Addition of diaryl disulfides to terminal alkynes catalysed by an MCM-41-supported bidentate phosphine palladium(0) complex

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A variety of (*Z*)-1,2-bis(arylthio)-substituted alkenes have been conveniently synthesised in high yields by the stereoselective addition of diaryl disulfides to terminal alkynes catalysed by an MCM-41-supported bidentate phosphine palladium(0) complex. This polymeric palladium catalyst can be recovered and reused many times without any loss of activity.

Keywords: vinylic sulfide, supported catalyst, palladium, MCM-41, catalysis

The development of environmentally friendly synthetic procedures has become a major concern throughout the chemical industry due to continuing depletion of natural resources and growing environmental awareness.[1-4] The high costs of transition-metal catalysts coupled with toxic effects associated with many transition metals has led to an increased interest in immobilising catalysts onto supports. This class of supported reagents can facilitate both the isolation and recycling of the catalysts by simple filtration, thus providing environmentally cleaner processes.[5,6]

Catalytic diaryl disulfide addition to terminal alkynes was discovered by Ogawa, Sonoda and coworkers.[7-9] The products of the addition reaction are of much practical interest in organic chemistry[10-12] and materials science.[13,14] The mechanism of this catalytic reaction has been extensively studied and proceeds via: (1) oxidative addition of the S–S bond to Pd(0); (2) the stereoselective insertion of acetylenes into the Pd–S bond and (3) C–S reductive elimination.[7-9] Recently, Ananikov and Beletskaya reported the solvent-free palladium-catalysed addition of diaryl disulfides to terminal alkynes[15] and palladium-catalysed addition of diaryl disulfides to terminal alkynes under microwave irradiation.[16] The reaction is usually catalysed by homogeneous palladium complexes such as $Pd(PPh_3)_4$. However, the homogeneous palladium catalysts are sensitive to air and moisture and cannot be recovered and reused. We reported that palladium-catalysed addition of diaryl disulfides to terminal alkynes can proceed smoothly in a room temperature ionic liquid ([bmim][PF_6]); high yields and stereoselectivity were observed for various alkynes and the ionic liquid and the palladium catalyst can be recycled four times.[17] Recently, Xu and coworkers described caesium hydroxide-catalysed addition of diaryl disulfides to terminal alkynes with high stereoselectivity and good yields.[18,19] From the standpoint of environmentally benign organic synthesis, development of immobilised palladium catalysts is challenging and important.[20-22] In an ideal system, they can be recovered from the reaction mixture by simple filtration and re-used indefinitely, and contamination of products by palladium is prevented. Beletskaya and coworkers have reported the first example of a polymer-supported palladium catalyst for stereoselective S-S bond addition to terminal alkynes.[23]

Recent developments on the mesoporous material MCM-41 provided a new possible candidate for a solid support for immobilisation of homogeneous catalysts.[24] MCM-41 has a regular pore diameter of *ca.*5 nm and a specific surface area > 700 $m^2\ g^{-1}$.[25] 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.[26-28] It is generally believed that high surface area of heterogeneous catalysts results in high catalytic activity. Considering the fact that MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that MCM-41-supported palladium catalysts will exhibit high activity and good reusability. To date, a few palladium complexes on functionalised MCM-41 supports have been prepared and successfully used in organic reactions.[29-32] Very recently, we have reported the synthesis of the MCM-41-supported bidentate phosphine palladium(0) complex [abbreviated as MCM-41-2P-Pd(0)] and found that this complex is a highly active and recyclable catalyst for Sonogashira reactions of aryl halides.[33] However, to the best of our knowledge, there has been no general study reported of the addition of diaryl disulfides to terminal alkynes catalysed by an MCM-41-supported palladium complex. We now report that a variety of (*Z*)-1,2-bis(arylthio)-substituted alkenes can be conveniently synthesised in high yields by the stereoselective addition of diaryl disulfides to terminal alkynes in the presence of a sub-stoichiometric amount of the MCM-41-supported bidentate phosphine palladium(0) complex [MCM-41-2P-Pd(0)].

MCM-41-2P-Pd(0) was prepared according to our previous procedure.[33] The phosphine and palladium contents were 1.15 and 0.52 mmol g^{-1}, respectively. Initially, to determine the optimum conditions, the addition of diphenyl disulfide to hex-1-yne (1.5 equiv.) was examined under different conditions. We found that, the addition reaction in benzene or toluene in the presence of 2 mol% MCM-41-2P-Pd(0) at 70 °C did not occur. However, the same reaction in toluene at 140 °C under sealed-tube conditions proceeded smoothly and stereoselectively to give (*Z*)-1,2-bis(phenylthio)hex-1-ene (**3a**) in 90% yield. The scope of the reaction was studied for different alkynes and diaryl disulfides (Scheme 1). The experimental results are summarised in Table 1. As shown in Table 1, the addition reactions of diaryl disulfides to a variety of terminal alkynes proceeded very smoothly to give the corresponding (*Z*)-1,2-bis(arylthio)-1- alkenes **3a–k** in high yields with high stereoselectivity (*Z*/*E*>99:1) after 2 hours. The purity of the products **3** was established by ^{1}H NMR, ^{13}C NMR and elemental analysis. The *Z*-configuration of the double bond of products **3** was determined by a 2D NOESY experiment. For example, irradiation of the methylene triplet at δ 2.23 of compound **3a** resulted in a 16% enhancement of the signal at δ 6.54 (vinyl singlet) and irradiation of the methylene triplet at δ 2.50 of compound **3k** resulted in a 18% enhancement of the signal at δ 6.73 (vinyl singlet). The NOE results indicate that compounds **3a** and **3k** have the expected *Z*-configuration. The reaction can tolerate a number of functional groups such as hydroxyl, amino, trimethylsilyl, and methoxyl.

The MCM-41-2P-Pd(0) catalyst can be easily recovered by simple filtration. We also investigated the possibility of reusing of the catalyst by using the addition reaction of diphenyl

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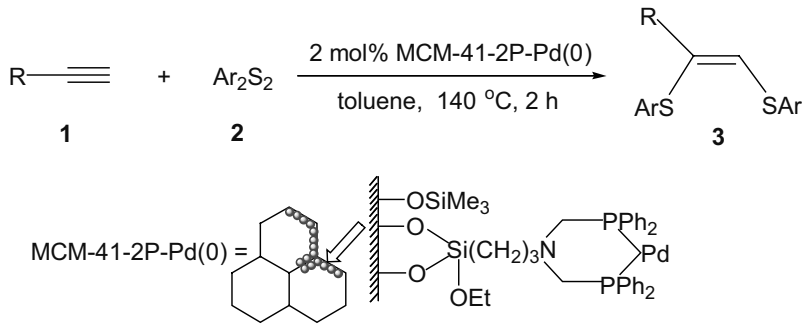

Scheme 1

disulfide to hex-1-yne (1.5 equiv.). In general, the continuous recycling of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within a five-recycle run. However, when 2 mol% of MCM-41-2P-Pd(0) was used in five consecutive runs for the addition of diphenyl disulfide to hex-1-yne (1.5 equiv.), (*Z*)-1,2-bis(phenylthio)-1-hexene (**3a**) was formed in 90, 89, 90, 90 and 88% yields, respectively. The high stability and excellent reusability of the catalyst may result from the chelating action of the bidentate phosphine ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from a practical point of view.

In conclusion, we have described the stereoselective addition of diaryl disulfides to terminal alkynes catalysed by an MCM-41-supported bidentate phosphine palladium(0) complex. High yields and stereoselectivities were observed for various alkynes. Easy product isolation and catalyst recycling are important advantages of the developed methodology.

Experimental

IR spectra were obtained using a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. Mass spectra (EI, 70 eV) were determined on a Finnigan 8230 mass spectrometer. Microanalyses were obtained using a Perkin-Elmer 240 elemental analyser. Benzene and toluene were freshly distilled from sodium before use; other reagents were used as received without further purification.

General procedure for the addition of diaryl disulfides to terminal alkynes

The Ar_2S_2 (1.0 mmol), the terminal alkyne (1.5 mmol) and 3 mL of degassed toluene were combined with the MCM-41-2P-Pd(0) (40 mg, 0.02 mmol) under Ar and the mixture was stirred at 140 °C for 2 h in a sealed tube. After cooling to room temperature, the mixture was filtered and the catalyst was washed with degassed toluene (2 × 5 mL) and reused in the next run. The combined organic solutions were concentrated under reduced pressure, and the residue was purified by preparative TLC on silica gel.

(Z)-1,2-Diphenylthiohex-1-ene (**3a**)**:** Oil. IR (neat): ν (cm^{-1}) 3059, 2957, 2928, 1582, 1478, 1439, 1024, 739, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.20 (m, 10H), 6.54 (s, 1H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.50–1.42 (m, 2H), 1.26–1.20 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 134.3, 133.8, 130.5, 129.7, 129.1, 129.0, 128.9, 126.8, 126.7, 36.8, 30.7, 21.9, 13.8; MS (EI): *m/z* 300 (M$^+$, 97), 147 (100); Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.95; H, 6.71. Found: C, 71.67; H, 6.63%.

(Z)-1,2-Bis[(4-methylphenyl)thio]hex-1-ene (**3b**): Oil. IR (neat): ν (cm^{-1}) 3020, 2956, 2928, 1564, 1491, 1453, 1401, 1091, 1018, 805; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 4H), 7.14–7.09 (m, 4H), 6.46 (s, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.20 (t, *J* = 7.4 Hz, 2H), 1.51–1.41 (m, 2H), 1.25–1.19 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 134.2, 132.4, 131.1, 130.2, 130.1, 129.9, 129.7, 128.7, 36.6, 30.7, 22.0, 21.2, 21.1, 13.9; MS (EI): *m/z* 328 (M$^+$, 65), 195 (100); Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36. Found: C, 72.86; H, 7.15%.

(Z)-2,3-Diphenylthioprop-2-en-1-ol (**3c**)[7]: Oil. IR (neat): ν (cm^{-1}) 3382, 3057, 1716, 1581, 1478, 1439, 1091, 1024, 740, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.21 (m, 10H), 7.03 (s, 1H), 4.14 (s, 2H), 2.01 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 134.7, 133.2, 130.5, 129.9, 129.3, 129.2, 127.5, 127.0, 65.5; MS (EI): *m/z* 274 (M$^+$, 47), 135 (100).

(Z)-2,3-Bis[(4-methylphenyl)thio]prop-2-en-1-ol (**3d**): Oil. IR (neat): ν (cm^{-1}) 3391, 3020, 1714, 1564, 1491, 1091, 1017, 805; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.28 (m, 4H), 7.14–7.09 (m, 4H), 6.89 (s, 1H), 4.09 (s, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 1.98 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.3, 134.3, 131.4, 130.8, 130.6, 130.1, 130.0, 129.4, 65.4, 21.1; MS (EI): *m/z* 302 (M$^+$, 98), 91 (100); Anal. Calcd for $C_{17}H_{18}OS_2$: C, 67.51; H, 6.00. Found: C, 67.33; H, 6.05%.

(Z)-1,2-Bis[(4-methylphenyl)thio]-3-methoxyprop-1-ene (**3e**)**:** Oil. IR (neat): ν (cm^{-1}) 3021, 1714, 1564, 1491, 1119, 1091, 1017, 806; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.30 (m, 4H), 7.16–7.10 (m, 4H), 6.86 (s, 1H), 3.90 (s, 2H), 3.27 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 137.1, 134.1, 131.6, 130.8, 130.7, 129.9, 129.8, 129.6, 127.3, 74.4, 58.0, 21.1; MS (EI): *m/z* 316 (M$^+$, 59), 161 (100); Anal. Calcd for $C_{18}H_{20}OS_2$: C, 68.31; H, 6.37. Found: C, 68.38; H, 6.29%.

Table 1 Addition of Ar_2S_2 to various acetylenes catalysed by MCM-41-2P-Pd(0)[a]

Entry	R	Ar	Product	Yield[b]/%
1	*n*-C_4H_9	Ph	**3a**	90
2	*n*-C_4H_9	4-$CH_3C_6H_4$	**3b**	91
3	$HOCH_2$	Ph	**3c**	88
4	$HOCH_2$	4-$CH_3C_6H_4$	**3d**	85
5	CH_3OCH_2	4-$CH_3C_6H_4$	**3e**	87
6	Ph	4-$CH_3C_6H_4$	**3f**	89
7	*n*-C_6H_{13}	4-$CH_3C_6H_4$	**3g**	92
8	H_2NCH_2	Ph	**3h**	86
9	*n*-C_6H_{13}	Ph	**3i**	93
10	Me_3Si	Ph	**3j**	90
11	$HOCH_2CH_2$	Ph	**3k**	89

[a]Reactions were conducted under the conditions of 1.5 mmol of acetylene **1** and 1.0 mmol of Ar_2S_2 **2** in the presence of MCM-41-2P-Pd(0) (2 mol%) in toluene (3 mL) at 140 °C for 2 h.
[b]Isolated yield based on the Ar_2S_2 **2** used.

(Z)-1,2-Bis[(4-methylphenyl)thio]styrene (**3f**)**:** Oil. IR (neat): ν (cm^{-1}) 3020, 1714, 1539, 1490, 1091, 1017, 803; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–6.97 (m, 14H), 2.35 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 137.7, 136.8, 135.8, 131.8, 131.1, 131.0, 130.0, 129.6, 129.2, 128.6, 128.3, 127.4, 126.8, 21.1, 21.0; MS (EI): *m/z* 348 (M^+, 47), 123 (100); Anal. Calcd for $C_{22}H_{20}S_2$: C, 75.82; H, 5.78. Found: C, 75.57; H, 5.63%.

(Z)-1,2-Bis[(4-methylphenyl)thio]oct-1-ene (**3g**)**:** Oil. IR (neat): ν (cm^{-1}) 3020, 2956, 2926, 1563, 1492, 1455, 1400, 1091, 1017, 806; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.26 (m, 4H), 7.14–7.09 (m, 4H), 6.44 (s, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.19 (t, J = 7.4 Hz, 2H), 1.50-1.43 (m, 2H), 1.26-1.15 (m, 6H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.9, 134.4, 132.5, 131.2, 130.1, 129.9, 129.8, 129.7, 128.5, 36.9, 31.5, 28.5, 22.5, 21.1, 21.0, 14.1; MS (EI): *m/z* 356 (M^+, 35), 195 (100); Anal. Calcd for $C_{22}H_{28}S_2$: C, 74.10; H, 7.92. Found: C, 73.89; H, 7.78%.

(Z)-2,3-Diphenylthioprop-2-enyl amine (**3h**)[7]**:** Oil. IR (neat): ν (cm^{-1}) 3374, 3055, 1654, 1582, 1478, 816, 745, 691; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.22 (m, 10H), 6.87 (s, 1H), 3.38 (s, 2H), 1.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.2, 133.7, 133.2, 132.1, 130.3, 130.0, 129.2, 129.1, 127.3, 126.9, 47.7; MS (EI): *m/z* 273 (M^+, 100).

(Z)-1,2-Diphenylthiooct-1-ene (**3i**)**:** Oil. IR (neat): ν (cm^{-1}) 3073, 2955, 2927, 1582, 1478, 1439, 1092, 1024, 740, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.19 (m, 10H), 6.56 (s, 1H), 2.24 (t, J = 7.4 Hz, 2H), 1.51–1.45 (m, 2H), 1.26–1.21 (m, 6H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 134.5, 133.9, 130.5, 129.7, 129.1, 129.0, 128.9, 126.8, 126.7, 37.2, 31.5, 28.6, 28.5, 22.6, 14.1; MS (EI): *m/z* 328 (M^+, 95), 147 (100); Anal. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36. Found: C, 73.24; H, 7.29%.

(Z)-1,2-Diphenylthio-1-(trimethylsilyl)ethene (**3j**)[7]**:** Oil. IR (neat): ν (cm^{-1}) 3059, 2953, 2925, 1583, 1478, 1439, 1249, 838, 739; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.13 (m, 11H), 0.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 135.8, 135.2, 130.7, 130.0, 129.2, 128.7, 128.4, 127.5, 125.7, –1.2; MS (EI): *m/z* 316 (M^+, 100).

(Z)-3,4-Diphenylthiobut-3-en-1-ol (**3k**)[7]**:** Oil. IR (neat): ν (cm^{-1}) 3353, 3055, 2931, 1582, 1478, 1439, 1024, 742; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.20 (m, 10H), 6.73 (s, 1H), 3.71 (t, J = 6.4 Hz, 2H), 2.50 (t, J = 6.4 Hz, 2H), 1.69 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 133.4, 133.0, 130.4, 130.1, 129.2, 129.1, 129.0, 127.2, 127.0, 60.8, 40.1; MS (EI): *m/z* 288 (M^+, 29), 135 (100).

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