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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,