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Imidazolium-Salt-Functionalized Ionic-CNT-Supported Ru−Carbene/Palladium Nanoparticles for Recyclable Tandem Metathesis/Hydrogenation Reactions in Ionic Liquids

Sujin Lee, Ju Yeon Shin, and Sang-gi Lee*[a]

Interest in the development and application of tandem catalytic reactions continues to grow for obvious reasons.[1] Tandem catalytic processes allow several transformations to be performed in a one-pot operation, thereby negating the need for handling and isolating intermediates. Furthermore, the substantial decrease in waste generation that accompanies tandem process has significant benefits on the environment. One class of reaction that has come to prominence in tandem reactions is the olefin-metathesis reaction. Grubbs and co-workers elegantly developed tandem metathesis/hydrogenation processes by using Grubbs's 1st- (**A**) or 2nd-generation Ru complexes (**B**).[2] It has been proposed that, under the hydrogenation conditions, Ru complexes **A** or **B** are transformed into their corresponding Ru−hydride complexes, which are effective hydrogenation catalysts. Numerous other tandem processes have also been developed by combining Ru-catalyzed metathesis reactions with hydrogenation reactions,[3] aza-Michael reactions,[4] Claisen rearrangements,[5] Diels–Alder reactions,[6] Kharasch additions,[7] dihydroxylations,[8] Wittig olefinations,[9] etc.[10] However, most of these reported metathesis-based tandem transformations employ homogeneous catalysis. The use of supported catalysts that enable their recovery and reuse could make tandem catalysis more sustainable.[11]

In recent years, the hybridization of imidazolium-based ionic liquids (ILs) with carbon nanotubes (CNTs) and/or metal nanoparticles (MNPs) has found increasing use in many areas of technology and science.[12,13] In this context, we previously reported that palladium nanoparticles (Pd NPs) that were supported on imidazolium-salt-functionalized ionic multi-walled carbon nanotubes (IM-*f*-MWCNTs) showed high reactivity and recyclability in an ionic liquid.[14] More recently, we found that Ru−carbene complexes that were supported on IM-*f*-MWCNTs also showed excellent catalytic activity and recyclability in ring-closing metathesis (RCM) reactions.[15,16] Based on these observations, we envisioned that the immobilization of both Ru−carbene complexes and Pd NPs onto the same IM-*f*-MWCNTs could allow us to devise a new supported, dual-function catalyst for tandem metathesis/hydrogenation reactions in an ionic liquid. Herein, we report the immobilization of a Hoveyda-type Ru−carbene catalyst and Pd NPs onto imidazolium-salt-functionalized ionic multi-walled carbon nanotubes (Ru−carbene/PdNP@IM-*f*-MWCNT) as a recyclable catalyst for tandem metathesis/hydrogenation reactions in an ionic liquid.

First, we investigated the stability of Ru complexes **A**–**D** and imidazolium-salt-tagged complex **E** under hydrogenation conditions (Figure 1). As reported by Grubbs and co-

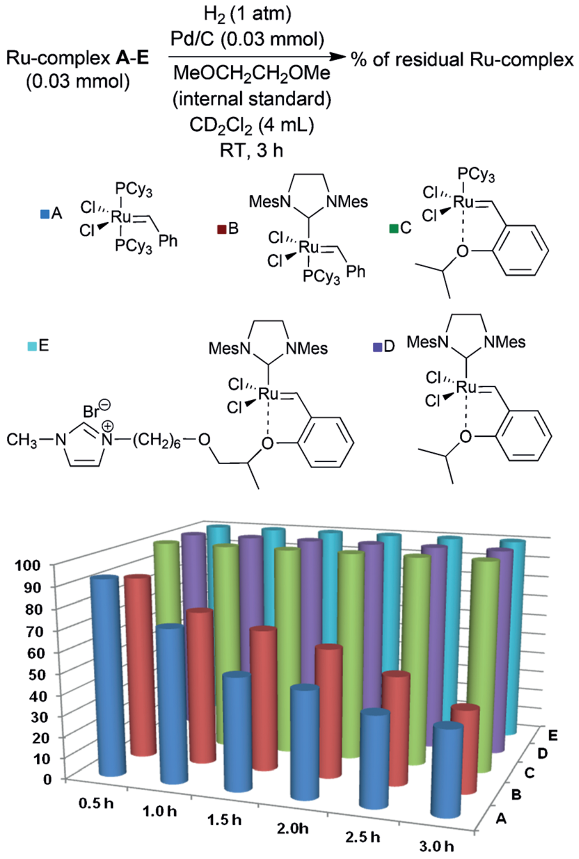

Figure 1. Plot that shows the stability of Ru−carbene complexes **A**–**E** under hydrogenation conditions (1 atm H_2, RT, 3 h, in the presence of 1.0 equiv Pd/C); the percentage residual Ru−complex was determined by ^{1}H NMR analysis with 1,2-dimethoxyethane as an internal standard.

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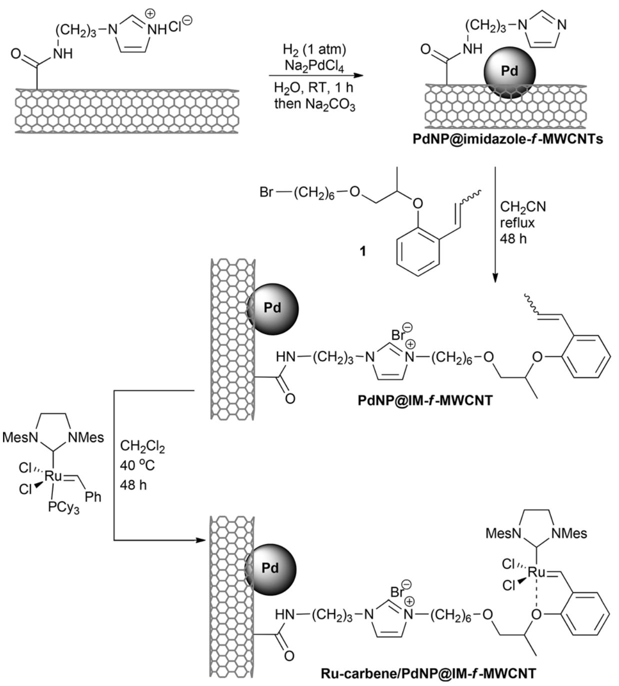
workers, Ru complexes **A** and **B** were labile under the hydrogenation conditions[2] and, thus, only 30 % of the Ru complex remained after 3 h under 1 atm H_2 in the presence of one equivalent of Pd/C at room temperature. In contrast, the chelated Ru complexes (**C**–**E**) were stable under the hydrogenation conditions. These results suggested that the Hoveyda-type Ru–carbene complexes were promising candidates for our study.

The preparation of the supported Ru–carbene/PdNP@IM-*f*-MWCNT catalyst is shown in Scheme 1. First, the immobilization of Pd NPs onto imidazole-functionalized MWCNTs (PdNP@imidazole-*f*-MWCNT) was achieved by the hydrogenation (1 atm) of Na_2PdCl_4 with imidazolium-chloride-functionalized MWCNTs in water at room temperature. Then, the reaction of PdNP@imidazole-*f*-MWCNT with bromide **1**, followed by metathesis with Grubbs′ 2nd-generation Ru–carbene complex **B**, afforded the supported Ru–carbene/PdNP@IM-*f*-MWCNT (for details, see the Supporting Information). Notably, this result represents the first example of an immobilized dual-functional Ru/Pd catalyst on CNTs for tandem metathesis/hydrogenation catalysis.



Scheme 1. Synthesis of the supported dual-functional Ru–carbene/PdNP@IM-*f*-MWCNT.

High-resolution transmission electron microscopy (HR-TEM, Figure 2 a) and X-ray diffraction (XRD, Figure 2 b) analyses of the Ru–carbene/PdNP@IM-*f*-MWCNT catalyst clearly indicated that highly crystalline Pd NPs were densely decorated over the MWCNTs. X-ray photoelectron spectroscopy (XPS) analysis showed that the oxidation states of both Ru^{IV} (Ru $3p_{(3/2)}$ at 462.4 eV, Ru $3p_{(1/2)}$ at 485.8 eV) and Pd^0 remained unchanged during the anchoring process of the Ru–carbene complex (Figure 2 c,d).[17] ICP-MS analysis indicated that 0.13 mmol g^{-1} Ru and 0.42 mmol g^{-1} Pd were incorporated onto the Ru–carbene/PdNP@IM-*f*-MWCNT catalyst. Moreover, this supported catalyst was highly disper-

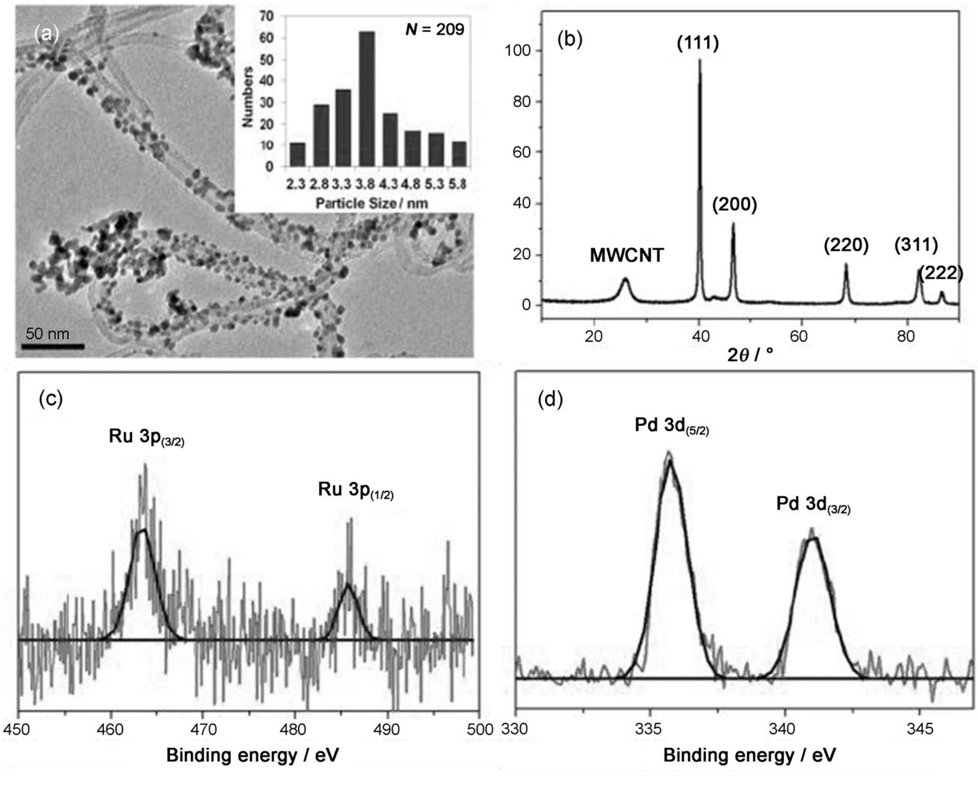


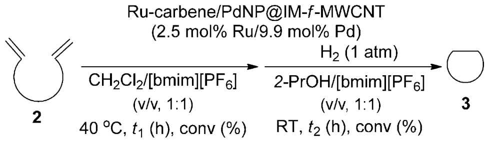
Figure 2. a) HR-TEM image, b) XRD pattern, and XPS data of the c) Ru and d) Pd regions of Ru–carbene/PdNP@IM-*f*-MWCNT.

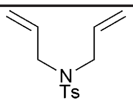
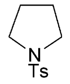
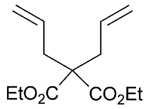
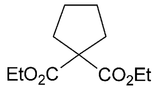
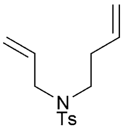
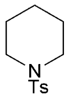
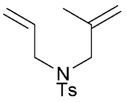
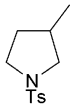
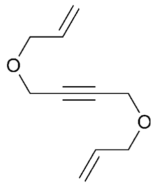
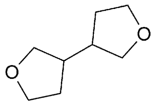
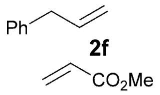
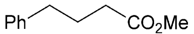
sible in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]).

Next, we investigated the catalytic activity of the supported catalyst for tandem metathesis/hydrogenation reactions (Table 1). As shown in Table 1, the supported Ru–carbene/PdNP@IM-*f*-MWCNT catalyst could efficiently catalyze the RCM of dienes **2a**–**2d** in CH_2Cl_2/[bmim][PF_6] (1:1 v/v). For the tandem hydrogenation reaction, the CH_2Cl_2 solvent was evaporated and then 2-propanol was added to the remained ionic-liquid phase that contained the catalyst and the metathesis product. Then, the solution was subjected to 1 atm H_2 pressure at room temperature to afford compounds **3a**–**3d** in up to 97% overall yield (over two steps; Table 1, entries 1–3). This tandem procedure can be successfully applied to the RCM/hydrogenation of dienyne **2e** and the cross-metathesis/hydrogenation of compound **2f** with methyl acrylate, thereby affording compounds **3e** and **3f**, respectively (Table 1, entries 5 and 6).

Finally, the recyclability of the Ru–carbene/PdNP@IM-*f*-MWCNT catalyst was investigated in the tandem RCM/hydrogenation reactions of N-tosylated bisallylamine (**2a**). After the tandem RCM/hydrogenation process, the ionic liquid phase, which contained the catalyst, was easily separated with 2-propanol, which was immiscible with [bmim][PF_6], by extraction of the ionic-liquid phase with 2-propanol three times. As shown in Table 2, the Ru–carbene/PdNP@IM-*f*-MWCNT catalyst was retained in the ionic-liquid layer, which could be reused up to four times. However, the catalytic activity of the Ru catalyst started to decline during the 4th run. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the 2-propanol layer indicated that no leaching of Pd was observed, but about 100 ppm Ru leached out during each run, which was ascribed to an ineffective return of the active Ru species to its initial resting state and/or to a rapid decomposition of the Ru species.

Table 1. Tandem metathesis/hydrogenation reactions catalyzed by the supported Ru–carbene/PdNP@IM-*f*-MWCNT.[a]



Entry	2	t_1 [h] (conversion [%])[b]	t_2 [h] (conversion [%])[b]	3	Yield [%][c]
1	 **2a**	1.5 (96)	0.5 (>99)	 **3a**	95
2	 **2b**	1.0 (97)	0.5 (>99)	 **3b**	96
3	 **2c**	1.0 (98)	0.5 (>99)	 **3c**	97
4	 **2d**	1.5 (99)	24 (85)	 **3d**	83
5	 **2e**	2.5 (80)	12 (95)	 **3e**	71
6	 **2f**	3.0 (>99)	1.0 (>99)	 **3f**	95

[a] The metathesis step was performed with the diene (0.05 mmol) in CH_2Cl_2/[bmim][PF_6] (1 mL/1 mL) at 40°C and the hydrogenation step was performed in 2-PrOH/[bmim][PF_6] (1 mL/1 mL) at RT. [b] Determined by GC or ^1H NMR analysis. [c] Yield of isolated product.

In summary, we have immobilized both a Ru–carbene complex and Pd nanoparticles onto the same imidazolium-functionalized ionic CNTs for recyclable tandem metathesis/hydrogenation reactions. The supported dual-function catalyst, Ru–carbene/PdNP@IM-*f*-MWCNT, showed excellent catalytic activity in tandem metathesis/hydrogenation reactions in an ionic liquid. This catalyst could be easily recovered and reused up to four times. The decreased catalytic activity in the fourth run was ascribed to leaching of Ru the species. To address this problem, variation in the anchoring positions of the Ru catalyst is currently under investigation.

Experimental Section

To a flask that contained Ru–carbene/PdNP@IM-*f*-MWCNT (30 mg, 2.5×10^{-3} mmol, Ru content: 2.5 mol%) was added a solution of substrate **2** (0.05 mmol) in CH_2Cl_2/[bmim][PF_6] (v:v=1:1, 2 mL) through a syringe and the mixture was stirred at 40°C for 1 h. After completion of metathesis step (by GC), the CH_2Cl_2 was evaporated, 2-propanol (1 mL) was added, and the

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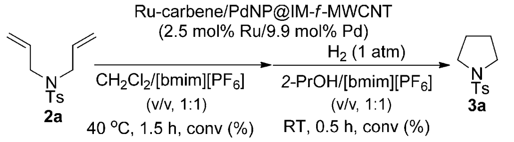
Table 2. Catalyst-recycling experiments.[a]



2a **3a**

Run	RCM [%][b]	Hydrogenation [%][b]	Yield [%][c]
1	96	>99	96
2	94	99	93
3	94	98	93
4	76	98	71

[a] The metathesis step were performed with compound **2a** (0.05 mmol) in CH_2Cl_2/[bmim][PF_6] (1 mL/1 mL) at 40°C for 1.5 h. After the evaporation of CH_2Cl_2, 2-PrOH (1 mL) was added and the hydrogenation step was performed for 30 min at RT. For the catalyst recovery and reuse, the 2-PrOH layer was separated and the ionic-liquid layer, which contained the catalyst, was extracted with 2-propanol (1 mL × 3) and reused in the next run by the addition of compound **2a** and CH_2Cl_2 (1 mL). [b] Determined by GC. [c] Yield of isolated product.

reaction mixture was stirred vigorously under 1 atm H_2 (balloon) at RT. After completion of the hydrogenation step (by GC), the top (2-propanol) layer was separated and ionic-liquid layer was extracted three times with Et_2O (3 × 3 mL). The combined extract was concentrated under vacuum and the residue was purified by column chromatography on silica gel to give the corresponding product (**3**). For the recycling experiments, CH_2Cl_2 (1 mL) and substrate **2a** were added into the remained ionic-liquid layer, which contained the catalyst, and the metathesis and hydrogenation reactions were repeated.

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Keywords: heterogeneous catalysis · hydrogenation · nanotubes · ring-closing metathesis · tandem reactions

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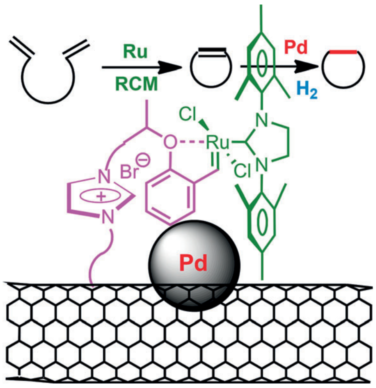
NP and tuck: Two different catalysts, a Ru−carbene complex and palladium nanoparticles, were immobilized onto the same imidazolium-salt-functionalized ionic CNTs. These supported dual-function catalysts showed excellent catalytic activity in tandem metathesis/hydrogenation reactions in an ionic liquid and could be recovered and reused four times. RCM = ring-closing metathesis.



Heterogeneous Catalysis

Sujin Lee, Ju Yeon Shin,
*Sang-gi Lee** ______ ■■■■–■■■■

Imidazolium-Salt-Functionalized Ionic-CNT-Supported Ru−Carbene/Palladium Nanoparticles for Recyclable Tandem Metathesis/Hydrogenation Reactions in Ionic Liquids