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Active Ruthenium Catalysts Based on Phosphine-Modified Ru/CeO_2 for the Selective Addition of Carboxylic Acids to Terminal Alkynes

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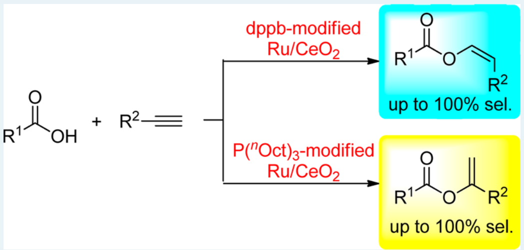
Supporting Information

ABSTRACT: The modification of ruthenium species supported on ceria in the presence of suitable phosphines under H_2 at 100 °C was found to generate catalytically active Ru species that were effective for the regio- and stereoselective addition of carboxylic acids to terminal alkynes. The reactions in the presence of a catalytic amount of Ru/CeO_2 modified with 1,4-bis(diphenylphosphino)butane gave the anti-Markovnikov adducts in high yields with excellent (*Z*)-isomer selectivities. On the other hand, the reactions with the trioctylphosphine-modified catalyst gave the Markovnikov adducts as major products. Among the catalysts examined, only ceria- or zirconia-supported catalysts were effective, and hot filtration tests using the phosphine-modified Ru/CeO_2 catalyst suggested that soluble ruthenium species showed quite a high catalytic activity. Very small amounts of ruthenium species were detected in the solution. The solid Ru/CeO_2 could be repeatedly used as a reservoir of active catalysts without a significant loss of activity.



KEYWORDS: *supported catalyst, ruthenium, ceria, alkynes, carboxylic acids, vinyl esters, phosphine modification*

INTRODUCTION

The development of highly selective catalytic reactions with high atom efficiencies is quite important, since such processes should give the desired products without byproduct or waste.[1] To achieve such goals, transition-metal complexes have been widely applied as homogeneous catalysts, mainly because fine-tuning of their active sites by ligands or additives can induce excellent activities and selectivities. In this context, ruthenium-complex catalysts together with suitable phosphine ligands have been used to achieve the regio- and stereoselective addition of carboxylic acid to alkynes,[2−21] which is the most atom-economical route for the synthesis of vinyl esters.[22−31]

The use of solid catalysts, particularly oxide-supported metal catalysts, is quite attractive because of their simple preparation, high stability, and facile reusability, as well as minimal contamination of the products by metallic species.[32−41] Recently, we developed recyclable Ru/CeO_2 catalysts that are quite effective for various C−C bond-forming reactions.[42−47] Our latest spectroscopic investigations showed that Ru(IV)=O species on CeO_2 were transformed into low-valent Ru species with high catalytic activities.[46,47] In the course of these studies, we found that the heating of Ru/CeO_2 catalysts in a hydrogen atmosphere in the presence of a small amount of phosphines (phosphine modification route) greatly improved the activities of the resulting Ru catalysts for the arylation[44] and alkylation[45] of aromatic C−H bonds. Furthermore, unmodified Ru/CeO_2 catalysts were found to be effective for the addition of carboxylic acids to terminal alkynes to give the (*E*)-isomer of vinyl esters as major products.[48] On the basis of these results as well as those using immobilized Ru catalysts,[49] we expected the modification of Ru/CeO_2 by suitable phosphines to generate highly active Ru catalysts for the regio- and stereoselective synthesis of vinyl esters via the addition of carboxylic acids to alkynes.

We report here a simple method for the preparation of active Ru catalysts that can be used for the selective addition of carboxylic acids to terminal alkynes by phosphine-modification of Ru/CeO_2. The conditions of the pretreatment of Ru/CeO_2 greatly affected their catalytic behavior, and the regio- and stereoselectivities of the products can be controlled by the choice of the phosphines used for pretreatment.

RESULTS AND DISCUSSION

Effects of dppb-Modification of Ru/CeO_2 or Ru/ZrO_2 on the Anti-Markovnikov Addition of Carboxylic Acids to Terminal Alkynes. The methods used to prepare supported Ru catalysts are summarized in Scheme 1. The CeO_2-supported Ru catalysts (Ru/CeO_2) were prepared by impregnation of a solution of a Ru precursor, such as $RuCl_3{\cdot}nH_2O$ or $Ru(acac)_3$, on CeO_2 followed by calcination in air at 400 °C for 30 min. The Ru/CeO_2 catalyst was then heated at 100 °C for 20 min under a hydrogen atmosphere (1 atm) without any solvent in the presence of phosphines to give *x*phosphine-Ru/CeO_2 (*phosphine modification*), where *x* shows the molar ratio of phosphine to ruthenium. In contrast, the Ru/CeO_2 catalyst that was reduced under similar conditions in the

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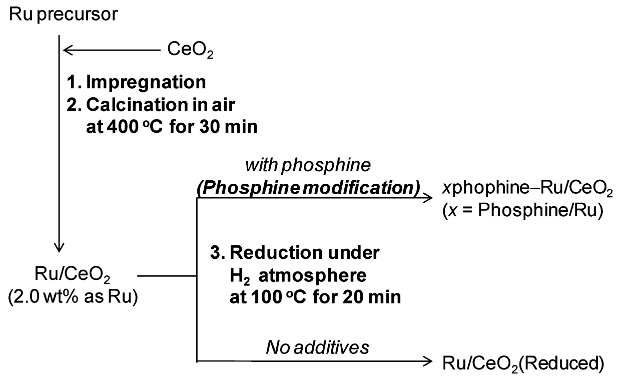
Scheme 1. Method for the Preparation of Phosphine-Modified Ru/CeO_2



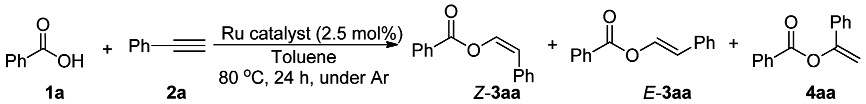
absence of any additives was designated as Ru/CeO_2(Reduced).

The 1,4-bis(diphenylphosphino)butane-modified Ru/CeO_2 catalyst (2dppb-Ru/CeO_2) showed excellent activity for the selective addition of benzoic acid (**1a**) to ethynylbenzene (**2a**) to afford the corresponding vinyl ester **3aa** quantitatively, with high selectivity for the (*Z*)-isomer (Table 1, entry 1). Preliminary experiments revealed that the optimum ratio of dppb to ruthenium is about 2. On the other hand, the reaction catalyzed by unmodified Ru/CeO_2 without any external additives mainly gave the (*E*)-isomer of **3aa** (entry 2). As reported in our previous study, the Ru/CeO_2-catalyzed reaction at 130 °C gave the product *E*-**3aa** in a high yield.[48] Ruthenium complexes with the dppb ligand have been reported to act as effective homogeneous catalysts to give the (*Z*)-isomer of vinyl esters with excellent selectivities,[12,13] while a recent report on the selective Markovnikov addition of carboxylic acids to internal alkynes catalyzed by dppb-coordinated Ru complexes[14] stated that factors other than coordinating ligands might affect the selectivity of the reaction. The addition of dppb to the unmodified Ru/CeO_2-catalyzed system produced the (*Z*)-isomer of **3aa** with a high selectivity, whereas the total yield of vinyl esters was very low (entry 3). The prereduction of Ru/CeO_2 with molecular hydrogen did not have a positive effect (entry 4), and the reaction of **1a** with **2a** under a hydrogen atmosphere resulted in a moderate total yield of **3** (entry 5). These results indicated that the reductive treatment of Ru/CeO_2 catalysts *in the presence of phosphine* is essential for generating Ru species with high catalytic activity and selectivity. The effects of modification by other phosphines are summarized in Table S2 of the Supporting Information.

The Ru precursors for Ru/CeO_2 affected the catalytic activities (entries 1 and 6−9). The solid Ru catalyst prepared using Ru(acac)$_3$ showed the highest selectivity, and the reaction was complete in the shortest time (8 h, entry 9). The Ru/ZrO_2 catalyst modified by dppb also showed catalytic activity for selective addition (entry 10). In contrast, dppb-modified Ru catalysts supported on SiO_2, Al_2O_3, TiO_2, or MgO did not show any activity (entries 11−14). Such a marked effect of the support has been observed in our previous studies on C−C bond-forming reactions[42−46] as well as in the addition of carboxylic acids to alkynes by unmodified catalysts.[48] As discussed in our previous reports,[46−48] highly dispersed Ru(IV)-oxo species is selectively formed on the surface of ceria and zirconia, and this would be a good precursor for the catalytically active Ru species. In contrast, Ru species formed on the surface of the other supports had a microstructure similar to that of crystalline RuO_2, which could not be transformed into the active catalysts.

To examine the nature of the ruthenium species on Ru/CeO_2 before and after modification with dppb, Ru K-edge X-ray absorption near edge structure (XANES) spectra were recorded, and the results are shown in Figure 1 together with the spectra of RuO_2 and Ru metal. The XANES spectrum of unmodified Ru/CeO_2 showed a characteristic pre-edge peak at around 22110 eV, which can be assigned to Ru(IV) species with a distorted coordination structure bearing a Ru═O bond.[46,50] After dppb-treatment, the pre-edge peak disappeared, and the absorption-edge of the catalyst shifted to a lower energy but did not coincide with that of Ru metal. This

Table 1. Effect of Pretreatment of Supported Ru Catalysts on the Anti-Markovnikov Addition[a]



1a **2a** *Z*-**3aa** *E*-**3aa** **4aa**

entry	Ru catalyst	Ru precursor	total yield (%)[b]	selectivity (%)[c] *Z*-**3aa**:*E*-**3aa**:**4aa**
1	2dppb-Ru/CeO_2	$RuCl_3 \cdot nH_2O$	99	90:10:0
2	Ru/CeO_2	$RuCl_3 \cdot nH_2O$	24	13:83:4
3	Ru/CeO_2 + 2dppb	$RuCl_3 \cdot nH_2O$	18	89:11:0
4	Ru/CeO_2(Reduced) + 2dppb	$RuCl_3 \cdot nH_2O$	18	90:10:0
5[d]	Ru/CeO_2 + 2dppb	$RuCl_3 \cdot nH_2O$	50	90:10:0
6	2dppb-Ru/CeO_2	$[RuCl_2(p\text{-cymene})]_2$	64	97:3:0
7	2dppb-Ru/CeO_2	$[RuCl_2(CO)_3]_2$	99	91:9:0
8	2dppb-Ru/CeO_2	$Ru_3(CO)_{12}$	83	91:9:0
9[e]	2dppb-Ru/CeO_2	Ru(acac)$_3$	99	98:2:0
10	2dppb-Ru/ZrO_2	Ru(acac)$_3$	71	98:2:0
11	2dppb-Ru/SiO_2	Ru(acac)$_3$	0	
12	2dppb-Ru/Al_2O_3	Ru(acac)$_3$	trace	
13	2dppb-Ru/TiO_2	Ru(acac)$_3$	0	
14	2dppb-Ru/MgO	Ru(acac)$_3$	0	

[a] Reaction *conditions*: **1a** 1.0 mmol, **2a** 1.3 mmol, toluene 1.0 cm^3, 0.025 mmol as Ru, dppb 0.050 mmol, at 80 °C for 24 h under Ar. [b] Total yield of **3aa** and **4aa** based on **1a**, determined by GLC. [c] Molar ratio of isomers determined by GLC. [d] Reaction under H_2 (1 atm). [e] Reaction for 8 h.

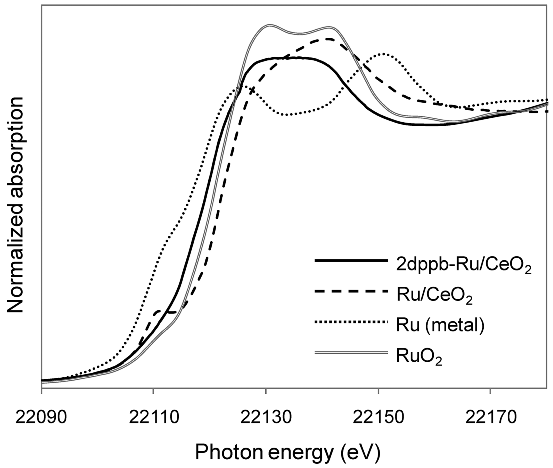


Figure 1. Ru K-edge XANES spectra of the catalysts.

result indicates that the Ru(IV) species are reduced to low-valent Ru species, probably Ru(II) species, with a loss of the Ru═O structure.

The amount of ruthenium species leached from the solid Ru catalysts into the liquid phase after the reactions of **1a** with **2a** under the condition shown in Table 1 was examined by inductively coupled plasma atomic emission spectrometry (ICP-AES). From the 2dppb-Ru/CeO_2 catalyst, 0.54 μmol of Ru species were found to be leached into toluene solution after it was allowed to cool to room temperature, which corresponds to 2.2% of ruthenium species in the fresh 2dppb-Ru/CeO_2 catalyst. There was no sign of the formation of Ru nanoparticles in solution by the transmission electron microscopy (TEM) study. The amount of ruthenium species leached from the zirconia-supported catalyst was below the limit of detection in the ICP-AES measurement. The ^{31}P {^{1}H} NMR spectrum of the filtrate and washings showed a large singlet of dppb (88% of dppb used for the modification) albeit with trace peaks of intractable phosphorus compounds, indicating that a major part of the dppb ligand was kept intact even after the catalytic reaction (see Supporting Information, Figure S2). Note that the leaching of Ru species from 2dppb-Ru/CeO_2 after heating in toluene (1.0 cm^3) for 8 h without any substrates was very low (0.35% of Ru species in the fresh catalyst), indicating that the substrates and/or products induce the leaching of Ru species, while the ^{31}P {^{1}H} NMR study showed that 91% of dppb used for the modification remained unchanged in the solution.

To investigate the contribution of the soluble ruthenium species generated from the 2dppb-Ru/CeO_2 catalyst, the effects of the removal of the solid catalysts by hot filtration through a PTFE filter (pore size 0.45 μm) were examined.[51−55] Figure 2 shows the time-course of the reactions with or without hot filtration. Removal of the solid catalyst after the reaction for 1 h did not stop further progress of the reaction. ICP-AES showed that the solution after hot filtration contained 1.3% of Ru species in the fresh catalyst. The results of the present hot filtration tests are very different from those observed in the C−C bond-forming reactions by PPh_3-modified Ru/CeO_2 catalyst, where removal of the solid catalysts stopped further progress of the reactions.[46] These results suggest that the contribution of dissolved ruthenium species depends on the type of the reaction, and that in the present catalytic reaction, surface low-valent Ru species derived from Ru/CeO_2 acted as an excellent source for extremely active, soluble ruthenium species.

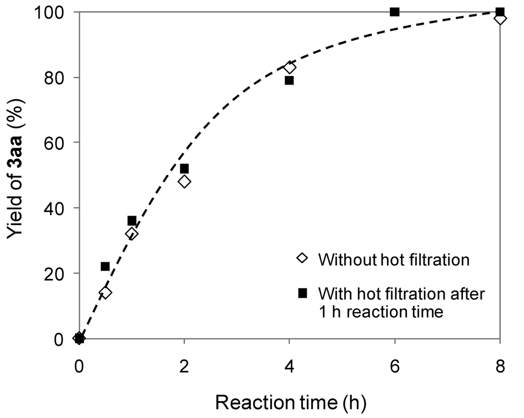
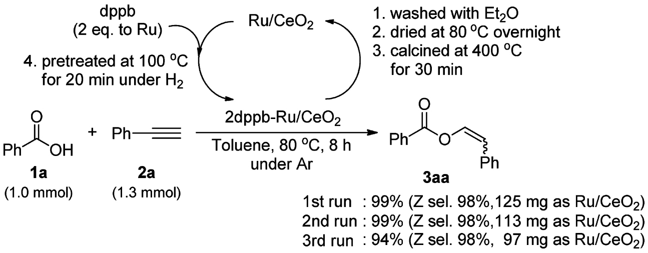


Figure 2. Time-course of the reaction of **1a** with **2a** at 80 °C with or without the removal of 2dppb-Ru/CeO_2 by hot filtration.

As a reflection of the low level of leaching of Ru species, solid Ru/CeO_2 could be repeatedly used as a reservoir of active catalysts after a suitable regeneration procedure. Scheme 2 shows an outline of the successful regeneration procedure and the results of catalytic reactions with the recycled Ru/CeO_2. After the reaction, the catalyst was washed with diethyl ether (10 cm^3, 3 times), dried in air at 80 °C, and then calcined in air at 400 °C to be recovered as Ru/CeO_2. The thus-obtained solid was remodified with dppb under a hydrogen atmosphere to give the regenerated 2dppb-Ru/CeO_2 for the next catalytic run. Although slightly decreased amounts of the recycled catalyst were used, *Z*-**3aa** was successfully obtained in excellent yields and selectivities in the second and third runs. On the other hand, the reaction using recovered Ru catalysts without calcination or further dppb-modification resulted in a low yield of **3aa**. The detailed effects of the recycling procedure are presented in Table S3 of the Supporting Information.

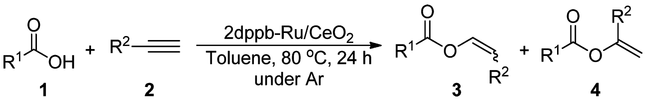
Scheme 2. Recycling of the dppb-Modified Ru/CeO_2 Catalyst

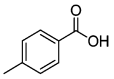
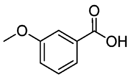
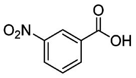
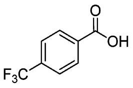
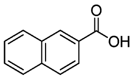
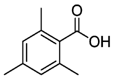
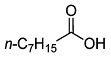
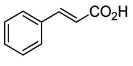
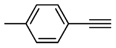
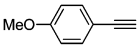
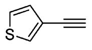


As discussed above, a small amount of leached ruthenium species, probably bearing dppb ligand(s), is considered to be responsible for the catalysis. The effectiveness of the catalysts greatly depends on the modification conditions. Ru/CeO_2 reduced in the absence of dppb did not show significant activity for the catalytic run even in the presence of dppb (entry 4 of Table 1). Therefore, dppb would play a critical role in generating partially reduced Ru species on the surface. Ru/CeO_2 was heated in H_2 together with phosphines in the absence of any solvents during phosphine-modification (see Experimental Section). Therefore, we believe that 2 equiv of phosphines are required to ensure contact with Ru species on ceria during the modification procedure. From these surface Ru species, truly active soluble Ru species would be produced during the catalytic runs, although their exact chemical nature is not yet clear.

The results of the reactions of various carboxylic acids with terminal alkynes by the dppb-modified Ru/CeO$_2$ catalyst are summarized in Table 2. The reaction with aromatic carboxylic acids bearing an electron-donating or -withdrawing substituent on the phenyl ring as well as 2-naphthoic acid proceeded smoothly to afford the corresponding vinyl esters in high yields with excellent (*Z*)-isomer selectivities. The reaction with an aliphatic carboxylic acid (**1h**) also gave the desired (*Z*)-adduct with high selectivity. An *α*,*β*-unsaturated acid (**1i**) could also be used in the present catalytic system. The reactions of **1a** with aromatic and heteroaromatic terminal alkynes also produced the (*Z*)-isomer of the adducts with excellent selectivities, while the reaction with an alkyl-substituted terminal alkyne (**2e**) proceeded very slowly. Formation of the Markovnikov adducts (**4**) was not observed at all except for the case shown in entry 12, and there were no signs of byproduct other than traces of the dimers of the alkynes in the reactions shown in Table 2.

Table 2. *Z*-Selective Addition of Carboxylic Acids to Terminal Alkynes by 2dppb-Ru/CeO$_2$ Catalyst[a]



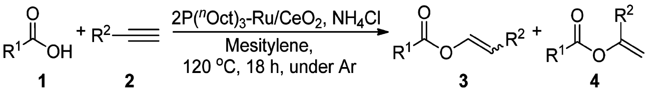
entry	1	2	product	total yield (%)[b]	selectivity (%)[c] *Z*-3: *E*-3 : 4
1	 **1b**	**2a**	**3ba**	88	98 : 2 : 0
2	 **1c**	**2a**	**3ca**	95	100 : 0 : 0
3	 **1d**	**2a**	**3da**	76	98 : 2 : 0
4	 **1e**	**2a**	**3ea**	61	98 : 2 : 0
5	 **1f**	**2a**	**3fa**	90	93 : 7 : 0
6	 **1g**	**2a**	**3ga**	42	85 : 15 : 0
7	 **1h**	**2a**	**3ha**	48	94 : 6 : 0
8	 **1i**	**2a**	**3ia**	92	94 : 6 : 0
9	**1a**	 **2b**	**3ab**	65	100 : 0 : 0
10	**1a**	 **2c**	**3ac**	66	98 : 2 : 0
11	**1a**	 **2d**	**3ad**	94	100 : 0 : 0
12	**1a**	n-C$_6$H$_{13}$—≡ **2e**	**3ae** + **4ae**	10[d]	(88 : 6 : 6)[d]

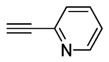
[a]Reaction *conditions*: **1** 1.0 mmol, **2** 1.3 mmol, toluene 1.0 cm^3, Ru/CeO$_2$ catalyst 0.025 mmol as Ru (prepared from Ru(acac)$_3$), dppb 0.050 mmol, at 80 °C for 24 h under Ar. [b]Isolated yield of **3** and **4** based on **1**. [c]Molar ratio of isomers determined by ^{1}H NMR. [d]Determined by GLC

On the other hand, the reaction of 4-hydroxybenzoic acid with **1a** did not proceed under the present conditions (data not shown in Table 2). Similarly, the reaction of **1a** with aliphatic terminal alkynes bearing hydroxy groups such as 2-methyl-3-butyn-2-ol and but-3-yn-1-ol did not proceed at all. Only trace amounts of adducts were observed after the reaction of **1a** with methyl propiolate. In contrast to previous studies using dppb-Ru complex catalysts in which trimethylsilylacetylene was a good substrate,[12,13] trimethylsilylacetylene could not be used in the present catalytic system: only trace amounts of adducts were obtained after the reaction under the present conditions.

We then focused on the selective production of Markovnikov-adducts **4** with the use of Ru/CeO$_2$ catalysts. By screening suitable phosphines and reaction conditions, we found that trioctylphosphine-modified Ru/CeO$_2$ together with a small amount of ammonium chloride as an external additive induced Markovnikov-selective addition (Table 3). The use of Ru complexes with chloro ligands or RuCl$_3$·nH$_2$O was advantageous in terms of selectivity for Markovnikov adducts (see Table S7 in the Supporting Information). Cl atoms remained on the surface of calcined Ru/CeO$_2$ prepared using Cl-containing Ru precursors, as reported in our previous study.[48] The detailed effects of the additives and reaction conditions for Markovnikov additions by 2P(^{n}Oct)$_3$-Ru/CeO$_2$ catalysts are presented in Tables S5, S6, and S8 of the Supporting Information. Although there is still room for further optimization of the reaction conditions, Markovnikov adducts

Table 3. Addition of Various Carboxylic Acids with Terminal Alkynes by P(^{n}Oct)$_3$-Ru/CeO$_2$[a]



entry	1	2	products	total yield (%)[b]	selectivity (%)[c] *Z*-3: *E*-3 : 4
1[d]	**1a**	**2a**	**3aa** + **4aa**	99	15: 8 : 77
2[e]	**1a**	**2a**	**3aa** + **4aa**	99	26 : 27 : 47
3	**1c**	**2a**	**3ca** + **4ca**	80	18 : 33 : 49
4	**1d**	**2a**	**3da** + **4da**	68	5 : 4 : 91
5	**1i**	**2a**	**3ia** + **4ia**	88	36 : 3 : 61
6	**1a**	**2b**	**3ab** + **4ab**	81	9 : 6 : 85
7	**1a**	**2c**	**3ac** + **4ac**	69	11 : 4 : 85
8	**1a**	**2e**	**4ae**	74	0 : 0 : 100
9	**1a**	 **2f**	**3af** + **4af**	37	0 : 9 : 91

[a]Reaction *conditions*: **1** 1.0 mmol, **2** 1.3 mmol, mesitylene 1.0 cm^3, Ru/CeO$_2$ catalyst 0.025 mmol as Ru (prepared from Ru(acac)$_3$), P(^{n}Oct)$_3$ 0.050 mmol, NH$_4$Cl 0.10 mmol, at 120 °C for 18 h under Ar. [b]Isolated yield. [c]Molar ratio of isomers determined by ^{1}H NMR. [d]Reaction for 6 h. [e]Reaction without NH$_4$Cl.

4 were obtained in good to high selectivities under the present conditions. For example, the reaction of **1d** with **2a** in the presence of 2P(^{n}Oct)$_3$-Ru/CeO$_2$ catalyst together with NH_4Cl in mesitylene at 120 °C produced **4da** with 91% selectivity (entry 4). Remarkably, the addition of **1a** to 1-octyne (**2e**) proceeded smoothly to afford **4ae** with a complete regio-selectivity (entry 8). A hot filtration test on 2P(^{n}Oct)$_3$-Ru/CeO$_2$ also indicated that dissolved catalytically active Ru species made a major contribution.

CONCLUSIONS

The simple modification of Ru/CeO$_2$, that is, reduction under a hydrogen atmosphere in the presence of suitable phosphines, generates Ru catalysts that are effective for the regio- and stereoselective addition of carboxylic acids to alkynes. The regio-selectivity of the addition was controlled by the added phosphines, as in homogeneous catalysis. The reactions in the presence of a catalytic amount of 2dppb-Ru/CeO$_2$ gave (*Z*)-isomers of anti-Markovnikov adducts with excellent selectivities. On the other hand, P(^{n}Oct)$_3$-modified Ru/CeO$_2$ catalysts gave the Markovnikov adducts as major products. These catalytic systems could be used for a variety of carboxylic acids and terminal alkynes. While hot filtration tests suggest that ruthenium species in the solution phase acted as catalysts, very small amounts of Ru species were detected in solutions by ICP-AES analyses, and Ru/CeO$_2$ could be repeatedly used without a significant loss of effectiveness. The present study demonstrates a new and facile method for the generation of soluble ruthenium species with excellent catalytic activity and tunable regio- and stereoselectivity from solid oxides. Studies on the further application of phosphine-modified Ru/CeO$_2$ as well as Ru/ZrO$_2$ in other organic synthetic reactions and a detailed investigation of the structure and generation of soluble catalytically active species are now in progress.

EXPERIMENTAL SECTION

General Information. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Dehydrated methanol, tetrahydrofuran (THF), and toluene were used as received. Other organic and inorganic reagents were obtained commercially and used without further purification. Cerium oxide was prepared by treatment of a solution of cerium(III) nitrate hexahydrate (12.6 g, 29 mmol) in 400 cm^3 of deionized water with 40 cm^3 of 3 M KOH aqueous solution with stirring for 2 h at room temperature. The resulting precipitate was collected by centrifugation and then air-dried overnight at 80 °C. The product was heated in a box furnace at a rate of 10 °C min^{-1} and maintained at 400 °C for 30 min to afford ceria in an excellent ceramic yield. Zirconium oxide and magnesium oxide were prepared by the same method using zirconium oxynitrate and magnesium nitrate hexahydrate, respectively. Titanium oxide (JRC-TIO-4) and γ-alumina (JRC-ALO-8) were obtained from the Catalysis Society of Japan. Silica (CAB-O-SIL) was obtained from Cabot and used as received.

^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at room temperature at 400 MHz, 100.4 MHz, and 161.9 MHz, respectively. The amounts of recovered phosphines were estimated using OP(OPh)$_3$ as an internal standard. High-resolution mass spectra (FAB) were recorded with *m*-nitrobenzyl alcohol as a matrix. TEM photographs were obtained on JEOL JEM-1400 electron microscope. Ru K-edge X-ray absorption fine structure (XAFS) measurements were performed at the beamline BL01B1 at SPring-8 operated at 8 GeV using a Si(311) two-crystal monochromator at room temperature. X-ray absorption near edge structure (XANES) spectra were analyzed using Rigaku REX 2000 (version 2.5).

The leaching of ruthenium species from the catalysts during the reaction was investigated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The products of catalytic runs were analyzed by GC–MS (Zebron ZB-1 capillary column, i.d. 0.25 mm, length 30 m, at 50–250 °C) and gas–liquid chromatography (Inertcap 17 capillary column, i.d. 0.25 mm, length 30 m at 50–250 °C).

Preparation of Supported Ruthenium Catalysts. Supported catalysts were prepared by the impregnation method using various supports and ruthenium complexes. A typical procedure is as follows: 1.0 g of metal oxide was added to a solution of 79 mg (0.20 mmol, 20 mg as Ru) of Ru(acac)$_3$ in 10 cm^3 of THF under air at room temperature. For $Ru_3(CO)_{12}$ and [RuCl$_2$(CO)$_3$]$_2$, THF was used as a solvent, while $RuCl_3 \cdot nH_2O$ and [RuCl$_2$(*p*-cymene)]$_2$ were impregnated from their methanol solutions. After impregnation and drying overnight in air at 80 °C, the resulting powder was calcined in air at 400 °C for 30 min to afford the Ru(2.0 wt %)/support catalyst.

Modification of the Catalysts by Phosphines. The Ru/support catalysts were modified by dppb as follows: 125 mg (0.025 mmol as Ru) of Ru/support and $Ph_2P(CH_2)_4PPh_2$ (dppb, 22 mg, 0.050 mmol) were heated at 100 °C for 20 min under a hydrogen atmosphere (1 atm) without any solvent. The resulting catalysts were designated as *x*dppb-Ru/support (*x* = molar ratio of dppb to Ru). P(^{n}Oct)$_3$-modified Ru/support catalysts were prepared by the same method using 19 mg (0.050 mmol) of P(^{n}Oct)$_3$ instead of dppb. These phosphine-modified Ru/CeO$_2$ were used for the catalytic reaction without exposure to open air.

General Procedure for the Addition of Carboxylic Acids to Terminal Alkynes. All of the reactions were performed with the use of hot stirrers equipped with cooling blocks for refluxing the solution. A typical reaction procedure is as follows: A mixture of carboxylic acid (1.0 mmol) and terminal alkyne (1.3 mmol) in toluene (1.0 cm^3) was placed in a 20-cm^3 glass Schlenk tube with a balloon under an Ar atmosphere together with the phosphine-modified Ru(2.0 wt %)/CeO$_2$ catalyst (0.025 mmol as Ru, 125 mg as Ru/CeO$_2$). The reaction mixture was stirred at 80 °C for 24 h, and then cooled rapidly in an ice bath. After the reaction, the solid catalyst was removed by passing the mixture through a 0.45 μm PTFE filter, and the filtrate was concentrated under reduced pressure. The products were isolated by column chromatography (silica gel, 4:1; hexane/EtOAc, v/v), identified by GC–MS, ^{1}H and ^{13}C NMR, HRMS, and quantified by GLC analyses using biphenyl as an internal standard.

Recovery of the 2dppb-Ru/CeO$_2$ Catalyst. After the reaction, the solid was separated from the reaction mixture by centrifugation and washed three times with 10 cm^3 of diethyl ether. The resulting solid was dried overnight at 80 °C and calcined in air at 400 °C for 30 min to recover Ru/CeO$_2$. Ru was then modified by 2 equiv of dppb through the aforementioned procedure to give the 2dppb-Ru/CeO$_2$ catalyst for reuse.

Hot Filtration Test. A 20-cm^3 Schlenk tube was charged with benzoic acid (**1a**, 2.0 mmol), ethynylbenzene (**2a**, 2.6 mmol), toluene (2.0 cm^3), and the 2dppb-Ru(2.0 wt %)/CeO$_2$

catalyst (0.050 mmol as Ru) together with an internal standard (biphenyl, ca. 46 mg) under an argon atmosphere. After the reaction was allowed to proceed for 1 h at 80 °C, the mixture was filtered through a 0.45-μm syringe filter into another preheated Schlenk tube. The filtrate was stirred at 80 °C, and the conversion and yields of the product after filtration were monitored by GC and GC−MS analyses.

Characterization Data of the Products. The formation of *Z*-**3ea**[21] has been reported before, and the data for *Z*-**3ha** well agree with that previously reported.[56] Small amounts of *Z*-**3ca**, *Z*-**3ad**, *Z*-**3da**, *Z*-**3fa**, and **4da** have been produced as minor isomers of the reactions catalyzed by unmodified Ru/CeO$_2$.[48]

*(Z)-Styryl 3-methoxybenzoate (Z-**3ca**).* Orange oil. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, 7.74 (m, 1H), 7.65 (m, 3H), 7.53 (d, J = 7.1 Hz, 1H), 7.37 (m, 3H), 7.25 (m, 1H), 7.13 (m, 1H), 5.83 (d, J = 7.1 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, 163.1, 159.6, 134.1, 134.0, 130.1, 129.6, 129.1, 128.4, 127.3, 122.4, 120.4, 114.2, 112.5, 55.2. FT-IR (neat, cm^{-1}) 1694, 1728. HRMS: Calculated for $C_{16}H_{15}O_3$ (M+H): 255.1021; found: 255.1027.

*Styryl 3-Nitrobenzoate (a Mixture of Z-**3da** and E-**3da** (98:2)).* Yellowish white solid. FT-IR (neat, cm^{-1}) 1654, 1738. HRMS: Calculated for $C_{15}H_{11}NO_4$ (M): 269.0688; found: 269.0680. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, *Z*-**3da**: 9.02 (m, 1H), 8.48 (m, 2H), 7.74 (t, J = 8.3 Hz, 1H), 7.65 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.0 Hz, 1H), 7.44 (t, J = 8.3 Hz, 2H), 7.32 (m, 1H), 5.95 (d, J = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, *Z*-**3da**: 161.4, 147.0, 135.6, 133.7, 133.5, 130.8, 130.1, 129.2, 128.6, 128.1, 127.8, 125.1, 113.8.

*Styryl 4-(Trifluoromethyl)benzoate (a Mixture of Z-**3ea** and E-**3ea** (98:2)).* Light yellow solid. FT-IR (neat, cm^{-1}) 1660, 1746. HRMS: Calculated for $C_{16}H_{11}F_3O_2$ (M): 292.0711; found: 292.0717.

^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, *Z*-**3ea**: 8.25 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 7.0 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.29 (m, 1H), 5.89 (d, J = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, *Z*-**3ea**: 162.3, 135.1 (q, J = 33.1 Hz), 133.9, 133.8, 132.2 (m), 131.5, 130.5, 129.2, 128.5, 127.6, 125.8 (m), 113.4.

*Styryl 2-Naphthoate (a Mixture of Z-**3fa** and E-**3fa** (93:7)).* Light yellow solid. FT-IR (neat, cm^{-1}) 1740. HRMS: Calculated for $C_{19}H_{15}O_2$ (M+H): 275.1072; found: 275.1064.^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, *Z*-**3fa**: 8.75 (br s, 1H), 8.17 (dd, J = 1.5, 8.3 Hz, 1H), 8.01−7.91 (m, 3H), 7.73 (d, J = 7.3 Hz, 2H), 77.66−7.57 (m, 3H), 7.43 (t, J = 7.8 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 5.91 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, *Z*-**3fa**: 163.6, 135.9, 134.3, 134.2, 132.5, 132.2, 129.5, 129.3, 128.8, 128.6, 128.5, 127.9, 127.4, 127.0, 126.1, 125.2, 112.7.

*Styryl Octanoate (a Mixture of Z-**3ha** and E-**3ha** (96:4))).* Orange oil. FT-IR (neat, cm^{-1}) 1706. HRMS: Calculated for $C_{16}H_{23}O_2$ (M+H): 247.1698; found: 247.1685. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, *Z*-**3ha**: 7.58 (d, J = 7.3 Hz, 2H), 7.36−7.22 (m, 4H), 5.69 (d, J = 7.3 Hz, 1H), 2.52 (t, J = 7.3 Hz, 2H), 1.73 (m, 2H), 1.40−1.28 (m, 8H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, *Z*-**3ha**: 170.3, 134.1, 133.9, 129.1, 128.4, 127.2, 111.7, 34.2, 21.6, 29.0, 28.9, 24.7, 22.6, 14.0.

*(Z)-2-(Thiophen-3-yl)vinyl Benzoate (Z-**3ad**).* Dark brown oil. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, 8.26 (d, J = 7.3 Hz, 2H), 7.63 (m, 1H), 7.53−7.46 (m, 5H), 7.33 (dd, J = 2.9, 4.9 Hz, 1H), 5.94 (d, J = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, 163.4, 134.8, 133.7, 133.2, 130.0, 129.0, 128.7, 128.4, 125.4, 124.2, 107.2. FT-IR (neat, cm^{-1}) 1660, 1692, 1732. HRMS: Calculated for $C_{13}H_{10}O_2S$ (M): 230.0402; found: 230.0405.

*1-Phenylvinyl 3-Nitrobenzoate (a Mixture of **4da**, E-**3da**, and Z-**3da** (91:4:5)).* Orange oil. For **4da**, ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ, 9.03 (m, 1H), 8.51 (m, 2H), 7.73 (t, J = 7.8 Hz, 1H), 7.52 (m, 2H), 7.38 (m, 3H), 5.63 (d, J = 2.5 Hz, 1H), 5.21 (d, J = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ, 162.7, 153.0, 148.4, 135.7, 133.7, 131.2, 129.9, 129.3, 128.7, 128.0, 125.0, 124.9, 102.8. FT-IR (neat, cm^{-1}) 1643, 1702, 1742.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of the supported ruthenium catalysts, effects of phosphines for modification, effects of the procedure for recycling of 2dppb-Ru/CeO$_2$ catalyst, optimization of the P(^{n}Oct)$_3$-modified Ru/CeO$_2$ catalyst, results of the ^{31}P NMR study, and ^{1}H and ^{13}C NMR spectra of the products. 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 interest.

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