Supplementary Material (ESI) for Chemical Communications

A novel Heck reaction catalyzed by Co hollow nanospheres in ligand-free condition

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Experimental

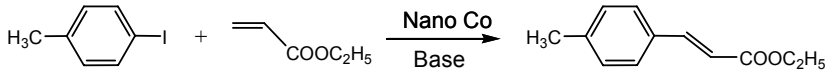
Reagents and instruments

The reagents used in the experiments were bought from Aldrich or the Shanghai Chemical Reagent Company. The characterization of the Co hollow nanospheres was performed by means of X-ray diffraction (XRD) using a D/Max-RA diffractometer with Cu Kα radiation, transmission electron microscopy (JEM-200CX TEM, working at 100 KV). Energy dispersive spectroscopy (EDS) was performed on the microscope with a PV9100 scanning electron microanalyzer. For the structural determination of the Heck reaction products, ^{1}H NMR spectra were determined on a Bruker AV 300 or AV 400 spectrometer (300 or 400 MHz) with TMS as the internal standard. FTIR spectra were obtained with a Nexus 670 spectrometer. MS spectra were determined on a Varian 3800 GC-MS apparatus. Melting points are uncorrected.

Synthesis and characterization of nano-sized Co hollow spheres

In a typical experiment, 5.0 g polyethylene glycol (0.25 mmol) was first dissolved into the 20 mL of deionized water to form solution A. Then 0.056g $CoSO_4 \cdot 7H_2O$ (0.2 mmol), 0.025g NH_4F (0.675 mmol) and 0.125g H_3BO_3 (2.02 mmol) were dissolved in the 10 mL of solution A to form solution B, and 0.006g $NaBH_4$ (0.159 mmol) was added into the 6 mL of solution A to form solution C. Then, the solution B was injected slowly into the solution C within 5 min under sonication at 30 ^oC. During the injection, the color of the mixture turned from pink to black gradually. After the injection was complete, the mixture was sonicated continuously for 10 min. Finally, the mixture was separated by centrifugation. The deposit was collected, washed with deionized water and ethanol several times, then dried to give the Co hollow spheres.

The affection of solvent and base to the Heck reaction[a]



Entry	Solvent	Base	Yield(%)
1	*p*-xylene	K_2CO_3	25
2	DMF	K_2CO_3	60
3	DMF	KOH	52
4	NMP	K_2CO_3	85
5	NMP	Na_2CO_3	70
6	NMP	KOH	78
7	NMP	NaOH	72

[a] Aryl halide (1 mmol), alkene (1.3 mmol), base (0. 6 mmol), Co (0.02 mmol) in 2 mL solvent at 130 °C with stirring for 10 hrs.

General procedure of Co nanoparticles catalyzed Heck reaction

To 2 mL of NMP were added 1 mmol of aryl halide and 1.3 mmol of alkene, then 0.02 mmol of cobalt nanoparticle and 0. 6 mmol of K_2CO_3 were added in turn. The mixture was stirred at 130 °C under nitrogen atmosphere for an appropriate time (see Table 1, monitored by TLC) till the reaction was complete, then centrifuged. The solution was separated and the precipitate was washed with ether (5 mL x 3). The solutions were combined and washed with water for three times. The product was then yielded by column chromatography on silica gel with hexane/ethyl acetate (20 : 1) as eluent. The precipitate was further washed sufficiently with methanol and ether then dried, and the cobalt nanoparticles were recovered. After being reused three times, the yield of the product did not obviously decrease.

(*E*)-Ethyl cinnamate:[1]
Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.71 (d, *J* = 16.0 Hz, 1H), 7.53-7.56 (m, 2H), 7.39-7.41 (m, 3H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); MS (m/e): 176 (77, M^+), 131 (100), 103 (45); IR (neat): 1708, 1635, 1309, 1169 cm^{-1}.

(*E*)-Ethyl 4-methylcinnamate:[1]
Pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (d, *J* = 16.0 Hz, 1H) ,7.44 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); MS (m/e): 190 (74, M^+), 145 (100), 117 (48); IR (neat): 1709, 1635, 1310, 1165 cm^{-1}.

(*E*)-Ethyl 3-methylcinnamate:[1]
Pale orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.20-7.35 (m, 4H), 6.45

(d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); MS (m/e): 190 (72, M^+), 145 (100), 117 (52); IR (neat): 1710, 1638, 1311, 1174 cm^{-1}.

(*E*)-Ethyl 2-methylcinnamate:[1]
Pale yellow oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.00 (d, *J* = 15.9 Hz, 1H), 7.57 (d, *J*=7.1 Hz, 1H), 7.20-7.31 (m, 3H), 6.38 (d, J = 15.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); MS (m/e): 190 (75, M^+), 145 (100), 117 (46); IR (neat): 1709, 1633, 1311, 1164 cm^{-1}.

(E)-Ethyl 4-chlorocinnamate:[2]
Pale yellow oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.65 (d, *J* = 16.0 Hz, 1H),7.47 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); MS (m/e): 212 (25, M^++2), 210 (74, M^+), 165 (100), 137 (43); IR (neat): 1708, 1638, 1312, 1166 cm^{-1}.

(*E*)-Ethyl 2-chlorocinnamate:[3]
Pale yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.11(d, J=16.0 Hz,1H), 7.64-7.62 (m, 1H), 7.44-7.22 (m, 1H), 7.32-7.29 (m, 2H), 6.45 (d, J=16.0 Hz, 1H), 4.29 (q, J=7.1 Hz, 2H), 1.36 (t, J= 7.1Hz, 3H); MS (m/e): 212 (26, M^++2), 210 (79, M^+), 165 (100), 137 (42); IR (neat): 1705, 1642, 1310, 1162 cm^{-1}.

(*E*)-Methyl cinnamate:[3]
Pale yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J*=16.0 Hz, 1H), 7.55-7.54 (m, 2H), 7.41-7.39 (m, 3H), 6.46 (d, *J*=16.0 Hz, 1H), 3.84 (s, 3H); MS (m/e): 162 (75, M^+), 131 (100), 103 (51); IR (neat) 1710, 1635, 1314, 1172 cm^{-1}.

(*E*)-Methyl 4-methylcinnamate:[4]
Colorless crystals. mp 52-54°C (lit 50-52 °C); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.69 (d, *J*=16.0 Hz, 1H), 7.43 (d, *J*=8.1 Hz, 2H), 7.20 (q, *J*=8.1 Hz, 2H), 6.41 (d, *J*=16.0 Hz, 1H), 3.81 (s, 3H), 2.39 (s, 3H); MS (m/e): 176 (73, M^+), 145 (100), 117 (45); IR (CCl_4): 1702, 1632, 1606, 1315, 1165 cm^{-1}.

(*E*)-Methyl 3-methylcinnamate:[5]
Pale yellow oil. ^1H NMR ($CDCl_3$, 400MHz): δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.20-7.35 (m, 4H), 6.44 (d, *J* =16.0 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H); MS (m/e): 176 (71, M^+), 145 (100), 117 (46); IR (neat) 1704, 1643, 1610, 1312, 1165 cm^{-1}.

(*E*)-Methyl 4-chlorocinnamate:[4]
Colorless crystals; mp 71-73 °C (lit 74-75°C); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J*=16.0 Hz, 1H), 7.46 (d, *J*=8.5 Hz, 2H), 7.37 (d, *J*=8.5 Hz, 2H), 6.42 (d, *J*=16.0 Hz, 1H), 3.82 (s, 3H); MS (m/e): 198 (24, M^++2), 196 (75, M^+), 165 (100), 137 (42); IR (KBr): 1702, 1634, 1592, 1332, 1167 cm^{-1}.

Methyl 2-methyl-3-*p*-tolylacrylate:[6]
Pale yellow oil. ^1H NMR ($CDCl_3$, 400MHz): δ 7.71 (s ,1H), 7.34 (d, *J*=7.4 Hz, 2H), 7.23 (d, *J*=7.4 Hz, 2H), 3.84 (s, 3H), 2.40 (s, 3H), 2.17 (s, 3H); MS (m/e): 190 (72, M^+), 159 (100), 131 (46); IR

(neat): 1711, 1632, 1335, 1168 cm^{-1}.

Methyl 2-methyl-3-*m*-tolylacrylate:[7]

Pale yellow oil. ^1H NMR ($CDCl_3$, 400MHz): δ 7.68 (1H, s), 7.15-7.32 (m, 4H), 3.84 (s, 3H), 2.39 (s, 3H), 2.13 (s, 3H); MS (m/e): 190 (71, M^+), 159 (100), 131 (44); IR (neat): 1708, 1632, 1332, 1173 cm^{-1}.

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