Catal Lett (2012) 142:803–808
DOI 10.1007/s10562-012-0781-9

Diphosphino-Functionalized MCM-41-Immobilized Rhodium Complex: A Highly Efficient and Recyclable Catalyst for the Hydrophosphinylation of Terminal Alkynes

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Received: 12 December 2011 / Accepted: 30 January 2012 / Published online: 4 April 2012

Abstract Diphosphino-functionalized MCM-41-immobilized rhodium complex (MCM-41-2P-RhCl$_3$) was conveniently synthesized from commercially available and cheap γ-aminopropyltriethoxysilane via immobilization on mesoporous MCM-41, followed by reacting with diphenylphosphinomethanol and rhodium chloride. It was found that this heterogeneous rhodium complex is a highly efficient catalyst for the hydrophosphinylation of terminal alkynes with diphenylphosphine oxide and can be recovered and recycled by a simple filtration of the reaction solution and used for at least 10 consecutive trials without any decreases in activity.

Keywords Supported rhodium catalyst · Functionalized MCM-41 · Phosphine rhodium complex · Hydrophosphinylation · Heterogeneous catalysis

1 Introduction

Alkenylphosphine oxides are key synthetic intermediates for the preparation of various phosphine ligands and present in numerous biologically active products [1–6]. In addition, a variety of heteroatom nucleophiles such as alcohols [7], thiols [8], primary and secondary amines [9–11], and phosphines [12] readily add to the double bond in alkenylphosphine oxides to afford versatile bifunctional compounds, which allow further synthetic transformations. Alkenylphosphine oxides have also been used for the formation of carbon–carbon bond via reactions with carbanion species [13] or carbon-centered radicals [14, 15]. Transition-metal-catalyzed addition of an P–H bond to alkynes is a straightforward method for the generation of alkenylphosphorus compounds [16–20], but this transformation always results in a mixture of *E/Z* configurations, and it is difficult to obtain one single product. Han et al. [21] described a rhodium-catalyzed regio- and stereoselective hydrophosphinylation of alkynes with Ph$_2$P(O)H, which provides a new convenient and clean method for the preparation of (*E*)-alkenylphosphine oxides. However, industrial applications of homogeneous rhodium complexes remain a challenge because they are expensive, cannot be recycled, and difficult to separate from the product mixture, which is a particularly significant drawback for their application in the pharmaceutical industry. The immobilization of catalytically active species, i.e., organometallic complexes, onto a solid support to produce a molecular heterogeneous catalyst is one potential solution to the latter two problems [22].

The high costs of the transition metal catalysts coupled with toxic effects associated with many transition metals has led to an increased interest in immobilizing catalysts onto a support. Heterogeneous catalysis also helps to minimize wastes derived from reaction workup, contributing to the development of green chemical processes [23, 24]. Supported rhodium catalysts have successfully been used for hydrogenation [25, 26], hydroformylation [27–29], hydrosilylation [30, 31], polymerization of aromatic acetylenes [32] and hydrothiolation of acetylenes [33]. Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [34–36].

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MCM-41 has a regular pore diameter of ca. 5 nm and a specific surface area >700 m^2 g^{-1} [37]. Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [38–40]. It is generally believed that high surface area of heterogeneous catalyst results in high catalytic activity. Considering the fact that the MCM-41 support has an extremely high surface area and the catalytic rhodium species is anchored on the inner surface of the mesopore of MCM-41 support, we expect that MCM-41-immobilized rhodium catalyst will exhibit high activity and good reusability. Shyu et al. [41] reported phosphinated MCM-41-supported rhodium complex for catalytic hydrogenation of olefins and found that it is an excellent hydrogenation catalyst with turnover frequency (TOF) three times higher than that of $RhCl(PPh_3)_3$ in the hydrogenation of cyclohexene. However, to the best of our knowledge, no hydrophosphinylation of alkynes with diphenylphosphine oxide catalyzed by MCM-41-immobilized phosphine rhodium complex has been reported until now. In this paper, we wish to report the synthesis of diphosphino-functionalized MCM-41-immobilized rhodium complex (MCM-41-2P-$RhCl_3$) and its catalytic properties in the hydrophosphinylation reaction of alkynes with diphenylphosphine oxide.

2 Experimental

All chemicals were reagent grade and used as purchased. The mesoporous material MCM-41 was prepared according to a literature procedure [42]. All reactions were performed under an inert atmosphere of dry argon using distilled dried solvents. All hydrophosphinylation products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were determined on a Perkin-Elmer 683 instrument. ^1H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. Rhodium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). X-ray powder diffraction patterns were obtained on Damx-rA (Rigaka). The BET surface area and pore analysis were performed on ASAP2010 (micromeritics) by N_2 physical adsorption–desorption at 77.4 K. X-ray photoelectron spectra were recorded on XSAM 800 (Kratos).

2.1 Preparation of MCM-41-NH_2

A solution of γ-aminopropyltriethoxysilane (2.20 g, 10 mmol) in dry chloroform (18 mL) was added to a suspension of the mesoporous support MCM-41 (2.80 g) in dry toluene (180 mL). The mixture was stirred for 48 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of Me_3SiCl (4.36 g, 40 mmol) in dry toluene (150 mL) at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 120 °C for 5 h to obtain 3.54 g of hybrid material MCM-41-NH_2. The nitrogen content was found to be 1.27 mmol/g by elemental analysis.

2.2 Preparation of MCM-41-2P

A Schlenk flask was charged with paraformaldehyde (0.701 g, 23.3 mmol), dry MeOH (20 mL) and diphenylphosphine (4.340 g, 23.3 mmol). The reaction mixture was heated to 60 °C under Ar until the white suspension formed a colorless solution. After removal of MeOH in vacuo the remaining viscous oil was diluted in dry toluene (20 mL). This solution was added to a suspension of MCM-41-NH_2 (3.020 g) in dry toluene (60 mL) and the reaction mixture was heated to 105 °C under Ar for 24 h. In the cooler regions of the flask the water-toluene azeotrope separated indicating the reaction progress. After cooling to room temperature the solid product was collected by filtration under Ar, washed with dry toluene (4 × 30 mL), CH_2Cl_2/THF (1/1) (2 × 30 mL), CH_2Cl_2 (2 × 30 mL) and dried in vacuo (100 °C) for 5 h to give 4.08 g of the light yellow MCM-41-2P. The nitrogen and phosphine content was found to be 0.76 and 1.44 mmol/g, respectively.

2.3 Preparation of MCM-41-2P-$RhCl_3$

To a solution of $RhCl_3$ (0.171 g) in acetone (40 mL) was added MCM-41-2P (1.85 g). The mixture was heated at reflux under Ar for 72 h. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 3 h to give 1.91 g of the brown yellow polymeric rhodium complex (MCM-41-2P-$RhCl_3$). The phosphine and rhodium content was 1.23 and 0.29 mmol/g, respectively.

2.4 Hydrophosphinylation Reaction of Alkynes with Diphenylphosphine Oxide

A mixture of terminal alkyne (1.0 mmol), diphenylphosphine oxide (1.0 mmol), toluene (3 mL), and the MCM-41-2P-$RhCl_3$ complex (105 mg, 0.03 mmol of Rh) was stirred under Ar in an oil bath at 80 °C for 4–12 h. The mixture was cooled, diluted with Et_2O (30 mL) and filtered. The MCM-41-2P-$RhCl_3$ complex was washed with EtOH (2 × 10 mL) and Et_2O (2 × 10 mL) and reused in the next run. The ether solution was concentrated under a reduced pressure, and the residue was purified by column chromatography on silica gel (EtOAc/hexane = 1/1).

2.5 The Recyclability of the MCM-41-2P-RhCl$_3$ and Rhodium Leaching Tests

After carrying out the reaction, the mixture was vacuum filtered using a sintered glass funnel and the residue washed with EtOH (2 × 10 mL) and Et$_2$O (2 × 10 mL). After being dried in an oven, the catalyst can be reused directly without further purification. The rhodium content of the catalyst was determined by ICP analysis to be 0.29 mmol/g after ten consecutive runs, no rhodium leaching from the MCM-41 support was observed.

3 Results and Discussion

The novel diphosphino-functionalized MCM-41-immobilized rhodium complex (MCM-41-2P-RhCl$_3$) was conveniently synthesized from commercially available and cheap γ-aminopropyltriethoxysilane via immobilization on MCM-41, followed by reacting with diphenylphosphinomethanol which resulted from adduct formation between diphenylphosphine and paraformaldehyde, and rhodium chloride (Scheme 1). X-ray powder diffraction (XRD) patterns of the parent MCM-41 and the modified materials MCM-41-2P, MCM-41-2P-RhCl$_3$ are displayed in Fig. 1. Small angle X-ray powder diffraction of the parent MCM-41 gave peaks corresponding to hexagonally ordered mesoporous phases. For MCM-41-2P and MCM-41-2P-RhCl$_3$, the (100) reflection of the parent MCM-41 with decreased intensity remained after functionalization, while the (110) and (200) reflections became weak and diffuse, which could be due to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results indicated that the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation. The nitrogen adsorption studies demonstrated that a significant decrease in pore size by virtue of silylation of the MCM-41 channels was observed. Additionally, upon modification the surface area and pore volume decreased obviously. These results are in good agreement with the fact that the surface modification indeed occurred inside

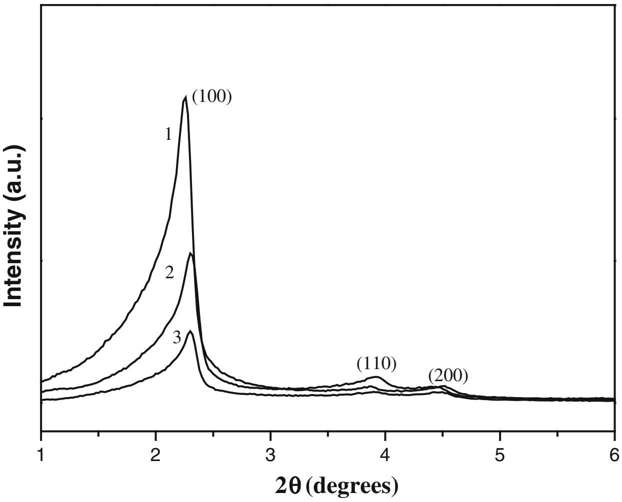
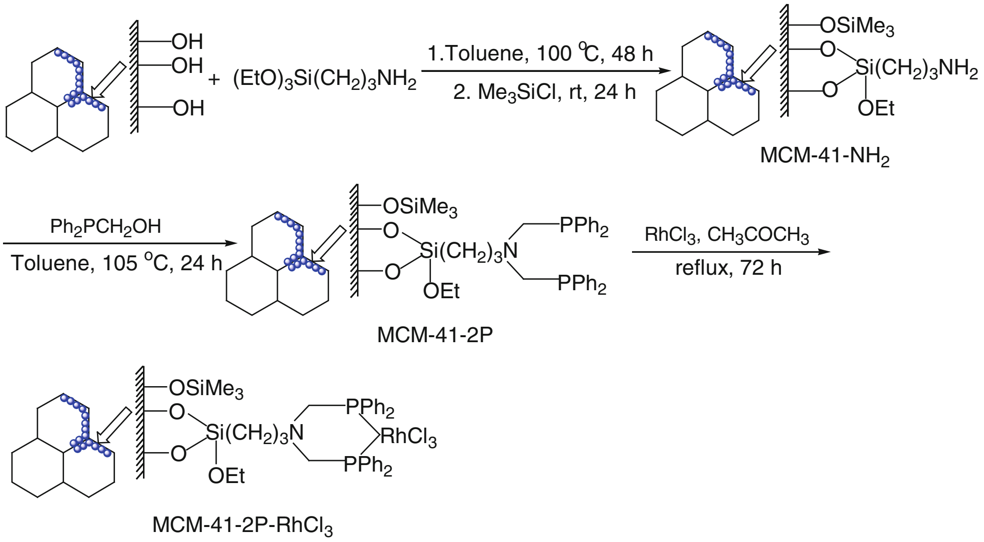


Fig. 1 XRD patterns of the parent MCM-41 (*1*), MCM-41-2P (*2*), and MCM-41-2P-RhCl$_3$ (*3*)



Scheme 1 Preparation of the MCM-41-2P-RhCl$_3$

the primary mesopores of the parent MCM-41. The results in detail are summarized in Table 1.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterize this heterogeneous rhodium complex. The P: Rh mole ratio of the MCM-41-2P-$RhCl_3$ was determined to be 4.24. The XPS data for MCM-41-2P-$RhCl_3$, MCM-41-2P, $RhCl_3$ and Rh foil are listed in Table 2. It can be seen that the binding energies of N_{1s}, Si_{2p} and O_{1s} of MCM-41-2P-$RhCl_3$ are similar to those of MCM-41-2P and the binding energy of Cl_{2p} of MCM-41-2P-$RhCl_3$ is similar to that of $RhCl_3$. However, the difference of P_{2p} binding energies between MCM-41-2P-$RhCl_3$ and MCM-41-2P is 0.5 eV. The binding energy of Rh_{3d} in MCM-41-2P-$RhCl_3$ is 1.9 eV less than that in $RhCl_3$, but 1.4 eV larger than that in Rh foil. These results show that a coordination bond between P and Rh is formed.

Table 1 Textural parameters of the catalytic materials

Materials	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)	Diameter[c] (nm)
MCM-41	904.6	0.84	2.7
MCM-41-2P	617.5	0.47	1.9
MCM-41-2P-$RhCl_3$	564.7	0.41	1.8

[a] BET surface area; [b] Single point total pore volume; [c] Pore diameter according to the maximum of the BJH pore size distribution

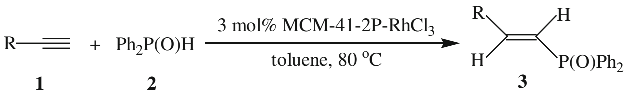
Table 2 XPS data for MCM-41-2P-$RhCl_3$, MCM-41-2P, $RhCl_3$ and Rh foil (in eV)

Sample	Rh_{3d}	P_{2p}	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-2P-$RhCl_3$	308.5	133.5	399.2	103.4	532.7	199.6
MCM-41-2P		133.0	399.1	103.4	532.7	
$RhCl_3$	310.4					199.7
Rh foil	307.1					

The binding energies are referenced to C_{1s}(284.6 eV), and the energy differences were determined with an accuracy of ±0.2 eV

The hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide was chosen as a model reaction, and the influences of various reaction parameters such as solvent, reaction temperature, and rhodium catalyst quantity on the reaction were tested. The results are summarized in Table 3. For the temperatures evaluated (25, 40, 60, 80, and 100 °C), 80 °C gave the best result and no reaction occurred at 25 or 40 °C. Other reaction temperatures such as 60 and 100 °C were substantially less effective. We then turned our attention to investigate the effect of solvents on the hydrophosphinylation reaction. Among the solvents used (THF, dioxane, toluene, and benzene), toluene was the best choice. Increasing the amount of rhodium catalyst could shorten the reaction time, but did not increase the yield of (*E*)-1-(diphenylphosphinyl)-1-octene (entry 9). The low rhodium concentration usually led to a long period of reaction, which was consistent with our experimental results (entries 10 and 11). Taken together, good result was obtained when the hydrophosphinylation reaction was carried out with 3 mol% of the catalyst in toluene at 80 °C (entry 4).

To examine the scope for this heterogeneous hydrophosphinylation reaction, we have investigated the reaction using a variety of terminal alkynes as the substrates under the optimized reaction conditions (Scheme 2) and the results are outlined in Table 4. As shown in Table 4, this heterogeneous rhodium complex-catalyzed hydrophosphinylation reaction can be readily applied to a variety of



Scheme 2 Hydrophosphinylation of terminal alkynes with diphenylphosphine oxide catalyzed by MCM-41-2P-$RhCl_3$

Table 3 Reaction condition screening for the hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide

Entry	Solvent	MCM-41-2P-$RhCl_3$ (mol%)	Temp. (°C)	Time (h)	Yield[a] (%)
1	Toluene	3.0	25	24	0
2	Toluene	3.0	40	24	Trace
3	Toluene	3.0	60	24	74
4	Toluene	3.0	80	4	90
5	Toluene	3.0	100	3	85
6	THF	3.0	60	8	78
7	Benzene	3.0	80	8	73
8	Dioxane	3.0	80	8	64
9	Toluene	5.0	80	3	89
10	Toluene	1.5	80	12	87
11	Toluene	1.0	80	24	82

All reactions were performed using 1.0 mmol of 1-octyne, 1.0 mmol of diphenylphosphine oxide in 3.0 mL of solvent under Ar

[a] Isolated yield

Table 4 Hydrophosphinylation of terminal alkynes catalyzed by MCM-41-2P-$RhCl_3$

Entry	R	Time (h)	Product	Yield[a] (%)
1	n-C_6H_{13}	4	3a	90
2[b]	n-C_4H_9	6	3b	87
3	Ph	6	3c	89
4	4-MeC_6H_4	6	3d	86
5	4-FC_6H_4	5	3e	88
6	2-ClC_6H_4	10	3f	81
7	4-$CH_3OC_6H_4$	8	3g	84
8	$HOCH_2CH_2$	6	3h	87
9	$MeOCH_2CH_2$	6	3i	85
10	1-Hydroxycyclohexyl	5	3j	87
11	$ClCH_2CH_2CH_2$	10	3k	84
12	$NCCH_2CH_2CH_2$	10	3l	86
13[b]	Me_3SiCH_2	12	3m	78
14	n-Bu_2NCH_2	12	3n	82
15	Thiophen-2-yl	8	3o	89
16	Pyridin-2-yl	6	3p	85
17	t-$BuCO_2CH_2CH_2$	6	3q	83
18	1-Cyclohexenyl	5	3r	88

All reactions were performed using 1.0 mmol of terminal alkyne, 1.0 mmol of diphenylphosphine oxide, and 3 mol% MCM-41-2P-$RhCl_3$ in 3.0 mL of toluene at 80 °C under Ar

[a] Isolated yield; [b] At 70 °C

terminal alkynes, proving to be a practically useful method for the stereoselective synthesis of (*E*)-alkenylphosphine oxides which are not readily available by conventional methods. The hydrophosphinylation reaction of aliphatic terminal alkynes with $HP(O)Ph_2$ proceeded smoothly at 80 °C to afford the corresponding (*E*)-adducts by the regioselective addition of the phosphorus atom at the terminal carbon of the triple bond in good to high yields (entries 1, 2, 8, 9, 11, 12, 17). The catalytic activity of this heterogeneous rhodium complex catalyst is comparable to that of homogeneous $RhCl_3$. For example, the hydrophosphinylation of 1-octyne in the presence of 3 mol% of MCM-41-2P-$RhCl_3$ in toluene at 80 °C under Ar for 4 h gave a 90% yield of the addition product **3a** (entry 1), the same reaction in the presence of 3 mol% $RhCl_3$ in toluene at 80 °C under Ar for 3 h gave **3a** in 91% yield [21]. Under the above reaction conditions, aromatic terminal alkynes reacted efficiently with $HP(O)Ph_2$ affording the corresponding (*E*)-alkenylphosphine oxides **3c**–**3g** in good to high yields (entries 3–7). The reactions of propargylic alcohol, silane and amine with $HP(O)Ph_2$ proceeded readily to give the corresponding (*E*)-adducts **3j**, **3m** and **3n** in good yields (entries 10, 13 and 14). A variety of functionalities such as chloro, cyano, amino, alkoxycarbonyl, hydroxyl, silyl, fluoro, methyl, and methoxy groups were all tolerant under the present reaction conditions. The reactions of heteroarylacetylenes such as 2-ethynylthiophene and 2-ethynylpyridine also proceeded efficiently under same reaction conditions to give the desired addition products **3o** and **3p** in high yields (entries 15 and 16). 1-Ethynylcyclohexene underwent hydrophosphinylation exclusively at the triple bond to afford the corresponding (1*E*)-1,3-dienylphosphine oxide **3r** in high yield (entry 18). The formation of the *anti*-Markovnikov β-adduct from 1-ethynylcyclohexene is noteworthy since the related palladium-catalyzed reaction afforded the Markovnikov α-adduct instead [43].

In order to determine whether the catalysis was due to the MCM-41-2P-$RhCl_3$ complex or to a homogeneous rhodium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test [44]. We focused on the hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide. We filtered off the MCM-41-2P-$RhCl_3$ complex after 2 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (80 °C) in order to avoid possible recoordination or precipitation of soluble rhodium upon cooling. We found that, after this hot filtration, no further reaction was observed and no rhodium could be detected in the hot filtered solution by ICP-AES. This result suggests that the rhodium catalyst remains on the support at elevated temperatures during the reaction and points to a process of heterogeneous nature.

For a heterogeneous transition-metal catalyst, it is very important to examine its ease of separation, good of recoverability and reusability. We also investigated the recyclability of the MCM-41-2P-$RhCl_3$ by using the reaction of 1-octyne with diphenylphosphine oxide. This heterogeneous rhodium catalyst can be easily recovered by simple filtration and washed with ethanol and diethyl ether. After being air-dried, it can be reused directly without further purification. The recovered rhodium catalyst was used in the next run, and almost consistent activity was observed for ten consecutive cycles (Table 5). In addition,

Table 5 Hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide catalyzed by recycled catalyst

Cycle	Yield[a] (%)	Cycle	Yield[a] (%)
1	90	2	89
3	89	4	90
5	89	6	88
7	87	8	89
9	88	10	87

Reaction conditions: 1.0 mmol of 1-octyne, 1.0 mmol of diphenylphosphine oxide, and 3.0 mol% MCM-41-2P-$RhCl_3$ in 3.0 mL of toluene at 80 °C for 4 h under Ar

[a] Isolated yield

rhodium leaching in the supported catalyst was also determined. The rhodium content of the catalyst was found by ICP analysis to be 0.29 mmol/g after ten consecutive runs, no rhodium had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst should result from the chelating action of bidentate phosphine ligand on rhodium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability and the easy accessibility of the MCM-41-2P-$RhCl_3$ make them a highly attractive heterogeneous rhodium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

4 Conclusions

In summary, we have developed a novel, practical and environmentally friendly catalyst system for the hydrophosphinylation of terminal alkynes with diphenylphosphine oxide by using diphosphino-functionalized MCM-41-immobilized rhodium complex as catalyst under mild conditions. The reactions generated stereoselectively the corresponding (*E*)-alkenylphosphine oxides in good to high yields. This novel heterogeneous rhodium catalyst can be easily prepared from commercially available and cheap reagents and exhibits high catalytic activity and can be reused at least 10 times without any decreases in activity. The hydrophosphinylation of terminal alkynes with diphenylphosphine oxide catalyzed by the MCM-41-2P-$RhCl_3$ complex provide a better and practical procedure for the synthesis of a variety of (*E*)-alkenylphosphine oxides.

Acknowledgments We gratefully acknowledge the financial support of this work by the National Natural Science Foundation of China (Project No. 20862008) and the Natural Science Foundation of Jiangxi Province in China (Project No. 2010GZH0062).

References

1. Niu M, Fu H, Jiang Y, Zhao Y (2007) Chem Commun 272
2. Inoue H, Nagaoka Y, Tomioka K (2002) J Org Chem 67:5864
3. Rahman MS, Oliana M, Hii KK (2004) Tetrahedron Asymmetr 15:1835
4. Barbaro P, Bianchini C, Giambastiani G, Togni A (2002) Chem Commun 2672
5. Han L-B, Zhao C-Q (2005) J Org Chem 70:10121
6. Nicolaou KC, Maligres P, Shin J, de Leon E, Rideout D (1990) J Am Chem Soc 112:7825
7. Johnson CR, Imamoto T (1987) J Org Chem 52:2170
8. Pietrusiewicz KM, Wisniewski W, Zablocka M (1989) Tetrahedron 45:337
9. Pietrusiewicz KM, Zablocka M (1988) Tetrahedron Lett 29:1991
10. Brunner H, Limmer S (1991) J Organomet Chem 417:173
11. Cavalla D, Warren S (1982) Tetrahedron Lett 23:4505
12. Brunner H, Limmer S (1991) J Organomet Chem 413:55
13. Pietrusiewicz KM, Zablocka M (1988) Tetrahedron Lett 29:937
14. Keck GE, Byers JH, Tafesh AM (1988) J Org Chem 53:1127
15. Brandi A, Cicchi S, Goti A (1991) Tetrahedron Lett 32:3265
16. Han L-B, Mirzael F, Zhao C-Q, Tanaka M (2000) J Am Chem Soc 122:5407
17. Zhao C-Q, Han L-B, Tanaka M (2000) Organometallics 19:4196
18. Zhao C-Q, Han L-B, Coto M, Tanaka M (2001) Angew Chem Int Ed 40:1929
19. Han L-B, Hua R, Tanaka M (1998) Angew Chem Int Ed 37:94
20. Han L-B, Zhang C, Yazawa H, Shimada S (2004) J Am Chem Soc 126:5080
21. Han L-B, Zhao C-Q, Tanaka M (2001) J Org Chem 66:5929
22. Iwasawa Y (1986) Tailored metal catalysts. Reidel D Publishing Company, Dordrecht
23. Poliakoff M, Fitzpatrick JM, Farren TR, Anastas PT (2002) Science 297:807
24. Kirschnig A, Monenschein H, Wittenberg R (2001) Angew Chem Int Ed 40:650
25. Sander AJ, Reek JNH, Kamer PCJ, van Leeuwen PWNM (2001) J Am Chem Soc 123:8468
26. Merckle C, Blumel J (2003) Adv Synth Catal 345:584
27. Zhou W, He DH (2009) Green Chem 11:1146
28. Bourque SC, Mlatais F, Xiao WJ, Tardif O, Alper H, Arya P, Manzer LE (1999) J Am Chem Soc 121:3035
29. Marras F, Wang J, Coppens MO, Reek JNH (2010) Chem Commun 46:6587
30. Sayah R, Framery E, Dufaud V (2009) Green Chem 11:1694
31. Marciniec B, Szubert K, Fiedorow R, Kownacki I, Potrzebowski MJ, Dutkiewicz M, Franczyk A (2009) J Mol Catal A Chem 310:9
32. Balcar H, Sedlacek J, Cejka J, Vohlidal J (2002) Macromol Rapid Commun 23:32
33. Yang Y, Rioux RM (2011) Chem Commun 47:6557
34. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Nature 359:710
35. Taguchi A, Schuth F (2005) Micropor Mesopor Mater 77:1
36. Martin-Aranda RM, Cejka J (2010) Top Catal 53:141
37. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL (1992) J Am Chem Soc 114:10834
38. Zhou W, Thomas JM, Shephard DS, Johnson BFG, Ozkaya D, Maschmeyer T, Bell RG, Ge Q (1998) Science 280:705
39. Maschmeyer T, Rey F, Sankar G, Thomas JM (1995) Nature 378:159
40. Liu C-J, Li S-G, Pang W-Q, Che C-M (1997) Chem Commun 65
41. Shyu S-G, Cheng S-W, Tzou D-L (1999) Chem Commun 2337
42. Lim MH, Stein A (1999) Chem Mater 11:3285
43. Han L-B, Chol N, Tanaka M (1996) Organometallics 15:3259
44. Lempers HEB, Sheldon RA (1998) J Catal 175:62