Copper and ligand free Sonogashira reaction catalyzed by Pd(0) nanoparticles at ambient conditions under ultrasound irradiation

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SUPPORTING INFORMATION

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General Considerations

All sonochemical reactions were carried out in an argon atmosphere. All of the ionic liquids were prepared by the method reported by us.¹ All chemicals were of research grade and used without further purification. The reactions were carried out in a thermostated (30 ± 1 °C) ultrasonic cleaning bath at 50 kHz. The ultrasonic cleaner had an output power of 120 W and a power supply of 450 W. The tank dimensions were 290 x 240 x 150 mm with a liquid holding capacity of 9.5 L. The reactions were carried out in a RB flask of 10 mL capacity suspended at the centre of the cleaning bath, 5 cm below the surface of the liquid. The melting points of the products were uncorrected and compared with the reported literature values. The TEM analysis was carried out in a Transmission Electron Microscope operating at 100 kV at different magnifications varying from 100 to 300 k.

Sample Preparation and TEM analysis

After completion of the reaction a sample is removed from the reaction mixture and after appropriate dilution with isopropyl alcohol was directly deposited on carbon coated 400 mesh Cu TEM grids. TEM pictures of each sample were taken at 100 kV operating voltage at multiple random locations in the sample and at two different magnifications. The size distribution histogram was obtained on the basis of about 100 particles.

TEM Measurements in acetone medium

Fig. 1

Fig. 2

TEM images of Pd(0) nanoparticles in acetone medium at different magnifications

Fig. 3

Fig. 4

Histogram and SAED pattern of Pd(0) nanoparticles in acetone medium

The micrograph shows the presence of polydispersed Pd(0) nanoparticles varying in size from 3-8 nm and of irregular morphology and spherical in shape (Figs. 1 and 2). The average size of the grains obtained from the TEM picture from acetone medium is about 4.18 nm (Fig. 3).

The inset picture of Fig. 4 show the SAED (Selected Area Electron Diffraction) pattern of the palladium nanoparticles in the acetone medium. It is clear from SAED pattern that the Pd particles are polycrystalline in nature and it can be indexed as the (111), (200), (220), (311) allowed reflections from face-centered cubic (fcc) palladium.

TEM Measurements in ionic liquid medium

Fig. 5

Fig. 6

TEM images of Pd(0) nanoparticles in ionic liquid medium at different magnifications

Fig. 7

Fig. 8

Histogram and SAED pattern of Pd(0) nanoparticles in IL medium

In the TEM images (Figs. 5 and 6) obtained from the ionic liquid medium, after the reaction of 1-ethynylbenzene with iodobenzene, it is observed that the palladium nanoparticles are almost spherical in nature and the boundaries are clear. They are well dispersed and the histogram (Fig. 7) shows the size to be in the range of 10-13 nm. The SAED pattern (Fig. 8) indicates the polycrystalline nature of the nanoparticles and can be indexed as the (111), (200), (220), (222), (331) allowed reflections from the fcc palladium.

Experimental

Preparation of Acetylene Derivatives

General Procedure for the Sonogashira Reaction in Acetone medium

A mixture of 4-iodotoluene (1 mmol), 1-ethynylbenzene (1 mmol), PdCl₂ (0.02 mmol) and triethylamine (1.5 mmol) in 5 mL of acetone was sonicated for the appropriate time under argon at 30 °C. The reaction was monitored by TLC, and after completion of reaction, acetone was removed from reaction mixture under reduced pressure. The residue was dissolved in 10% ethyl acetate in petroleum ether (bp 60-80 °C), clarified by filtration through Celite filter bed, and washed with water. The organic layer was separated and dried over anhyd Na₂SO₄ and concentrated in a vacuum. The crude product obtained was further purified by column chromatography through a column of silica gel using petroleum ether (bp 60-80 °C) or an appropriate mixture of petroleum ether and ethyl acetate as eluent to afford the pure product.

General Procedure for the Sonogashira Reaction in [bbim]BF₄

A mixture of 4-iodotoluene (1 mmol), phenylacetylene (1 mmol), PdCl₂ (0.02 mmol), and triethylamine (1.5 mmol) in 2 mL of dry ionic liquid was sonicated for the

appropriate time under argon at 30 °C. The reaction was monitored by TLC, and after completion of reaction, the product was selectively extracted with 10% ethyl acetate in petroleum ether (bp 60-80 °C) from the reaction mixture leaving behind the ionic liquid consisting of the Pd catalyst as an immiscible layer. The hydrophobic ionic liquid layer was washed with water to remove the amine hydrochloride salt, and the ionic liquid was dried under reduced pressure at 60 °C for 30 min and used as such for further reaction. The separated organic layer was dried over anhyd Na_2SO_4 and concentrated in a vacuum. The crude product obtained was further purified by column chromatography through a column of silica gel using petroleum ether (bp 60-80 °C) or an appropriate mixture of petroleum ether and ethyl acetate as eluent to afford the pure product.

Characterization data:

Diphenylacetylene² (Table 1, entry 1): (white solid); mp 60 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.27-7.24 (m, 6H), 7.48-7.43 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 131.6, 128.3, 128.2, 123.3, 89.4. Anal. Calcd for C₁₄H₁₀: C, 94.34; H, 5.66. Found: C, 94.23; H, 5.70.

1-Fluoro-3-(phenylethynyl)benzene³ (Table 1, entry 2): (white solid); mp 36 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.58-7.54 (m, 2H), 7.39-7.31 (m, 5H), 7.27-7.23 (m, 1H), 7.11-7.01 (m, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 162.3 (d, *J* = 246.27), 131.62, 129.8 (d, *J* = 8.42 Hz), 128.4, 128.3, 127.4 (d, *J* = 2.56 Hz), 125.08 (d, *J* = 9.52 Hz), 122.7, 118.3 (d, *J* = 23.05 Hz), 115.5 (d, *J* = 21.22 Hz), 90.2, 88.0 (d, *J* = 2.93 Hz). Anal. Calcd for C₁₄H₉F: C, 85.70; H, 4.62; F, 9.68. Found: C, 85.78; H, 4.54; F, 9.75.

4-(phenylethynyl)toluene² (Table 1, entry 3): (white solid); mp 70 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.45-7.40 (m, 2H), 7.33 (d, *J* = 8.22 Hz, 2H), 7.27-7.21 (m, 3H), 7.05 (d, *J* = 8.22 Hz, 2H), 2.28 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 138.3, 131.5, 131.4, 129.0, 128.8, 128.0, 123.4, 120.1, 89.5, 88.7, 21.6. Anal. Calcd for C₁₅H₁₂: C, 93.71; H, 6.29. Found: C, 93.70; H, 6.29.

1-phenylethynylcyclohexanol⁴ (Table 1, entry 4): (white solid); mp 64 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.44-7.30 (m, 5H), 2.00 (s, 1H), 1.74-1.43 (m, 10 H); ¹³C NMR (CDCl₃, 50 MHz) δ 131.5, 128.0, 127.9, 122.9, 92.9, 84.2, 68.8, 39.9, 25.1, 23.2. Calcd. for C₁₄H₁₆O: C, 83.96; H, 8.05. found: C, 83.92; H, 8.10.

1-Fluoro-3-(phenylethynyl)toluene (Table 1, entry 6): (white solid); mp 61 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.25-7.16 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.02-6.90 (m, 1H), 2.30 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 162.4 (d, *J* = 246.47 Hz), 138.7, 131.5, 130.1 (d, *J* = 9.22 Hz), 129.8 (d, *J* = 9.22 Hz), 129.1, 128.4, 127.3, 125.4 (d, *J* = 11.52 Hz), 119.7, 119.2 (d, *J* = 23.03 Hz), 118.2 (d, *J* = 20.73 Hz), 116.8 (d, *J* = 20.73 Hz), 115.3 (d, *J* = 20.73 Hz), 90.5, 87.5, 21.4. Anal. Calcd for C₁₅H₁₁F: C, 85.69; H, 5.27; F, 9.04. Found: C, 85.63; H, 5.32; F, 9.19.

Di-*p*-tolylacetylene⁵ (Table 1, entry 7): (white solid); mp 139 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.44 (d, *J* = 8Hz, 4H), 7.17 (d, *J* = 8Hz, 4H), 2.38 (s, 6H); ¹³C NMR (CDCl₃, 50 MHz) δ 138.1, 131.3, 129.0, 120.3, 88.8, 21.4. Anal. Calcd for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 93.23; H, 6.70.

1-*p*-Tolylethynylcyclohexanol (Table 1, entry 8): (white solid); mp 103 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.31 (d, *J* = 8.22 Hz, 2H), 7.09 (d, *J* = 8.20 Hz, 2H), 2.34 (s, 3H), 1.98 (s, 1H), 1.73-1.57 (m, 10 H); ¹³C NMR (CDCl₃, 50 MHz) δ 138.0, 131.5, 128.9, 119.8, 92.1, 84.4, 68.9, 40.0, 25.2, 23.4, 21.4. Anal. Calcd for C₁₅H₁₈O: C, 84.07; H, 8.47. Found: C, 84.03; H, 8.52.

1-Nitro-(4-phenylethynyl)benzene⁶ (Table 1, entry 9): (yellow solid); mp 119 °C; ¹H NMR (CDCl₃, 200 MHz) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.57-7.55 (m, 2H), 7.40-7.37 (m, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 146.9, 132.2, 131.8, 130.2, 129.2, 128.5, 123.6, 122.0, 94.6, 87.6. Anal. Calcd for C₁₄H₉NO₂: C, 75.33; H, 4.06. Found: C, 75.27; H, 4.13.

1-Fluoro-3-(phenylethynyl)nitrobenzene (Table 1, entry 10): (pale yellow solid); mp 139 °C; ¹H NMR (CDCl₃, 200 MHz) δ 8.24 (d, *J* = 8.5Hz, 2H), 7.67 (d, *J* = 8.5Hz, 2H), 7.41-7.08 (m 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 162.3 (d, *J* = 247.61 Hz), 147.1, 132.3, 130.1 (d, *J* = 9.60 Hz), 129.5, 127.6 (d, *J* = 3.83 Hz), 123.8 (d, *J* = 9.60 Hz), 123.6, 118.5 (d, *J* = 23.03 Hz), 116.5, (d, *J* = 21.22 Hz), 96.09, 88.19. Anal. Calcd for C₁₄H₈FNO₂: C, 69.71; H, 3.34; F, 7.88; N, 5.81. Found: C, 69.70; H, 3.40; F, 7.79; N, 5.74.

1-Methyl-4-(phenylethynyl)nitrobenzene (Table 1, entry 11): (yellow solid); mp 157 °C; ¹H NMR (CDCl₃, 200 MHz) δ 8.23 (d, *J* = 8.61 Hz, 2H), 7.66 (d, *J* = 7.43 Hz, 2H), 7.42 (d, *J* = 7.44 Hz, 2H), 7.21 (d, *J* = 7.82 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 146.7, 139.6, 132.0, 131.6, 130.4, 129.2, 123.5, 118.9, 95.0, 87.0, 21.5. Anal. Calcd for C₁₅H₁₁NO₂: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.97; H, 4.59; N, 5.82.

1-(4-Nitro-phenylethynyl)cyclohexanol (Table 1, entry 12): (white solid); mp 101 °C; ¹H NMR (CDCl₃, 200 MHz) δ 8.15 (d, *J* = 8.25 Hz, 2H), 7.54 (d, *J* = 8.25 Hz, 2H), 2.01 (s, 1H), 1.76-1.55 (m, 10H); ¹³C NMR (CDCl₃, 50 MHz) δ 146.9, 132.3, 129.8, 123.4, 98.3, 82.4, 69.0, 39.7, 25.0, 23.2. Anal. Calcd for C₁₄H₁₅NO₃: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.48; H, 6.22; N, 5.68.

1-Chloro-4-(phenylethynyl)benzene⁶ (Table 1, entry 13): (white solid); mp 83 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.29-7.23 (m, 5H), 7.48-7.37 (m, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 134.2, 132.7, 131.6, 128.6, 128.4, 128.3, 122.9, 121.8, 90.3, 88.2. Anal. Calcd for C₁₄H₉Cl: C, 79.07; H, 4.27; Cl, 16.67. Found: C, 79.01; H, 4.23; Cl, 16.78.

1-Fluoro-3-(phenylethynyl)chlorobenzene (Table 1, entry 14): (white solid); mp 86 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.39 (d, *J* = 8.33 Hz), 7.31-7.11 (m, 5H), 7.03-6.93 (m, 1H); ¹³C NMR (CDCl₃, 50 MHz) δ 162.4 (d, *J* = 246.48 Hz), 134.6, 132.8, 131.5, 129.9 (d, *J* = 6.91 Hz), 128.7, 128.3, 127.4, 124.8 (d, *J* = 9.21 Hz), 121.31, 118.3 (d, *J* = 23.03 Hz), 115.7 (d, *J* = 20.73 Hz), 89.0 (d, *J* = 9.22 Hz); Anal. Calcd for C₁₄H₈ClF: C, 72.90; H, 3.50; Cl, 15.37; F, 8.24. Found: C, 72.83; H, 3.45; Cl, 15.45; F, 8.19.

1-Chloro-4-(phenylethynyl)toluene⁷ (Table 1, entry 15): (white solid); mp 149 °C; ¹H NMR (CDCl₃, 200 MHz) 7.39-7.32 (m, 4H), 7.26-7.17 (m, 2H), 7.08 (d, *J* = 7.83, 2H Hz), 2.29 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 138.6, 134.0, 132.7, 131.5, 129.1, 128.6, 122.1, 119.9, 90.5, 87.6, 21.4. Anal. Calcd for C₁₅H₁₁Cl: C, 79.47; H, 4.89; Cl, 15.64. Found: C, 79.42; H, 4.91; Cl, 15.59.

1-(4-Chloro-phenylethynyl)cyclohexanol (Table 1, entry 16): (white solid); mp 78 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.31-7.18 (m, 4H), 1.92 (s, 1H), 1.68-1.49 (m, 10 H); ¹³C NMR (CDCl₃, 50 MHz) δ 134.2, 132.6, 128.5, 121.3, 93.8, 83.8, 69.0, 39.9, 25.1, 23.3. Anal. Calcd for C₁₄H₁₅ClO: C, 71.64; H, 6.44; Cl, 15.10. Found: C, 71.58; H, 6.38; Cl, 15.12.

1-(4-Phenylethynyl-phenyl)ethanone² (Table 1, entry 17): (white solid); mp 95-96 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.87 (d, *J* = 8.72 Hz, 2H), 7.54 (d, *J* = 8.59 Hz, 2H), 7.50 - 7.46 (m, 2H), 7.31-7.28 (m, 3H), 2.54 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 197.1, 136.0, 131.6, 131.5, 128.7, 128.3, 128.1, 128.0, 122.5, 92.6, 88.5, 26.4. Anal. Calcd for C₁₆H₁₂O: C, 87.25; H, 5.49. Found: C, 87.31; H, 5.42.

1-[4-(3'-Fluoro-phenylethynyl)-phenyl]ethanone (Table 1, entry 18): (white solid); mp 90-91 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.87 (d, *J* = 8.79 Hz, 2H), 7.53 (d, *J* = 8.06 Hz, 2H), 7.27-6.99 (m, 4H), 2.54 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 197.1, 162.2 (d, *J* = 247.0 Hz), 136.3, 131.6, 129.9 (d, *J* = 8.78 Hz), 128.1, 127.56, 127.50, 124.3 (d, *J* = 9.52 Hz), 118.3 (d, *J* = 23.05 Hz), 116.05 (d, *J* = 21.22 Hz), 91.1, 89.3, 26.4. Anal. Calcd for C₁₆H₁₁FO: C, 80.66; H, 4.65; F, 7.97. Found: C, 80.64; H, 4.66; F, 7.90.

1-(4-*p*-Tolylethynyl-phenyl)ethanone⁸ (Table 1, entry 19): (white solid); mp 126-127 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.86 (d, *J* = 8.59 Hz, 2H), 7.52 (d, *J* = 8.59 Hz, 2H), 7.37 (d, *J* = 8.08 Hz, 2H), 7.10 (d, *J* = 7.83 Hz, 2H), 2.54 (s, 3H), 2.31 (s, 3H); ¹³C NMR (CDCl₃, 50 MHz) δ 197.2, 139.0, 135.9, 131.57, 131.53, 129.1, 128.3, 128.1, 119.4, 92.9, 88.0, 26.5, 21.5. Anal. Calcd for C₁₇H₁₄O: C, 87.15; H, 6.02. Found: C, 87.16; H, 5.98.

1-[4-(1'-Hydroxy-cyclohexylethynyl)-phenyl]ethanone (Table 1, entry 20): (white solid); mp 82-83 °C; ¹H NMR (CDCl₃, 200 MHz) δ 7.88 (d, *J* = 8.79 Hz, 2H), 7.48 (d, *J* = 8.79 Hz, 2H), 2.58 (s, 3H), 1.99 (s, 1H), 1.7-1.54 (m, 10 H); ¹³C NMR (CDCl₃, 50 MHz) δ 197.4, 136.0, 131.7, 128.1, 127.8, 96.3, 83.4, 69.0, 39.8, 26.5, 25.0, 23.2. Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.35; H, 7.44.

Pd-biscarbene Complex [A]⁹: white amorphous powder; ¹H NMR (CDCl₃, 200 MHz) δ 6.81 (s, 4H), 4.52 (t, 8H), 2.08 (m, 8H), 1.47 (m, 8H), 1.01 (t, 12H); ¹³C NMR (CDCl₃, 50 MHz) δ 169.2, 119.8, 50.1, 32.6, 19.6, 13.3. MS: *m/z* 466 [M⁺ - BF₄]. Anal. Calcd for C₁₂H₂₄N₄Pd: C, 43.58; H, 7.31; N, 16.94. Found: C, 43.55; H, 7.27; N, 16.97.

Aromatic region (Entry 2)

4-Methyl diphenylacetylene

6 Dec 2004
Wed-2ac-017
Atul R Ghosh

Aromatic region (Entry 3)

Aromatic region (Entry 6)

Entry 6

25 Dec 2004
F14 av2#005
Dr Lahoti, IH

Aromatic region (Entry 9)

6 Dec 2004
Fri-2ao-032
Atul R Ghosh

3 Dec 2004
Atul R Ghalap

4-Chloro-diphenylacetylene

Aromatic region (Entry 13)

4-Chloro-3'-fluoro-diphenylacetylene

Aromatic region (Entry 14)

Aromatic region (Entry 15)

15 Feb 2005
atul ghosh

Aromatic region (Entry 19)

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