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Note

Highly regio- and stereoselective hydrophosphinylation of acetylenes with diphenylphosphine oxide catalyzed by immobilization of rhodium in MCM-41

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ABSTRACT

Highly regio- and stereoselective hydrophosphinylation of a wide range of acetylenes with diphenylphosphine oxide was achieved in toluene at 70 °C in the presence of 2 mol% of an MCM-41-immobilized bidentate phosphine rhodium complex [MCM-41-2P-RhCl(PPh_3)], yielding a variety of (*E*)-alkenylphosphine oxides in good to excellent yields. This heterogeneous rhodium catalyst can be easily recovered and recycled by a simple filtration of the reaction solution and used for at least 10 consecutive trials without significant loss of activity or selectivity.

1. Introduction

Alkenyl di(phenyl)phosphine oxides are useful synthetic intermediates for the preparation of various phosphine ligands and present in numerous biologically active products [1–6]. In addition, the addition of a variety of heteroatom nucleophiles such as alcohols [7], thiols [8], primary and secondary amines [9–11], and phosphines [12] to alkenylphosphine oxides was readily achieved to give useful 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 P–H bonds to acetylenes has provided a new and clean methodology for the preparation of alkenylphosphorus compounds [16–22], but some transformations result in a mixture of *E*/*Z* configurations, and it is difficult to obtain one single product [17,18]. Yorimitsu et al. described rhodium-catalyzed reaction of 1-alkenylphosphines with water yielding (*E*)-1-alkenylphosphine oxides in moderate to good yields, but the scope of substrates is limited [23]. Very recently, Yang et al. reported Cu(I)-catalyzed decarboxylative coupling of various (*E*)-cinnamic-acid derivatives with diphenylphosphine oxide to afford stereoselectively the corresponding (*E*)-1-alkenylphosphine oxides in good yields, but the reaction of vinyl carboxylic acids did not occur [24]. The rhodium-catalyzed hydrophosphinylation of acetylenes with diphenylphosphine oxide has provided a convenient and clean method for the regio- and stereoselective preparation of (*E*)-alkenylphosphine oxides [19–22]. 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. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. 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 [25,26]. So far, supported palladium catalysts have successfully been used for the Heck reaction, the Suzuki–Miyaura reaction, the Sonogashira reaction, and the Stille reaction, etc [27–29]. However, carbon–carbon bond or carbon–heteroatom bond formation reactions catalyzed by heterogeneous rhodium complexes have received less attention [30–34].

Developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [35]. MCM-41 has a regular pore diameter

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of ca. 5 nm and a specific surface area >700 $m^2 g^{-1}$ [36]. 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 [37–39]. 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 complex catalyst will exhibit high activity and good reusability. Shyu et al. 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 [40]. Wagner et al. reported Al-MCM-41-immobilized chiral phosphine rhodium complexes for enantioselective hydrogenation [41]. Huang et al. described the synthesis of aminated MCM-41-tethered rhodium complexes and their catalytic properties in the hydroformylation reaction of 1-hexene [42]. However, to the best of our knowledge, no hydrophosphinylation of acetylenes with diphenylphosphine oxide catalyzed by an MCM-41-immobilized phosphine rhodium complex has been reported until now. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesize a new diphosphino-functionalized MCM-41-immobilized rhodium(I) complex [MCM-41-2P-RhCl(PPh_3)], which was used as an effective rhodium catalyst for the hydrophosphinylation reaction of acetylenes with diphenylphosphine oxide.

2. Experimental

2.1. General remarks

Acetylenes are either commercially available or prepared by a reported procedure [43]. The diphosphino-functionalized mesoporous material MCM-41-2P was prepared according to our previous procedure, the phosphine content was 1.44 mmol/g [44]. Other chemicals were reagent grade and used as purchased. 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. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker ARX-300 instrument (300 MHz for ^1H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P NMR spectroscopy). Unless otherwise noted, $CDCl_3$ was used as the solvent. Chemical shift values for ^1H and ^{13}C are referenced to Me_4Si (0 ppm), and these for ^{31}P are referenced to H_3PO_4 (85% solution in D_2O, 0 ppm). ^{31}P one-pulse experiments were performed on a Bruker AMX 400 spectrometer at a ^{31}P frequency of 161.98 MHz at room temperature. Chemical shifts were referenced to Na_2HPO_4 at 0 ppm. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. Melting points were not corrected.

2.2. Preparation of the MCM-41-2P-RhCl(PPh_3)

To a solution of $RhCl(PPh_3)_3$ (1.109 g, 1.2 mmol) in benzene (50 mL) was added MCM-41-2P (2.04 g). The mixture was stirred under an argon atmosphere at 25 °C for 48 h. The solid product was filtered by suction, washed with benzene (5 × 10 mL), and dried at 70 °C/26.7 Pa under an argon atmosphere for 3 h to give 2.34 g of the light yellow rhodium complex [MCM-41-2P-RhCl(PPh_3)]. The phosphine and rhodium content was 1.74 mmol/g and 0.39 mmol/g, respectively.

2.3. General procedure for hydrophosphinylation reaction of terminal acetylenes with diphenylphosphine oxide

A mixture of terminal acetylene (1.0 mmol), diphenylphosphine oxide (1.0 mmol), toluene (3 mL), and the MCM-41-2P-RhCl(PPh_3) complex (51 mg, 0.02 mmol of Rh) was stirred under Ar in an oil bath at 70 °C for 3–12 h. The mixture was cooled, diluted with Et_2O (30 mL) and filtered. The MCM-41-2P-RhCl(PPh_3) complex was washed with EtOH (2 × 5 mL) and Et_2O (2 × 5 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).

2.3.1. (E)-1-(Diphenylphosphinyl)-1-octene, **3a**

White solid, mp 70–71 °C (lit [45]. mp 68–69 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.67 (m, 4H), 7.54–7.44 (m, 6H), 6.78–6.69 (m, 1H), 6.22 (dd, J = 17.2, J_{HP} = 24.4 Hz, 1H), 2.32–2.27 (m, 2H), 1.49–1.44 (m, 2H), 1.35–1.20 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 153.0 (J_{CP} = 2.0 Hz), 133.1 (J_{CP} = 105.3 Hz), 131.7 (J_{CP} = 3.1 Hz), 131.3 (J_{CP} = 10.1 Hz), 128.5 (J_{CP} = 12.0 Hz), 121.9 (J_{CP} = 103.1 Hz), 34.5 (J_{CP} = 17.1 Hz), 31.5, 28.8, 27.8, 22.5, 14.0 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.9 ppm.

2.3.2. (E)-1-(Diphenylphosphinyl)-1-hexene, **3b**

White solid, mp 65–66 °C (lit [46]. mp 64–65 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.67 (m, 4H), 7.54–7.45 (m, 6H), 6.77–6.68 (m, 1H), 6.23 (dd, J = 16.8, J_{HP} = 24.4 Hz, 1H), 2.31–2.28 (m, 2H), 1.49–1.43 (m, 2H), 1.38–1.30 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 152.9, 133.2 (J_{CP} = 104.3 Hz), 131.7 (J_{CP} = 2.1 Hz), 131.3 (J_{CP} = 10.0 Hz), 128.5 (J_{CP} = 12.1 Hz), 121.5 (J_{CP} = 103.3 Hz), 34.2 (J_{CP} = 17.0 Hz), 30.0, 22.3, 13.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.8 ppm.

2.3.3. (E)-1-(Diphenylphosphinyl)-3,3-dimethyl-1-butene, **3c**

White solid, mp 156–157 °C (lit [19]. mp 157–158 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.65 (m, 4H), 7.51–7.41 (m, 6H), 6.75 (dd, J = 17.4, J_{HP} = 24.7 Hz, 1H), 6.10 (dd, J = 17.4, J_{HP} = 20.4 Hz, 1H), 1.09 (s, 9H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.4, 133.4 (J_{CP} = 104.5 Hz), 131.5 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 10.4 Hz), 128.4 (J_{CP} = 11.4 Hz), 116.5 (J_{CP} = 103.5 Hz), 35.2 (J_{CP} = 14.5 Hz), 28.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 24.2 ppm.

2.3.4. (E)-1-(Diphenylphosphinyl)-2-phenylethene, **3d**

White solid, mp 167–168 °C (lit [45]. mp 168–169 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.74 (m, 4H), 7.56–7.47 (m, 9H), 7.39–7.37 (m, 3H), 6.84 (dd, J = 17.6, J_{HP} = 22.4 Hz, 1H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.6 (J_{CP} = 3.1 Hz), 135.1 (J_{CP} = 17.0 Hz), 132.9 (J_{CP} = 105.1 Hz), 131.9 (J_{CP} = 3.1 Hz), 131.4 (J_{CP} = 10.0 Hz), 130.1, 128.8 (J_{CP} = 17.1 Hz), 128.6, 127.8, 119.2 (J_{CP} = 104.5 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 24.4 ppm.

2.3.5. (E)-1-(Diphenylphosphinyl)-4-hydroxy-1-butene, **3e**

Colorless oil [45]. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.66 (m, 4H), 7.52–7.45 (m, 6H), 6.79–6.68 (m, 1H), 6.33 (dd, J = 17.2, J_{HP} = 24.4 Hz, 1H), 3.73 (t, J = 6.0 Hz, 2H), 3.19 (br, 1H), 2.54–2.48 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 149.8, 132.8 (J_{CP} = 105.1 Hz), 131.8 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 10.0 Hz), 128.6 (J_{CP} = 12.1 Hz), 123.8 (J_{CP} = 102.3 Hz), 60.5, 37.8 (J_{CP} = 16.7 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 24.3 ppm.

2.3.6. (E)-1-(Diphenylphosphinyl)-4-methoxy-1-butene, **3f**

White solid, mp 85–86 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.67 (m, 4H), 7.55–7.44 (m, 6H), 6.73–6.68 (m, 1H), 6.32 (dd, J = 16.8, J_{HP} = 24.4 Hz, 1H), 3.52 (t, J = 6.6 Hz, 2H), 3.34 (s, 3H), 2.60–2.56 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 149.0,

132.8 (J_{CP} = 105.1 Hz), 131.8 (J_{CP} = 3.1 Hz), 131.3 (J_{CP} = 10.0 Hz), 128.5 (J_{CP} = 12.1 Hz), 123.7 (J_{CP} = 102.5 Hz), 70.6, 58.7, 34.8 (J_{CP} = 17.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.7 ppm. Anal. Calcd for $C_{17}H_{19}O_2P$: C, 71.31; H, 6.69. Found: C, 71.10; H, 6.44.

2.3.7. (E)-4-(Diphenylphosphinyl)-3-butenyl 2,2-dimethylpropanoate, ***3g***

White solid, mp 104–105 °C (lit [19]. mp 103–104 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.62 (m, 4H), 7.52–7.41 (m, 6H), 6.74–6.63 (m, 1H), 6.30 (dd, J = 17.1, J_{HP} = 24.0 Hz, 1H), 4.18 (t, J = 6.4 Hz, 2H), 2.65–2.59 (m, 2H), 1.09 (s, 9H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 178.5, 147.7, 132.5 (J_{CP} = 105.5 Hz), 131.8 (J_{CP} = 3.1 Hz), 131.2 (J_{CP} = 9.3 Hz), 128.6 (J_{CP} = 12.4 Hz), 124.5 (J_{CP} = 102.4 Hz), 62.2, 38.8, 33.6 (J_{CP} = 17.6 Hz), 27.2 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.2 ppm.

2.3.8. (E)-5-Chloro-1-(diphenylphosphinyl)-1-pentene, ***3h***

White solid, mp 92–93 °C (lit [19]. mp 93–94 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.63 (m, 4H), 7.51–7.40 (m, 6H), 6.70 (ddt, J = 6.4, 17.1, J_{HP} = 19.2 Hz, 1H), 6.29 (dd, J = 17.1, J_{HP} = 24.4 Hz, 1H), 3.53–3.50 (m, 2H), 2.45–2.43 (m, 2H), 1.93–1.90 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 150.5, 133.1 (J_{CP} = 104.5 Hz), 131.9 (J_{CP} = 2.1 Hz), 131.3 (J_{CP} = 10.3 Hz), 128.7 (J_{CP} = 11.6 Hz), 122.8 (J_{CP} = 102.5 Hz), 44.1, 31.6 (J_{CP} = 16.5 Hz), 30.6 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.1 ppm.

2.3.9. (E)-5-Cyano-1-(diphenylphosphinyl)-1-pentene, ***3i***

White solid, mp 64–65 °C (lit [45]. mp 65–66 °C). ^{1}H NMR (300 MHz, C_6D_6): δ = 7.77–7.39 (m, 10H), 6.71–6.59 (m, 1H), 6.31 (dd, J = 17.0, J_{HP} = 24.2 Hz, 1H), 2.45–2.37 (m, 2H), 2.31 (t, J = 7.0 Hz, 2H), 1.84–1.75 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 149.0 (J_{CP} = 2.1 Hz), 132.9 (J_{CP} = 92.0 Hz), 131.9 (J_{CP} = 2.8 Hz), 131.2 (J_{CP} = 10.0 Hz), 128.6 (J_{CP} = 12.1 Hz), 124.4 (J_{CP} = 101.4 Hz), 119.1, 32.9 (J_{CP} = 7.1 Hz), 23.7, 16.6 ppm. ^{31}P NMR (121.5 MHz, C_6D_6): δ = 22.6 ppm.

2.3.10. (E)-1-(Diphenylphosphinyl)-2-(4-methylphenyl)ethene, ***3j***

White solid, mp 205–206 °C (lit [45]. mp 203–204 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.73 (m, 4H), 7.53–7.51 (m, 2H), 7.49–7.41 (m, 7H), 7.18 (d, J = 8.0 Hz, 2H), 6.78 (dd, J = 17.1, J_{HP} = 22.4 Hz, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 147.5 (J_{CP} = 3.0 Hz), 140.4, 133.5 (J_{CP} = 105.2 Hz), 132.4 (J_{CP} = 18.1 Hz), 131.9 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 10.1 Hz), 129.5 (J_{CP} = 81.5 Hz), 128.4 (J_{CP} = 10.0 Hz), 127.7, 118.3 (J_{CP} = 105.5 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 24.7 ppm.

2.3.11. (E)-3-(Dibutylamino)-1-(diphenylphosphinyl)-1-propene, ***3k***

White solid, mp 85–86 °C (lit [19]. mp 84–86 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.63 (m, 4H), 7.50–7.40 (m, 6H), 6.74–6.65 (m, 1H), 6.50 (dd, J = 17.1, J_{HP} = 24.2 Hz, 1H), 3.27 (br, 2H), 2.41 (t, J = 7.6 Hz, 4H), 1.41–1.35 (m, 4H), 1.28–1.20 (m, 4H), 0.84 (t, J = 7.6 Hz, 6H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 150.2, 133.1 (J_{CP} = 104.5 Hz), 131.7 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 10.4 Hz), 128.5 (J_{CP} = 12.4 Hz), 123.6 (J_{CP} = 104.5 Hz), 57.1 (J_{CP} = 17.6 Hz), 54.3, 29.4, 20.7, 14.0 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.8 ppm.

2.3.12. (E)-1-(Diphenylphosphinyl)-3-trimethylsilylpropene, ***3l***

White solid, mp 88–89 °C (lit [19]. m.p. 89–90 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.65 (m, 4H), 7.49–7.41 (m, 6H), 6.69 (ddt, J = 8.6, 16.7, J_{HP} = 19.6 Hz, 1H), 6.02 (dd, J = 16.7, J_{HP} = 24.4 Hz, 1H), 1.83 (d, J = 8.6 Hz, 2H), 0.13 (s, 9H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 150.9, 133.7 (J_{CP} = 104.5 Hz), 131.6 (J_{CP} = 3.0 Hz), 131.3 (J_{CP} = 10.3 Hz), 128.6 (J_{CP} = 12.4 Hz), 119.2 (J_{CP} = 106.5 Hz), 27.5 (J_{CP} = 16.6 Hz), −1.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 23.8 ppm.

2.3.13. (E)-1-(Diphenylphosphinyl)-2-trimethylsilylethene, ***3m***

White solid, mp 114–115 °C (lit [19]. mp 113–114 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.64 (m, 4H), 7.52–7.44 (m, 6H), 7.25 (dd, J = 20.4, J_{HP} = 29.5 Hz, 1H), 6.83 (dd, J = 20.4, J_{HP} = 32.6 Hz, 1H), 0.13 (s, 9H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 155.2 (J_{CP} = 5.1 Hz), 137.0 (J_{CP} = 91.0 Hz), 132.7 (J_{CP} = 102.5 Hz), 131.8, 131.4 (J_{CP} = 9.1 Hz), 128.6 (J_{CP} = 12.1 Hz), −1.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 22.9 ppm.

2.3.14. (E)-1-(Diphenylphosphinyl)-2-(2-thienyl)ethene, ***3n***

Pale yellow solid, mp 143–145 °C (lit [19]. mp 145–146 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.70 (m, 4H), 7.62–7.41 (m, 7H), 7.33 (d, J = 4.9 Hz, 1H), 7.16 (d, J = 3.4 Hz, 1H), 7.07–6.89 (m, 1H), 6.57 (dd, J = 17.1, J_{HP} = 21.3 Hz, 1H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 140.9 (J_{CP} = 20.7 Hz), 139.9, 132.9 (J_{CP} = 106.6 Hz), 131.9 (J_{CP} = 2.1 Hz), 131.3 (J_{CP} = 9.3 Hz), 130.2, 128.6 (J_{CP} = 12.4 Hz), 128.1, 128.0, 117.8 (J_{CP} = 106.6 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 24.1 ppm.

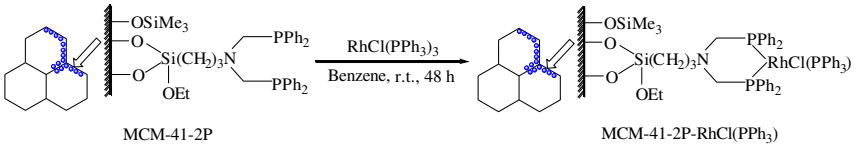
2.3.15. (E)-1-(Cyclohexen-1-yl)-2-(diphenylphosphinyl)ethene, ***3o***

White solid, mp 126–127 °C (lit [19]. mp 126–128 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.57 (m, 4H), 7.42–7.30 (m, 6H), 6.92 (dd, J = 17.4, J_{HP} = 19.5 Hz, 1H), 5.98 (dd, J = 17.4, J_{HP} = 22.4 Hz, 1H), 5.96 (br, 1H), 2.08–2.05 (m, 4H), 1.61–1.55 (m, 2H), 1.51–1.46 (m, 2H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 151.1 (J_{CP} = 4.1 Hz), 137.9, 135.2 (J_{CP} = 17.6 Hz), 133.4 (J_{CP} = 105.5 Hz), 131.6 (J_{CP} = 2.0 Hz), 131.3 (J_{CP} = 9.3 Hz), 128.4 (J_{CP} = 11.4 Hz), 114.5 (J_{CP} = 106.6 Hz), 26.3, 24.1, 22.1, 22.0 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 25.2 ppm.

3. Results and discussion

3.1. Synthesis and characterization of MCM-41-2P-RhCl(PPh_3)

The novel MCM-41-immobilized bidentate phosphine rhodium complex [MCM-41-2P-RhCl(PPh_3)] was conveniently synthesized by the reaction of diphosphino-functionalized MCM-41 (MCM-41-2P) with RhCl(PPh_3)$_3$ (Scheme 1). Small angle X-ray powder diffraction (XRD) analysis of the MCM-41-2P-RhCl(PPh_3) indicated that, the (100) reflection of MCM-41-2P-RhCl(PPh_3) had lower intensity compared to that of the parent MCM-41, 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. Therefore, the basic structure of the parent MCM-41 was not damaged in the whole process of catalyst preparation. Elemental



Scheme 1. Preparation of MCM-41-2P-RhCl(PPh_3) complex.

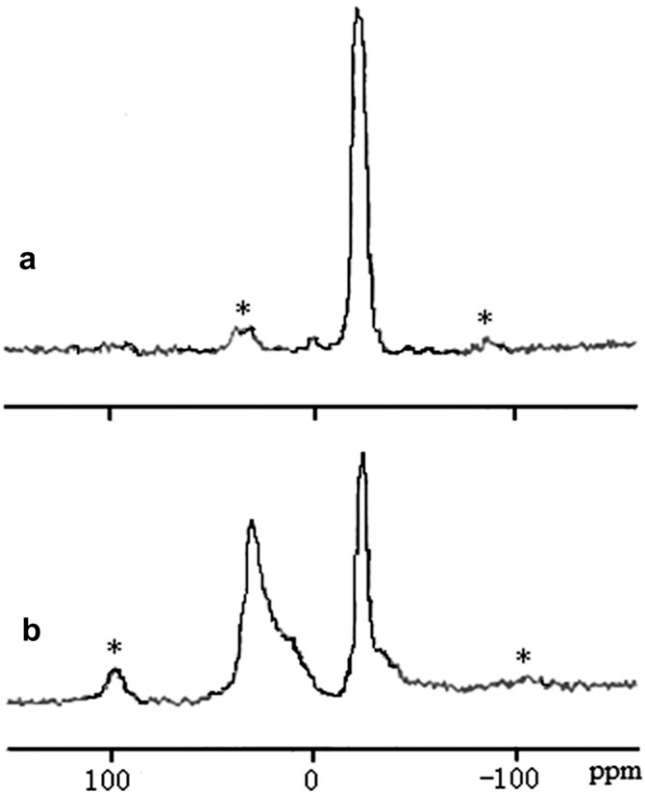


Fig. 1. Solid state ^{13}P NMR spectra of (a) MCM-41-2P and (b) MCM-41-2P-RhCl(PPh_3). Signals arising from side bands are marked with asterisks.

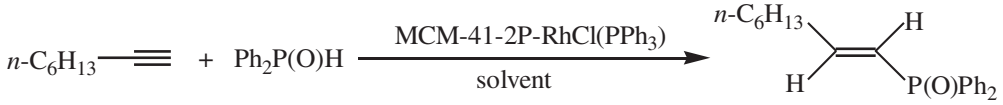
analyses and solid state ^{31}P NMR were used to characterize the supported rhodium complex [MCM-41-2P-RhCl(PPh_3)]. The P:Rh mole ratio of the MCM-41-2P-RhCl(PPh_3) was determined to be 4.5. Blumel et al. investigated the silica-supported phosphine rhodium complexes by solid state ^{31}P NMR spectroscopy [47,48]. Solid state ^{31}P NMR of MCM-41-2P showed a signal at δ −23.1 ppm, which further indicates that the mesoporous material MCM-41-2P contains phosphorus. Solid state ^{31}P NMR of MCM-41-2P-RhCl(PPh_3) showed three signals at δ −23.1, 12.2, 31.3 ppm, respectively [Fig. 1(b)]. One of these corresponds to the unreacted anchoring ligand while the other two are assigned to the anchoring ligand and triphenylphosphine ligand coordinated to the Rh complex since they are shifted relative to the ^{31}P signal of RhCl(PPh_3)$_3$. However, exact assignments cannot be concluded. These observations indicate that Rh has been successfully immobilized on the mesoporous material MCM-41.

3.2. Heterogeneous hydrophosphinylation reaction of terminal alkynes with diphenylphosphine oxide

In our initial screening experiments, the hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide was investigated to optimize the reaction conditions, and the results are summarized in Table 1. At first, the temperature effect was examined, and a significant temperature effect was observed. For the temperatures evaluated [25, 40, 60, 70, and 80 °C], 70 °C gave the best result and the reaction proceeded very slowly at 25 °C. Other reaction temperatures such as 60 and 80 °C also gave good results. Our next studies focused on the effect of solvent on the model reaction. Among the solvents used [THF, dioxane, benzene, and toluene], toluene was the best choice. Increasing the amount of rhodium catalyst could shorten the reaction time, but didn't 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, excellent result was obtained when the hydrophosphinylation reaction was carried out with 2 mol% of the catalyst in toluene at 70 °C (entry 4).

With this promising result in hand, we started to investigate the scope of this reaction under the optimized conditions. The results are summarized in Table 2. As shown in Table 2, MCM-41-2P-RhCl(PPh_3) complex-catalyzed hydrophosphinylation reaction can be readily applied to a variety of terminal acetylenes, proving to be an efficient and practical method for the regio- and stereoselective synthesis of (*E*)-alkenylphosphine oxides which are not readily available by conventional methods. The hydrophosphinylation reaction of aliphatic terminal acetylenes with $Ph_2P(O)H$ proceeded very smoothly at 70 °C to afford the corresponding (*E*)-alkenylphosphine oxides by the regioselective addition of the phosphorus atom at the terminal carbon of the triple bond in good to excellent yields (entries 1–3, 5–9). The catalytic activity of the MCM-41-2P-RhCl(PPh_3) complex is comparable to that of homogeneous RhBr(PPh_3)$_3$. For example, the hydrophosphinylation of 1-octyne in the presence of 2 mol% of MCM-41-2P-RhCl(PPh_3) in toluene at 70 °C under Ar for 3 h gave a 91% yield of the addition product **3a** (entry 1), the same reaction in the presence of 3 mol% RhBr(PPh_3)$_3$

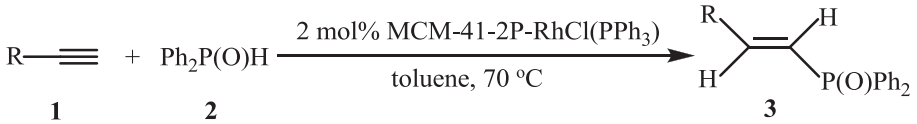
Table 1
Reaction condition screening for the hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide.[a]



Entry	Solvent	Rh catalyst amount (mol%)	Temp. (°C)	Time (h)	Yield[b] (%)
1	Toluene	2.0	25	24	Trace
2	Toluene	2.0	40	24	57
3	Toluene	2.0	60	6	82
4	Toluene	2.0	70	3	91
5	Toluene	2.0	80	2.5	88
6	THF	2.0	60	5	81
7	Benzene	2.0	70	4	86
8	Dioxane	2.0	70	6	72
9	Toluene	4.0	70	2	90
10	Toluene	1.0	70	8	88
11	Toluene	0.5	70	24	85

[a] 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.
[b] Isolated yield.

Table 2
Hydrophosphinylation of terminal acetylenes with $Ph_2P(O)H$ catalyzed by MCM-41-2P-RhCl(PPh_3).[a]



1 **2** **3**

Entry	R	Time (h)	Product	Yield[b] (%)
1	*n*-C_6H_{13}	3	**3a**	91
2	*n*-C_4H_9	3	**3b**	92
3[c]	*t*-C_4H_9	3	**3c**	89
4	Ph	4	**3d**	90
5	$HOCH_2CH_2$	3	**3e**	92
6	$CH_3OCH_2CH_2$	3	**3f**	88
7	*t*-$BuCO_2CH_2CH_2$	6	**3g**	86
8	$ClCH_2CH_2CH_2$	4	**3h**	87
9	$NCCH_2CH_2CH_2$	12	**3i**	91
10	4-$CH_3C_6H_4$	4	**3j**	89
11	*n*-Bu_2NCH_2	10	**3k**	87
12	Me_3SiCH_2	10	**3l**	82
13[d]	Me_3Si	12	**3m**	88
14	Thiophen-2-yl	7	**3n**	91
15	1-Cyclohexenyl	4	**3o**	92

[a] All reactions were performed using 1.0 mmol of terminal acetylene, 1.0 mmol of diphenylphosphine oxide, and 2 mol% MCM-41-2P-RhCl(PPh_3) in 3.0 mL of toluene at 70 °C under Ar.
[b] Isolated yield.
[c] In a sealed tube.
[d] At 60 °C.

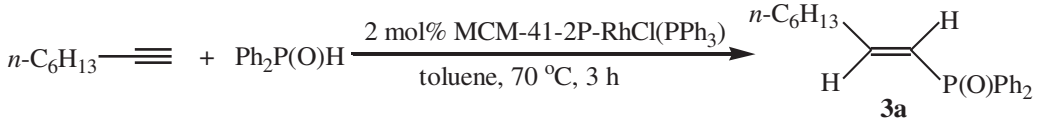
in toluene at 25 °C under Ar for 40 min gave **3a** in 91% yield [19]. Under the above reaction conditions, aromatic terminal acetylenes reacted efficiently with $Ph_2P(O)H$ affording the corresponding (*E*)-alkenylphosphine oxides **3d** and **3j** in high yields (entries 4 and 10). The reactions of propargylic amine and silane with $Ph_2P(O)H$ proceeded readily to afford the desired (*E*)-adducts **3k** and **3l** in good yields (entries 11 and 12). It is obvious that the hydrophosphinylation reaction of acetylenes catalyzed by the MCM-41-2P-RhCl(PPh_3) complex tolerates a variety of functional groups such as chloro, cyano, amino, alkoxycarbonyl, hydroxy, silyl and methoxy. The reaction of 2-ethynylthiophene with $Ph_2P(O)H$ also proceeded efficiently under same reaction conditions to give the desired addition product **3n** in 91% yield (entry 14). The hydrophosphinylation of 1-ethynylcyclohexene occurred exclusively at the triple bond to afford the corresponding (1*E*)-1,3-dienylphosphine oxide **3o** in 92% yield (entry 15). The formation of the *anti*-Markovnikov β-adduct from the hydrophosphinylation of 1-ethynylcyclohexene is noteworthy since the palladium-catalyzed same reaction afforded the Markovnikov α-adduct instead [45]. It can be seen from Table 2 that yields, selectivities, conditions, solvent, substrates, functional group compatibilities, structure of the catalyst in our catalytic system are similar to those reported by Han et al. [19]. We tried to use internal alkynes as substrates, but the hydrophosphinylation reaction under the same conditions did not occur.

A further objective of our studies was to determine whether the catalysis was due to the MCM-41-2P-RhCl(PPh_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 [49]. We focused on the hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide. We filtered off the MCM-41-2P-RhCl(PPh_3) complex after 1 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (70 °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.

3.3. Recycling of the catalyst

For a heterogeneous transition-metal catalyst, it is very important to examine its ease of separation, good of recoverability and reusability. The MCM-41-2P-RhCl(PPh_3) complex can be easily recovered by a simple filtration of the reaction solution and washed with ethanol and diethyl ether. After being air-dried, it can be reused directly in the next run without further purification. In

Table 3
Hydrophosphinylation reaction of 1-octyne with diphenylphosphine oxide catalyzed by recycled catalyst.[a]



3a

Entry	Catalyst cycle	Isolated yield (%)	TON
1	1st	91	45.5
2	10th	89	44.5
3	1st–10th consecutive	Av. 90	Total of 450

[a] The reaction was performed using 1.0 mmol of 1-octyne, 1.0 mmol of diphenylphosphine oxide, and 2 mol% MCM-41-2P-RhCl(PPh_3) in 3.0 mL of toluene at 70 °C for 3 h under Ar.

general, the continuous recycle of resin-immobilized transition-metal catalysts is difficult owing to leaching of the metal species from the polymer supports, which often reduces their activity within five recycles. However, when the reaction of 1-octyne with diphenylphosphine oxide was performed even with 2 mol% of MCM-41-2P-RhCl(PPh_3), the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the 10th recycled catalyst gave **3a** in 89% yield (entry 2, Table 3). The average yield of **3a** in consecutive reactions promoted by the 1st through the 10th recycled catalyst was 90% (entry 3, Table 3). The high stability and excellent reusability of the catalyst should result from the chelating action of the 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(PPh_3) complex make them a highly attractive supported rhodium catalyst for the parallel solution phase synthesis of diverse libraries of compounds.

4. Conclusion

In summary, we have developed a novel, practical and environmentally friendly method for the stereoselective synthesis of (*E*)-alkenylphosphine oxides through the addition reaction of $Ph_2P(O)H$ to terminal acetylenes by using MCM-41-immobilized bidentate phosphine rhodium complex [MCM-41-2P-RhCl(PPh_3)] as catalyst under mild reaction conditions. The reactions generated the corresponding (*E*)-alkenylphosphine oxides regio- and stereoselectively in good to excellent yields. This heterogeneous rhodium catalyst could be easily recovered and recycled by a simple filtration of the reaction solution and reused for 10 cycles without significant loss of activity or selectivity, thus making this procedure environmentally more acceptable.

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