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Rhodium-grafted hydrotalcite catalyst for heterogeneous 1,4-addition reaction of organoboron reagents to electron deficient olefins†

Ken Motokura,[‡] Norifumi Hashimoto,^a Takayoshi Hara,[§] Takato Mitsudome,^a Tomoo Mizugaki,^a Koichiro Jitsukawa^a and Kiyotomi Kaneda^{*a,b}

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A rhodium-grafted hydrotalcite (Rh/HT) was prepared by the treatment of a Mg–Al mixed hydroxide (hydrotalcite, HT) with an aqueous RhCl₃·nH₂O solution. The formation of the Rh^{III} species on the HT surface was confirmed by X-ray absorption fine structure spectroscopy. The Rh/HT catalyst was demonstrated to effectively promote the 1,4-addition reaction of organoboron reagents to electron-deficient olefins in both organic and aqueous solvents. The strong surface basicity of HT facilitates the formation of a Rh–OH species, which possesses high nucleophilicity, leading to an efficient transmetalation with organoboron reagents. This catalyst system is also applicable in the one-pot three-component synthesis of 2-cyano-3,3-diphenyl propionate due to the bifunctionality of the Rh/HT surface.

Introduction

The use of nanostructured, heterogeneous catalysts in organic synthesis enables not only facile recovery and recycling of expensive transition metals but also highly efficient organic transformations due to the unique properties of the solid surfaces.¹ Recently, layered clay minerals have received much attention as macro ligands. Our group has focused on a basic layered clay of hydrotalcite (HT), because HT shows strong surface basicity, adsorption capacity, and ion exchange properties.^{2.3} We and others have demonstrated that highly active metal species (*i.e.*, Ru, Mn, Pd, W, Os, Ni, and Cu) can be deposited on the HT surface and that a variety of organic reactions using these HT-supported metal catalysts can be conducted.

Since Miyaura and co-workers discovered the Rh-catalyzed 1,4-addition reaction of aryl boronic acids to electron deficient olefins,⁴ various homogeneous Rh complexes have been

developed for the carbon-carbon bond formation.⁵ In 2002, Hayashi and co-workers reported that the Rh species possessing a hydroxide ligand demonstrated outstanding catalytic activity.5b The key step in the 1,4-addition is the transmetallation between Rh-OH and Ar-B(OH)₂ to form Aryl-Rh species^{5b} In spite of these excellent advancements in the homogeneous reaction systems, there remain a few examples of the heterogeneous counterparts, which additionally enable facile recovery of the expensive Rh catalyst.6 Here, we report the use of a Rh-grafted hydrotalcite (Rh/HT) as an efficient heterogeneous catalyst in the 1,4-addition reaction of organoboron reagents to electron deficient olefins (Chart 1, eqn (1)).7 The associated benefits with the use of the basic HT as a support is not only the development of a recoverable heterogeneous Rh catalyst, but also the ability to form the active Rh-OH species by the basic hydroxyl groups on the HT surface.3b,c,f The Rh/HT catalyst system represents an environmentally friendly organic transformation distinguished by the following advantages: (i) high catalytic activity and selectivity is observed, (ii) phosphane ligands are not required, and (iii) both organic solvents and water are compatible with the catalyst. In addition, this report includes a one-pot



^aDepartment of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, Japan. E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: (+81) 6-6850-6260

^bResearch Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka, 560-8531, (Japan)

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[‡]Current address: Interdisciplinary Graduate School of Science and Engineering, Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan.

[§] Current address: Graduate School of Engineering, Chiba University, 1-33 Yayoi, Inage, Chiba, 263-8522, Japan.

synthesis of 2-ethoxycarbonyl-3-phenylnitriles, capitalizing on the bifunctional nature of the Rh/HT catalyst.



Results and discussion

Catalyst preparation and characterization

The preparation of the catalyst by deposition of the Rh species onto the HT surface took places as follows. Treatment of the HT with an aqueous solution of $RhCl_3 \cdot nH_2O$ at room temperature afforded Rh/HT as a pink powder (Rh content: 2.0 wt%). XRD patterns of Rh/HT indicated retention of the original HT interlayer distance, which confirmed that the Rh species were deposited onto the HT surface (Fig. 1). The features of the Rh K-edge XANES spectrum and the edge energy of a fresh Rh/HT (Fig. 2, c) did not resemble those of Rh^o foil (Fig. 2, a), but were similar to those of Rh₂O₃ (Fig. 2, b). This similarity indicates that the Rh species present in the Rh/HT is in the +3 oxidation state. In the Fourier transform of the k^3 -weighted Rh K-edge EXAFS spectrum of the Rh/HT (Fig. 3, c), a strong peak around 0.16 nm was observed (Fig. 3, b). The FT peak around 0.16 nm was well fitted by the use of a Rh-O shell parameter with six oxygen atoms at 0.204 nm, as shown in Table 1. In addition, the peaks around 0.20–0.30 nm were also well fitted by the use of a Rh-O-Mg shell parameter with three Mg atoms at 0.317 nm (Table 1). These results indicate that the monomeric Rh species on HT is highly dispersed on the HT surface coordinated with oxygen ligands. The strong basicity of the HT surface may serve to facilitate the introduction of a hydroxyl group on the Rh site. It was reported that hydroxyl groups can be introduced to surface Rh site by treatment with aqueous NaOH solution8 Conclusively, the RhIII species bearing a hydroxy group (Rh-OH) and two additional water molecules is linked with three Rh-O bonds (covalent or coordinative) onto the HT surface (Rh-O-Mg).



Fig. 1 XRD patterns of (a) parent HT, (b) fresh Rh/HT, and (c) recovered Rh/HT.

| Table 1 | Curve-fitting analysis for the Rh/HT catalyst |
|---------|---|
|---------|---|

| Sample | Shell | C. N." | <i>r</i> (nm) ^{<i>b</i>} | σ (nm) ^c |
|--------|---|------------|-----------------------------------|----------------------------|
| Rh/HT | Rh–O ^d Rh–(O)–Mg ^e | 6.4 3.3 | 0.204 0.317 | $0.0070 \\ 0.0066$ |

^{*a*} Coordination number. ^{*b*} Bond distance. ^{*c*} Debye–Waller factor. ^{*d*} Curvefitting analysis was performed with the inverse FT of the 0.112 nm < r < 0.193 nm range. ^{*c*} 0.221 nm < r < 0.292 nm.



Fig. 2 A series of Rh K-edge XANES spectra for (a) Rh foil, (b) Rh_2O_3 , (c) fresh Rh/HT, (d) recovered Rh/HT, and (e) Rh/HT during the reaction.

1,4-Addition reaction using the Rh/HT catalyst

The 1,4-addition reaction of phenylboronic acid (2a) and 2cyclohexen-1-one (1a) proceeded smoothly in the presence of the Rh/HT catalyst and a small amount of 1,5-cyclooctadiene (1,5-cod) in 1,4-dioxane to afford 3-phenylcyclohexanone (3a) in 98% yield, as shown in Table 2, entry 1. In the case of MgO as a catalyst support, a moderate yield of 3a was obtained (entry 6). Also, the $Rh(OH)_x/Al_2O_3$ having hydroxo ligand gave a good yield of 3a (entry 11).8 On the other hands, other supported Rh catalysts such as Rh/Mg(OH)₂, Rh/Al₂O₃, Rh/Al(OH)₃, and Rh-carbon were found to be less active (entires 7-10). The catalyst precursor $RhCl_3 \cdot nH_2O$ or the parent HT alone did not show any catalytic activities (entries 12 and 13). The effect of the additives on the Rh/HT-catalyzed addition was also examined, as shown in Table 3. This reaction occurred only to a slight extent in the absence of 1,5-cod (entry 1). The dienes 1,5-cod (entry 3) and 2,5-norbornadiene (entry 4) accelerated the 1,4addition reaction;9 however, no conversion was observed in the presence of other additives, such as triphenylphosphane or



Fig. 3 FT of k^3 -weighted Rh K-edge EXAFS spectra for (a) Rh foil, (b) Rh₂O₃, (c) fresh Rh/HT, (d) recovered Rh/HT, and (e) Rh/HT during the reaction.

1,4-*bis*(diphenylphosphano)butane (dppb), due to their strong coordination to the Rh species (entries 5–8). The effect of solvents on the 1,4-addition, under otherwise identical reaction conditions as used for entry 1 in Table 2 was examined: 1,4-dioxane, ethanol, and DME were found to be good solvents (Table 4, entries 1–3). However, toluene, DMF, n-heptane, and THF were not effective (entries 4–7).

With optimized conditions using 1,5-COD and 1,4-dioxane, the scope of the reaction was examined using a variety of electron deficient olefin substrates (Table 5). Both cyclic and acyclic aliphatic α . β -unsaturated ketones worked well as acceptors in the reaction with 2a (entries 1, 5–7). An aromatic ketone (e.g., chalcone) also served as an efficient acceptor, providing 1,3,3triphenylpropan-1-one in an excellent yield (entry 8). In the case of cinnamaldehyde, the corresponding 1,4-addition product was obtained without formation of the 1,2-addition product (entry 9).¹⁰ This methodology was applicable with an α , β -unsaturated nitrile (entry 10) as well. The scope of the donor substrate was expanded to various *p*-substituted phenylboronic acids (entries 12-14). Good to excellent yields of products were obtained in the reactions of p-substituted phenylboronic acids. A large-scale reaction of 2a with 1a afforded 3a with a TOF of 580 h⁻¹ and a TON of 3500 (entry 4), which are considerably higher than those previously reported for a heterogeneous Rh catalyst system (TOF, 11 h⁻¹; TON, 32).⁶

The Rh/HT catalyst was easily separated from the reaction mixture by filtration and the recovered Rh/HT was washed

| Ĵ | + B(OH)2 - | catalyst 1,5-cod, 1,4-dioxane | - |
|-----------------|----------------------|-------------------------------------|--|
| _1a | 2a | | 3a 🎽 |
| Entry | Catalyst | | Yield of 3a (%) ^{<i>b</i>} |
| 1 | Rh/HT | | 98 |
| 2 ^c | Rh/HT | | 2 |
| 3 ^d | Rh/HT | | 94 |
| 4^e | Rh/HT | | 14 |
| 51 | Rh/HT | | Trace |
| 6 | Rh/Mg | C | 55 |
| 7 | Rh/Mg | $(OH)_2$ | 20 |
| 8 | Rh/Al ₂ | D ₃ | Trace |
| 9 | Rh/Al(0 | OH) ₃ | 0 |
| 10 | Rh-Carl | Rh-Carbon | |
| 11 ^g | Rh(OH) | $Rh(OH)_x/Al_2O_3$ | |
| 12 | Rh_2O_3 | | Trace |
| 13 | RhCl ₃ ·n | $RhCl_3 \cdot nH_2O$ | |
| 14 ^h | HT | | 0 |
| 15 | None | | 0 |

 Table 2
 1,4-Addition of 2a to 1a using various catalysts^a

^{*a*} **1a** (1.0 mmol), **2a** (1.0 mmol), Rh catalyst (6.0×10^{-2} g, Rh: 1.2×10^{-2} mmol), 1,5-cod (1.2×10^{-2} mmol), 1,4-dioxane (2 mL), 100 °C, Ar, 4 h. ^{*b*} Determined by GC. ^{*c*} Without 1,5-cod. ^{*d*} 70 °C. ^{*c*} 60 °C. ^{*f*} 40 °C. ^{*s*} Rh(OH)_x/Al₂O₃ was prepared by the reported procedure^{8 *h*} HT (0.06 g) was used.

Table 3 1,4-Addition of 2a to 1a using various ligands^a

 $1a + 2a \xrightarrow{\text{Rh/HT}} 3a$

| Entry | Additive | Yield of 3a (%) ^b | |
|----------------|---|-------------------------------------|--|
| 1 | None | 2 | |
| 2 ^c | None | 32 | |
| 3 | 1,5-Cyclooctadiene (1,5-cod) | 98 | |
| 4 | 2,5-Norbornadiene | 49 | |
| 5 ^c | 1,3-Cyclohexadiene | No reaction | |
| 6 ^c | Triphenylphosphane | No reaction | |
| 7 | 1,4-Bis(diphenylphosphano)butane (dppb) | No reaction | |
| 8 | Acetyl acetone | Trace | |

^{*a*} Reaction condition: Rh/HT (Rh: 1.2×10^{-2} mmol), **1a** (1.0 mmol), **2a** (1.0 mmol), 1,4-dioxane (2.0 mL), ligand (1.0 equiv of Rh), 100 °C, 4 h, Ar. ^{*b*} GC yield. ^{*c*} Rh/HT (Rh: 1.2×10^{-2} mmol), **1a** (0.4 mmol), **2a** (2.0 mmol), 1,4-dioxane (3.0 mL), 24 h.

Table 41,4-Addition of 2a to 1a using various solvents^a

| $1a \pm 2a$ | Rh/HT | . 30 |
|-------------|------------------|------|
| 1a + 2a - | 1,5-cod, solvent | → Ja |

| Entry | Solvent | Yield of 3a (%) ^b |
|-------|-----------------------------|-------------------------------------|
| 1 | 1,4-Dioxane | 98 |
| 2 | Ethanol | 98 |
| 3 | DME (dimethoxyethane) | 97 |
| 4 | Toluene | 36 |
| 5 | DMF (N,N-dimethylformamide) | 33 |
| 6 | <i>n</i> -Heptane | 28 |
| 7 | THF | 26 |

^{*a*} 1a (1.0 mmol), 2a (1.0 mmol), Rh/HT (6.0×10^{-2} g, Rh: 1.2 × 10⁻² mmol), 1,5-cod (1.2×10^{-2} mmol), solvent (2 mL), 100 °C, Ar, 4 h. ^{*b*} Determined by GC.

| R ¹ | + Ar- ۳R ² | –B(OH) ₂ – 2 | Rh/HT 1,5-cod, 1,4-dioxane | $- R^{1} \xrightarrow{O} R^{2} R^{2}$ |
|-----------------------|--------------------------|-----------------------------------|----------------------------------|---|
| Entry | Acceptor | Donor | Time (h) | Yield of 3 (%) ^{<i>b</i>} |
| 1 | 1a | 2a | 4 | 92 |
| 2^{c} | 1a | 2a | 4 | 92 |
| 3 ^{<i>d</i>} | 1a | 2a | 4 | 92 |
| 4 ^e | 1a | 2a | 6 | 70 |
| 5 ^{f,g} | 1b | 2a | 5 | 75 |
| 6 | 1c | 2a | 4 | 92 |
| $7^{f,g,h}$ | 1d | 2a | 8 | 76 |
| $8^{f,g,h}$ | 1e | 2a | 24 | 99 |
| 9 ^g | 1f | 2a | 4 | 74 ⁱ |
| 10 ^g | 1g | 2a | 8 | 61 ^{<i>i</i>} |
| 11 | 1h | 2a | 4 | 61 ⁱ |
| 12 | 1a | 2b | 4 | 99 |
| 13 | 1a | 2c | 4 | 75 |
| 14 | 1a | 2d | 4 | 78 |

^{*a*} **1** (1.0 mmol), **2** (1.0 mmol), Rh/HT (6.0×10^{-2} g, Rh: 1.2×10^{-2} mmol), 1,5-cod (1.2×10^{-2} mmol), 1,4-dioxane (2 mL), Ar, 100 °C. ^{*b*} Isolated yield. ^{*c*} Reuse 1. ^{*d*} Reuse 2. ^{*e*} **1** (20 mmol), **2** (20 mmol), Rh/HT (2.0×10^{-2} g, Rh: 4.0×10^{-3} mmol), 1,5-cod (4.0×10^{-3} mmol), 1,4-dioxane (2 mL), H₂O (0.36 mL), Ar. ^{*f*} 1.5 equiv of **2** was used. ^{*g*} 150 °C. ^{*h*} Rh/HT (0.12 g, Rh: 2.4×10^{-2} mmol) was used. ^{*i*} GC yield.

with 1,4-dioxane and reused under same reaction conditions; the first and second runs afforded 92% and 92% yield of the product, respectively (entries 2 and 3). After the completion of the catalytic reaction using Rh/HT, ICP-AES analysis of the filtrate showed a 2% leaching of Rh. However, the addition reaction completely stopped after the hot-filtration of Rh/HT at 50% conversion of **1a**.

Reaction pathway

XANES spectra of the Rh species from the recovered Rh/HT (Fig. 2, d) and Rh/HT during the reaction (Fig. 2, e) showed the same peak shape and E_0 value as the freshly prepared Rh/HT catalyst (Fig. 2, c). A similar spectrum of the recovered Rh/HT (Fig. 3, d) to that of the Rh/HT during the reaction (Fig. 3, e) was obtained by Fourier transform of the k^3 -weighted Rh K-edge EXAFS analysis. These results indicate the retention of the +3 oxidation state in the local structure of the Rh species during the 1,4-addition reaction. As confirmed by the above hot-filtration experiment, the leached Rh species did not have catalytic activity. The Rh(OH)_x/Al₂O₃ acts as a good catalyst

compared to Rh/Al₂O₃ for the 1,4-addition reaction under the same reaction conditions (vide supra). These results strongly support that the surface Rh^{III}-OH is an active species for the Rh/HT-catalyzed 1,4-addition reaction. The reaction may involve (i) transmetalation between the surface Rh-OH species and the arylboronic acid providing a Ar-Rh species, followed by (ii) insertion of an olefin into the Ar-Rh bond yielding an oxa- π -allyl rhodium enolate, which is readily protonated by water generating (iii) the desired addition product with concomitant regeneration of the Rh-OH catalyst (Scheme 1). When the reaction was conducted in 1,4-dioxane, the conjugate addition smoothly proceeded without addition of water. Adsorbed water on the HT surface and the water generated by the dehydration reaction of $B(OH)_3$ are expected to be consumed by the hydrolysis step of the oxa- π -allyl rhodium in the proposed catalytic cycle. In 20 mmol scale reaction (Table 5, entry 4), addition of a small amount of water accelerates the 1,4-addition reaction. The proposed reaction mechanism is agreement with that previously reported for the homogeneous Rh catalyst system.5b The surface basicity of the HT could promote the formation of basic Rh hydroxide species.[vide supra] In competitive addition reactions of para-substituted phenylboronic acids with 1a, the reaction rates decreased with electron-rich phenylboronic acids (eqn (2)). This suggests that the reaction mechanism involves nucleophilic attack of the OH group on the Rh species to boron atom of the arylboronic acid thereby facilitating the transmetallation. Kinetic studies in 1,4dioxane demonstrated a first-order dependence of 2a and a zeroorder relationship in 1a, indicating that transmetallation of 2a may be the rate-determining step (Fig. 4S, ESI[†]). This is also in agreement with the proposed mechanism previously reported for the homogeneous Rh catalyst system.5g

1,4-Addition reaction in water

To minimize or eliminate the use of harmful organic reagents is a promising synthetic approach to environmentally friendly chemistry.¹¹ The use of water as a solvent is recognized as a significant challenge, and additionally reveals unique catalytic activities and selectivities not observed under anhydrous conditions.¹² We examined water as a solvent in place of 1,4-dioxane in the Rh/HT-catalyzed 1,4-addition reaction. A poor yield of the desired product was obtained under the previously optimized reaction conditions for the Rh/HT-1,4dioxane system, but the use of a small excess of **2a** was found to significantly enhance the yield of **3a** (eqn (3)).







L = 1,5-cod or oxy ligand on the HT surface

Scheme 1

The conjugate additions of a variety of arylboronic acids to electron deficient olefins were examined using water as a solvent (Table 6). Interestingly, olefins that have poor solubility in water readily reacted with **2a** to provide the conjugate addition products in excellent to moderate yields (entries 1–8). *p*-Substituted arylboronic acids also served as excellent substrates in water (entries 9–12).¹³ The product yields are similar to those of the cases in 1,4-dioxane (Table 5).

One-pot three component synthesis

Because the Rh/HT catalyst possesses both a Rh site and a surface base site, it was envisioned that the Rh/HT could

Table 61,4-Addition of 2 to 1 in water^a

| | $1+2 (1.5 \text{ equiv.}) \xrightarrow{\text{Rh/HT}} 3$ | | | |
|----------------|---|-------|------------------------------------|--|
| Entry | Acceptor | Donor | Yield of 3 (%) ^b | |
| 1 | 1a | 2a | 90 | |
| 2 | 1b | 2a | 80 | |
| 3 ^c | 1c | 2a | 75 | |
| 4 | 1d | 2a | 87 | |
| 5 ^d | 1e | 2a | 90 | |
| 6 | 1f | 2a | 88 | |
| 7 | 1g | 2a | 91 | |
| 8 | 1 h | 2a | 40 | |
| 9 | 1a | 2b | 95 | |
| 10 | 1a | 2c | 95 | |
| 11 | 1a | 2d | 90 | |
| 12 | 1a | 2e | 60 | |

^{*a*} **1** (1.0 mmol), **2** (1.5 mmol), Rh/HT (6.0×10^{-2} g, Rh: 1.2×10^{-2} mmol), 1,5-cod (1.2×10^{-2} mmol), water (2 mL), 100 °C, Ar, 4 h. ^{*b*} Isolated yield based on **1**. ^{*c*} 80 °C, 12 h. ^{*d*} 5 h.

| be used as a bifunctional catalyst for the one-pot synthesis |
|--|
| containing several organic reactions; ^{3,4,4} a condensation reaction |
| could be catalyzed by the base site of HT surface, followed |
| by the conjugate addition of the organoboron reagent to the |
| electrophilic olefin, catalyzed by Rh-catalysis, to provide highly |
| functionalized products in a one-pot (Table 7). For example, |
| after the Knoevenagel condensation of ethyl cyanoacetate with |
| benzaldehyde catalyzed by the surface base site of the Rh/HT, |
| further transformation with 2a in the same flask gave 88% |
| overall yield of 2-cyano-3,3-diphenyl propionate, a precursor to |
| the important amino acid (2R)-3,3-diphenyl-2-methylalanine) |
| (entry 1).14 The water generated by the Konoevenagel con- |
| densation reaction might accelerate the following 1,4-addition |
| reaction. We also investigated a variety of aldehydes, such as |
| substituted benzaldehyde and heteroaromatic aldehydes (entries |
| 2-5). In all cases, one-pot reaction products were obtained in |
| high yields. Not only aromatic aldehyde, but also aliphatic ones, |
| such as 1-octanal, acted as good substrates with 2a provided |
| the corresponding 3-phenylnitrile in moderate yields (entries 6 |
| and 7). |

Conclusion

Rh-grafted hydrotalcite (Rh/HT) has been developed as a highly active heterogeneous catalyst for the implementation in 1,4-addition reactions of various arylboronic acids to electron deficient olefins. Furthermore, the one-pot synthesis of an important amino acid precursor using Rh/HT as a bifunctional catalyst was also demonstrated. Heterogeneous transition metal catalysts using the HT support will allow for environmentally friendly chemical transformations.

Experimental

General

¹H and ¹³C NMR spectra were obtained on JEOL GSX-270 of JNM-AL400 spectrometers at 270 or 400 MHz in CDCl₃ with TMS as an internal standard. Analytical GLC and GC-mass were performed using Shimadzu GC-8A PF with flame ionization detector equipped with KOCL 3000T, Silicon SE-30, and OV-17 columns, and a Shimadzu GCMS QP5050A equipped with ULBON HR-1 columns. Powder X-ray diffraction patterns were recorded using Philips X'Pert-MPD with Cu-K α radiation. Inductively coupled plasma (ICP-AES) measurement was performed using a SII NanoTechnology SPS7800. Rh K-edge X-ray absorption fine structure spectra were recorded at room temperature in transmission mode with a Si(311) double crystal monochromator at the beam line NW-10A

| | NC [^] CO₂Et + R [^] O - | (i) | Et $\begin{array}{ c c c } \hline Rh \ species \\ \hline (ii) \ 2a \end{array} \qquad \begin{array}{c} Ph \\ \hline CO_2 Et \\ CN \end{array}$ | |
|-------|--|------------------|--|------------------------|
| Entry | Aldehyde | Time of (ii) (h) | Product | Isolated Yield (%) |
| 1 | \bigcirc | 12 | Ph CO ₂ Et CN | 88 |
| 2 | CI CI CI | 12 | CI CN CO2Et | 84 |
| 3 | NC | 24 | NC Ph CO ₂ Et | 63 |
| 4 | Meo | 12 | MeO Ph CO ₂ Et | 74 ^{<i>b</i>} |
| 5 | | 24 | CN Ph CO ₂ Et CN | 51* |
| 6 | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ | 20 | Ph CO ₂ Et CN | 61 |
| 7 | $\sim \sim \sim \circ$ | 20 | Ph CO ₂ Et CN | 64 |

| Fable 7 | Three-component | one-pot synthesis of | 2-ethoxycarbonyl-3 | -phenylnitriles | using the Rh/H | HT as a bifunctional catalyst ^a |
|---------|-----------------|----------------------|--------------------|-----------------|----------------|--|
|---------|-----------------|----------------------|--------------------|-----------------|----------------|--|

^{*a*} (i) Ethyl cyanoacetate (1.0 mmol), aldehyde (1.0 mmol), 1,5-cod (1.2×10⁻² mmol), Rh/HT (6.0×10⁻² g; Rh: 1.2×10⁻² mmol), 1,4-dioxane (2.0 mL), 8 h, 100 °C, Ar. (ii) **2a** (1.5 mmol), 100 °C. ^{*b*} GC yield.

station with 6.5 GeV storage ring energy of the Photon Factory, AR, Tsukuba, Japan. (KEK-PF, proposal No. 2009G069). The resulting EXAFS spectra were analyzed with REX2000 ver 2.5.7 (Rigaku Co.). Fourier transforms of k^3 -weighted EXAFS spectra were performed in the 0.30 nm⁻¹ < k < 1.55 nm⁻¹ range.

A hydrotalcite (HT), $Mg_{0.827}Al_{0.173}(OH)_{1.930}(CO_3)_{0.090}(Cl)_{0.063}$. 0.62H₂O, was obtained from TOMITA Pharmaceutical Co. Ltd, Japan. MgO, Mg(OH)₂, Al(OH)₃, and Rh–Carbon were purchased from Wako Pure Chemicals. γ -Al₂O₃ (JRC-ALO-4) was also used. Olefins, aryl boronic acids, and solvents were purchased from Wako, Tokyo Kasei, and Aldrich, and purified by the standard procedures prior to experiments. The identities of products were confirmed by comparison with reported mass and NMR data.

Preparation of the Rh/HT

The HT (1.0 g) was added to 100 mL of an aqueous solution of RhCl₃·nH₂O (Rh: 2.0 × 10⁻³ M), and the heterogeneous mixture was stirred at room temperature for 0.5 h. The solid product was separated by filtration, washed thoroughly with deionized water, and dried under vacuum at room temperature, affording Rh/HT as a pink powder. Other supported Rh catalysts, such as Rh/MgO and Rh/Al₂O₃, were synthesized by similar procedures. $Rh(OH)_x/Al_2O_3$ was prepared according to the report by Mizuno and co-workers.⁸

1,4-Addition of arylboronic acids to electron-deficient olefins

Into a pyrex glass reactor were combined **1a** (1.0 mmol), **2a** (1.0 mmol), Rh/HT (0.06 g, Rh: 0.012 mmol), 1,5-cod (0.012 mmol), and 1,4-dioxane (2.0 mL). The reaction mixture was vigorously stirred at 100 °C under Ar for 4 h. After the reaction was complete, the catalyst was removed by filtration, and the filtrate was evaporated. The crude product was purified by silica gel column chromatography (n-hexane/ethyl acetate, 9:1), thus affording **3a** as a colorless oil (92% isolated yield). The recovered Rh/HT catalyst was washed with 1,4-dioxane and reused under same reaction conditions; the first and second runs afforded 92% and 92% yield of the product, respectively.

Large-scale 1,4-addition of 2a to 1a

Into a pyrex glass reactor were combined **1a** (20 mmol), **2a** (20 mmol), Rh/HT (0.02 g, Rh: 0.004 mmol), 1,5-cod

(0.004 mmol), 1,4-dioxane (20 mL), and water (0.36 mL). The reaction mixture was vigorously stirred at 100 °C under Ar for 6 h. After the reaction was complete, the catalyst was removed by filtration, and the filtrate was evaporated. The crude product was purified by distillation, thus affording **3a** as a colorless oil (70% isolated yield).

1,4-Addition of arylboronic acids to electron-deficient olefins in water

Into a pyrex glass reactor were combined 1a (1.0 mmol), 2a (1.5 mmol), Rh/HT (0.06 g, Rh: 0.012 mmol), 1,5-cod (0.012 mmol), and water (2.0 mL). The reaction mixture was vigorously stirred at 100 °C under Ar for 4 h. After the reaction was complete, the catalyst was removed by filtration, and the filtrate was extracted with ethyl acetate. The organic layers were combined and concentrated by evaporation to give the crude product, which was purified by silica gel column chromatography (n-hexane/ethyl acetate, 9:1), thus affording 3a as a colorless oil (90% isolated yield).

One-pot three-component synthesis

A mixture of benzaldehyde (1.0 mmol), ethyl cyanoacetate (1.0 mmol), Rh/HT (0.060 g, Rh: 0.012 mmol), 1,5-cod (0.012 mmol), and 1,4-dioxane (2.0 mL) was vigorously stirred at 100 °C under Ar for 8 h. Then, **2a** (1.5 mmol) was added to the same flask, and allowed to further react at 100 °C under Ar for 12 h. After the reaction, the catalyst was separated by filtration. The filtrate was evaporated and the crude product was purified by silica gel column chromatography (n-hexane/ethyl acetate, 9:1) to afford a pure ethyl2-cyano-3,3-diphenylpropionate (88% isolated yield).

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