Journal of Organometallic Chemistry 840 (2017) 38–46

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

A highly efficient heterogeneous ruthenium(III)-catalyzed reaction of diaryl diselenides with alkyl halides leading to unsymmetrical diorganyl selenides

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ARTICLE INFO

Article history:
Received 24 September 2016
Received in revised form
16 March 2017
Accepted 8 April 2017
Available online 11 April 2017

Keywords:
Supported ruthenium catalyst
Diorganyl selenide
Diaryl diselenide
Functionalized MCM-41
Heterogeneous catalysis

ABSTRACT

A highly efficient heterogeneous ruthenium(III)-catalyzed reaction of diaryl diselenides with alkyl halides was achieved in DMF at 100 °C in the presence of 2 mol% of an MCM-41-immobilized bidentate nitrogen ruthenium(III) complex [MCM-41-2N-$RuCl_3$] and zinc, yielding a variety of unsymmetrical diorganyl selenides in good to excellent yields. This new heterogeneous ruthenium catalyst can easily be prepared via a simple two-step procedure from commercially readily available and inexpensive reagents, and recovered by filtration of the reaction solution and recycled for at least eight times without a significant loss of activity.

1. Introduction

Diorganyl selenides are of considerable interest in academia and industry because they have been widely used as versatile reagents in modern organic synthesis and catalysis [1–4]. In addition, the biological activities and medicinal properties of selenium and organoselenium compounds such as antioxidant, antitumor, antimicrobial, and antiviral properties have also been reported [5–9] and, thus, much effort has been devoted to accomplishing the synthesis of these compounds. Diorganyl selenides are generally prepared by chemical cleavage of Se–Se bonds, especially cleavage of diphenyl or other diaryl diselenides, employing common reducing agents such as $NaBH_4$, $LiAlH_4$, Na/NH_3, Bu_3SnH, and other expensive metal sources such as La, In, Yb, Sm, etc [10–17]. Recently, catalytic procedures for preparation of functional diorganyl selenides have received much attention since many functional groups cannot withstand the harsh conditions for chemical cleavage of Se–Se bonds. CuI-bipyridine complex-catalyzed reaction of diaryl diselenides with arylboronic acids or reaction of diaryl diselenides with aryl iodides in the presence of magnesium gave unsymmetrical diaryl selenides [18,19]. InI-mediated synthesis of diorganyl selenides was achieved by cleavage of diaryl diselenides and subsequent condensation with alkyl halides or acyl chlorides [20–22]. $NiBr_2$-catalyzed cross-coupling of diaryl diselenides with aryl iodides was realized in the presence of a polymer-bound borohydride [23]. In the presence of a bimetallic [Sn(II)/Cu(II)] catalytic system, reactive bromides such as allyl, propargyl, benzyl, and alkynyl bromides were reacted with diorganyl diselenides to furnish unsymmetrical diorganyl selenides [24]. Ruthenium-catalyzed reaction of dibenzyl or diphenyl diselenides with alkyl halides in the presence of zinc provides an efficient one-pot method for the construction of unsymmetrical diorganyl selenides [25]. CuI-catalyzed direct arylselenation of arylamines with diaryl diselenides afforded arylselanyl anilines via C–H bond cleavage of aryl amines [26]. Braga et al. described an iodine-catalyzed solvent- and metal-free approach to synthesis of unsymmetrical diorganyl chalcogenides from arylboronic acids and diorganyl dichalcogenides under microwave irradiation [27]. Palladium(0)-catalyzed synthesis of diorganyl selenides via cleavage of diphenyl diselenides or cross-coupling reaction of $PhSeSnBu_3$ with aryl and alkyl halides was also reported [28–30].

Although these metal-catalyzed cleavages of Se–Se bonds are

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http://dx.doi.org/10.1016/j.jorganchem.2017.04.004
0022-328X/

highly efficient for construction of diorganyl selenides, separation of the soluble metal catalyst from the product and reaction medium remains difficult, especially for expensive and/or toxic heavy metal complexes. In addition, the use of homogeneous metal catalysts might result in unacceptable metallic species contamination of the desired isolated product. These problems are of particular economic and environmental concerns in chemical and pharmaceutical industries. Catalyst recycle is one of the most important features for many green synthetic methods. To overcome these problems, the development of highly efficient and recyclable heterogeneous catalysts, for example by immobilization of catalytically active species onto an ideal solid support to generate a molecular heterogeneous catalyst is highly desirable [31–33]. In the past decades, heterogeneous catalysts have received more and more attention because of the advantages of high catalytic efficiency and easy recycling, which are important for precious metal catalysts and flow chemistry processes [34–36]. Recently, mesoporous MCM-41 materials have emerged as smart and promising supports with great industrial potential for immobilization due to their outstanding advantages such as extremely high surface areas, combined with large and defined pore sizes of mesoporous materials, compared with other solid supports [37–39]. During recent years, some functionalized MCM-41-supported palladium [40–45], rhodium [46], molybdenum [47,48], gold [49–51], and copper [52–54] complexes have been prepared and successfully utilized as potentially green and sustainable catalysts in organic reactions. However, to the best of our knowledge, no example of an MCM-41-immobilized bidentate nitrogen ruthenium complex has been reported until now.

In continuation of our efforts to develop economical and eco-friendly synthetic pathways for organic transformations from the viewpoint of green and sustainable chemistry [43–45,52–54], here we wish to report the first synthesis of MCM-41-immobilized bidentate nitrogen ruthenium(III) complex [MCM-41-2N-$RuCl_3$] and its successful application to C–Se coupling reaction between diaryl diselenides and alkyl halides leading to unsymmetrical diorganyl selenides. The new heterogeneous ruthenium complex exhibits excellent catalytic activity in the reaction and can easily be recovered by a simple filtration of the reaction solution, and its catalytic efficiency remains unaltered even after recycling eight times.

2. Experimental

2.1. General remarks

All chemicals were reagent grade and used as purchased. DMF was distilled before use. The products were purified by flash chromatography on silica gel. Light petroleum ether (30–60 °C) or a mixture of light petroleum ether (30–60 °C) and CH_2Cl_2 (ca. 10:1, v/v) was generally used as eluent. All products were characterized by comparison of their spectra and physical data with authentic samples. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer in $CDCl_3$ as solvent. HRMS spectra were recorded on a Finnigan MAT8430 spectrometer. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer. X-ray diffraction (XRD) measurements were carried out at room temperature using an X-ray powder diffractmeter. X-ray energy dispersive spectroscopy (EDS) was performed using a microscope. X-ray photoelectron spectra (XPS) were recorded on XSAM 800 (Kratos). EPR measurements were carried out on a Radiopan SE/X 2742 spectrometer (X-band) with cylindrical TM_{110} resonator and 100 kHz magnetic field modulation. FT-IR spectra were recorded using a Nicolet FT-IR (510P) spectrophotometer. Mesoporous material MCM-41 was prepared according to a literature method [55].

2.2. Preparation of the catalyst

2.2.1. Preparation of MCM-41-2N

A solution of 1.54 g of 3-(2-aminoethylamino)propyltrimethoxysilane in 18 mL of dry chloroform was added to a suspension of 2.2 g of the MCM-41 in 180 mL of dry toluene. The mixture was stirred for 24 h at 100 °C. Then the solid was filtered and washed by $CHCl_3$ (2 × 20 mL), and dried in vacuum at 160 °C for 5 h. The dried white solid was then soaked in a solution of 3.1 g of Me_3SiCl in 100 mL of dry toluene at room temperature under stirring for 24 h. Then the solid was filtered, washed with acetone (3 × 20 mL) and diethyl ether (3 × 20 mL), and dried in vacuum at 120 °C for 5 h to obtain 3.49 g of hybrid material MCM-41-2N. The nitrogen content was found to be 1.84 mmol/g by elemental analysis.

2.2.2. Preparation of MCM-41-2N-$RuCl_3$ complex

In a Schlenk tube, 2.3 g of the above-functionalized MCM-41 (MCM-41-2N) was mixed with 0.339 g (1.3 mmol) of $RuCl_3 \cdot 3H_2O$ in 50 mL of dry acetone. The mixture was refluxed for 72 h under an argon atmosphere. The solid product was filtered by suction, washed with acetone, distilled water and acetone successively and dried at 70 °C/26.7 Pa under Ar for 5 h to give 2.52 g of a gray ruthenium complex [MCM-41-2N-$RuCl_3$]. The nitrogen and ruthenium content was found to be 1.65 mmol/g and 0.47 mmol/g, respectively.

2.3. General procedure for the heterogeneous ruthenium-catalyzed reaction of diaryl diselenides with alkyl halides

Under argon atmosphere, to a mixture of diaryl diselenide (0.5 mmol), zinc (52 mg, 0.8 mmol), and MCM-41-2N-$RuCl_3$ (2 mol %) were successively added DMF (3 mL) and alky halide (1.2 mmol). The mixture was stirred at 100 °C for 2 h. The reaction mixture was cooled to room temperature and diluted with EtOAc (20 mL) and filtered. The MCM-41-2N-$RuCl_3$ catalyst was washed with diluted hydrochloric acid (2 × 5 mL), distilled water (2 × 5 mL), and EtOH (2 × 5 mL) and reused in the next run. The filtrate was washed with brine (2 × 10 mL), dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography using light petroleum ether or light petroleum ether/CH_2Cl_2 (ca. 10:1, v/v) as the eluent to afford the desired product **3**.

2.3.1. Heptyl phenyl selenide, ***3a*** [15]

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.2 Hz, 2H), 7.26–7.20 (m, 3H), 2.91 (t, J = 7.4 Hz, 2H), 1.73–1.66 (m, 2H), 1.43–1.20 (m, 8H), 0.87 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4, 130.8, 129.0, 126.6, 31.7, 30.2, 29.8, 28.8, 28.0, 22.6, 14.1.

2.3.2. Pentyl phenyl selenide, ***3b*** [16]

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 6.8 Hz, 2H), 7.27–7.20 (m, 3H), 2.91 (t, J = 7.4 Hz, 2H), 1.74–1.67 (m, 2H), 1.40–1.26 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4, 130.7, 129.0, 126.6, 32.0, 29.9, 27.9, 22.2, 14.0.

2.3.3. Dodecyl phenyl selenide, ***3c*** [17]

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 6.4 Hz, 2H), 7.27–7.19 (m, 3H), 2.91 (t, J = 7.4 Hz, 2H), 1.75–1.64 (m, 2H), 1.41–1.22 (m, 18H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 132.4, 130.7, 129.0, 126.6, 31.9, 30.2, 29.9, 29.7, 29.6, 29.5, 29.4, 29.1, 28.0, 22.7, 14.2.

2.3.4. (2-Ethylhexyl) phenyl selenide, ***3d***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.27–7.18 (m, 3H), 2.95 (d, *J* = 6.0 Hz, 2H), 1.65–1.53 (m, 1H), 1.47–1.21 (m, 8H), 0.89–0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4, 131.4, 128.9, 126.5, 39.7, 33.6, 33.1, 28.9, 26.3, 23.0, 14.1, 10.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{22}Se^+$ [M^+] 270.0887; found 270.0892.

2.3.5. Phenylethyl phenyl selenide, ***3e*** *[20]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.33–7.15 (m, 8H), 3.17–3.12 (m, 2H), 2.99 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 132.7, 130.3, 129.2, 128.6, 128.5, 126.9, 126.5, 36.7, 28.8.

2.3.6. Butyl phenyl selenide, ***3f*** *[16]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 7.2 Hz, 2H), 7.27–7.20 (m, 3H), 2.92 (t, *J* = 7.6 Hz, 2H), 1.73–1.62 (m, 2H), 1.47–1.36 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.4, 130.7, 129.0, 126.6, 32.3, 27.6, 23.0, 13.6.

2.3.7. 6-(Phenylselanyl)hexan-1-ol, ***3g***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.41 (m, 2H), 7.28–7.19 (m, 3H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 1.75–1.68 (m, 2H), 1.59–1.50 (m, 2H), 1.49–1.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.5, 130.6, 129.0, 126.7, 62.8, 32.6, 30.1, 29.6, 27.8, 25.2. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}OSe^+$ [M^+] 258.0523; found 258.0519.

2.3.8. Ethyl 6-(phenylselanyl)hexanoate, ***3h***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 6.4 Hz, 2H), 7.27–7.20 (m, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.75–1.59 (m, 4H), 1.48–1.40 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 132.5, 130.5, 129.0, 126.7, 60.2, 34.2, 29.8, 29.2, 27.6, 24.4, 14.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{20}O_2Se^+$ [M^+] 300.0629; found 300.0627.

2.3.9. Benzyl phenyl selenide, ***3i*** *[16]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 2H), 7.18–7.10 (m, 8H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 133.6, 130.5, 129.1, 128.9, 128.5, 127.4, 126.9, 32.3.

2.3.10. (4-Methoxybenzyl) phenyl selenide, ***3j*** *[20]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 2H), 7.26–7.20 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.80–6.75 (m, 2H), 4.08 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6, 133.5, 130.7, 130.6, 130.0, 129.0, 127.2, 113.9, 55.3, 31.8.

2.3.11. (4-Methylbenzyl) phenyl selenide, ***3k*** *[16]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2H), 7.25–7.21 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 4.08 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6, 135.5, 133.4, 130.8, 129.2, 129.0, 128.8, 127.2, 32.0, 21.1.

2.3.12. (4-Chlorobenzyl) phenyl selenide, ***3l*** *[20]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2H), 7.25–7.17 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.03 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.4, 133.9, 132.6, 130.1, 129.8, 129.1, 128.5, 127.6, 31.5.

2.3.13. 4-(Phenylselanylmethyl)benzonitrile, ***3m***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 6.8 Hz, 2H), 7.31–7.21 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 134.4, 132.1, 129.4, 129.2, 128.9, 128.0, 118.8, 110.5, 31.7. HRMS (ESI) *m/z* calcd for $C_{14}H_{11}NSe^+$ [M^+] 273.0057; found 273.0058.

2.3.14. (2-Methylbenzyl) phenyl selenide, ***3n*** *[16]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.42 (m, 2H), 7.26–7.20 (m, 3H), 7.13–7.10 (m, 2H), 7.06–6.99 (m, 2H), 4.10 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.4, 136.3, 133.9, 130.5, 129.7, 129.0, 127.4, 127.3, 126.0, 30.5, 19.2.

2.3.15. (4-Bromobenzyl) phenyl selenide, ***3o***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.41 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.26–7.21 (m, 3H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 133.9, 131.5, 130.5, 129.8, 129.1, 127.6, 120.7, 31.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}BrSe^+$ [M^+] 325.9209; found 325.9211.

2.3.16. Heptyl p-tolyl selenide, ***3p***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.25 (s, 3H), 1.67–1.57 (m, 2H), 1.30–1.18 (m, 8H), 0.80 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 133.0, 130.1, 129.8, 31.7, 30.2, 29.8, 28.8, 28.4, 22.6, 21.1, 14.1. HRMS (ESI) *m/z* calcd for $C_{14}H_{22}Se^+$ [M^+] 270.0887; found 270.0882.

2.3.17. Pentyl p-tolyl selenide, ***3q***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 1.69–1.64 (m, 2H), 1.41–1.26 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 133.0, 129.8, 126.7, 32.0, 29.9, 28.3, 22.2, 21.1, 14.0. HRMS (ESI) *m/z* calcd for $C_{12}H_{18}Se^+$ [M^+] 242.0574; found 242.0577.

2.3.18. Dodecyl p-tolyl selenide, ***3r***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 1.71–1.63 (m, 2H), 1.41–1.22 (m, 18H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6, 133.0, 129.8, 126.7, 32.0, 30.2, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 28.4, 22.7, 21.1, 14.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{32}Se^+$ [M^+] 340.1669; found 340.1665.

2.3.19. (2-Ethylhexyl) p-tolyl selenide, ***3s***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.90 (d, *J* = 6.0 Hz, 2H), 2.31 (s, 3H), 1.57–1.53 (m, 1H), 1.46–1.23 (m, 8H), 0.89–0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5, 132.9, 129.8, 127.4, 39.7, 34.0, 33.1, 28.9, 26.3, 23.0, 21.1, 14.1, 10.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{24}Se^+$ [M^+] 284.1043; found 284.1046.

2.3.20. Phenylethyl p-tolyl selenide, ***3t***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.6 Hz, 2H), 7.31–7.15 (m, 5H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 137.0, 133.2, 130.0, 128.5, 128.4, 126.4, 126.3, 36.7, 29.1, 21.2. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}Se^+$ [M^+] 276.0417; found 276.0423.

2.3.21. Butyl p-tolyl selenide, ***3u***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.69–1.62 (m, 2H), 1.44–1.37 (m, 2H), 0.89 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 133.0, 129.8, 126.7, 32.3, 28.0, 23.0, 21.1, 13.6. HRMS (ESI) *m/z* calcd for $C_{11}H_{16}Se^+$ [M^+] 228.0417; found 228.0415.

2.3.22. Benzyl p-tolyl selenide, ***3v*** *[16]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.0 Hz, 2H), 7.24–7.16 (m, 5H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.06 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 137.4, 134.1, 129.8, 128.8,

128.4, 126.8, 126.5, 32.6, 21.2.

2.3.23. (4-Chlorophenyl) heptyl selenide, ***3w***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 2H), 7.25–7.21 (m, 2H), 2.89 (t, J = 7.4 Hz, 2H), 1.71–1.63 (m, 2H), 1.46–1.23 (m, 8H), 0.87 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 133.8, 129.1, 128.9, 31.7, 30.1, 29.8, 28.8, 28.3, 22.6, 14.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{19}ClSe^+$ [M^+] 290.0341; found 290.0337.

2.3.24. (4-Chlorophenyl) pentyl selenide, ***3x***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.88 (t, J = 7.4 Hz, 2H), 1.72–1.65 (m, 2H), 1.42–1.23 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 133.8, 129.1, 128.9, 32.0, 29.8, 28.3, 22.2, 14.0. HRMS (ESI) *m/z* calcd for $C_{11}H_{15}ClSe^+$ [M^+] 262.0027; found 262.0035.

2.3.25. (4-Chlorophenyl) dodecyl selenide, ***3y***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.88 (t, J = 7.4 Hz, 2H), 1.71–1.64 (m, 2H), 1.42–1.20 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.8, 132.8, 129.1, 128.9, 31.9, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 28.3, 22.7, 14.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{29}ClSe^+$ [M^+] 360.1123; found 360.1125.

2.3.26. (4-Chlorophenyl) (2-ethylhexyl) selenide, ***3z***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.92 (d, J = 6.4 Hz, 2H), 1.58–1.52 (m, 1H), 1.46–1.22 (m, 8H), 0.90–0.83 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.8, 132.7, 129.5, 129.1, 39.7, 34.0, 33.0, 28.8, 26.3, 22.9, 14.1, 10.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{21}ClSe^+$ [M^+] 304.0497; found 304.0495.

2.3.27. (4-Chlorophenyl) (phenylethyl) selenide, ***3a'***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.33–7.14 (m, 7H), 3.13 (t, J = 8.0 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 134.1, 133.1, 129.3, 128.6, 128.4, 126.6, 36.6, 29.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}ClSe^+$ [M^+] 295.9871; found 295.9867.

2.3.28. Butyl (4-chlorophenyl) selenide, ***3b'***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.89 (t, J = 7.4 Hz, 2H), 1.70–1.62 (m, 2H), 1.46–1.36 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 133.8, 129.1, 128.9, 32.2, 28.0, 22.9, 13.6. HRMS (ESI) *m/z* calcd for $C_{10}H_{13}ClSe^+$ [M^+] 247.9871; found 247.9876.

2.3.29. Benzyl (4-chlorophenyl) selenide, ***3c'*** *[16]*

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.31 (m, 2H), 7.26–7.15 (m, 7H), 4.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3, 135.2, 133.7, 129.2, 128.9, 128.5, 128.3, 127.1, 32.6.

2.3.30. (4-Chlorophenyl) (pent-4-ynyl) selenide, ***3d'***

Oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.35 (m, 2H), 7.27–7.19 (m, 2H), 2.99 (t, J = 7.2 Hz, 2H), 2.36–2.28 (m, 2H), 1.97 (t, J = 2.6 Hz, 1H), 1.92–1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 134.1, 129.2, 128.1, 83.1, 69.2, 28.6, 26.9, 18.4. HRMS (ESI) *m/z* calcd for $C_{11}H_{11}ClSe^+$ [M^+] 257.9714; found 257.9722.

3. Results and discussion

3.1. Synthesis and characterization of MCM-41-2N-RuCl$_3$

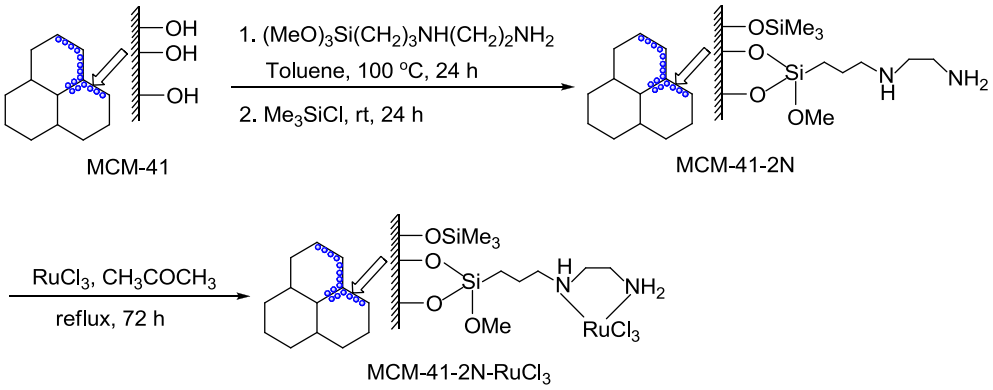
The new MCM-41-immobilized bidentate nitrogen ruthenium(III) complex [MCM-41-2N-$RuCl_3$] was conveniently prepared from commercially readily available and inexpensive reagents according to the procedure summarized in Scheme 1. Firstly, the 3-(2-aminoethylamino)propyl-functionalized MCM-41 (MCM-41-2N) was obtained by the condensation of mesoporous material MCM-41 with 3-(2-aminoethylamino)propyltrimethoxysilane in toluene at 100 °C for 24 h, followed by the silylation with Me_3SiCl in toluene at room temperature for 24 h. The MCM-41-2N was then reacted with $RuCl_3$ in acetone under reflux for 72 h to produce the MCM-41-immobilized bidentate nitrogen ruthenium(III) complex (MCM-41-2N-$RuCl_3$) as a gray powder, the ruthenium content of the complex was found to be 0.47 mmol g^{-1} according to the ICP-AES measurements.

Small angle X-ray powder diffraction (XRD) analysis of the MCM-41-2N-$RuCl_3$ indicated that, the (100) reflection of MCM-41-2N-$RuCl_3$ had lower intensity compared to that of the parent MCM-41 [37], while the (110) and (200) reflections became weak and diffuse (see ESI). According to related references [55–57], the intensity reduction may be attributed to contrast matching between the silicate framework and organic moieties which are located inside the channels of MCM-41. These results demonstrate that the structure of the mesoporous MCM-41 remains intact through the functionalization procedure. The energy dispersive X-ray spectroscopy (EDS) shows the elements present in the material. EDS analysis of fresh MCM-41-2N-$RuCl_3$ complex shows the presence of Si, O, C, N, Cl, and Ru elements (see ESI).

Morphological changes of MCM-41 and MCM-41-2N-$RuCl_3$ were investigated by scanning electron microscopy (SEM). As shown in Fig. 1, the morphology of MCM-41-2N-$RuCl_3$ (Fig. 1b) is similar to the particle form of MCM-41 (Fig. 1a), suggesting a high possibility in the modification of ruthenium complex on the inner channel of MCM-41 pores without any significant change in the manner of MCM-41. The FT-IR spectrum of MCM-41-2N-$RuCl_3$ (Fig. 2) shows the N–H stretching vibration absorption at 3430 cm^{-1} and the N–H bending vibration absorption at 1641 cm^{-1}, which confirming the presence of H on Ru attached N atoms. XPS analysis of MCM-41-2N-$RuCl_3$ was performed to analyze the oxidation state of the Ru metal (Fig. 3). It can be seen that although the Ru 3d signal is obscured by the C 1s signal of a carbon contaminant at 284.6 eV, the deconvoluted spectrum shows three ruthenium states characterized by Ru $3d^{5/2}$ binding energy of 280.6 eV, 281.3 eV, and 282.1 eV. The first Ru $3d^{5/2}$ binding energy of 280.6 eV is probably assigned to $RuCl_3$ anchored by means of three N atoms coordinating to one Ru atom; the second Ru $3d^{5/2}$ binding energy of 281.3 eV is assigned to $RuCl_3$ anchored by means of bidentate two N atoms coordinating to one Ru atom [58]; while the third Ru $3d^{5/2}$ binding energy of 282.1 eV may be assigned to $RuCl_3$ anchored by means of one N atom coordinating to one Ru atom [59]. This assignment is based on the XPS data for $RuCl_3$ [60]. The electron binding energy analysis shown in Fig. 3 indicated that the oxidation state of ruthenium in MCM-41-2N-$RuCl_3$ was Ru(III). The EPR spectrum recorded for MCM-41-2N-$RuCl_3$ complex is shown in Fig. 4. The observed EPR signal at g = 1.991 can also confirm that the oxidation state of ruthenium in MCM-41-2N-$RuCl_3$ was Ru(III) [61].

3.2. Heterogeneous ruthenium(III)-catalyzed reaction of diaryl diselenides with alkyl halides

The MCM-41-immobilized bidentate nitrogen ruthenium(III) complex [MCM-41-2N-$RuCl_3$] was then used as catalyst for the reaction of diaryl diselenides with alkyl halides in the presence of zinc. Initial experiments with diphenyl diselenide (**1a**) and 1-bromoheptane (**2a**) were performed to optimize the reaction conditions, and the results are summarized in Table 1. At first, the temperature effect was examined in the presence of 5 mol% of



Scheme 1. Preparation of MCM-41-2N-$RuCl_3$ complex.

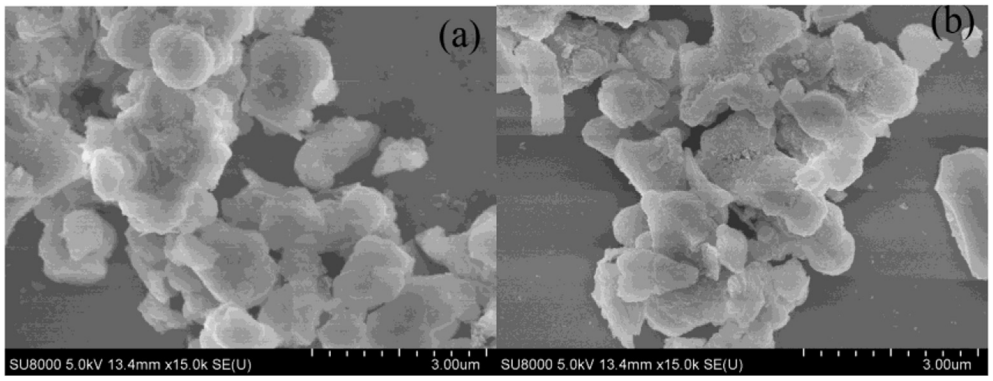


Fig. 1. SEM images of MCM-41 (a) and MCM-41-2N-$RuCl_3$ (b).

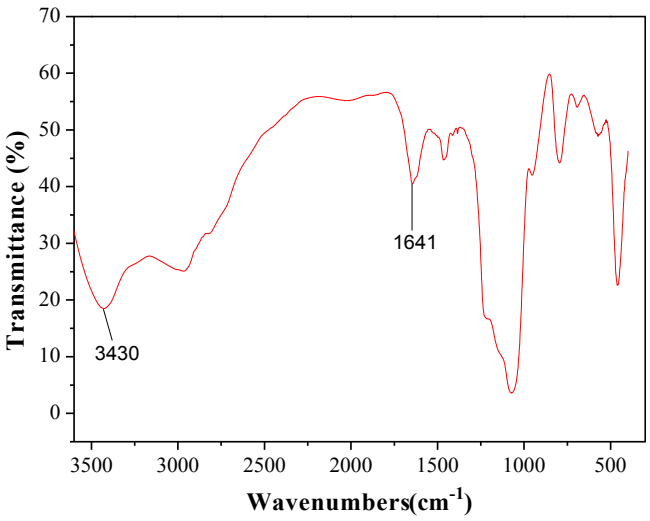


Fig. 2. FT-IR spectrum of the MCM-41-2N-$RuCl_3$ complex.

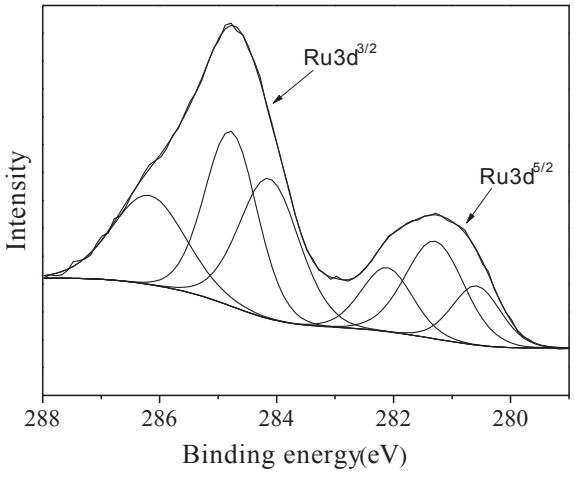


Fig. 3. XPS of the MCM-41-2N-$RuCl_3$ complex.

MCM-41-2N-$RuCl_3$ in DMF with 1.0 equiv of Zn as reductive reagent and a significant temperature effect was observed. At ambient temperature the catalytic reaction did not work (entry1). The reaction at 60 °C gave a trace of desired product **3a** (entry 2) and a low yield was obtained even at 80 °C (entry 3). However, when reaction temperature was raised to 100 °C, the reaction proceeded smoothly to afford the desired product **3a** in 76% yield within 4 h (entry 4). But further increasing reaction temperature to 120 °C did not improve the yield (entry 5). The results of control experiments reveal that both ruthenium catalyst and zinc are necessary for the described phenylselenation to undergo, and the use of a homogeneous $RuCl_3 \cdot 3H_2O$ as catalyst also gave good yield (entries 6–8). We then turned our attention to investigate the effect of the amount of zinc on the model reaction. It was found that the yield of **3a** increased with the increase in the amount of zinc and the use of 1.6 equiv of Zn gave a 96% yield (entries 4 and 9–12). In the presence of 1.6 equiv of Zn, homogeneous $RuCl_3 \cdot 3H_2O$ also afforded **3a** in 95% yield (entry 13), which indicating that the catalytic activity of MCM-41-2N-$RuCl_3$ was comparable to that of homogeneous

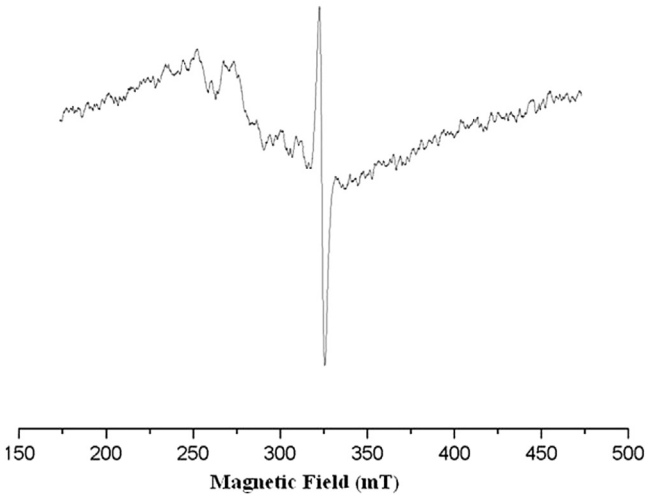
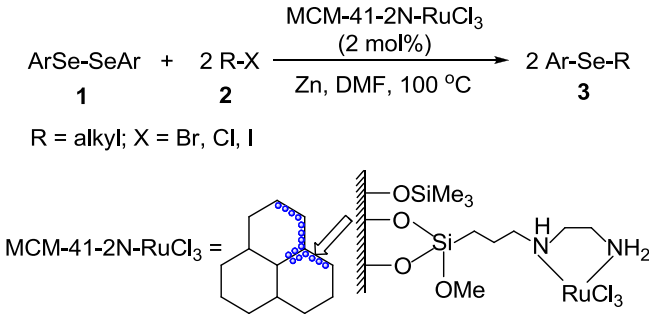


Fig. 4. EPR spectrum of the MCM-41-2N-$RuCl_3$ complex, ν = 9.40 GHz.

$RuCl_3 \cdot 3H_2O$ complex. The effect of solvent on the model reaction was also examined (entries 14–17). The use of DMAc or DMSO as solvent gave good results, but dioxane afforded a low yield and toluene was ineffective, so, DMF was the best choice. We next screened the amount of the supported ruthenium catalyst and were pleased to find that there was no change in yield when the catalyst amount was decreased to 2 mol% (entry 18). The reaction still proceeded smoothly even with only 1 mol% catalyst (entry 19). Thus, the optimized reaction conditions for this transformation are the MCM-41-2N-$RuCl_3$ (2 mol%), 1.6 equiv of Zn in DMF at 100 °C under Ar for 2 h (entry 18).

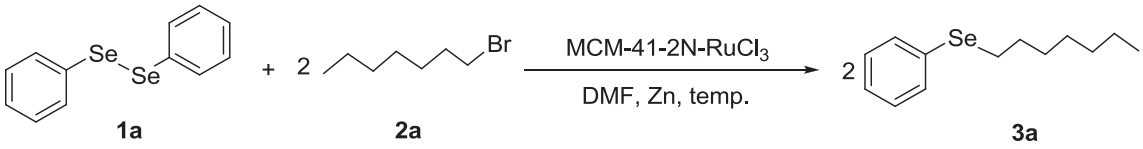
With this promising result in hand, we started to investigate the scope of this heterogeneous ruthenium-catalyzed C–Se coupling reaction of diaryl diselenides with alkyl halides under the optimized conditions (Scheme 2). Firstly, reactions of diphenyl diselenides (**1a**) with a wide range of alkyl halides were examined and the results are summarized in Table 2. A variety of alkyl bromides underwent the phenylselenation reaction effectively to afford the corresponding unsymmetrical diorganyl selenides **3a-3e** in excellent yields. The reaction of alkyl iodides such as 1-iodobutane also proceeded smoothly to give the desired product **3f** in 92% yield. Unreactive chlorides, such as 1-chloroheptane, did not undergo the same type of phenylselenation. Surprisingly, addition of sodium bromide could promote the reaction of 1-chloroheptane with **1a** remarkably to furnish the desired **3a** in 90% yield. Interestingly, alkyl bromides with functional groups such as hydroxy and ester were also good coupling partners and gave the desired products **3g** and **3h** in excellent yields. In addition, reactive benzyl chlorides or bromides also underwent the phenylselenation with **1a** efficiently to provide the corresponding benzyl phenyl selenides **3i-3o** in good to excellent yields. Both electron-donating and electron-withdrawing groups such as methyl, methoxy, chloro, bromo and cyano on benzene ring were tolerated well.

Encouraged by the above-mentioned results, we next turned



Scheme 2. Heterogeneous Ru-catalyzed synthesis of diorganyl selenides.

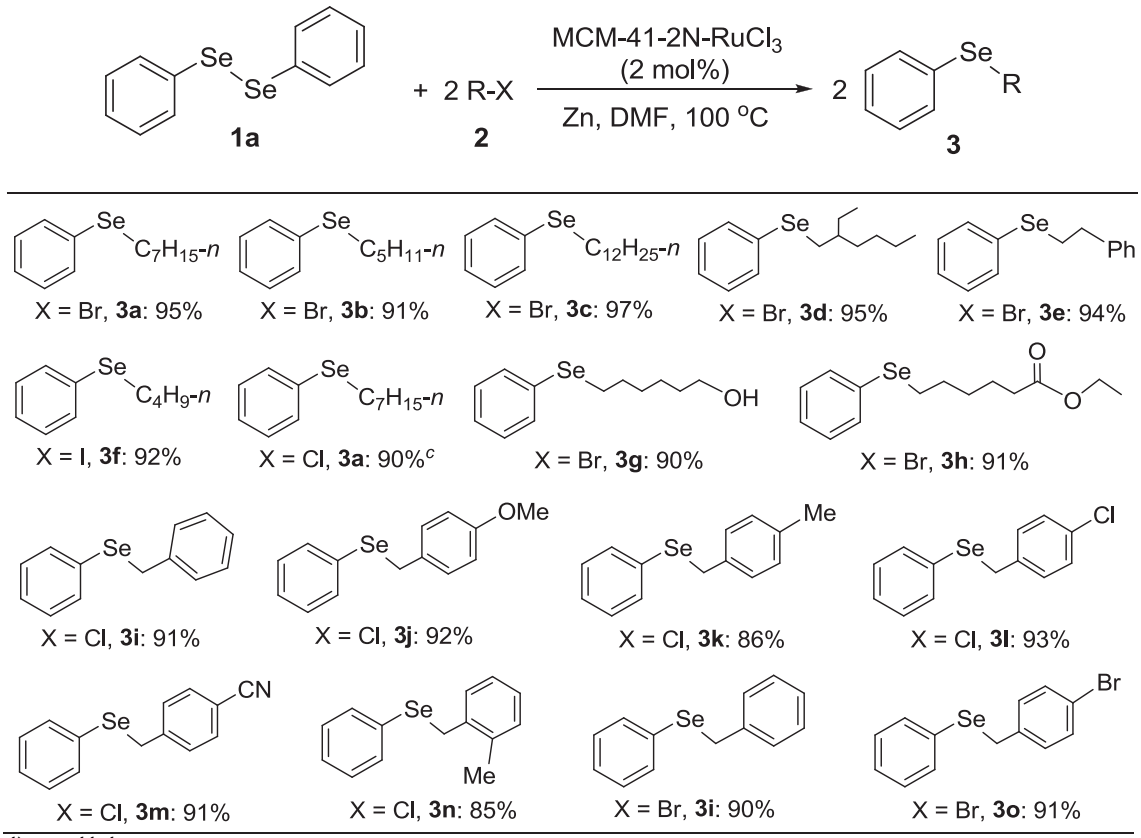
Table 1
Optimization of the reaction conditions of the C–Se bond formation reaction catalyzed by MCM-41-2N-$RuCl_3$.[a]



Entry	Ru(III) (mol%)	Temp. (°C)	Zn (equiv)	Solvent	t/h	Yield (%)[b]
1	MCM-41-2N-$RuCl_3$ (5)	30	1.0	DMF	24	0
2	MCM-41-2N-$RuCl_3$ (5)	60	1.0	DMF	24	trace
3	MCM-41-2N-$RuCl_3$ (5)	80	1.0	DMF	24	27
4	MCM-41-2N-$RuCl_3$ (5)	100	1.0	DMF	4	76
5	MCM-41-2N-$RuCl_3$ (5)	120	1.0	DMF	3	75
6	MCM-41-2N-$RuCl_3$ (5)	100	0	DMF	24	0
7	None	100	1.0	DMF	24	trace
8	$RuCl_3 \cdot 3H_2O$ (5)	100	1.0	DMF	4	78
9	MCM-41-2N-$RuCl_3$ (5)	100	1.2	DMF	3	84
10	MCM-41-2N-$RuCl_3$ (5)	100	1.4	DMF	2	89
11	MCM-41-2N-$RuCl_3$ (5)	100	1.6	DMF	1	96
12	MCM-41-2N-$RuCl_3$ (5)	100	1.8	DMF	1	93
13	$RuCl_3 \cdot 3H_2O$ (5)	100	1.6	DMF	1	95
14	MCM-41-2N-$RuCl_3$ (5)	100	1.6	DMAc	1	86
15	MCM-41-2N-$RuCl_3$ (5)	100	1.6	DMSO	1	71
16	MCM-41-2N-$RuCl_3$ (5)	100	1.6	dioxane	12	34
17	MCM-41-2N-$RuCl_3$ (5)	100	1.6	toluene	24	trace
18	MCM-41-2N-$RuCl_3$ (2)	100	1.6	DMF	2	95
19	MCM-41-2N-$RuCl_3$ (1)	100	1.6	DMF	4	89

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.2 mmol), solvent (3 mL) under Ar.
[b] Isolated yield.

Table 2
Reactions of diphenyl diselenide with alkyl halides catalyzed by MCM-41-2N-$RuCl_3$.[a,b]



[c] NaBr (1.2 mmol) was added.
[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.2 mmol), Zn (0.8 mmol), MCM-41−2N-$RuCl_3$ (2 mol%), DMF (3 mL) at 100 °C under Ar for 2 h.
[b] Isolated yield.

our attention to examine reactions of substituted diphenyl diselenides such as di(4-methylphenyl) diselenide **1b** and di(4-chlorophenyl) diselenide **1c** with various alkyl halides under the optimized conditions and the results are listed in Table 3. As shown in Table 3, the reactions of substituted diphenyl diselenides **1b** and **1c** with a variety of alkyl halides also proceeded smoothly to give the corresponding unsymmetrical diorganyl selenides **3p-3d'** in good to excellent yields. The results indicated that the electronic effect of substituents on the benzene ring has limited influence on this heterogeneous Ru-catalyzed C−Se coupling reaction. It is noteworthy that, for 5-chloro-1-pentyne with a terminal alkynyl group, the reaction with **1c** proceeded effectively in the presence of NaBr to furnish the desired 5-(4-chlorophenylseleno)-1-pentyne **3d'** in 86% yield with good tolerance of terminal alkynyl group. The method provides a quite general route for the synthesis of unsymmetrical diorganyl selenides having various functionalities.

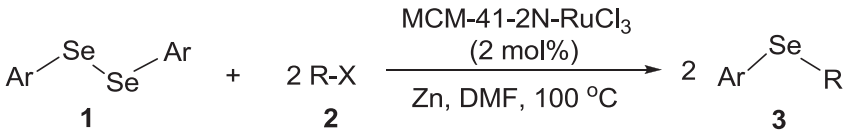
To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-2N-$RuCl_3$ or to a leached ruthenium species in solution, we carried out the hot filtration test [62]. We focused on the coupling reaction of diphenyl diselenide (**1a**) with 1-bromoheptane (**2a**). We removed the MCM-41-2N-$RuCl_3$ complex from the reaction mixture by filtration after 0.5 h of reaction time and allowed the filtrate to react further at 100 °C in the presence of zinc. The catalyst filtration was performed at 100 °C to avoid possible recoordination or precipitation of soluble ruthenium upon cooling. It was found that, in this case, no significant increase in conversion of diphenyl diselenide (**1a**) was observed, indicating that leached ruthenium species from the supported catalyst (if any) are not responsible for the observed activity. In addition, ICP-AES analysis showed that no ruthenium species could be detected in the hot filtered solution. These results rule out any contribution to the observed catalysis from a homogeneous ruthenium species, demonstrating that the reaction catalyzed by ruthenium was intrinsically heterogeneous.

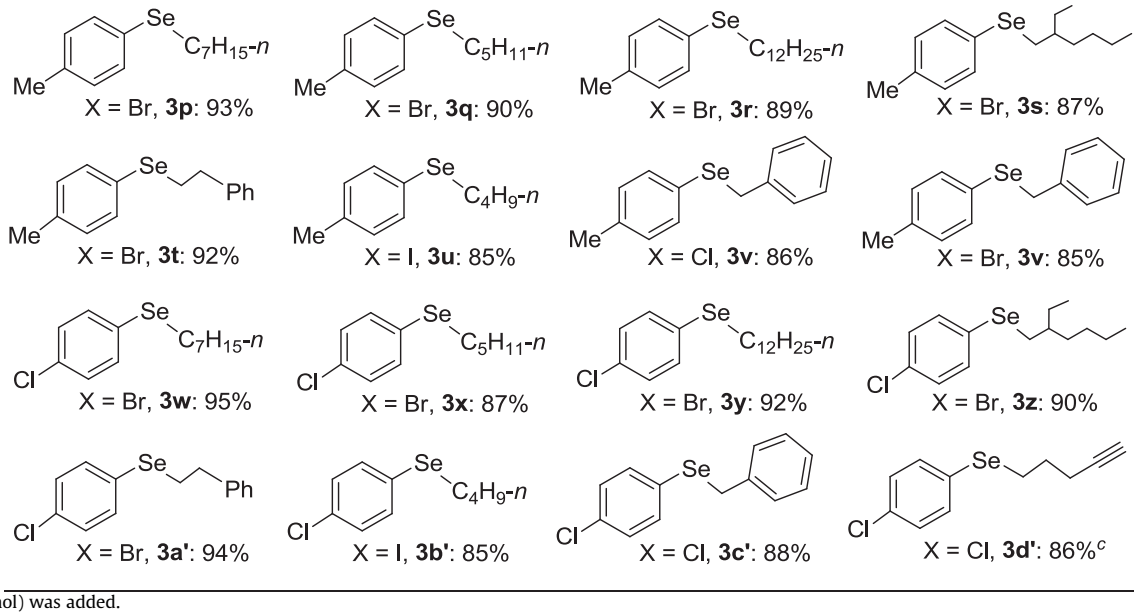
A plausible mechanism for this heterogeneous ruthenium-catalyzed C−Se coupling reaction of diaryl diselenides with alkyl halides is illustrated in Scheme 3. First, elemental zinc reacts with diaryl diselenide **1** to form di(arylselenyl)zinc **A**. The MCM-41-2N-RuX_3 then reacts with **A** to afford an MCM-41-bound $(ArSe)_2Ru(III)X$ complex intermediate **B**, which undergoes coupling with alkyl halide **2**, generating unsymmetrical diorganyl selenide **3** and an MCM-41-bound $ArSeRu(III)X_2$ complex intermediate **C**. Further reaction of intermediate **C** with alkyl halide **2** gives the desired product **3** and regenerates the MCM-41-2N-RuX_3 complex ($X_3 = Cl_3$, $ClBr_2$, or ClI_2 depending on the starting alkyl halides) to complete the catalytic cycle.

3.3. Recycling of the catalyst

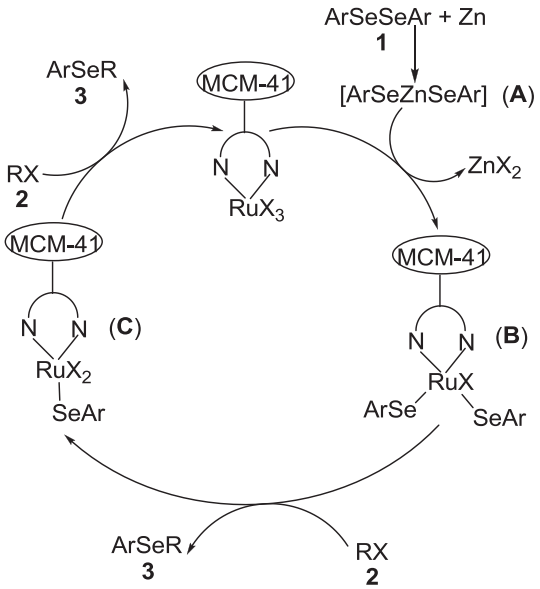
For the practical application of a heterogeneous precious metal catalyst, its ease of separation, good recoverability and reusability are important factors. The MCM-41-2N-$RuCl_3$ can be easily separated and recovered by a simple filtration of the reaction solution. We next investigated the recycle of the catalyst by using the reaction of diphenyl diselenide **1a** with 1-bromododecane **2c**. After completion of the reaction, the catalyst was recovered by a simple

Table 3
Reactions of diaryl diselenides with various alkyl halides catalyzed by MCM-41-2N-$RuCl_3$.[a,b]





[c] NaBr (1.2 mmol) was added.
[a] Reaction conditions: **1** (0.5 mmol), **2** (1.2 mmol), Zn (0.8 mmol), MCM-41-2N-$RuCl_3$ (2 mol%), DMF (3 mL) at 100 °C under Ar for 2 h.
[b] Isolated yield.



Scheme 3. A possible mechanism for this Ru-catalyzed C–Se coupling reaction.

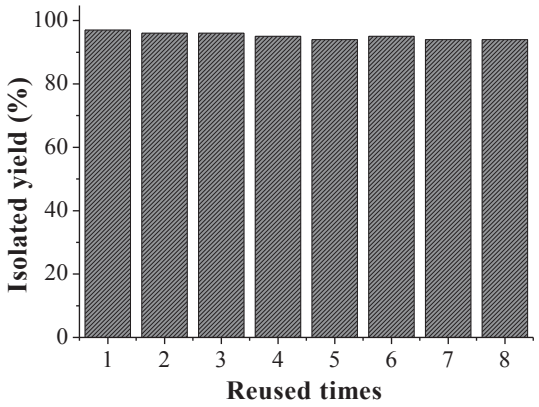


Fig. 5. Recycle of the MCM-41-2N-$RuCl_3$ complex.

filtration and washed with diluted hydrochloric acid, distilled water, and EtOH. After being air-dried, it can be reused directly without further purification. The recovered ruthenium catalyst was used in the next run, and almost consistent activity was observed for eight consecutive cycles (Fig. 5). In addition, the ruthenium leaching in the supported catalyst was also determined by ICP analysis. The ruthenium content of the catalyst was found to be 0.46 mmol/g after eight consecutive runs, indicating that only 2% of ruthenium had been lost from the MCM-41 support.

4. Conclusion

In conclusion, we have developed a novel, efficient and practical method for the synthesis of unsymmetrical diorganyl selenides through the C–Se coupling of diaryl diselenides with alkyl halides using an MCM-41-immobilized bidentate nitrogen ruthenium(III) complex [MCM-41-2N-$RuCl_3$] as the catalyst in the presence of zinc.

The reactions generated a variety of unsymmetrical diorganyl selenides in good to excellent yields and were applicable to organic iodides, reactive or unreactive organic bromides and chlorides. In addition, this new heterogeneous ruthenium catalyst can easily be prepared via a simple two-step procedure from commercially readily available and inexpensive reagents, and recovered by filtration of the reaction solution and recycled for at least eight times without a significant loss of activity, thus making this procedure economically and environmentally more acceptable.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21462021) and Key Laboratory of Functional Small Organic Molecule, Ministry of Education (No. KLFS-KF-201409) for financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.04.004.

References

[1] T.G. Back, Organoselenium Chemistry: a Practical Approach, Oxford University Press, New York, 1999.
[2] E.M. McGarrigle, E.L. Myers, O. Illa, M.A. Shaw, S.L. Riches, V.K. Aggarwal, Chem. Rev. 107 (2007) 5841–5883.
[3] G. Perin, E.J. Lenardao, R.G. Jacob, R.B. Panatieri, Chem. Rev. 109 (2009) 1277–1301.
[4] D.M. Freudendahl, S. Santoro, S.A. Shahzad, C. Santi, T. Wirth, Angew. Chem. Int. Ed. 48 (2009) 8409–8411.
[5] C.W. Nogueira, G. Zeni, J.B.T. Rocha, Chem. Rev. 104 (2004) 6255–6286.
[6] B.K. Sarma, G. Mugesh, Org. Biomol. Chem. 6 (2008) 965–974.
[7] E.E. Alberto, V. Nascimennto, A.L. Braga, J. Braz, Chem. Soc. 21 (2010) 2032–2041.
[8] C.W. Nogueira, J.B.T. Rocha, J. Braz, Chem. Soc. 21 (2010) 2055–2071.
[9] C.W. Nogueira, J.B.T. Rocha, Arch. Toxicol. 85 (2011) 1313–1359.
[10] D. Crich, D. Grant, J. Org. Chem. 70 (2005) 2384–2386.
[11] K.K. Bhasin, N. Singh, R. Kumar, D.G. Deepali, S.K. Mehta, T.M. Klapoetke, M.-J. Crawford, J. Organomet. Chem. 689 (2004) 3327–3334.
[12] X.H. Xu, X. Huang, Chin. Chem. Lett. 6 (2000) 473–474.
[13] M. Yoshimatsu, T. Sato, H. Shimizu, M. Hori, T. Kataoka, J. Org. Chem. 59 (1994) 1011–1019.
[14] I. Andreadou, W.M.P.B. Menge, J.N.M. Commandeur, E.A. Worthington, N.P.E. Vermeulen, J. Med. Chem. 39 (1996) 2040–2046.
[15] M. Sakakibara, K. Katsumata, Y. Watanabe, T. Toru, Y. Ueno, Synthesis (1992) 377–379.
[16] S. Narayanaperumal, E.E. Alberto, K. Gul, O.E.D. Rodrigues, A.L. Braga, J. Org. Chem. 75 (2010) 3886–3889.
[17] T. Nishino, M. Okada, T. Kuroki, T. Watanabe, Y. Nishiyama, N. Sonoda, J. Org. Chem. 67 (2002) 8696–8698.
[18] N. Taniguchi, J. Org. Chem. 72 (2007) 1241–1245.
[19] N. Taniguchi, T. Onami, J. Org. Chem. 69 (2004) 915–920.
[20] B.C. Tanu, T. Mandal, S. Samanta, Org. Lett. 5 (2003) 1439–1441.
[21] B.C. Tanu, T. Mandal, J. Org. Chem. 69 (2004) 5793–5795.
[22] S. Narayanaperumal, E.E. Alberto, F.M. de Andrade, E.J. Lenardao, P.S. Taube, A.L. Braga, Org. Biomol. Chem. 7 (2009) 4647–4650.
[23] C. Millois, P. Diaz, Org. Lett. 2 (2000) 1705–1708.
[24] A. Kundu, S. Roy, Organometallics 19 (2000) 105–107.
[25] X. Zhao, Z. Yu, S. Yan, S. Wu, R. Liu, W. He, L. Wang, J. Org. Chem. 70 (2005) 7338–7341.
[26] V.G. Ricordi, S. Thurow, F. Penteado, R.F. Schumacher, G. Perin, E.J. Lenardao, D. Alves, Adv. Synth. Catal. 357 (2015) 933–939.
[27] S. Saba, J. Rafique, A.L. Braga, Adv. Synth. Catal. 357 (2015) 1446–1452.
[28] D.J. Knapton, T.Y. Meyer, J. Org. Chem. 70 (2005) 785–796.
[29] Y. Nishiyama, K. Tokunaga, N. Sonoda, Org. Lett. 1 (1999) 1725–1727.
[30] I.P. Beletskaya, A.S. Sigeev, A.S. Peregudov, P.V. Petrovskii, J. Organomet. Chem. 605 (2000) 96–101.
[31] Y. Iwasawa, Tailored Metal Catalysis, Reidel D. Publishing Company, Dordrecht, Holland, 1986.
[32] R.M. Rioux, Model Systems in Catalysis from Single Crystals to Enzyme Mimics, Springer, 2010.
[33] Y. Yang, R.M. Rioux, Chem. Commun. 47 (2011) 6557–6559.
[34] R. Akiyama, S. Kobayashi, Chem. Rev. 109 (2009) 594–642.
[35] M.J. Climent, A. Corma, S. Iborra, Chem. Rev. 111 (2011) 1072–1133.
[36] A. Molnar, Chem. Rev. 111 (2011) 2251–2320.
[37] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710–714.
[38] A. Corma, Top. Catal. 4 (1997) 249–260.
[39] R.M. Martin-Aranda, J. Cejka, Top. Catal. 53 (2010) 141–153.
[40] P.C. Mehnert, D.W. Weaver, J.Y. Ying, J. Am. Chem. Soc. 120 (1998) 12289–12296.
[41] J.Y. Ying, C.P. Mehnert, M.S. Wong, Angew. Chem. Int. Ed. 38 (1999) 56–77.
[42] K. Mukhopadhyay, B.R. Sarkar, R.V. Chaudhari, J. Am. Chem. Soc. 124 (2002) 9692–9693.
[43] M. Cai, G. Zheng, G. Ding, Green Chem. 11 (2009) 1687–1693.
[44] M. Cai, J. Peng, W. Hao, G. Ding, Green Chem. 13 (2011) 190–196.
[45] W. Hao, H. Liu, L. Yin, M. Cai, J. Org. Chem. 81 (2016) 4244–4251.
[46] S.-G. Shyu, S.-W. Cheng, D.-L. Tzou, Chem. Commun. (1999) 2337–2338.
[47] M. Jia, A. Seifert, W.R. Thiel, Chem. Mater 15 (2003) 2174–2180.
[48] C.D. Nunes, A.A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romao, J. Rocha, I.S. Goncalves, J. Mater. Chem. 12 (2002) 1735–1742.
[49] A. Corma, E. Gutierrez-Puebla, M. Iglesias, A. Monge, S. Perez-Ferreras, F. Sanchez, Adv. Synth. Catal. 348 (2006) 1899–1907.
[50] A. Corma, C. Gonzalez-Arellano, M. Iglesias, F. Sanchez, Angew. Chem. Int. Ed. 46 (2007) 7820–7822.
[51] G. Villaverde, A. Corma, M. Iglesias, F. Sanchez, ACS Catal. 2 (2012) 399–406.
[52] R. Xiao, H. Zhao, M. Cai, Tetrahedron 69 (2013) 5444–5545.
[53] H. Zhao, W. He, R. Yao, M. Cai, Adv. Synth. Catal. 356 (2014) 3092–3098.
[54] H. Zhao, W. He, L. Wei, M. Cai, Catal. Sci. Technol. 6 (2016) 1488–1495.
[55] M.H. Lim, A. Stein, Chem. Mater 11 (1999) 3285–3295.
[56] W. Hammond, E. Prouzet, S.D. Mahanti, T.J. Pinnavaia, Microporous Mesoporous Mater 27 (1999) 19–25.
[57] P. Ferreira, I.S. Goncalves, F.E. Kuhn, M. Pillinger, J. Rocha, A. Thursfield, W.M. Xue, G. Zhang, J. Mater. Chem. 10 (2000) 1395–1401.
[58] D. Duraczynska, A. Drelinkiewicz, E.M. Serwicka, D. Rutkowska-Zbik, E. Bielanska, R. Socha, A. Bukowska, W. Bukowski, React. Funct. Polym. 70 (2010) 382–391.
[59] R.B. Nasir, M.N. Nadagouda, R.S. Varma, Green. Chem. 16 (2014) 2122–2127.
[60] B. Folkesson, Acta Chem. Scand. 27 (1973) 287–302.
[61] J. Goslar, M. Wojciechowska, M. Pietrowski, M. Zielinski, Res. Chem. Intermed. 33 (2007) 841–845.
[62] H.E.B. Lempers, R.A. Sheldon, J. Catal. 175 (1998) 62–69.