## Rhodium/Chiral Urea Relay Catalysis Enables an Enantioselective Semipinacol Rearrangement/Michael Addition Cascade

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The combined use of rhodium and cinchona-based squaramide has first been introduced for asymmetric relay catalysis, enabling a highly enantioselective semipinacol rearrangement/Michael addition cascade.

The rearrangement reaction represents one of the most attractive fashions for the formation of new chemical bonds, especially in the creation of sterically congested quaternary carbon centers.<sup>1</sup> The semipinacol rearrangement, as a variant of the pinacol rearrangement, has been intensively studied since 1923, thanks to its diverse active species with electrophilic carbocenters, which would enable subsequent various cascade transformations, together with its wide applications in elegant total synthesis of natural products (Scheme 1).<sup>2</sup> Remarkably, Tu and coworkers have successfully developed a series of practical tandem semipinacol rearrangement transformations, including alkylation, bromination, and hydroamination.<sup>2b,3</sup> Maruoka and others have also established intermolecular

Scheme 1. Profiles of Semipinacol Rearrangement



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semipinacol-type ring expansions exploring diazo compounds.<sup>4</sup> Despite these elegant achievements, some other promising active species for this rearrangement are unexpectedly fading before flourishing, such as the classical rhodium carbenoid,<sup>5</sup> which would lead to unprecedented chemical processes.

The asymmetric metal/organo combined catalysis<sup>6</sup> has been a unique strategy to circumvent the challenges that the conventional single type of chiral catalysts encountered. In particular, asymmetric relay catalysis

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 $(ARC)^{7-11}$  that emphasized independent but methodical activations of different substrates has been accepted as a robust generic concept, capable of creating otherwise inaccessible enantioselective cascade reactions with high step efficiency. We and others have disclosed a range of hybrid metal/organo binary systems including transition metals, such as gold,<sup>8</sup> ruthenium,<sup>9</sup> and rhodium,<sup>10</sup> basically combined with Brønsted acids, such as chiral phosphoric acids. In contrast, nitrogen or sulfur containing bifunctional organocatalysts have been exploited to a lesser extent in ARC presumably due to the deactivation effect of both catalytic cycles.<sup>6b</sup> Herein, we will report the first combined use of a rhodium complex and cinchonabased bifunctional catalyst<sup>12</sup> rendering a highly enantioselective relay catalytic semipinacol rearrangement/ Michael addition cascade that is unrealizable otherwise.

Diazoalcohols of type 1 have been found to undergo semipinacol rearrangement through 1,2-H or 1,2-C migration

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in the presence of transition metal complexes, including copper and rhodium complexes, to give  $\beta$ -keto esters III via intermediates I and II.<sup>5c-5g</sup> We proposed that the resultant keto ester intermediate III *in situ* generated would undergo an enantioselecitive Michael addition with nitroalkenes under the influence of chiral bifunctional urea.<sup>13</sup> As such, a relay catalytic semipinacol rearrangement/Michael addition cascade would likely be driven by a transition metal/chiral urea collaboration (Scheme 2).

The initial experiment to validate our hypothesis explored the reaction of 1a with 2a under the catalysis of 5 mol % of copper salt and 10 mol % of chiral bifunctional urea (in  $CH_2Cl_2$ , 25 °C, Table 1, entries 1–3). However, the combination of either CuBr or CuSO<sub>4</sub> · 5H<sub>2</sub>O with 4a gave disappointing results presumably due to the low solubility (entries 1-2). To our delight, the presence of Cu(OTf)<sub>2</sub> led to generation of the desired product 3aa in a 29% isolated yield and with 73% and 79% ee respectively for two diastereomers (entry 3). Interestingly, the conventional highly active Rh<sub>2</sub>(OAc)<sub>4</sub>, in combination with 4a, rendered the tandem reaction to proceed completely within 2 h, almost quantitatively affording 4a (97% yield) with 82%/88% ee (entry 4). The great advantage of Rh<sub>2</sub>(OAc)<sub>4</sub> encouraged us to improve the stereocontrol by evaluating a series of ureas or thioureas incorporated with different chiral scaffolds (entries 5-7). Basically, in comparison with thiourea organocatalysts 4b and 4d, urea analogues 4a and 4c gave similar levels of enantioselectivity, but much higher yields (entry 4 vs 5 and entry 6 vs 7). In particular, 4a showed the most efficient catalytic activity (entry 4). Subsequently, a variety of solvents were evaluated and we found that toluene could further accelerate the whole process, however, at the cost of a significantly eroded yield (entry 8). Neither tetrahydrofuran (THF) or ethyl ether (Et<sub>2</sub>O) was able to enhance the stereocontrol (entries 9 and 10), and CH<sub>2</sub>Cl<sub>2</sub> was therefore the solvent of choice. More interestingly, a quinine-based squaramide  $4e^{13d}$  substantially improved the enantioselectivity to 99%/99% ee (entry 11). Notably, the combination of 0.5 mol % Rh<sub>2</sub>(OAc)<sub>4</sub> and 2 mol % 4e provided an even better result (entry 12).

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Table 1. Investigation of Binary Catalysts<sup>a</sup>



entry	catalyst I	4	<i>t</i> (h)	yield $(\%)^b$	$\mathrm{d}\mathbf{r}^c$	$ee^d$
1	CuBr	4a	48	_	_	_
2	$CuSO_4 \cdot 5H_2O$	4a	48	N.R	_	_
3	Cu(OTf) <sub>2</sub>	4a	24	29	1:1	73/79
4	Rh <sub>2</sub> (OAc) <sub>4</sub>	4a	2	97	1:1	82/88
5	Rh <sub>2</sub> (OAc) <sub>4</sub>	<b>4b</b>	<b>2</b>	74	1:1	88/90
6	Rh <sub>2</sub> (OAc) <sub>4</sub>	<b>4c</b>	4	71	1:1	-82/-82
7	Rh <sub>2</sub> (OAc) <sub>4</sub>	<b>4d</b>	4	43	1:1	-80/-83
$8^e$	Rh <sub>2</sub> (OAc) <sub>4</sub>	4a	0.5	70	1:1	84/88
9 <sup>f</sup>	Rh <sub>2</sub> (OAc) <sub>4</sub>	4a	12	59	1:1	18/33
$10^g$	Rh <sub>2</sub> (OAc) <sub>4</sub>	4a	12	78	1:1	73/80
11	$Rh_2(OAc)_4$	<b>4e</b>	1	94	1:1	99/99
$12^{h,i}$	Rh <sub>2</sub> (OAc) <sub>4</sub>	<b>4e</b>	1	97	1:1	99/99
$13^h$	Rh <sub>2</sub> (OAc) <sub>4</sub>	_	48	N.R.	_	_
$14^h$		<b>4e</b>	48	N.R.	_	_

<sup>*a*</sup> Unless indicated otherwise, reactions of **1a** (0.15 mmol), **2a** (0.10 mmol), catalyst I (0.005 mmol), and **4** (0.010 mmol) were carried out in DCM (1 mL). <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Determined by crude H<sup>1</sup> NMR. <sup>*d*</sup> Determined by HPLC analysis. <sup>*e*</sup> In toluene. <sup>*f*</sup> In THF. <sup>*g*</sup> In Et<sub>2</sub>O. <sup>*h*</sup> 0.5 mol % Rh<sub>2</sub>(OAc)<sub>4</sub> and 2.0 mol % **4e** were used. <sup>*i*</sup> 0.20 mmol scale in DCM (1 mL).

As anticipated, neither  $Rh_2(OAc)_4$  or **4e** could catalyze this tandem reaction alone (entries 13–14).

With the optimal conditions in hand, we investigated the generality of this protocol for diazoalcohols (Table 2). Very high levels of enantioselectivity were achieved for various secondary alcohol substrates (entries 1–7). Both the ester group and substituents on the  $\alpha$ -position of the hydroxyl influenced the diastereoselectivity slightly because of the nature of monosubstituted  $\beta$ -keto esters. Significantly, the protocol was amenable to diazoalcohols bearing a spectrum of functional groups, including alkynyl, alkenyl, and protected hydroxyl, to furnish the corresponding products in high yields and with excellent enantioselectivities, which would allow further synthetic applications by virtue of the rich chemistry in these functionalities (entries 4–6).

The enantioselective creation of quaternary stereogenic centers has long received much attention for their ubiquity in natural products and molecules with significant bioactivity.<sup>14</sup> In this regard, various tertiary diazoalcohols were subjected to this relay catalytic cascade reaction,

Table 2. Scope for Multifunctionalized Diazoalcohols<sup>a</sup>



entry	1	3	yield (%) <sup>b</sup>	$dr^c$	$ee^d$
1	OH O 1b N <sub>2</sub> Ot-Bu	O O Ot-Bu 3ba Ph	76	3:1	97/99
2	OH O OH O OMe OMe 1c N <sub>2</sub>	3ca 2h NO2	81	1.7:1	98/94
3	$\begin{array}{c} OH & O \\ Ph & & \\ 1d & 2 \\ N_2 \end{array} OMe$	O O Ph 3da Ph NO <sub>2</sub>	87	4.5:1	98/96
4	OH O 1e 2 OMe	3ea 2 Mo2	91	1.5:1	98/98
5	OH O H 1f N <sub>2</sub> OMe	3fa Ph NO <sub>2</sub>	95	2.5:1	99/99
6	BnO H 1g N <sub>2</sub> OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH O OH OH	BnO 3ga Ph NO <sub>2</sub>	95	1.2:1	99/99
7	OH O Ph OMe <b>1h</b> N <sub>2</sub>	Ph OMe 3ha Ph NO <sub>2</sub>	90	1.7:1	96/99
8	0H № 1i	MeO <sub>2</sub> C	99	20:1	91
9 <sup>e</sup>	1j CO <sub>2</sub> Me	MeO <sub>2</sub> C O 3ja	60	50:1	98
10	1k CO <sub>2</sub> Me	MeO <sub>2</sub> C O 3ka	90	12:1	91
11		MeO <sub>2</sub> C 3la	73	6:1	88/68
12	OH № 1m → CO <sub>2</sub> Me	3maNO <sub>2</sub>	89	3:1	99/97

<sup>*a*</sup> Unless indicated otherwise, reactions of **1** (0.30 mmol), **2a** (0.20 mmol),  $Rh_2(OAc)_4$  (0.001 mmol), and **4e** (0.004 mmol) were carried out in 1 mL of DCM for 1 h. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Determined by crude H<sup>1</sup> NMR. <sup>*d*</sup> Determined by HPLC analysis. <sup>*e*</sup> The reaction was conducted in 0.5 mL of DCM for 24 h.

Ph

creating two vicinal carbon stereocenters involving a quaternary one in one step (Table 2, entries 8–12). Generally, the desired ring-expanded products were obtained in excellent yields and with high levels of stereoselectivity for cyclic substrates within 1 h (entries 8, 10, and 11), except that **1j** and **2a** required a higher concentration and prolonged time to accomplish a complete process (60% yield, 50:1 dr, 98% ee; entry 9). Moreover, the acyclic tertiary substrate like **1m** was also able to participate in the tandem reaction to provide **3ma** in 89% yield and with 99%/97% ee (entry 12).

The generality for nitroalkenes was also explored. A variety of nitroalkenes were treated with **1i** under the

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Table 3. Generality for (E)-Nitroalkenes<sup>a</sup>



<sup>*a*</sup> Unless indicated otherwise, reactions of **1** (0.30 mmol), **2a** (0.20 mmol),  $Rh_2(OAc)_4$  (0.001 mmol), and **4e** (0.004 mmol) were carried out in 1 mL of DCM for 1 h. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Determined by crude H<sup>1</sup> NMR. <sup>*d*</sup> Determined by HPLC analysis. <sup>*e*</sup> The reaction time was 12 h.

optimized conditions to generate a diverse spectrum of Michael adducts in almost quantitative yields and with excellent diastereoselectivities, ranging from 20:1 to 99:1 dr (Table 3). For any nitroalkenes, the stereochemical control became sensitive to the substitution pattern while it was somewhat independent of the electron feature. For example, either *ortho*- or *meta*-substituents of the  $\beta$ -nitrostyrene provided higher enantioselectivities than para-substituted nitroolefins (entries 1-2 vs 3-6) while the presence of the electron-donating or -withdrawing substituents gave comparable enantioselectivities (entry 1 vs 2 and entries 4-5 vs 6). In addition, for the naphthyl, heteroaryl, and alkyl nitroalkene, 2h, 2i, and 2j also underwent clean relay catalytic cascade reactions to give the desired products in high yields and with excellent stereochemical outcomes (entries 7-9).

The highly functionalized products obtained could be conveniently converted into synthetically important chiral molecules by using classical reactions. For instance, in the presence of a catalytic amount of *p*-toluenesulfonic acid

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Scheme 3. Synthetic Application of Tethered Functional Group



hydrate (*p*-TSA·H<sub>2</sub>O), the carbon–carbon triple bond and keto group in the compound **3ea** underwent a cyclization to form **5** bearing a furan moiety. Followed by a cascade selective reduction/transesterification of **5** with a combined reagent of NiCl<sub>2</sub>·6H<sub>2</sub>O and NaBH<sub>4</sub>,<sup>15</sup> 3,4-disubstituted  $\gamma$ -lactam **6** was furnished in an overall 71% yield in two steps and with maintained enantioselectivity (Scheme 3).

In summary, we have, for the first time, demonstrated that rhodium and chiral bifunctional urea are highly compatible and can be combined for asymmetric relay catalysis. This binary chiral catalyst system rendered a highly enantioselective semipinacol rearrangement/ Michael addition cascade reaction to proceed cleanly. Remarkably, the relay catalytic process showed excellent tolerance to various functionalities and enabled direct access to highly functionalized chiral nitro compounds that are basically impracticable otherwise. Moreover, the presence of the multiple functionalities in the products allows further transformations into biologically interesting optically pure molecules.

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**Supporting Information Available.** Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.