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# Decarbonylation *via* Aldehydic C–H Bond Cleavage by Cationic Iridium Catalyst

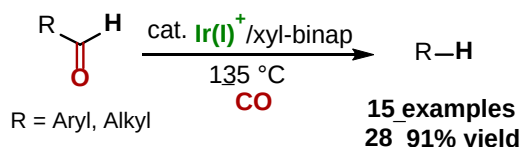
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**Abstract** We report the decarbonylation of aldehydes *via* aldehydic C–H bond cleavage catalyzed by cationic iridium/bisphosphine catalyst. The reaction proceeds under relatively mild reaction conditions, providing the corresponding hydrocarbon products in moderate to high yields. In addition, this cationic iridium catalyst system can be applied to asymmetric ketone hydroacylation reaction.

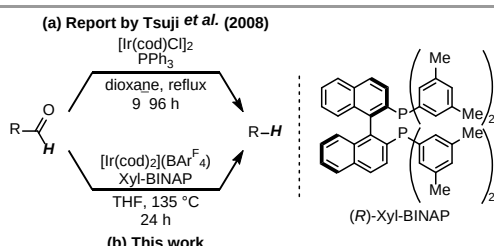
**Key words** decarbonylation, cationic iridium, benzaldehyde, C–C bond cleavage, asymmetric acylation, ketone

Transition metal-catalyzed carbonylation using inexpensive carbon monoxide (CO gas) is one of the most common industrial processes to synthesize the bulk and fine chemicals.<sup>1</sup> Similarly, transition metal-catalyzed decarbonylation of carbonyl compounds is the fundamental reaction in synthetic chemistry because it can be applied to beneficial C–C bond formations such as cross-coupling reactions.<sup>2–4</sup> In addition, decarbonylation reaction is also regarded as an efficient method for attractive carbon–carbon bond cleavage.<sup>5</sup> Among them, decarbonylation of aldehyde is most basic decarbonylation reaction and have been known for a long time. The stoichiometric rhodium-mediated simple decarbonylation for aldehydes have first developed by Tsuji and Ohno in 1965.<sup>6</sup> Decarbonylation of aldehydes was well-

established, and was realized by use of various transition metal catalysts.<sup>5a, 6b, 7–12</sup> In 2008, Tsuji and co-workers reported that aromatic and aliphatic aldehydes react in the presence of a neutral iridium catalyst to give corresponding decarbonylated products in good yield (Scheme1 (a)).<sup>10c</sup> A wide range of functional group were tolerant for this reaction. Recently, earth-abundant nickel-catalyzed decarbonylation of aldehydes was also developed.<sup>11</sup> More recently, cobalt-mediated decarbonylation of aldehydes has been reported by Tonzetich.<sup>12</sup> Although there are many active catalyst systems for decarbonylation, a common feature of most of these reactions is to use neutral metal complex. However, it is known that cationic complex promotes the decarbonylation by decreasing  $\pi$ -back-donation from metal center to an antibonding orbital of CO.<sup>7a</sup> As a new entry for catalytic decarbonylation of aldehydes, herein we describe the development of a cationic iridium-catalyzed decarbonylation reaction of aldehydes with high substituent

**Table 1** Screening of Reaction Conditions for Catalytic Decarbonylation

| entry | cat.                                       | ligand                 | solvent | yield (%) <sup>a</sup> |
|-------|--------------------------------------------|------------------------|---------|------------------------|
| 1     | [Ir(cod)] <sub>2</sub> (BAR <sub>4</sub> ) | <i>rac</i> -binap      | Toluene | 68                     |
| 2     | [Ir(cod)] <sub>2</sub> (BF <sub>4</sub> )  | <i>rac</i> -binap      | Toluene | 32                     |
| 3     | [IrCl(cod)] <sub>2</sub>                   | <i>rac</i> -binap      | Toluene | 18                     |
| 4     | [Ir(cod)] <sub>2</sub> (BAR <sub>4</sub> ) | ( <i>R</i> )-tol-binap | Toluene | 69                     |
| 5     | [Ir(cod)] <sub>2</sub> (BAR <sub>4</sub> ) | ( <i>R</i> )-xyl-binap | Toluene | 75                     |
| 6     | [Ir(cod)] <sub>2</sub> (BAR <sub>4</sub> ) | ( <i>R</i> )-segphos   | Toluene | 61                     |
| 7     | [Ir(cod)] <sub>2</sub> (BAR <sub>4</sub> ) | dppf                   | Toluene | 7                      |
| 8     | [Ir(cod)] <sub>2</sub> (BAR <sub>4</sub> ) | PPh <sub>3</sub>       | Toluene | 4                      |



**Scheme 1** Iridium-catalyzed Decarbonylation of Aldehydes

|    |                                                      |                        |             |    |
|----|------------------------------------------------------|------------------------|-------------|----|
| 9  | $[\text{Ir}(\text{cod})_2](\text{BAR}^{\text{F}}_4)$ | ( <i>R</i> )-xyl-binap | THF         | 78 |
| 10 | $[\text{Ir}(\text{cod})_2](\text{BAR}^{\text{F}}_4)$ | ( <i>R</i> )-xyl-binap | DME         | 64 |
| 11 | $[\text{Ir}(\text{cod})_2](\text{BAR}^{\text{F}}_4)$ | ( <i>R</i> )-xyl-binap | 1,4-Dioxane | 77 |

<sup>a</sup> GC yield against internal standard (methyl 3-nitrobenzoate)

compatibility (Scheme 1(b)). Initially, we choose 2-ethoxybenzaldehyde (**1a**) as a model substrate and attempted the decarbonylation in the presence of  $[\text{Ir}(\text{cod})_2](\text{BAR}^{\text{F}}_4)$  (5 mol%) and *rac*-BINAP (5.5 mol%) in toluene at 135 °C (Note; we previously confirmed that the chirality of ligand does not affected the reactivity). Under these conditions, the decarbonylation proceeded to give the product **2a** in 68% yield (Table 1, entry 1).

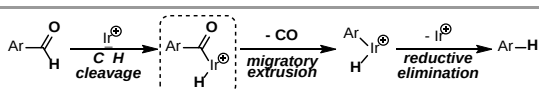
**Table 2** Cationic Iridium-Catalyzed Decarbonylation of Aldehydes

| entry | aldehyde ( <b>1a–1n</b> ) | product ( <b>2a–2n</b> ) | yield <sup>a</sup>                     |
|-------|---------------------------|--------------------------|----------------------------------------|
| 1     |                           |                          | 78%                                    |
| 2     |                           |                          | 35% <sup>b</sup><br>69% <sup>b,c</sup> |
| 3     |                           |                          | n.r.                                   |
| 4     |                           |                          | 71%                                    |
| 5     |                           |                          | 28%                                    |
| 6     |                           |                          | 37% <sup>b</sup>                       |
| 7     |                           |                          | 63% <sup>b</sup>                       |
| 8     |                           |                          | 91% <sup>b</sup><br>49% <sup>d</sup>   |
| 9     |                           |                          | 32% <sup>b</sup>                       |
| 10    |                           |                          | 65% <sup>b</sup>                       |
| 11    |                           |                          | 59%                                    |
| 12    |                           |                          | 72%                                    |
| 13    |                           |                          | 83%                                    |
| 14    |                           |                          | 49%                                    |
| 15    |                           |                          | 49%                                    |
| 16    |                           |                          | 71%                                    |

Reaction conditions: aldehyde **1** (0.25 mmol), Ir cat (5 mol%), and (*R*)-Xyl-BINAP (1.1 equiv to Ir) in THF, stirred for 24 h at 135 °C in sealed tube.  
<sup>a</sup> GC yield, <sup>b</sup> isolated yield, <sup>c</sup> 48 h, n.r. = no reaction. <sup>d</sup>  $[\text{IrCl}(\text{cod})]_2/\text{PPh}_3$  system was used for the sake of comparison.

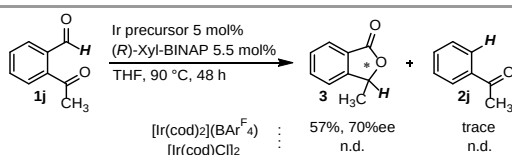
The reaction with  $[\text{Ir}(\text{cod})_2](\text{BF}_4)$  as catalyst precursor resulted in an apparent decrease in the product yield (entry 2). Note also that the neutral iridium/*rac*-binap complex performed poorly for decarbonylation under optimized conditions (entry 3). It is known that the decarbonylation by  $[\text{Ir}(\text{coe})_2\text{Cl}]_2/\text{rac}$ -BINAP system requires the higher temperature (>160 °C) to obtain the desired product because this transformation by neutral Ir/bisphosphine complex likely proceeds *via* partial ligand dissociation of *rac*-BINAP to generate a coordinatively unsaturated active species, as reported by Madsen group.<sup>10f</sup> Furthermore, both Tsuji group<sup>10c</sup> and Madsen group<sup>10f</sup> elucidated that the active species in neutral Ir-catalyzed decarbonylation contain less than two phosphines coordinated to iridium. The change of *rac*-binap to its analogues (entries 4–6), in particular, (*R*)-tol-binap and (*R*)-xyl-binap, led to further improvement of reactivity (69% and 75%, respectively; entries 4–5). However, dppf was not suitable ligand (entry 7). Furthermore, in contrast with the report by Tsuji, the use of monodentate phosphorus ligand such as  $\text{PPh}_3$  significantly lowered the decarbonylation efficiency (entry 8). The solvent had some effect for reactivity, and the highest yield was obtained the reaction using THF (entry 9). With an optimized catalytic system in hand, we next explored its versatility by employing a variety of aldehydes **1** (Table 2). Note that in all cases of low to moderate yields, the unreacted starting materials were recovered without affording byproducts including the Tishchenko reaction product.<sup>11</sup> 2-Alkoxybenzaldehydes (**1a–b**) were tolerated, and the corresponding hydrocarbons (**2a–b**) were produced in moderate to good yield (entries 1, 2). Unexpectedly, when conducted with the substrate **1c** having the acetoxy group, no reaction was observed and the starting materials **1c** was recovered quantitatively. The decarbonylation products **2d** and **2e** were obtained in moderate to good yield even in the presence of unprotected phenol or aniline. (entries 4, 5) Moreover, moderate to high yields were obtained from the reactions of benzaldehyde **1f–1j** possessing ester or amide, ketone substituents (entries 6–10). In particular, the use of cationic iridium system was beneficial for **1h** having coordinative amide substituent compared with the neutral iridium system ( $[\text{IrCl}(\text{cod})]_2/\text{PPh}_3$ ). Subsequent screening experiments were performed using *meta*- or *para*-substituted benzaldehyde **1k–1m**, affording the product **2a** in moderate to good yields (entry 11–13). This method can be applied to the reaction with sterically congested aldehyde **2n** (entry 14). In addition, aliphatic aldehydes **1o–1p** can be also applicable to decarbonylation in this catalytic system (**2o**, 49% yield and **2p**, 71% yield, entries 15, 16).

The mechanism of the decarbonylation has been already well-established as illustrated in Scheme 2. Lastly, we have also briefly investigated the application using reactive species for decarbonylation such as acyliridium–hydride intermediate generated *in situ* by aldehydic C–H bond cleavage.<sup>7f, 10f</sup> Because the asymmetric hydroacylation of ketones catalyzed by rhodium<sup>13a–d</sup> or cobalt<sup>13e</sup> complex was previously reported, we presumed that the asymmetric hydroacylation occurs *via* acyliridium–hydride complex. In fact, cationic iridium-catalyzed atom-economical asymmetric hydroacylation of benzaldehyde **1j** proceeded to give the corresponding chiral phthalide **3** in 57% conversion with good enantioselectivity (70%ee) (Scheme 3). The cationic property of iridium complex was beneficial for the use in an asymmetric hydroacylation, and the neutral complex



Scheme 2 Proposed Catalytic Cycle for the Decarbonylation of Aldehydes

did not catalyze the reaction. To our knowledge, this reaction represents the first example of iridium-catalyzed asymmetric hydroacylation of ketone *via* aldehydic C–H bond cleavage.<sup>14</sup>



Scheme 3 Asymmetric hydroacylation of ketone

In summary, we have reported a new efficient system for the decarbonylation *via* aldehydic C–H bond cleavage using a cationic iridium/bidentate phosphine catalyst.<sup>15</sup> The cationic iridium catalyst system is synthetically useful, as demonstrated by asymmetric hydroacylation of ketone providing convenient chiral five-membered lactones.<sup>16</sup> We are currently working to develop new cationic iridium-catalyzed synthetic methods *via* C–H bond cleavage.

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## Supporting Information

YES (this text will be updated with links prior to publication)

## Primary Data

NO (this text will be deleted prior to publication)

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(15) **Representative general procedure of decarbonylation – preparation of benzyl phenyl ether (2b)**

To an oven-dried sealed tube, [Ir(cod)<sub>2</sub>](BARF<sub>4</sub>) (0.0125 mmol, 5 mol%) and (*R*)-xyl-binap (0.0138 mmol, 5.5 mol%) and dry THF (1.0 mL) were added under N<sub>2</sub> atmosphere. The mixture was stirred at room temperature for 30 min, followed by the addition of benzaldehyde **1b** (0.25 mmol). The reaction mixture was then heated at 135 °C. After being stirred for 24 h, the mixture was purified with silica gel column chromatography (eluent: Hexane only) to afford pure decarbonylation product **2b** (35% yield)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27–7.45 (m, 7H), 6.96–7.00 (m, 3H), 5.07 (s, 3H)

**General procedure of asymmetric hydroacylation – preparation of 3-methylisobenzofuran-1(3*H*)-one (3)**

To an oven-dried 2-neck flask with condenser, [Ir(cod)<sub>2</sub>](BARF<sub>4</sub>) (0.0125 mmol, 5 mol%) and (*R*)-Xyl-BINAP (0.0138 mmol, 5.5 mol%) and dry THF (1.0 mL) were added under N<sub>2</sub> atmosphere. The solution was stirred at room temperature for 30 min, followed by the addition of benzaldehyde **1a** (0.25 mmol). The reaction mixture was then heated at 90 °C. After being stirred for 48 h, lactone (**3**) was confirmed by <sup>1</sup>H-NMR and conversion was determined by <sup>1</sup>H-NMR integration comparing to substrate peak.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.57 (q, *J* = 6.8 Hz, 1H), 1.65 (d, *J* = 6.4 Hz, 1H)

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