–Cl with KOH at room temperature for 24 h to form a hygroscopic solid, the elemental analysis of which showed a significant decrease in the amount of Cl, suggesting Rh–OH formation (see SI). The solid PS-diene Rh–OH thus prepared was first tested in the asymmetric 1,4-addition reaction of **2a** with **1a**. The reaction proceeded very rapidly to afford the desired adduct **3aa** quantitatively within 30 min; the TOF of the catalyst reached over 1,000 h^{−1} (91% for 10 min;

95% for 30 min; 96% for 1 h (99% ee)). We also conducted the reactions of acyclic α,β -unsaturated ketones **1b**, **1c**, and **1d**, and it was found that the yields were improved significantly (36%, 50%, 90%, respectively, Table 2, entry 8 in parentheses). Although the yields were improved, PS-diene Rh–OH was hygroscopic and its handling was not easy. We then intended to prepare PS-diene Rh–OH in situ from PS-diene Rh–Cl. After screening several additives (see SI), it was found that the use of and cinnamyl alcohol (1.0 mol%), **1b** and **1c** reacted with **2a** to afford cinnamyl alcohol was very effective for the reactions. In the presence of PS-diene Rh–Cl (0.5 mol%) and cinnamyl alcohol (1.0 mol%), **1b** and **1c** reacted with **2a** to afford the corresponding adducts **3ba** and **3ca** in 55% and 65% yields, respectively. The yields were further improved to 87% and 89%, respectively, by using 3 equiv. of **2a** while maintaining outstanding enantioselectivity (Table 2, entries 6 and 7 in parentheses). We assume that cinnamyl alcohol coordinates to Rh of PS-diene Rh–Cl to accelerate the formation of PS-diene Rh–OH. In this heterogeneous Rh-catalyzed asymmetric arylation of α,β -unsaturated carbonyl compounds without using additives, the efficiency of the reaction of esters and amides was better than that of ketones, despite the lower electrophilicity of unsaturated esters and amides. We assume that more Lewis basic esters and amides may also work as additives, coordinating to Rh of PS-diene Rh–Cl to accelerate the formation of PS-diene Rh–OH.^[32,33]

The application of PS-diene Rh–OH to a continuous-flow reaction was conducted (Scheme 3). A toluene solution of **1a** and an aqueous solution of **2a** were mixed in a T-shape joint and the biphasic flow was passed through the column containing PS-diene Rh–OH with back pressure. The desired product was continuously obtained in high yield without any decrease in enantioselectivity from batch reaction. However, clogging occurred after several hours. Further improvements to the catalysts are therefore required to enable continuous flow to be operated with a long lifetime; such a project is ongoing in our laboratory.



Scheme 2. Continuous-flow reaction.

In conclusion, we have developed ligand-immobilized heterogeneous chiral Rh complexes (PS-diene Rh–Cl) for asymmetric arylation reactions. A broad range of substrates, including α,β -unsaturated

ketones, α,β -unsaturated esters, α,β -unsaturated amides, nitroalkenes, and imines, could be arylated in high yields with excellent enantioselectivities, and the catalyst could be reused more than 10 times without any loss of yield or enantioselectivity. PS-diene Rh–Cl is robust and superior to previous-reported heterogeneous catalysts for the same type of reactions^[17–22] and has comparable performance with the corresponding homogeneous catalyst.^[13,16] These results indicated that the chiral diene with the tertiary alkyl amine-derived secondary amide moiety was successfully immobilized even under radical polymerization conditions. PS-diene Rh–Cl was further activated either by treatment with a base or in the presence of a Lewis basic additive. High TOF ($>1000\text{ h}^{-1}$) was achieved and the activated catalyst was applied to an asymmetric continuous-flow reaction.

Experimental Section

Representative procedure of asymmetric arylation catalyzed by PS-diene Rh catalyst.

PS-diene Rh (0.189 mmol/g, 7.9 mg, 0.0015 mmol), phenylboronic acid **2a** (53.7 mg, 0.45 mmol) and 2-cyclohexenone **1a** (28.8 mg, 0.3 mmol) were mixed with toluene (700 μL) and water (1400 μL). After the mixture was stirred at 100 °C for 16 h, the resulting mixture was diluted with Et₂O, washed with saturated aqueous Na₂CO₃ twice and dried over Na₂SO₄, and the solvent was removed *in vacuo*. The conversion was determined by ¹H NMR analysis with reference to an internal standard (1,1,2,2-tetrachloroethane). The crude product was purified by pTLC (hexane/ethyl acetate = 10:1) to afford the pure product **3aa** (51.2 mg, 98% yield). The ee value of the product was determined by chiral HPLC analysis (99% ee).

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COMMUNICATION

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