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Article

Controlled Reversible Immobilization of Ru Carbene on Single-Walled Carbon Nanotubes: A New Strategy for Green Catalytic Systems Based on a Solvent Effect on $\pi-\pi$ Interaction

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A pyrene-tagged ruthenium carbene **8** was synthesized and immobilized on single-walled carbon nanotubes (SWNTs) via $\pi-\pi$ stacking. These $\pi-\pi$ interactions were greatly affected by the reaction temperature and the solvent polarity, thus, offering a new reversible immobilization model that can be controlled by reaction temperature in polar solvents, such as acetone. SWNTs-supported ruthenium carbene **8** is a robust and recyclable catalyst system. Six to seven cycles were achieved for ring-closing metathesis of selected substrates. Importantly, after the complete loss of activity, the SWNTs can be easily recycled by washing with tetrahydrofuran. The recycled SWNTs can then be reloaded with **8**. The reusability of the catalyst supported on recycled SWNTs is comparable with that supported on fresh SWNTs.

Introduction

Development of cost-effective and environmentally benign catalytic systems is of primary importance in meeting the stringent and compelling demands for greener processes.[1] In this regard, immobilization of homogeneous catalysts on support materials is very attractive to facilitate the recycling and reuse of these types of catalysts. Recycling and reusing supporting materials would be a further step for green chemistry, but it is also one of the most challenging issues in the field of supported catalysts. Many different strategies including polymer-incarcerated catalysts,[2] microencapsulated catalysts,[3] polyurea-encapsulated catalysts,[4] dendrimer-supported catalysts,[5] and ship-in-a-bottle syntheses[6] were developed for this purpose. Recently, several methods for immobilizing catalysts using a noncovalent method via electrostatic interactions also have been reported.[7] Compared to traditional covalent bonding immobilization methods,[8] this method is simpler, and is more convenient for recycling and reuse of the support materials. Also, these catalysts are better for industrial continuous-flow processes. Up to now, noncovalent methods have been successfully used for the immobilization of transition metal catalysts and the development of efficient catalytic systems.[9] However, this method has its limitations since many of these catalysts are highly

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* Author to whom correspondence should be addressed. Phone: (+) 86-022-27892497. Fax: (+) 86-022-27403475. E-mail: wjh@tju.edu.cn.

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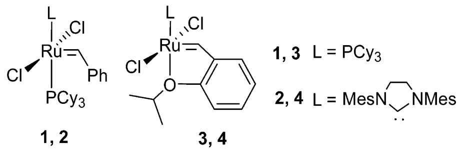
sensitive to ionic conditions. Therefore, there is a great need to design a more general reversible model for anchoring these sensitive complexes onto solid supporting materials.

Single-walled carbon nanotubes (SWNTs) are molecular wires that exhibit interesting structural, mechanical, electrical, and electromechanical properties.[10] Their rigid structures, as well as several of their properties like their nonswelling nature, insolubility in organic solvents, and large surface area, are attractive with regard to their application as a stationary phase in a continuous process. The sidewalls of SWNTs can be functionalized through covalent bonding or noncovalent bonding methods.[11,12] SWNTs have been widely used as an ideal solid support material for anchoring catalysts using covalent bonding methods.[13] However, there are only a few reports on the immobilization of catalysts on SWNTs via noncovalent $\pi-\pi$ stacking. In 2003, norbornene polymerization was selectively initiated on the surface of SWNTs via a specifically adsorbed pyrene-linked ring-opening metathesis polymerization (ROMP) initiator by Waymouth et al., resulting in a homogeneous noncovalent poly(norbornene) coating.[14] This was the first description of the support of a metathesis catalyst on carbon nanotubes (CNTs). But, noncovalent $\pi-\pi$ stacking has not been applied to the development of recyclable olefin metathesis catalysts. After a careful study of the effects of solvent polarity and temperature on the $\pi-\pi$ stacking interaction between pyrenyl groups and SWNTs, we have found a new strategy that uses solvents to control immobilization and to recycle the catalyst and the SWNTs. Herein, we report the application of noncovalent $\pi-\pi$ interactions to developing a recyclable olefin metathesis catalyst.

Since the discovery of well-defined modern ruthenium catalysts **1**−**4**,[15] olefin metathesis has gained a position of significance.[16] Various strategies have been employed to recycle and reuse these catalysts.[17] A Grubbs−Hoveyda boomerang catalyst was selected as the catalyst precursor and used to synthesize a pyrene-tagged olefin metathesis catalyst.



1, 2 **3, 4**

Results and Discussion

Preparation of Pyrene-Tagged Ruthenium Complex 8. Reaction of prepared (*E*)-(4-isopropoxy-3-(prop-1-enyl)phenyl)methanol **5** with the commercially available 4-(pyren-1-yl)butanoic acid **6** gave the pyrene-tagged ligand **7** in good yield (Scheme 1). Treatment of **7** with **2** in the presence of CuCl in CH_2Cl_2 at 40 °C, as described by Hoveyda and co-

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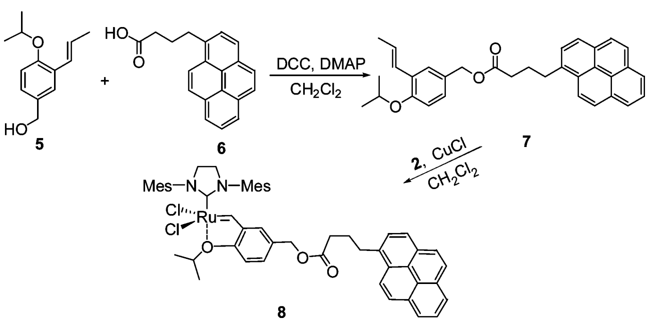
Scheme 1. Synthesis of Pyrene-Tagged Ruthenium Carbene **8**



workers[15c] resulted in the exchange of the styrene group to give the pyrene-tagged ruthenium complex **8** in good yield (68%) as a greenish crystalline solid.

Crystal Structure. Crystals suitable for X-ray detection were grown in toluene by slow evaporation at −15 °C. The structure of **8** is shown in Figure 1, and selected bond lengths and angles are given in Table 1 together with data for the analogous complex **4**.[17h] The structural data confirmed the predicted formation of **8**, which essentially resembled the overall geometry of complex **4**. However, a number of subtle, but significant differences involving the orientation of the O and Cl ligands are noteworthy. The C(1)−Ru−O(1) angle is 6.24° larger in **8** than in **4**, and the Cl(1)−Ru−Cl(2) angle is 3.77° more linear in **8** than in **4**. The Ru−O(1), and N(2)−C(1) bond distances in **8** are 2.236 and 1.338 Å, respectively, which are slightly shorter than the equivalent bond distances of 2.261 and 1.351 Å in **4**. However, the bond distances of Ru−Cl(2) 2.3492 Å and N(1)−C(1) 1.371 Å in **8** are slightly longer than the equivalent bond distances 2.328 and 1.350 Å found in **4**.

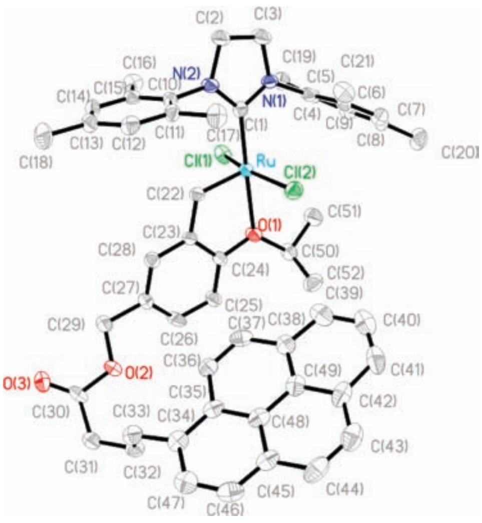


Figure 1. Crystal structure of **8**. For clarity, the solvent and all hydrogen atoms have been omitted. Displacement ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (°) for **4** and **8**

bond lengths	4	8	bond angles	4	8
Ru−C(1)	1.981	1.979	Cl(1)−Ru−Cl(2)	156.5	160.27
Ru−C(22)	1.828	1.834	C(1)−Ru−C(22)	101.5	102.7
Ru−O(1)	2.261	2.236	O(1)−Ru−C(1)	176.2	175.8
Ru−Cl(1)	2.340	2.3399	N(1)−C(1)−N(2)	106.9	106.3
Ru−Cl(2)	2.328	2.3492	N(2)−C(1)−Ru	131.6	135.3
N(1)−C(1)	1.350	1.371	N(1)−C(1)−Ru	120.8	118.1
N(2)−C(1)	1.351	1.338	C(1)−Ru−O(1)	79.28	85.52

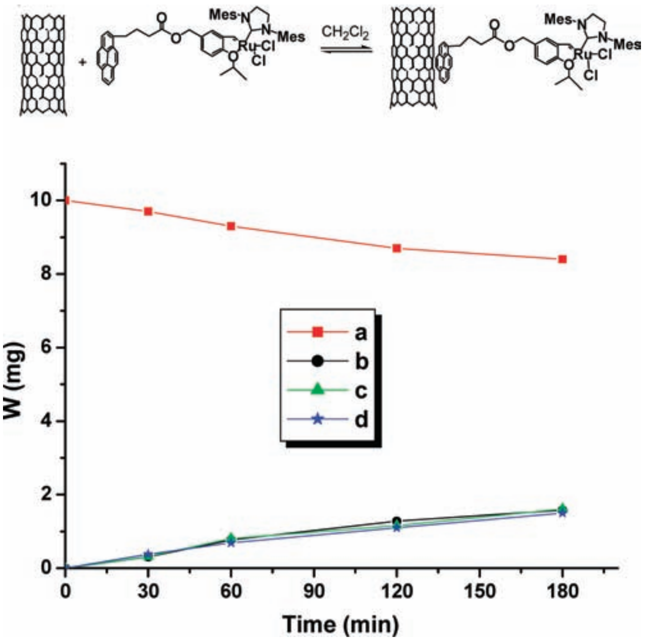


Figure 2. Content of **8** as a function of time (10 mg of **8** and 10 mg of SWNTs in 0.4 mL of CH_2Cl_2): (a) catalyst **8** in solution by UV; (b) catalyst **8** on the SWNTs by calculating; (c) catalyst **8** on the SWNTs by EDX; (d) catalyst **8** on the SWNTs by UV.

Immobilization of 8 on SWNTs. A typical experiment for the noncovalent immobilization of **8** onto the SWNTs was conducted in CH_2Cl_2. The concentration change of **8** in solution was monitored by UV spectroscopy. After 3 h, the concentration of **8** in solution did not change significantly. If the CNTs are left for a longer time, then there is no obvious change and the absorption tapers off because the SWNTs absorb the maximum that they can support. The concentration changes of **8** in the solution, as well as on the SWNTs, as a function of time are shown in Figure 2. The red line (a) was obtained in Figure 2 by Beer's law concentration calculations. The black line (b) was obtained by subtracting the solution concentration from the initial concentration. The green line (c) was obtained from the energy dispersive X-ray (EDX) spectra of the SWNTs. In order to prove the accuracy of the data, another experiment that immobilized catalyst **8** on the SWNTs at different time intervals was performed. The dry SWNTs-supported **8** were desorbed by dichloromethane at 45 °C, and the resulting solution was subjected to UV detection. The blue line (d) was obtained by calculating the desorbed **8** from the SWNTs. Since lines b, c, and d are almost identical, it could be concluded that the amount of Ru immobilized on the SWNTs can be easily calculated from the decrease of the Ru concentration in the solution. The results show that ~1.5 mg of **8** can be loaded for each 10 mg of SWNTs (Figure 2) under the defined conditions.

To further confirm the immobilization of **8** on the SWNTs, both the nonfunctionalized SWNTs and the functionalized SWNTs were characterized by transmission electron microscopy (TEM) and EDX (see Figure 3). The diameter of SWNTs is about 2 nm, and there is almost no difference between the TEM of the nonfunctionalized SWNTs (a) and

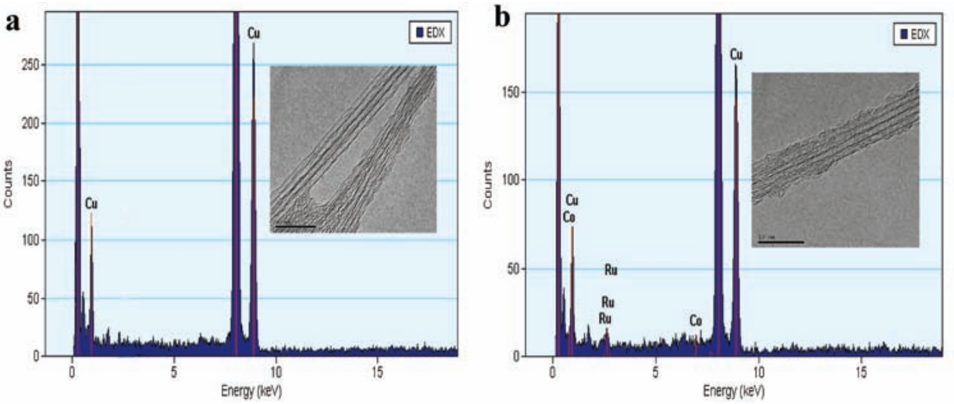


Figure 3. EDX analyses and TEM image of **8**. (a) SWNTs; (b) SWNTs after immobilization of **8**. The spectra were recorded ~10 nm from the surface.

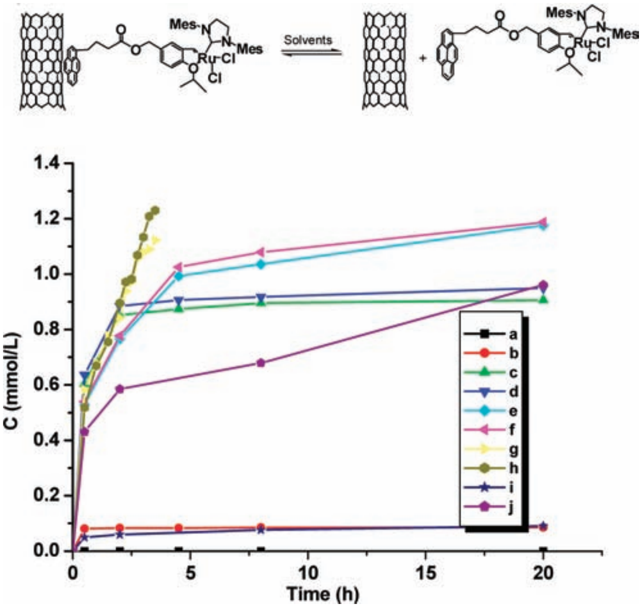


Figure 4. Desorption of **8** from SWNTs using different solvents (11.2 mg of SWNTs supporting catalysts containing 1.2 mg of **8** in 1.0 mL of solvent). With stirring at 25 °C: (a) acetone, (b) ethyl acetate, (c) toluene, (d) benzene, (e) CH_2Cl_2, (f) THF. With sonicating at 25 °C: (g) CH_2Cl_2, (h) THF. With stirring in acetone: (i) 35 °C and (j) 56 °C.

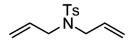
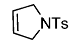
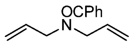
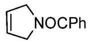
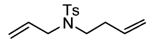
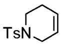
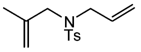
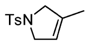
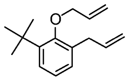
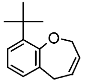
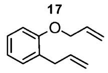
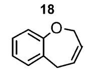
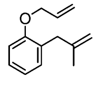
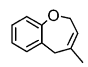
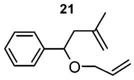
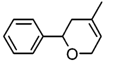
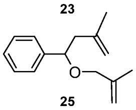
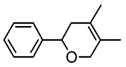
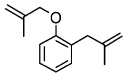
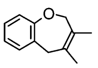
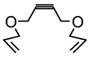
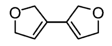
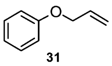
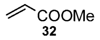
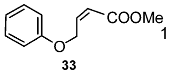
the functionalized SWNTs (b). However, there are differences in the EDX spectra. Ru is not observed in the EDX spectra of the nonfunctionalized SWNTs, whereas it is seen in the functionalized SWNTs. There is a very low signal for the Ru in the EDX measurements, so we repeated this experiment and measured the sample many times by EDX in order to minimize errors. These results prove that the Ru catalyst can be immobilized on the SWNTs. Co was picked up in the EDX spectrum because the SWNT contained it as an impurity (the SWNTs were prepared using Co complex as catalyst).

Desorption of 8 from SWNTs. Different solvents were used for desorption of the anchored ruthenium carbene complexes on SWNTs, and the results are shown in Figure 4. Significant amounts of **8** were desorbed from the SWNTs by nonpolar solvents, such as benzene and toluene, and by polar solvents, such as dichloromethane and THF. In contrast, only a small amount of **8** was desorbed from the SWNTs when a polar solvent, like ethyl acetate or acetone, was used. Desorption of the Ru complex from the SWNTs was also significantly affected by temperature (Figure 4 a,i,j). With acetone as the extracting phase, no detectable amount of **8** was extracted after 20 h at 25 °C. The same results were obtained at 0 °C. About 7% was desorbed at 35 °C, and about 80% was desorbed at 56 °C after 24 h. Desorption of **8** was accelerated when the mixture was sonicated (Figure 4 g,h). The concentration of **8** in solution reached its highest level within 4 h. The results showed that ~98% of **8** could be washed off the surface of the SWNTs when CH_2Cl_2 or THF was used as the extracting phase.

Furthermore, in acetone, the in situ desorbed **8** could be reimmobilized on the SWNTs when the solvent was concentrated at low temperature. These results clearly demonstrate that the $\pi-\pi$ stacking interaction between pyrene and SWNTs is reversible and is affected by the polarity of the solvents and by temperature. Based on these results, a new strategy was developed to control immobilization and to recycle both the catalyst and the SWNTs by using solvents at different temperatures.

Catalytic Study of SWNTs-Supported 8 in Acetone. A variety of representative ring-closing metathesis (RCM) substrates that led to the formation of various carbocyclic, as well as nitrogen- and oxygen-containing heterocyclic compounds, were examined to evaluate the performance of SWNTs-supported **8**. The results are shown in Table 2. Although the reaction time in acetone is longer than in the traditionally used CH_2Cl_2, SWNTs-supported **8** converts disubstituted dienes **11**, **13**, **17**, **19**, and trisubstituted dienes **15**, **21**, **23**, to five-, six-, or seven-membered rings in high yields at 35 °C. The enyne-RCM reaction of substrate **29** also proceeded with high conversion in acetone. Cross metathesis of **31** and **32** also was achieved in good yields using catalyst **8** at 35 °C. With low catalyst loading in acetone, low conversion of the tetra-substituted dienes **25** and **27** to the corresponding cyclic products occurred at 35 °C. However, high conversion (>94%) of these dienes was achieved using a high loading of SWNTs-supported **8** (5 mol % Ru) and a longer reaction time (24 h) at elevated temperature (56 °C). The low conversion of the sterically bulky substrates at low temperature (35 °C) may be attributed to two reasons. One is the use of the polar solvent acetone, and the other is the heterogeneous nature of the SWNTs-supported **8**. Although small amounts of **8** are desorbed from

Table 2. Model Reactions for Evaluating the SWNTs-Supported Catalyst **8** Using Different Substrates

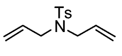
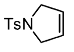
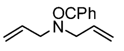
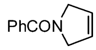
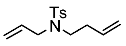
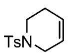
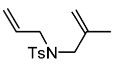
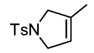
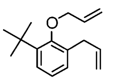
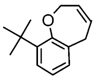
entry	diene	product	Ru mol%	conditions	convn.[a](yield)(%)
1	 **9**	 **10**	0.2	5.0 h, 35 °C	99 (98)
2	 **11**	 **12**	0.2	5.0 h, 35 °C	98 (97)
3	 **13**	 **14**	0.2	6.0 h, 35 °C	98 (97)
4	 **15**	 **16**	0.2	12 h, 35 °C	95 (93)
5	 **17**	 **18**	0.2	6.0 h, 35 °C	98 (96)
6	 **19**	 **20**	0.2	7.5 h, 35 °C	98 (97)
7	 **21**	 **22**	2.5	12 h, 35 °C	87 (85)
8	 **23**	 **24**	2.5	12 h, 35 °C	92 (90)
9	 **25**	 **26**	5.0	24 h, 56 °C	95 (92)
10	 **27**	 **28**	5.0	24 h, 56 °C	94 (90)
11	 **29**	 **30**	1.5	12 h, 35 °C	98 (95)
12	 **31**  **32**	 **33**	1.5	12 h, 35 °C	96 (95) *Z:E* (>20:1)

[a] Relative conversion rates of substrates were obtained by HPLC using SWNTs-supported catalysts **8** in acetone.

the SWNTs at 35 °C, there was not enough catalytically active species in solution to accomplish high conversions of these sterically bulky substrates. By contrast, high conversions of these sterically bulky substrates were achieved at elevated temperature, which was similar to other solid-supported catalysts. This is mainly due to the large amount of complex **8** being desorbed from the SWNTs, which contributes to the RCM. In acetone, SWNTs-supported **8** is a highly active catalyst for a wide range of RCM reactions and is tolerant to many functional groups, which is comparable to the parent compound **4**.

Recycle and Reuse of SWNTs-supported 8. Although some amount of catalyst was desorbed from the SWNTs at high temperature, the desorbed **8** was reanchored onto the SWNTs when stirred for ~ 30 min at 0 °C. Like other heterogeneous catalysts, the SWNTs-supported **8** can be separated by filtration or centrifugation (~94%). With low catalyst loading (1.5 mol % Ru), the SWNTs-supported catalyst **8** can be recycled and reused six or seven times for many di- or trisubstituted substrate dienes by using acetone as the solvent and by controlling the temperature between 0 – 35 °C. For the subsequent runs, gradual decrease in activity was observed compared with the activity for the first run. This is comparable to other solid-supported ruthenium carbene catalysts, and the catalysts are still very recyclable and are able to obtain high yields with longer reaction times.[17] Inductively coupled plasma mass spectrometry (ICP-MS) analysis of product **10** after the first recycle using the SWNT supported **8** indicated only 0.04% (by mass) Ru contamination in the unpurified product, which is similar to previously reported methods.[18] This value is substantially lower than that obtained for homogeneous-monomeric catalysts **2** or **4**, where all of the catalyst remains in the product mixture. Although the Ru contamination in the products is significantly lower using SWNT supported **8**, further purification is still needed to obtain pure product for medical purposes. The recycling capacity of SWNTs-supported **8** catalyst (1.5 mol % Ru) for different substrates is shown in Table 3. Not only is the SWNTs-supported **8** a good catalyst for RCM reactions, but also it is recyclable.

Table 3. Recycle Study of SWNTs Supported Catalyst **8** Using Different Substrates

substrate	product	cycle	conv.(%)[a] (time)		
 **9**	 **10**	1	99 (1 h)	5	93 (4 h)
		2	97 (1 h)	6	91 (9 h)
		3	96 (1.5 h)	7	89 (12 h)
		4	94 (2 h)	8	47 (24 h)
 **11**	 **12**	1	98 (1 h)	5	96 (11 h)
		2	98 (1 h)	6	96 (12 h)
		3	97 (3 h)	7	36 (24 h)
		4	97 (7 h)		
 **13**	 **14**	1	98 (1 h)	5	93 (12 h)
		2	97 (2 h)	6	91 (24 h)
		3	97 (2 h)	7	15 (24 h)
		4	95 (3 h)		
 **15**	 **16**	1	95 (2 h)	5	94 (12 h)
		2	95 (3 h)	6	82 (12 h)
		3	95 (7 h)	7	70 (24 h)
		4	95 (10 h)		
 **17**	 **18**	1	98 (1.5 h)	5	98 (24 h)
		2	98 (2 h)		
		3	98 (4 h)		
		4	98 (12 h)		

[a] Reaction was conducted in acetone at 35 °C; conversion was obtained by HPLC.

Importantly, the SWNTs can be easily reused and recycled after catalyst **8** completely loses activity by simply treating the deactivated catalyst twice with THF (sonicating for 4 h each time). About 98% of the SWNTs can be recovered from the deactivated supported **8**. These are then subjected to reloading with the new catalyst. The reusability of the catalyst supported on recycled SWNTs was comparable to that of catalyst supported on fresh SWNTs. The catalyst was reloaded on the recycled SWNTs up to six times, and consistent results were obtained as shown in Table 4.

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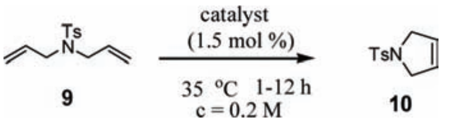
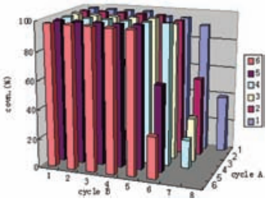
(18) (a) Kingsbury, J. S.; Garber, S. B.; Giftos, J. M.; Gray, B. L.; Okamoto, M. M.; Farrer, R. A.; Fourkas, J. T.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 4251–4256. (b) Michrowska, A.; Mennecke, K.; Kunz, U.; Kirschning, A.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128*, 13261–13267.

Table 4. Recycle Study of SWNTs Supported Catalyst **8** and Reuse Study of SWNTs



times	cycle (% convn.[a]) 1	2	3	4	5	6	7	8
1	98	98	98	98	95	95	90	39
2	98	98	98	98	98	98	95	55
3	98	98	98	98	98	95	30	
4	98	98	98	98	98	98	20	
5	98	98	98	98	98	60		
6	98	98	98	98	98	30		



[a] The experiment is based on the substrate **9** using SWNTs-supported **8** (1.5 mol Ru %) in acetone at 35 °C.

Although for each subsequent reuse the catalyst dies after fewer cycles (e.g., after seven cycles for the first use and after six cycles for the third use), the immobilization of **8** on the surface of SWNTs through $\pi-\pi$ stacking offers a new recycling model in which both the catalyst and the supporting materials can be reused. This immobilization model through $\pi-\pi$ stacking has vast advantages over the traditional immobilization method via covalent bonds: (1) The current immobilization method is a reversible immobilization model and is capable of promoting metathesis reactions in a homogeneous solution, thus, catalyzing the metathesis in higher reaction rates than any other solid-supported catalyst under similar conditions. (2) Although the reaction was performed in a homogeneous solution, the SWNTs-supported catalyst was recovered by just filtration after the reaction mixture was cooled down. This is easier than recovery of a catalyst system supported on soluble polymers. (3) Most importantly, the supporting material SWNTs can be recycled and reused by just washing with a polar solvent when the supported catalysts completely lost its activity. This recycle model offers a further step for green catalytic systems.

Study of in Situ Recovery of the Ru Catalyst from a Homogeneous RCM Reaction. A further study showed that the Ru catalyst can be recovered from a homogeneous RCM reaction mixture by adding SWNTs with attached ligand **7** and CuCl. A homogeneous RCM reaction in dry acetone was carried out using **2** or **4** and SWNTs with attached **7** and CuCl. After the end of the reaction, the reaction mixture was cooled to 0 °C and stirred for 30 min to allow the in situ generated pyrene-tagged Ru catalyst to attach onto the surface of the SWNTs. Then the SWNTs were separated and washed. After the sample was dried, the Ru on the SWNTs was analyzed by EDX. The results showed that 35% Ru (mol) was recovered from the SWNTs using **4** as the initial catalyst, whereas 90% Ru (mol) was recovered when **2** was employed as the initial catalyst. A great deal of **4** was still found in the solution due to an incomplete exchange of **4** and ligand **7**. For catalyst **2**, PCy_3 is a good leaving group, so the ligand exchange of **2** with **7** generates the pyrene-tagged **8** in high yield, which finally anchors onto the SWNT. So, the SWNTs and ligand **7** can be directly used for the recovery of the Ru catalyst from a homogeneous RCM reaction system when **2** is employed as the initial catalyst.

Experimental Section

Unless otherwise noted, all reactions were performed under an atmosphere of dry N_2 with oven-dried glassware and anhydrous solvents. Pentanes, hexanes, and diethyl ether were distilled from sodium benzophenone under a N_2 atmosphere. Dimethylformamide (DMF) and CH_2Cl_2 were dried over CaH_2 and distilled prior to use. All other solvents were dried over 4−8 Å mesh molecular sieves (Aldrich)and were either saturated with dry argon or degassed before use. Reactions were monitored by thin-layer chromatography on 0.20 mm silica gel plates, and spots were detected with UV light. Silica gel (200−300 mesh) (from Anhui Liangchen Chem. Company, Ltd.) was used for the flash chromatography. SWNTs were obtained from Shenzhen Bill technology Developing Co., Ltd. (SWNTs 90+ %; diameter, <2 nm; length, 5−40 μm; surface area, 407 m^2/g; density, 0.30 g/cm^3). Other chemicals or reagents were obtained from commercial sources. ^1H NMR and ^{13}C NMR spectra were acquired in $CDCl_3$ on Varian 500 spectrometers. If not otherwise noted, chemical shifts are reported as values in ppm relative to residual $CDCl_3$ (δ 7.26) for ^1H NMR spectra and relative to $CDCl_3$ (77.16 ppm) for ^{13}C NMR spectra. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, and m = multiplet. Coupling constants (J) are quoted in Hz at 400 or 500 MHz for ^1H NMR spectra. Infrared spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrophotometer and Nicolet Magna 550 FT-IR spectrophotometer. Elemental analyses were determined at Nankai University using a Perkin-Elmer-2400C instrument. Conversions were determined by HPLC analysis of the sample on an Agilent 1100 using an Eclipse XDB-C8 (4.6 × 150 mm) column (mobile phase: $CH_3OH/H_2O = 4:1$). The immobilization of **8** catalysts was monitored by UV spectroscopy. TEM was performed using a Philips CM200 field-emission gun TEM, operated at 200 kV.

Synthetic Procedures. All experiments were carried out in 25−100 mL glass round-bottom flasks, equipped with magnetic stirring bars and high-vacuum Teflon valves. Compounds in the products were identified by comparing their IR and ^1H NMR spectra with those of pure samples. (*E*)-4-Bromo-1-isopropoxy-2-(prop-1-enyl)benzene **5**, dienes **9**, **11**, **13**, **15**, **17**, **19**, **21**, **23**, **25**, **27**, and **29** were synthesized and purified according to the literature.[19] Catalyst **2** was also prepared according to a literature method.[20]

Synthesis of (*E*)-(4-Isopropoxy-3-(prop-1-enyl)phenyl) Methanol 5. A flask was charged with 1.50 g of (5.91 mmol) (*E*)-4-bromo-1-isopropoxy-2-(prop-1-enyl)benzene (precursor for **5**) and 5 mL of anhydrous diethyl ether. The solution was cooled to −78 °C, and 4.27 mL of *n*-BuLi (1.66 M in hexanes, 7.08 mmol, and 1.2 equiv) was slowly added via a syringe. The reaction mixture was then allowed to slowly warm to room temperature. After stirring for 1 h at room temperature, the reaction mixture was cooled to −78 °C. To this mixture, 0.43 g of DMF (5.91 mmol, 1 equiv) was added slowly via a syringe. The resulting solution was stirred for 1 h at this temperature. The mixture was then concentrated under vacuum to obtain a thick oil residue. A 20 mL portion of dichloromethane was added to this residue. After being washed four times with water, the organic layer was dried over magnesium sulfate. Removal of the solvent by filtration gave an oil residue. The residue was then dissolved in 15 mL of methanol, and 0.48 g of $NaBH_4$ (12.7 mmol, 2.5 equiv) was added. The mixture was stirred for 5 h at room temperature. After the mixture was concentrated under a vacuum, 20 mL of water and 100 mL of dichloromethane were added. The organic layer was washed four times with water, dried over magnesium sulfate, filtered, and concentrated. The residue was purified by silica gel chromatography using dichloromethane as the elutant. The desired (*E*)-(4-isopropoxy-3-(prop-1-enyl)phenyl) methanol **5** was obtained as a colorless oil (0.86 g, 4.20 mmol, 71%). Analytical data: Found (calcd) for $C_{13}H_{18}O_2$, C 75.60 (75.69), H 8.70 (8.80). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.351 (d, ^3J (H, H) = 6.0 Hz, 6H, CH_3), 1.906 (dd,^3J (H, H) = 1.6, ^3J (H, H) = 6.8 Hz, 3H, CH_3), 2.846 (s, 1H, O*H*), 4.476 (m, ^3J (H, H) = 6.0 Hz, 1H, C*H*), 4.537(s, 2H, CH_2), 6.208 (m, 1H, ^3J (H, H) = 6.8 Hz, C*H*), 6.714 ((dd, ^3J (H, H) = 1.6, ^3J (H, H) = 16 Hz, C*H*ar), 6.819 (d, 1H, ^3J (H, H) = 8.4 Hz, C*H*), 7.088 (dd, ^3J (H, H) = 2.0 Hz, ^3J (H, H) = 8.4 Hz, 1H, C*H*ar), 7.389 (d, ^3J (H, H) = 2 Hz, 1H, C*H*ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 19.2, 22.4, 65.0, 71.3, 114.7, 125.7, 126.1, 126.3, 126.8, 128.5, 133.5, 154.3. IR (CH_2Cl_2) *υ*: 3395, 3035, 2977, 2932, 2728, 2650, 1651, 1608, 1492, 1448, 1378, 1245, 1120, 1020, 967, 816, 623, 631, 519, 469 cm^{-1}.

Synthesis of (*E*)-4-Isopropoxy-3-(prop-1-enyl)benzyl-4-(pyren-1-yl)butanoate 7. To a solution of 0.15 g of **5** (0.73 mmol) and 0.21 g of 4-(pyren-1-yl)-butanoic acid **6** (0.73 mmol) in 20 mL of anhydrous CH_2Cl_2 at 0 °C were added 0.15 g of *N*, *N*′-dicyclohexylcarbodiimide (0.73 mmol) and 0.18 g of 4-dimethylaminopyridine (1.46 mmol). The reaction mixture was slowly warmed to room temperature and stirred for 12 h at this temperature. Then the insoluble material was filtered out, and the filtrates were concentrated under vacuum. The crude product was purified by flash column chromatography on silica using pentane/CH_2Cl_2 (1:1) as the eluant to provide 0.26 g of (*E*)-4-isopropoxy-3-(prop-1-enyl)benzyl-4-(pyren-1-yl)butanoate **7** as an orange oil (0.54 mmol, 74%). Analytical data: Found (calcd) for $C_{33}H_{32}O_3$, C 83.43 (83.16), H 6.32 (6.77). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.353 (d, ^3J (H, H) = 6.4 Hz, 6H, CH_3), 1.901 (dd,^3J (H, H) = 1.2, ^3J (H, H) = 6.8 Hz, 3H, CH_3), 2.210 (m, 2H,^3J (H, H) = 7.6 Hz, CH_2), 2.496 (t, 2H,^3J (H, H) = 7.6 Hz, CH_2), 3.373 (t, 2H,^3J (H, H) = 7.6 Hz, CH_2), 4.496(m, ^3J (H, H) = 6.4 Hz, 1H, C*H*), 5.097(s, 2H, CH_2), 6.237 (m, 1H, ^3J (H, H) = 6.4 Hz, C*H*), 6.713 ((dd,^3J (H, H) = 1.6, ^3J (H, H) = 16 Hz, 1H, C*H*ar), 6.828 (d, 1H, ^3J (H, H) = 8.4 Hz, C*H*), 7.155 (dd, ^3J (H, H) = 2.0 Hz, ^3J (H, H) = 8.4 Hz, 1H, C*H*ar), 7.454 (d, ^3J (H, H) = 1.6 Hz, 1H, C*H*ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 19.2, 22.4, 27.1, 32.9, 34.2, 66.6, 71.0, 114.2, 123.5, 124.9, 125.0, 125.1, 125.2, 125.3, 125.8, 126.0, 126.7, 126.9, 127.3, 127.5, 127.6, 127.7, 128.1, 128.3, 128.5, 128.9, 130.1, 131.1, 131.6, 135.9, 154.8, 173.6. IR (CH_2Cl_2) *υ*: 3040, 2971, 2933, 2877, 1730, 1652, 1605, 1493, 1449, 1378, 1245, 1181, 1120, 968, 844, 759, 719, 622, 474, 431 cm^{-1}.

Preparation of Pyrene-Tagged Ruthenium Carbene Complex 8. A 0.42 g sample of catalyst **2** (0.50 mmol) and 0.05 g of CuCl (0.50 mmol) were added to a flask under N_2. A 0.29 g of solution of **7** (0.6 mmol) in 25 mL of dry dichloromethane was poured into the reaction mixture under N_2. The resulting mixture was then refluxed for 20 min. After cooling to room temperature, the reaction mixture was filtered to collect the filtrate. Solvent from the filtrate was evaporated under vacuum to give a residue. The residue was purified by flash column chromatography on silica using CH_2Cl_2 as the elutant to give 0.32 g of the desired product **8** as a green crystalline solid (0.34 mmol, 68%). Analytical data: Found (calcd) for: $C_{52}H_{54}Cl_2N_2O_3Ru$ C 67.41 (67.38), H 6.01 (5.87), N 3.41 (3.02). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.256 (d, ^3J (H, H) = 6.0 Hz, 6H, CH_3), 2.205 (m, 2H,^3J (H, H) = 7.6 Hz, CH_2), 2.242 (s, 6H, CH_3), 2.453 (s, 12H, CH_3), 2.471 (t, 2H,^3J (H, H) = 7.6 Hz, CH_2), 3.401 (t, 2H, ^3J (H, H) = 7.6 Hz, CH_2), 4.165 (s, 4H, CH_2), 4.844 (m, ^3J (H, H) = 6.4 Hz, 1H, C*H*), 5.089 (s, 2H, CH_2), 6.724 (d, 1H, *J* (H, H) = 8.4 Hz, C*H*ar), 6.915 (s, 1H, C*H*ar), 7.016 (s, 4H, C*H*ar), 7.463 (d, ^3J (H, H) = 8.0 Hz, 1H, CHar). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 21.3, 27.0, 29.9, 33.0, 34.1, 51.7, 65.5, 75.6, 113.1, 123.1, 123.5, 125.0, 125.1, 125.2, 125.3, 126.0, 126.9, 127.6, 127.71, 127.73, 128.9, 129.6, 129.9, 130.2, 131.1, 131.6, 135.8, 139.0, 145.4, 152.3, 173.3, 211.1, 296.4.

Immobilization of Pyrene-Tagged Ruthenium Carbene Catalyst 8 on SWNTs. Under N_2 gas, a glass vial with a screw-cap septum top was charged with 10 mg of SWNTs and 0.4 mL CH_2Cl_2. The resulting mixture was sonicated for 1 h in a KQ 2200E 100W ultrasonicator at room temperature. Then 10 mg of catalyst **8** was added into the mixture, and the mixture was sonicated for another 5 min. The resulting mixture was allowed to stand for 3 h at room temperature. During this period, aliquots (10 μL) of the mixture were taken from the reaction mixture at different time intervals, using a microsyringe, and were diluted immediately with 10 mL of CH_2Cl_2. The resulting solution was then subjected to UV detection. The SWNTs with **8** were separated from the solution

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via centrifugation. The solid was rinsed three times with acetone. The resulting dark solid was dried under vacuum for 12 h and weighed. Complex **8** (~1.5 mg) was loaded for each 10 mg of SWNTs.

Desorption of 8 from SWNTs with Different Solvents. Under N_2 gas, a glass vial with a screw-cap septum top was charged with 11.2 mg of SWNTs-supported **8** catalyst (equal to 1.2 mg, 0.0012 mmol of **8**) and 1 mL of solvent. The resulting mixture was sonicated in a KQ 2200E 100W ultrasonicator and stirred at room temperature. During this time, aliquots (30 μL) were taken from the reaction mixture using a microsyringe and were immediately diluted with 10 mL of CH_2Cl_2. The resulting solution was subjected to UV detection.

Catalytic Study of SWNTs-Supported 8 for Different Substrates in Acetone. SWNTs-supported **8** catalysts (0.4 mg, 0.43 mmol) and a solution of substrate in dry acetone (0.5 mL) were mixed in a reaction flask under argon at different temperatures. The reaction mixture was stirred for 1−24 h. At the end of the reaction (monitored by TLC), the SWNTs-supported **8** catalyst was separated by centrifugation. The solution was evaporated to afford the crude cyclized product. The product was dissolved in CH_2Cl_2 to remove the trace amounts of Ru residue, and the solution was filtered through silica gel using CH_2Cl_2 as the eluant. The sample was analyzed by HPLC. Conversions were obtained by comparing the ratios of the starting materials with those of the products.

Recycle Study of SWNTs-Supported 8 in Acetone. SWNTs-supported **8** (19.4 mg) catalysts (equal to 2.4 mg, 0.0026 mmol of **8**) and a solution of the substrate (0.17 mmol) in dry acetone (0.5 mL) were mixed in a reaction flask under argon. The reaction mixture was stirred at 35 °C until the reaction was complete. At the end of the reaction (monitored by TLC), the reaction mixture was concentrated and stirred for 30 min at 0 °C, allowing the desorbed catalysts to be reimmobilized on the SWNTs. Then the SWNTs-supported **8** catalyst was separated by centrifugation and subjected to another cycle. The solution was evaporated to afford the crude cyclized product. The product was dissolved in CH_2Cl_2 to remove the trace amounts of Ru residue, and the solution was filtered through silica gel using CH_2Cl_2 as the eluant. The sample was analyzed by HPLC. Conversions were obtained by comparing the ratios of the starting materials with those of the products. When substrate **9** was used, the crude cyclized products **10** of the first cycle were subjected to ICP-MS analysis, and the ruthenium contamination was determined to be 0.04% (by mass).

Recycle and Reused SWNTs from Deactivated Catalyst. Catalyst **8** supported on the SWNTs (19.4 mg) (equal to 2.4 mg, 0.0026 mmol of **8**) was used for the recyclability study. When the recycle study of the supported **8** in acetone was finished, the SWNTs were separated by centrifugation and were suspended in 1 mL of THF in a 5 mL vial with a screw cap. The mixture was sonicated for 4 h. Then the solid was separated from the mixture via centrifugation and was washed again with 1 mL THF with sonication. SWNTs (16 mg) were obtained by drying under vacuum and weighed. According to the weight of SWNTs, catalysts of **8** were immobilized (quality, 1/1; concentration of solution, 0.027mol/L) again. The above operation was repeated at least six times.

In Situ Recovery of the Ru Catalyst from a Homogeneous RCM Reaction. SWNTs (10.8 mg) with attached **7** (0.8 mg, 0.0017 mmol), CuCl (0.0014mmol), and a solution of substrate **9** (0.17 mmol) in dry acetone (0.5 mL) were mixed in a reaction flask under argon. Then catalyst **2** (1.2 mg, 0.0014 mmol) or **4** (0.9 mg, 0.0014mmol) was added. The reaction mixture was stirred at 35 °C until the reaction was completed. At the end of the reaction (monitored by TLC), the reaction mixture was concentrated and stirred for 30 min at 0 °C, allowing the catalysts to anchor on the SWNTs. The supported catalyst was separated by centrifugation, and the amount of Ru recovered on the SWNTs from the reaction solution was determined by EDX.

Conclusion

A pyrene-tagged ruthenium carbene **8** was prepared. **8** can be anchored on the surface of SWNTs via $\pi-\pi$ interactions between the pyrene and the SWNTs. The $\pi-\pi$ interactions are greatly affected by the polarity of the solvent, thus offering a new way to recycle both the ruthenium catalysts and the supporting SWNTs. In view of the growing interest in the development of cost-effective and environmentally benign catalytic systems, this new strategy can be applied to the design of other recyclable transition metal-based catalysts, to template synthesis, and to other related research areas.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of the catalyst **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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