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Ruthenium-Catalyzed Intermolecular Hydroacylation of Internal Alkynes: The Use of Ceria-Supported Catalyst Facilitates the Catalyst Recycling

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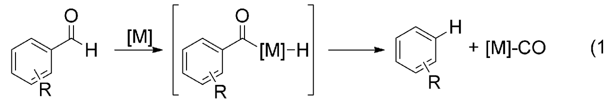
Carbon–carbon bond-forming reactions that involve the activation and subsequent functionalization of C−H bonds catalyzed by transition metals are the most important reactions in current organic chemistry.[1] Intermolecular hydroacylation of C−C triple bonds is a promising method for the preparation of conjugated enones because of its inherent 100 % atom efficiency.[2,3] Although transition-metal catalysts can cleave C−H bonds of formyl groups to give acyl–metal species, which are key intermediates in catalytic hydroacylation, these intermediates often undergo rapid decomposition into metal–carbonyl species and reduced molecules before coupling across C−C multiple bonds [Eq. (1)].

Decarbonylation of aldehydes

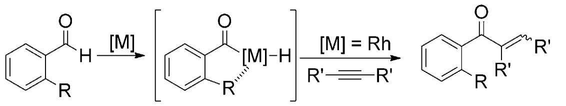


(1)

To suppress the decarbonylation and to obtain hydroacylation products in high yields without pressurization of carbon monoxide,[4] chelation-assisted strategies have been developed. In the case of the reaction of terminal alkynes, the use of the reaction system employing Rh complex and 2-amino-3-picoline is an efficient strategy for the production of conjugate enones.[5] On the other hand, Miura and coworkers, and Willis et al. independently developed the Rh-catalyzed hydroacylation of internal alkynes by the use of OH or SMe group on aldehydes as chelation-controlling substituents to give the corresponding enones in high yields [Eq. (2)].[6,7]

Catalytic hydroacylation without chelation assistance have also been reported. The reactions include the coupling of aldehydes with alkenyl–metal species generated by the hydrometalation of 2-alkynes [Eq. (3)].[8]

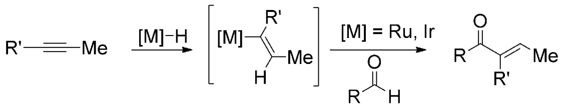
Intermolecular hydroacylation of alkynes with chelation assistance



(2)

(R = OH; by Miura et al.)
(R = SMe; by Willis et al.)

Intermolecular hydroacylation of 2-alkynes without chelaiton assistance

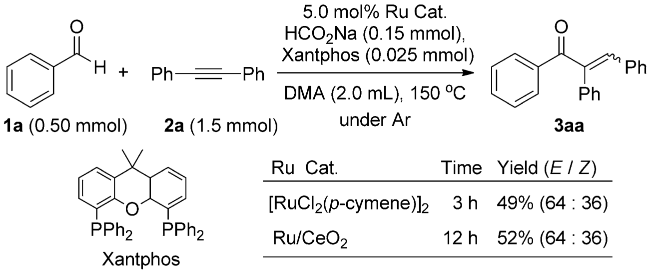


(3)

(M = Ru; by Krische et al.)
(M = Ir; by Ishii et al.)

However, the development of new catalytic systems that can broaden the scope of aldehydes and alkynes for intermolecular hydroacylation is still a challenge. Herein, we describe the catalytic intermolecular hydroacylation of alkynes in the presence of Ru catalysts. A wide range of aromatic aldehydes and internal alkynes can be used in the present catalytic system. The solid Ru catalysts are recyclable without a significant loss of activity.

The intermolecular coupling of benzaldehyde (**1a**) with diphenylacetylene (**2a**) took place in the presence of a catalytic amount of $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol % as Ru) together with 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) and HCO_2Na in *N*,*N*-dimethylacetamide (DMA) at 150 °C under an Ar atmosphere to give the corresponding conjugated enone **3aa** in a yield of 49 % (*E*/*Z* 64:36; Scheme 1). Recently, highly efficient organic transformation with recyclable solid catalysts has been regarded as an important research field from the perspective of green



Ru Cat.	Time	Yield (*E* / *Z*)
$[RuCl_2(p\text{-cymene})]_2$	3 h	49% (64 : 36)
Ru/CeO_2	12 h	52% (64 : 36)

Scheme 1. Ru-catalyzed hydroacylation of **2a** with **1a**.

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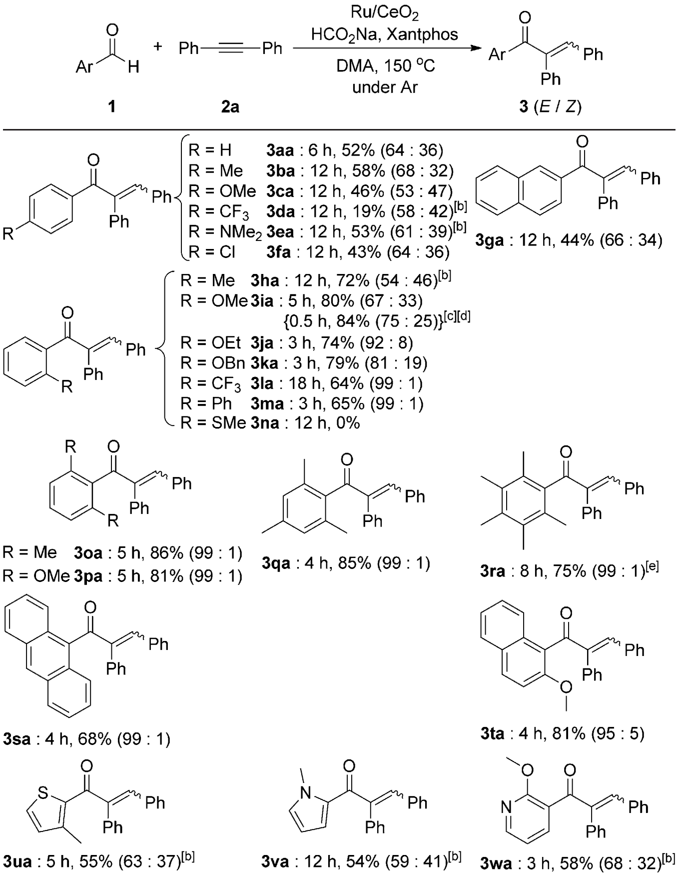
and sustainable chemistry.[9] We found that CeO_2-supported Ru catalysts (Ru/CeO_2) showed excellent catalytic performance and recyclability for various synthetic reactions.[10] For the present catalytic reaction, Ru/CeO_2 also showed activities to give **3aa** in the yields of 52%. On the other hand, other solid Ru catalysts supported on SiO_2, Al_2O_3, TiO_2, or MgO did not show any activities, and the reaction of **1a** with **2a** resulted in very low yields of **3aa** in the presence of other Ru, Rh, Ir, or Pd complex catalysts under the present conditions (Table S1 in the Supporting Information). Both Ru/CeO_2- and $[RuCl_2(p\text{-cymene})]_2$-catalyzed reactions in the absence of HCO_2Na did not take place at all. Phosphorous ligands, except for Xantphos, were totally ineffective (Table S2 in the Supporting Information).

Under the optimized reaction conditions, the intermolecular hydroacylation of **2a** with various aromatic aldehydes was examined by using the solid Ru/CeO_2 catalyst together with Xantphos and HCO_2Na (Table 1). From *para*-substituted aromatic aldehydes, the corresponding conjugated enones **3ba**–**3fa** were obtained in moderate yields. Note that these products, such as **3aa**, are available by the aldol condensation.[11] On the other hand, we fortunately found that the reactions of aromatic aldehydes having substituents at the *ortho*-position gave the desired products in good-to-high yields. Methyl, methoxy, ethoxy, benzyloxy, trifluoromethyl, and phenyl substituent suppressed side reactions, mainly decarbonylation, in the present catalytic system. The product **3ia** was also obtained in high yield by the reaction of **1i** and **2a** in the presence of $[RuCl_2(p\text{-cymene})]_2$ catalyst (Table S3 in the Supporting Information). In contrast, an *ortho*-methylsulfanyl-substituted aldehyde (**1n**) did not participate in the present catalytic reaction, although in Rh-complex-catalyzed reactions the products were obtained in high yields.[7] From aldehydes with substituents at both the *ortho*-positions of aromatic rings, the conjugated enones (**3oa**–**3ta**) were obtained in high yields with excellent *E* selectivities. The $[RuCl_2(p\text{-cymene})]_2$ catalyst also showed excellent *E* selectivity for the reaction of **1o** and **2a** (entries 8–10 of Table S3 in the Supporting Information), which suggest that the substituents of aldehydes significantly affect the stereoselectivity of the products. The *E*-structure of the major stereoisomer of **3ta** was confirmed by X-ray crystallographic study (Table S5 in the Supporting Information).[12] Heterocyclic aldehyde could also be used. Unfortunately, aliphatic aldehydes, such as 1-octanal, could not be used in the present catalytic system because of rapid aldol condensation.

The scope of alkynes was also investigated in the reaction of *ortho*-dimethyl-substituted benzaldehydes (**1o** or **1q**) by the use of Ru/CeO_2 catalyst (Table 2). Note that the products shown in Table 2 were obtained as *E* isomer stereoselectively ($E/Z > 99:<1$). The reaction of diarylacetylene

Table 1. Scope of aldehydes on the intermolecular hydroacylation of **2a** catalyzed by Ru/CeO_2.[a]



R = H **3aa** : 6 h, 52% (64 : 36)
R = Me **3ba** : 12 h, 58% (68 : 32)
R = OMe **3ca** : 12 h, 46% (53 : 47)
R = CF_3 **3da** : 12 h, 19% (58 : 42)[b]
R = NMe_2 **3ea** : 12 h, 53% (61 : 39)[b]
R = Cl **3fa** : 12 h, 43% (64 : 36)

3ga : 12 h, 44% (66 : 34)

R = Me **3ha** : 12 h, 72% (54 : 46)[b]
R = OMe **3ia** : 5 h, 80% (67 : 33)
{0.5 h, 84% (75 : 25)}[c][d]
R = OEt **3ja** : 3 h, 74% (92 : 8)
R = OBn **3ka** : 3 h, 79% (81 : 19)
R = CF_3 **3la** : 18 h, 64% (99 : 1)
R = Ph **3ma** : 3 h, 65% (99 : 1)
R = SMe **3na** : 12 h, 0%

R = Me **3oa** : 5 h, 86% (99 : 1)
R = OMe **3pa** : 5 h, 81% (99 : 1)

3qa : 4 h, 85% (99 : 1)

3ra : 8 h, 75% (99 : 1)[e]

3sa : 4 h, 68% (99 : 1)

3ta : 4 h, 81% (95 : 5)

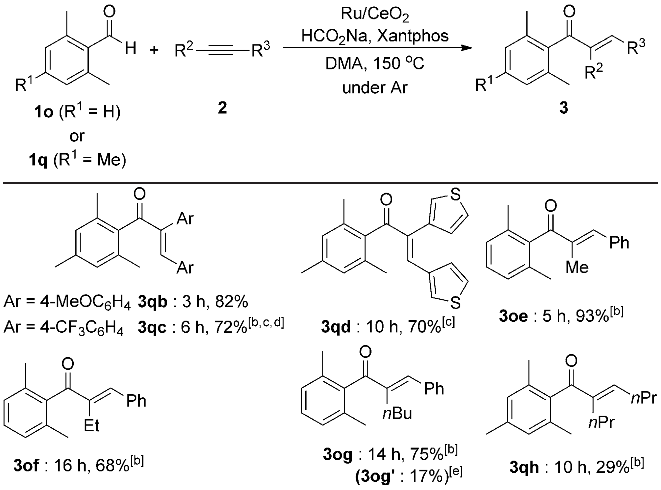
3ua : 5 h, 55% (63 : 37)[b]

3va : 12 h, 54% (59 : 41)[b]

3wa : 3 h, 58% (68 : 32)[b]

[a] Reaction conditions: **1** (0.50 mmol), **2a** (1.5 mmol), DMA (2.0 mL), Ru/CeO_2 (125 mg, 0.025 mmol as Ru), HCO_2Na (0.15 mmol), Xantphos (0.050 mmol) at 150 °C under Ar. Isolated yields were given. The numbers in parentheses show the selectivity of stereoisomer (*E*/*Z*) determined by ^1H NMR spectroscopy. [b] Structures of isomers were not determined. [c] $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol as Ru) was used instead of Ru/CeO_2. [d] Determined by GLC. [e] HCO_2Na (0.25 mmol) was used.

Table 2. Scope of alkynes in the Ru/CeO_2-catalyzed hydroacylation.[a]



Ar = 4-$MeOC_6H_4$ **3qb** : 3 h, 82%
Ar = 4-$CF_3C_6H_4$ **3qc** : 6 h, 72%[b,c,d]

3qd : 10 h, 70%[c]

3oe : 5 h, 93%[b]

3of : 16 h, 68%[b]

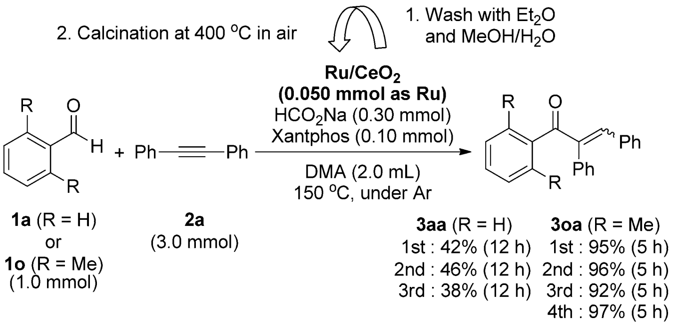
3og : 14 h, 75%[b]
(**3og'** : 17%)[e]

3qh : 10 h, 29%[b]

[a] Reaction conditions: **1** (0.50 mmol), **2** (1.5 mmol), DMA (2.0 mL), Ru/CeO_2 (125 mg, 0.025 mmol as Ru), HCO_2Na (0.15 mmol), Xantphos (0.050 mmol) at 150 °C under Ar. Isolated yields were given. [b] 0.25 mmol of HCO_2Na was used. [c] Reaction at 160 °C. [d] 250 mg of Ru/CeO_2 (0.50 mmol of Ru) was used. [e] Regioisomer of **3og** was obtained in 17% isolated yield.

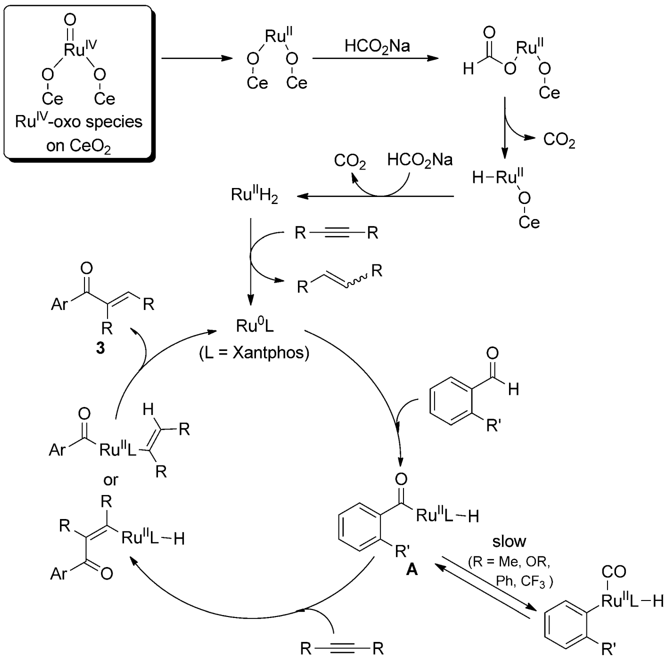
with methoxy or CF_3 substituent and dithienylacetylene occurred and the corresponding conjugated enones (**3qb–d**) were obtained in high yields. For alkyl-substituted alkynes, the reactions proceeded smoothly by using an increased amount of HCO_2Na to give the corresponding products (**3oe–g**) in good-to-high yields with high regioselectivity. The reaction of an aliphatic alkyne resulted in a low yield of the product **3qh**.

One of the most advantageous features of solid catalysts is their high recyclability. After the reaction of **1a** or **1o** with **2a**, the solid ruthenium catalyst was separated from the reaction mixture by centrifugation and washed with diethyl ether and water/methanol. The resulting powder was calcined in air at 400°C for 30 min to recover Ru/CeO_2 for subsequent catalytic runs. As shown in Scheme 2, the solid Ru/CeO_2 continued to show catalytic activity and gave **3aa** and **3oa** without significant decreases in yields for at least three times. Removal of the solid ruthenium catalyst by the hot filtration through a polytetrafluoroethylene (PTFE) filter (pore size 0.45 mm) after the reaction for 30 min partly retarded further progress of reaction of **1i** and **2a** (Figure S1 in the Supporting Information), which indicates a significant contribution of soluble ruthenium species to the catalysis. On the other hand, the amount of ruthenium species leached into the solution after the reaction of **1o** with **2a** by the fresh Ru/CeO_2 catalyst was 2.0% of the ruthenium species in the fresh catalyst (0.00050 mmol as Ru), and the same amount of $[RuCl_2(p\text{-cymene})]_2$ catalyst did not show significant activity (Table S3 in the Supporting Information).



Scheme 2. Recycling of the Ru/CeO_2 catalyst.

Although the reaction mechanisms in the present Ru/CeO_2 catalytic system are not yet fully understood, a possible mechanism is shown in Scheme 3.[2,4–7,13] As was described in our previous paper, a Ru^{IV}–oxo species is formed on the surface of CeO_2 or ZrO_2 before the catalytic reactions.[10e] An X-ray absorption fine structure (XAFS) study revealed that this Ru^{IV} species on CeO_2 is transformed into Ru^{II} species by treatment with HCO_2Na and Xantphos in DMA at 150°C (Figures S3–S5 in the Supporting Information). Darses and co-workers reported that the treatment of $[RuCl_2(p\text{-cymene})]_2$ with formate salts gave $Ru^{II}H_2$ species, which are easily reduced to Ru^0 species by the reaction with alkenes.[13] After the reaction of **2a** with Ru/CeO_2 catalyst, a catalytic amount of stilbene was detected by GC-MS analysis, indicating such Ru^{II} species should be reduced to Ru^0 species.[14] The in situ generated Ru^0 species cleaves the formyl C–H bonds to give acyl-Ru intermediate **A**. Alkynes then inserted into Ru–C or Ru–H bonds and reductive elimination gives conjugated enones **3** with the regeneration of Ru^0 species. The decarbonylation from intermediate **A** may be suppressed by the steric hindrance of substituents on the *ortho*-positions of aromatic aldehydes.[15]



Scheme 3. Possible reaction mechanism.

In summary, intermolecular hydroacylation of internal alkynes in the presence of Ru catalysts, namely Ru/CeO_2 and Ru complex catalysts, together with HCO_2Na and Xantphos was described. Even the reaction of aromatic aldehydes without coordinating groups gives the corresponding conjugated enones in good yields. In particular, various aromatic aldehydes with substituents at the *ortho*-positions of aromatic rings are transformed to the products in high yields. The present catalytic system by using solid Ru/CeO_2 shows high environmental compatibility because of their high recyclability and the very low contamination of the products by metallic species. Detailed mechanistic studies and expansion of the reaction scope are currently underway in our laboratory.

Experimental Section

2,6-Dimethylbenzaldehyde (**1o**; 67 mg, 0.50 mmol), diphenylacetylene **2a** (267 mg, 1.5 mmol), sodium formate (10.2 mg, 0.15 mmol), Xantphos (28.9 mg, 0.050 mmol), and *N*,*N*-dimethylacetamide (2.0 mL) were placed in a glass Schlenk tube under an argon atmosphere together with Ru/CeO_2 (125 mg, 0.025 mmol as Ru). The reaction mixture was stirred at 150°C for 5 h on a hot stirrer equipped with a cooling block. After the reaction, the solution was separated from the reaction mixture by centrifugation, and concentrated under reduced pressure. The products were isolated by a column chromatography (hexane/ethyl acetate 20:1) to give the product **3oa** as a white solid (yield 134.3 mg, 86%).

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Keywords: alkynes • C–H activation • hydroacylation • ruthenium • solid catalysts

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