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A facile synthesis of terminal arylacetylenes via Sonogashira coupling reactions catalyzed by MCM-41-supported mercapto palladium(0) complex

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Abstract

A variety of terminal arylacetylenes have been conveniently synthesized in good to high yields via Sonogashira coupling of aryl iodides with (trimethylsilyl)acetylene catalyzed by MCM-41-supported mercapto palladium(0) complex, followed by desilylation under mild conditions. This polymeric palladium catalyst can be reused many times without any decrease in activity.

Keywords: Sonogashira coupling; MCM-41-supported catalyst; Mercapto palladium(0) complex; Terminal arylacetylene; Heterogeneous catalysis

Terminal arylacetylenes are important synthetic intermediates [1] and usually prepared by classical methods such as the Vilsmeier method [2], the halogenation–dehydrohalogenation sequence of vinyl aromatics [3] and ketones [4], and the dehydrohalogenation of β,β-dihalo olefins [5]. However, these methods involve a tedious multistep synthetic procedure and the yields are poor to moderate. The Sonogashira reaction has become an extremely powerful tool for the formation of carbon–carbon bonds [6]. This coupling reaction has been widely applied in organic synthesis since a wide variety of functionality can be tolerated on either partner and the yields of coupled products are high. Lau and coworkers [7] reported that terminal arylacetylenes could be conveniently synthesized in good yields by palladium(0)-catalyzed Sonogashira coupling of aryl halides with (trimethylsilyl)acetylene, followed by desilylation under mild conditions. However, the Sonogashira reaction generally proceeds in the presence of a homogeneous palladium catalyst such as $Pd(PPh_3)_4$, which makes the catalyst recovery a tedious operation and might result in unacceptable palladium contamination of the product. From the standpoint of green chemistry, the development of more environmentally benign conditions for the reaction, for example, the use of a heterogeneous palladium catalyst would be desirable [8]. So far, polymer-supported palladium catalysts have successfully been used for the Heck reaction [9], the Suzuki reaction [10], and the Sonogashira reaction [11]. However, to the best of our knowledge, no report for the Sonogashira coupling of aryl halides with (trimethylsilyl)acetylene has been known using supported palladium

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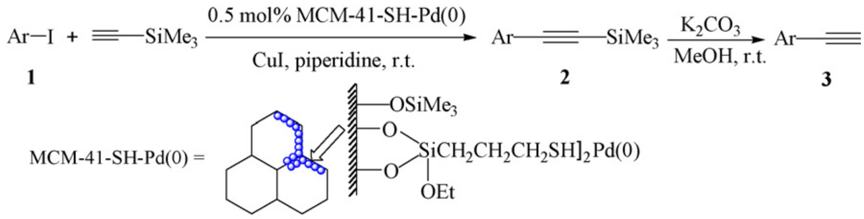

Scheme 1.

catalysts. Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilization of homogeneous catalysts [12]. MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area >700 $m^2 g^{-1}$ [13]. 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 [14]. We have found that MCM-41-supported thioether palladium(0) complex and sulfur palladium(0) complex can efficiently catalyze the Sonogashira coupling reaction [15]. Very recently, we have reported the synthesis of the first MCM-41-supported mercapto palladium(0) complex [abbreviated as MCM-41-SH-Pd(0)] and found that this complex is an efficient and recyclable catalyst for the heterogeneous Suzuki reaction [16]. Herein we wish to report that a variety of terminal arylacetylenes could be conveniently synthesized in good to high yields via Sonogashira coupling of aryl iodides with (trimethylsilyl)acetylene catalyzed by MCM-41-SH-Pd(0), followed by the desilylation under mild conditions (Scheme 1).

1. Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-P300 (300 MHz) spectrometer with TMS as an internal standard (δ in ppm). Mass spectra were determined on a Finnigan 8230 mass spectrometer. IR spectra were obtained on a PerkinElmer 683 instrument. Piperidine was dried and freshly distilled before use. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer.

*1.1. General procedure for the synthesis of 1-aryl-2-(trimethylsilyl)ethynes **2a–l***

Aryl iodide (1.0 mmol), MCM-41-SH-Pd(0) (13 mg, 0.005 mmol Pd), piperidine (3 mL), and CuI (0.05 mmol) were added to a flask under Ar, and the resulting mixture was stirred at room temperature for 5 min. To this suspension was added (trimethylsilyl)acetylene (1.5 mmol), and the reaction mixture was stirred at room temperature for 1–2.5 h. The mixture was dissolved in Et_2O (40 mL). The MCM-41-SH-Pd(0) catalyst was separated from the mixture by filtration, washed with distilled water (2× 10 mL), EtOH (3× 10 mL) and Et_2O (2× 10 mL) and reused in the next run. The ethereal solution was washed with water (2× 10 mL) and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel.

*1.2. General procedure for the synthesis of terminal arylacetylenes **3a–l***

A mixture of 1-aryl-2-(trimethylsilyl) ethyne (1.0 mmol), anhydrous potassium carbonate (0.09 mmol) in anhydrous MeOH (3 mL) was stirred at 25 °C under argon for 3 h. The solvent was evaporated under reduced pressure, and the residue was mixed with 2 mL of aqueous sodium bicarbonate and extracted with Et_2O (3× 10 mL). The combined organic fractions were dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography on silica gel.

2. Results and discussion

The MCM-41-SH-Pd(0) was prepared by our previous procedure [15]. The sulfur and palladium content was 0.81 and 0.38 mmol/g, respectively. The results of MCM-41-SH-Pd(0)-catalyzed cross-coupling of (trimethylsilyl)acetylene with a variety of aryl iodides are summarized in Table 1. As shown in Table 1, the coupling reaction of a variety