Letter

Rh(I)/Bisoxazolinephosphine-Catalyzed Regio- and Enantioselective Allylic Substitutions

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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.0c00712 • Publication Date (Web): 23 Mar 2020

Rh(I)/Bisoxazolinephosphine-Catalyzed Regio- and Enantioselective Allylic Substitutions

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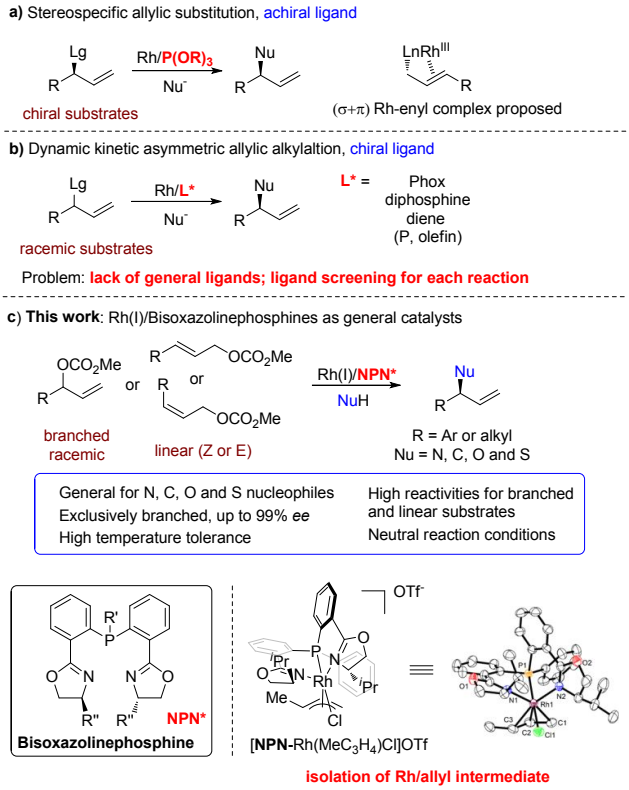
ABSTRACT: Rhodium(I)/bisoxazolinephosphine combination has been developed as a general catalyst to achieve the dynamic kinetic asymmetric allylation of a variety of nitrogen, carbon, oxygen and sulfur pronucleophiles from branched racemic allylic carbonates. Exclusively branch-selectivity and up to 99% enantiomeric excess could be obtained under neutral conditions. Linear allylic substrates (both *Z* and *E*) could be converted to the same chiral branched products with excellent regio- and enantioselectivities as well. Chiral π-allyl-Rh(III)/NPN intermediate was isolated and characterized to understand the origin of the high selectivities.

Keywords: Rhodium, allylic substitution, bisoxazolinephosphine, asymmetric catalysis, π-allyl-rhodium complex

Transition-metal-catalyzed asymmetric allylic substitution has become a powerful method to construct chiral building blocks with olefin functions.[1] Compared to frequently used Pd, Ir and Cu, Rh-catalyzed asymmetric allylic substitution is underexplored, although challenging aliphatic group substituted allylic compounds could be prepared by Rh.[2] The pioneering reports from Evans demonstrate that chiral branched allylic substrates could be converted to chiral products in a stereospecific manner with $Rh/P(OR)_3$ catalysts, in which a (σ+π)-allyl-Rh intermediate was proposed (Scheme 1, **a**).[3] The dynamic kinetic asymmetric allylation from racemic allylic precursors is more attractive for the easily accessible substrates and higher reactivities (Scheme 1, **b**). Hayashi's report on Rh/Phox-catalyzed selective carbon-carbon bond construction from malonates and racemic allylic esters indicates that this challenging process could be realized when suitable ligands and reaction conditions were selected.[4] The groups of Vrieze,[5] Nguyen,[6] Breit,[7] Guo[8] and You[9] developed the asymmetric allylation of several nucleophiles with chiral diphosphine, diene, or (P, olefin) ligands respectively. Nevertheless, the scope of allylic substrates and nucleophiles is still very limited. Moreover, extensive ligand screening is usually necessary when a new reaction is explored. A ligand which could be used in a general Rh-catalyzed highly enantioselective allylation for different nucleophiles is highly desired.

To develop a dynamic kinetic asymmetric allylation, a rapid π-σ-π isomerization before the new bond formation is mandatory. Inspired by our recently report on cobalt-catalyzed regio- and enantioselective allylic amination with bisoxazolinephosphine ligands,[10] we assume that the applying of tridentate ligand may help generate the σ-allyl-Rh intermediate and accelerate the interconversion of the chiral intermediates because of the third coordination atom. Herein, we report that bisoxazolinephosphines were identified as powerful ligands to control the expected selectivities. Rh(I)/bisoxazolinephosphine is able to catalyze the exclusively branch-selective asymmetric allylation with different nitrogen, carbon, oxygen and sulfur pronucleophiles in excellent enantioselectivities. Importantly, either racemic branched or linear (both *Z* and *E*) allylic substrates could be used as substrates (Scheme 1, **c**). An Rh/allyl/bisoxazolinephosphine complex was isolated and characterized by X-ray diffraction analysis, which could be used to interpret the high regio- and enantioselectivities.

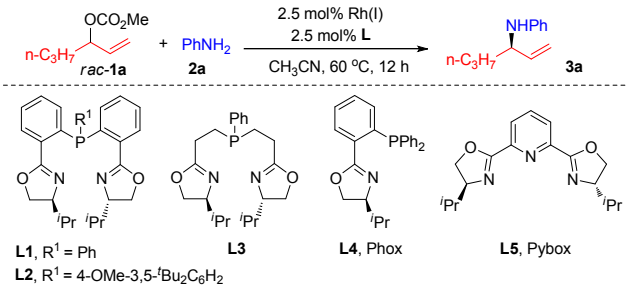
Scheme 1. Rh-Catalyzed Asymmetric Allylic Substitutions



We began our study by using racemic allylic carbonate **1a** and aniline **2a** in a 1 : 1 ratio as model substrates (Table 1). When the reaction was conducted with $Rh(cod)_2BF_4$ and **L1** in acetonitrile at 60 °C, excellent yield, exclusively branched regioselectivity and 99% *ee* were achieved (entry 1). Comparable yield and selectivity were

obtained with electron-richer and bulkier **L2** (entry 2). **L3** with the flexible linkers is also a suitable ligand with rhodium (90% yield, entry 3). However, only 10% *ee* was observed, which implies the rigid phenyl skeleton is crucial for the enantioselective process. Reactions with Phox **L4** and Pybox **L5** were not efficient (entries 4 and 5). The counter anion effect was also examined. Similar result was obtained when $[Rh(cod)Cl]_2$ was used (entry 6), while relatively lower conversion and *ee* were observed with $Rh(cod)_2OTf$ (entry 7). The reaction could also be conducted at room temperature and 50% of **3a** was isolated (entry 8). Finally, the reactivity of $[Ir(cod)Cl]_2$ and $Ir(cod)_2BF_4$ were checked under otherwise the identical condition.[11] However, much lower conversion and enantioselectivities were obtained (entries 9 and 10), which demonstrates the different reactivities of the metals. Acetonitrile is the best among solvents examined probably due to the coordination effect. Reactions from allylic acetate or phosphate lead to lower *ee*s, probably due to the π or σ complexation mode change caused by bidentate leaving groups (see SI).

Table 1. Optimization of Rhodium-Catalyzed Asymmetric Allylic Substitutions[a]

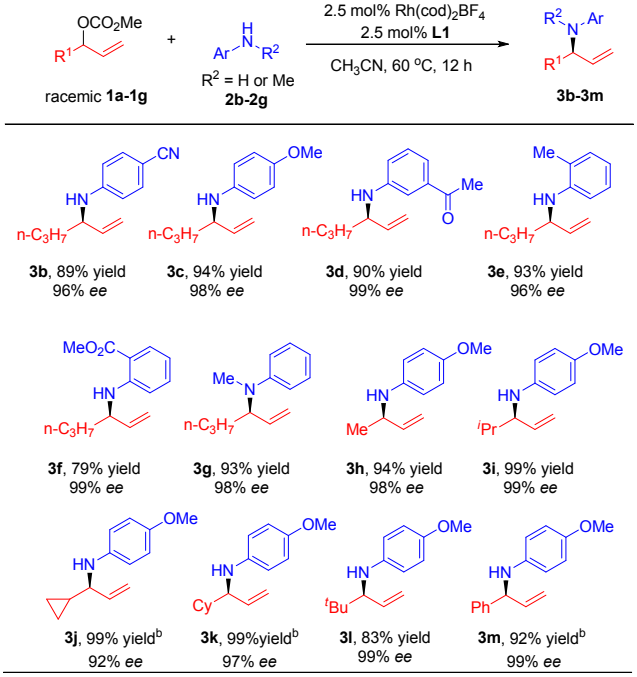


entry	metal salts	ligand	yield (%)[b]	*ee* of **3a** (%)[c]
1	$Rh(cod)_2BF_4$	**L1**	99	99
2	$Rh(cod)_2BF_4$	**L2**	99	99
3	$Rh(cod)_2BF_4$	**L3**	90	10
4	$Rh(cod)_2BF_4$	**L4**	< 5	-
5	$Rh(cod)_2BF_4$	**L5**	27	5
6[d]	$[Rh(cod)Cl]_2$	**L1**	92	99
7	$Rh(cod)_2OTf$	**L1**	83	95
8[e]	$Rh(cod)_2BF_4$	**L1**	50	99
9[d]	$[Ir(cod)Cl]_2$	**L1**	39	16
10	$Ir(cod)_2BF_4$	**L1**	16	7

[a]Conditions: **1a** (0.4 mmol, 1.0 equiv), **2a** (0.4 mmol, 1.0 equiv), Rh(I) (0.01 mmol, 0.025 equiv), ligand (0.01 mmol, 0.025 equiv), CH_3CN (2 mL). [b]Isolated yield. [c]The enantiomeric excess of **3a** was determined by HPLC with a chiral column. [d]1.25 mol% of catalyst precursor dimer was used. [e]Reaction was run at room temperature.

Under the optimized reaction condition (Table 1, entry 1), the substrate scope was examined by varying the substituents on anilines and the allylic carbonates (Table 2). Anilines containing electron-donating and electron-withdrawing functional groups react smoothly with completely branched selectivities and excellent enantioselectivities (**3b** to **3d**). ortho-Substituted anilines are also reactive in this transformation (**3e** and **3f**). Sterically more hindered N-methyl aniline was allylated to give **3g** efficiently with Rh. This protocol was amenable to a set of allylic carbonates bearing simple alkyl groups. Allylic amine **3g** with α-methyl was prepared with 98% *ee* and 94% yield. Allylic carbonates with α-branched isopropyl, cyclopropyl and cyclohexyl groups underwent the amination reaction to deliver **3i** to **3k** in excellent yields and *ee*s. It is worthwhile to mention that more challenging allylic carbonate with t-butyl group could also be used in this reaction to prepare **3l**. Phenyl-substituted racemic allyl carbonate reacts to provide the branched **3m** selectively when **L2** was used.

Table 2. Reaction Scope of Anilines[a]

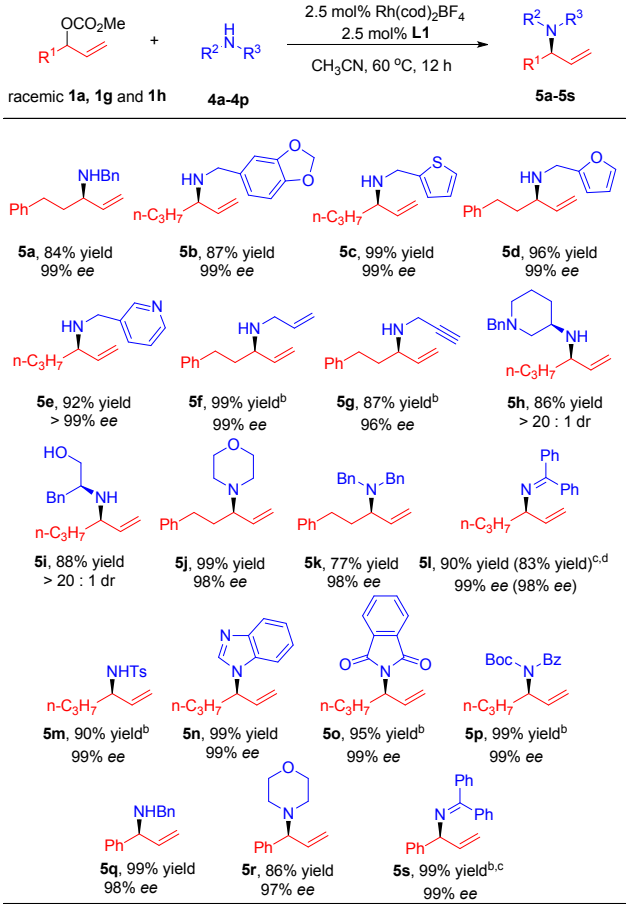


[a]Conditions: **1a** (0.4 mmol, 1.0 equiv), **2a** (0.4 mmol, 1.0 equiv), Rh(I) (0.01 mmol, 0.025 equiv), **L1** (0.01 mmol, 0.025 equiv), CH_3CN (2 mL). [b]$[Rh(cod)Cl]_2$(0.0125 equiv) and **L2** (0.025 equiv) were used.

Having established the efficient asymmetric allylation of anilines, we turned our attention to other nucleophiles (Table 3). Benzyl amine **4a** react smoothly to afford **5a** in high yield under the identical condition as anilines. Heterocycles could be tolerated to deliver secondary amines **5b** to **5e** in high selectivities. Carbon-carbon double and triple bonds were introduced in **5f** and **5g**, which allows further ring constructions. High diastereomeric ratios in **5h** and **5i** were obtained when chiral amines were used. Although sterically more hindered, morpholine and dibenzyl amine were successfully utilized to prepare tertiary amines **5j** and **5k**. Benzophenone imine could also be used as a nucleophile and primary amine with 99% *ee* was prepared after subsequent hydrolysis. To demonstrate the practicality of this transformation, a reaction at 10 mmol scale was conducted with 1.0 mol% catalyst. 83% of **5l** with 98% ee could be obtained after 48 hours. Tosylamide, benzimidazole, phthalimide and N-Boc-benzamide could also react to give the allylation products in high yields and *ee*s under the same condition (**5m** to **5p**). The absolute configuration of these compounds were assigned to be *R* by comparing with literature (see SI). Different from the basic aromatic and aliphatic amines, these acidic nitrogen containing molecules are more likely to react as good nucleophiles after deprotonation by the released carbonate or methoxide anion. Finally, not only aliphatic allylic carbonates, phenyl substituted allylic carbonate could also be used to produce chiral allylic amines **5q** to **5s** in highly efficiency.

Encouraged by the successful formation of **5m** to **5p**, we further examined the reactions of weakly acidic carbon, oxygen and sulfur pronucleophiles (Table 4). Under the neutral condition,

Table 3. Scope of Other Nitrogen Nucleophiles[a]

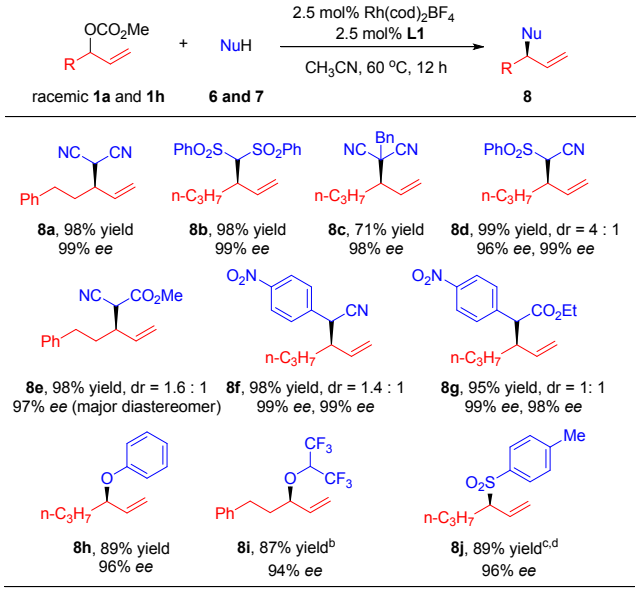


[a]Conditions: **1** (0.4 mmol, 1.0 equiv), 4 (0.4 mmol, 1.0 equiv), Rh(I) (0.01 mmol, 0.025 equiv), **L1** (0.01 mmol, 0.025 equiv), CH_3CN (2 mL). [b][Rh(cod)Cl]$_2$ (0.0125 equiv) and **L2** (0.025 equiv) were used. [c]The imine was hydrolyzed and protected as an amide. The *ee* was determined with the amide. [d]Data in brackets is for 10 mmol scale reaction and 1 mol% Rh catalyst was used.

malononitrile and bis(phenylsulfonyl)methane react smoothly to produce **8a** and **8b** with excellent yields and *ee*s. Substituted malononitrile could also be used to give **8c** with a quaternary carbon. 1 : 1 to 1.4 : 1 drs were obtained with unsymmetrical carbon nucleophiles which contain ester and ketone groups, while the regio- and enantioselectivities remain excellent (**8d** to **8g**). Acidic phenol, hexafluoropropan-2-ol and and 4-toluenethiol react to form **8h**, **8i** and **8j** in this base-free condition, which further extends the scope of this reaction to oxygen and sulfur pronucleophiles. $Et_3N{\cdot}3HF$ does not react under the same condition, probably due to its low acidity.

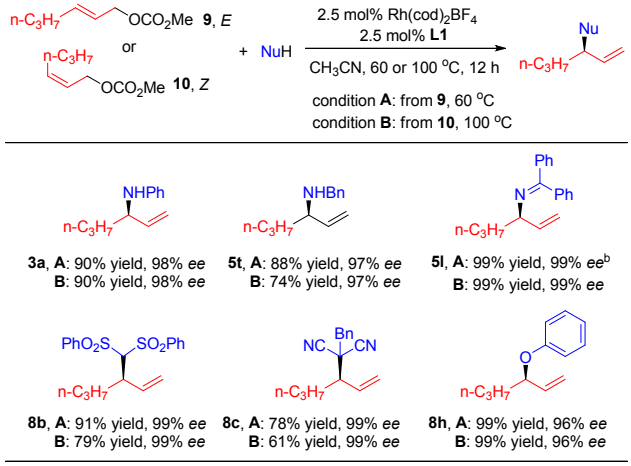
The previously-reported rhodium-catalyzed allylic substitution predominantly takes place predominantly at the position where the leaving group leaves. The dynamic kinetic asymmetric allylation performance for the rhodium/bisoxazolinephosphine catalyst inspires us to examine whether the Rh-catalyzed regiospecific allylation is also ligand dependent. As shown in Table 5, when *E*-linear allylic carbonate **9** was subjected to the reaction condition as above (60 °C), the same level of yield, regio- and enantioselectivity for **3a** were obtained. Reaction of *Z*-linear allylic carbonate **10** under the identical condition leads to the formation of **3a** as well, which is different from the *Z*-linear product formation under the catalysis of Ir.[12] However, the *ee* of **3a** drops to 86%. To our surprise, the *ee* could be improved to 98% by simply increasing the reaction temperature to 100 °C, which indicates that a higher reaction barrier to reach the same intermediate from **10** may exist. Under the optimized conditions for both **9** and **10**, different nucleophiles were examined. Aniline, benzyl amine, benzophenone imine, bis(phenylsulfonyl)methane, substituted malononitrile, and phenol all reacted to produce the allylation products **3a**, **5t**, **5l**, **8b**, **8c** and**8h** regio- and enantioselectively.

Table 4. Scope of Carbon, Oxygen and Sulfur Nucleophiles[a]



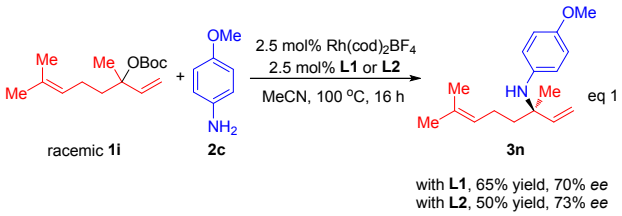
[a]Conditions: **1** (0.4 mmol, 1.0 equiv), **4** (0.4 mmol, 1.0 equiv), Rh(I) (0.01 mmol, 0.025 equiv), **L1** (0.01 mmol, 0.025 equiv). [b]**7b** (0.6 mmol, 1.5 equiv) was used. [c][Rh(cod)Cl]$_2$ (0.0125 equiv) and **L2** (0.025 equiv) were used. [d]The thio-ether was oxidized to sulfone to avoid the linear product formation and measure the *ee*.

Table 5. Scope of Linear Allylic carbonates[a]



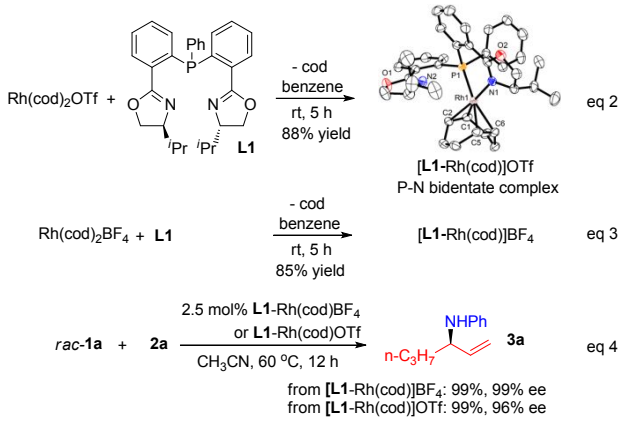
[a]Conditions: **9** or **10** (0.4 mmol, 1.0 equiv), **4** (0.4 mmol, 1.0 equiv), Rh(I) (0.01 mmol, 0.025 equiv), **L1** (0.01 mmol, 0.025 equiv), CH_3CN (2 mL). [b]The imine was hydrolyzed and protected as an amide.

Racemic tertiary allylic carbonate **1i** could also react with aniline **2c** to give **3n** with a tetrasubstituted carbon under the catalysis of the same rhodium complexes. The yield of **3n** was relatively lower and small amount of 1,3-dienes by elimination reaction could be observed. Two possible reasons may lead to the lower enantioselectivity of **3n**: 1) The slower interconversion between the two diastereomers of the π-allyl/Rh complex; 2) The difference of methyl group and CH_2R group becomes smaller than that of methyl group and hydrogen, which makes the face-selection be more difficult. Modification of the ligand to improve the enantioselectivity of tetrasubstituted carbons is under investigation.



To better understand the role of bisoxazolinephosphine ligand, characterization of Rh/ligand complex was conducted (scheme 2). By simply mixing $Rh(cod)_2BF_4$ or $Rh(cod)_2OTf$ with **L1** in benzene at room temperature, [**L1**-Rh(cod)]BF_4 and [**L1**-Rh(cod)]OTf were synthesized in high yields (eqs 2 and 3). A set of doublet peak at 30.2 ppm in ^{31}P NMR indicates only one rhodium complex formed. Recrystallization of [**L1**-Rh(cod)]OTf in pentane and acetone affords a crystal suitable for single crystal X-ray diffraction analysis. Solid-state

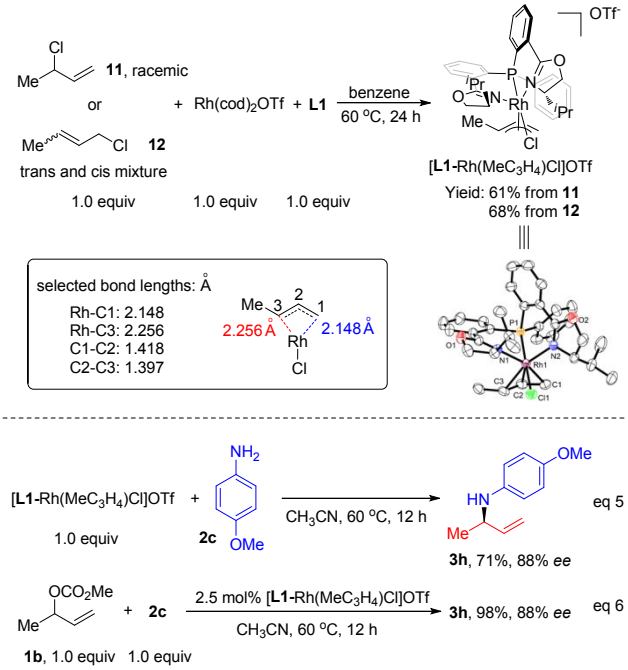
Scheme 2. Synthesis of [L1-Rh(cod)]OTf, [L1-Rh(cod)]BF_4 and Their Reactivities



structure reveals that **L1** coordinates with Rh(I) as only a P-N bidentate ligand, and one cod is still on the metal.[13] The rhodium complex adopts a distorted square planar geometry. The reactivities of these two complexes match with the in-situ generated catalysts (eq 4) (Table 1, entries 1 and 7).

To get more insight about the high selectities controlled by the bisoxazolinephosphine ligand, we further focused on the Rh(III)-allyl complex synthesis. After the unsuccessful attempts starting from either branched or linear allylic carbonates, we turned our attention to the allylic chloride. Both racemic 3-chlorobut-1-ene **11** and crotyl chloride **12** react with $Rh(cod)_2OTf$ and **L1** to form the same yellow solid (Scheme 3). The doublet peak at 40.5 ppm in ^{31}P-NMR indicates a new rhodium complex was generated and only one isomer exists in solution. Different from η^3-allyl-Ir-cod complex, no cyclooctadiene peaks could be found in this rhodium complex.[14,15] A crystal suitable for X-ray diffraction was obtained by slow diffusion of pentane into the acetone solution of the complex. [**L1**-Rh(MeC_3H_4)Cl]OTf adopts a distorted six-coordinate octahedral geometry, with the chloride located trans to the phosphorus atom in the axial direction. The two allyl termini carbons are oriented trans to one nitrogen atom on the oxazolines respectively. The Rh-C3 bond is longer than the Rh-C1 bond by 0.108 Å. The relatively weaker Rh-C3 bond and shielding effect at C1 by the isopropyl group at the right oxazoline ring may account for the excellent branch-selectivity. The excellent exo face-selectivity of the syn-methylallyl moiety could be interpreted by the size effect of the chloride anion on the rhodium. The steric repulsion between the methyl or C2-H and the chloride could make the endo-π-allyl-Rh(III) intermediate be less stable.[16] The role of the chloride could be replaced by the carbonate anion or methoxide when $Rh(cod)_2BF_4$ was used as the catalyst precursor, in which case no chloride exists. The formation of [**L1**-Rh(MeC_3H_4)Cl]OTf from both **11** and **12** as the most stable reaction intermediate is consistent with the observed facts that both branched

Scheme 3. Synthesis of [L1-Rh(MeC_3H_4)Cl]OTf and Reactivity



racemic and linear (*Z* and *E*) allylic carbonates lead to the same enantiomer of product.

The stoichiometric reaction of [**L1**-Rh(MeC_3H_4)Cl]OTf was studied (eq 5). **3h** with 88% *ee* was isolated in 71% yield after heating the complex with **2c** in acetonitrile for 12 hours.[17] The complex was also efficient in the catalytic reaction (eq 6), and the same 88% *ee* was obtained, which indicates that [**L1**-Rh(MeC_3H_4)Cl]OTf is involved as reaction intermediate of the catalysis. The absolute *R*-configuration of **3h** supports an outer-sphere attack on allyl carbon by nucleophiles opposite to the metal center. This possible mechanism could also explain the fact that the same level of enantioselectivities were obtained from sterically quite different nitrogen, carbon, oxygen and sulfur pronucleophiles.

In summary, we have developed a highly regio- and enantioselective allylic substitution based on rhodium and bisoxazolinephosphine ligands. This catalyst system provides a general reaction platform for different nitrogen, carbon and oxygen pronucleophiles. In contrast to the previous reported rhodium-catalyzed regiospecific allylic substitution, both challenging

branched racemic and linear (*Z* and *E*) allylic substrates bearing simple alkyl groups could be converted to the same chiral products. π-Allyl-Rh(III) intermediate was isolated to understand the origin of the high regio- and enantioselectivities. The modular synthesis of bisoxazolinephosphine ligands enables the fine tuning of the steric and electronic properties of the ligands, which is expected to broaden the scope of the nucleophiles and the allylic substrates in the future.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, characterization data, copies of ^{1}H, ^{13}C NMR spectra, HPLC spectra and X-ray crystal structure of [**L1**-Rh(cod)]OTf and [**L1**-Rh(MeC_3H_4)Cl]OTf. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work is supported National Natural Science Foundation of China (NSFC) (Grant 21602130) and Shanghai Jiao Tong University. We thank Prof. Yong Jian Zhang for the helpful discussion.

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