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Nanocatalysts for C–Se cross-coupling reactions

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This mini review is an attempt to highlight the most important contributions toward the applications of nanocatalysts in carbon–selenium cross-coupling reactions with the emphasis on the mechanistic aspects of the reactions. Literature has been surveyed from 2007 to 2017.

1. Introduction

Transition metal-catalyzed cross-coupling reactions have emerged as a powerful tool for the synthesis of a wide array of organic compounds with high atom and step economy.^{1–5} These reactions have a unique ability to form carbon–carbon and carbon–heteroatom (oxygen, nitrogen, sulfur, phosphorus, selenium, and tellurium) bonds under mild reaction conditions.^{6–9} In this context, extensive studies have been focused on the metal-catalyzed C–Se cross-coupling reactions for the synthesis of organo-selenium compounds,⁶ which are attractive synthetic targets for biochemists and synthetic chemists.^{10–13} Nanomaterial-based catalysts with high surface to volume ratio and reactive morphologies have been undergone tremendous growth during the past few decades.^{14–19} The use of nanoparticles

as catalysts offers several advantages: (i) improving product yield and selectivity; (ii) shortening the reaction time; (iii) decreasing the catalyst loading; and (iv) recyclability of catalyst.¹⁶ Recently, the use of nanoparticles as eco-friendly catalysts in C–Se cross coupling reactions has attracted a lot of attention (Fig. 1). Therefore rapid recent advance in nanoparticles catalyzed C–Se cross coupling reactions prompts us to review the most important reports in this interesting field with the aim of stimulating new development in this exciting research area. As a continuation of our previous works,¹⁶ in this review we have classified these reactions based on the reactions type (e.g. C–Se coupling of alkynes with diorganyl diselenides and C–Se coupling of aryl/alkyl halides with Se⁰) with special emphasis on the mechanistic aspects of the reactions.

2. C–Se coupling of aryl halides with diorganyl diselenides

Aryl halides are among the most commonly employed nucleophilic partners in the C–Se cross-coupling reactions. Metal-

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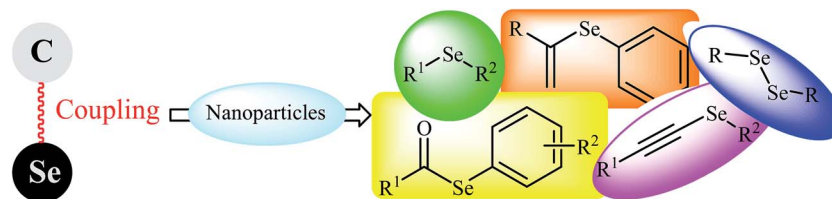
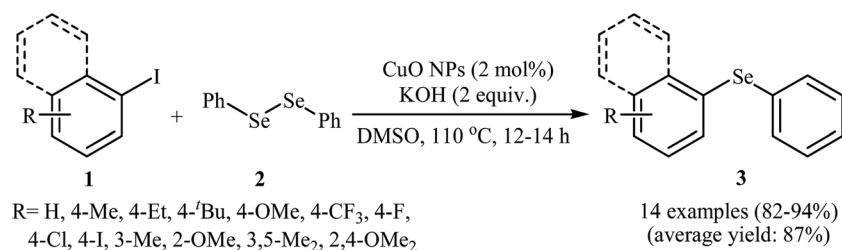


Fig. 1 Synthesis of organoselenides through nano-metal catalyzed C–Se cross-coupling reactions.



Scheme 1 Nano-CuO-catalyzed C–Se coupling of aryl iodides **1** with (PhSe)₂.

catalyzed Se-arylation reactions of diorganyl diselenides with aryl halides has been the subject of a number of recent studies.^{20–23} However, the number of reported examples on nanosized metal catalyzed reactions between aryl halides and diorganyl diselenides are few and more studies are needed in this interesting research arena.

In 2009, Rao and co-workers showed that nanocrystalline CuO was a viable catalyst for the Se-arylation of diaryl diselenides with aryl halides. Optimum yields attended the use of KOH as the base and DMSO as the solvent at 110 °C under an inert atmosphere. This optimized reaction condition was applied for the Se-arylation of a diverse set of aryl iodides **1** and diphenyl diselenides **2**, and the reaction gave high to excellent yields of the expected diaryl selenides **3** (Scheme 1). However, in the cases of aryl bromides and chlorides the yields were rather poor. Noteworthy, other nano-metal oxides such as ZnO, NiO, Fe₂O₃, Bi₂O₃, and In₂O₃ were also found to promote this ligand-

free reaction but in lower yields. According to the author proposed mechanistic pathway, the reaction may occur *via* oxidative addition followed by reductive elimination (Scheme 2).²⁴

Subsequently, the group of Rodrigues further improved the efficiency of this reaction in terms of yield, reaction time and temperature by performing the process in BMIM-BF₄ as a recyclable solvent. Thus, in the presence of 5 mol% of nano-CuO as catalyst and 2 equiv. of KOH as a base in BMIM-BF₄ at room temperature, C–Se coupling of aryl bromides **4** with diaryl diselenides **5** furnished corresponding diaryl selenides **6** in good to high yields (Scheme 3). The authors disclosed that alkyl bromides were also efficient electrophilic partners for this reaction. It is noted that the solvent was recycled over four runs without significant loss of efficiency (78–82% yield over all runs).²⁵

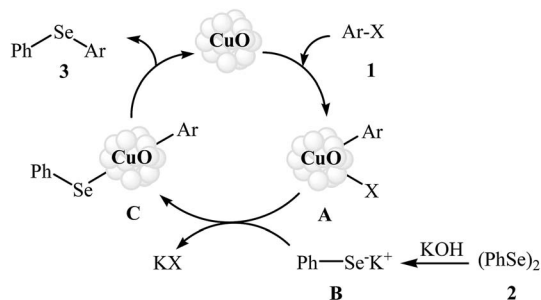
With the objective of designing a greener procedure to aryl selenides through aryl-selenylation of aryl halides, Saha and co-workers were able to demonstrate that a range of diaryl selenides **8** could be obtained from the reaction of aryl iodides **7** with diphenyl diselenides **2** in the most significant green solvent, water, employing copper(0) nanoparticle/Zn combination as cost-effective catalytic system under reflux conditions. Under optimized conditions [Cu NPs (20 mol%), Zn (1.5 equiv.), H₂O, 8–12 h], the expected diaryl selenides **8** were obtained in good to excellent yields (Scheme 4). The authors nicely showed the application of this green and sustainable procedure for the high yielding syntheses of aryl vinyl selenides *via* treatment of vinyl bromides with corresponding diaryl diselenides. The author proposed a mechanistic pathway for the formation of diaryl selenides **8** is shown in Scheme 5.²⁶ Very recently, this research team elegantly showed that iron(0) nanoparticles catalyzed reaction of aryl amines and diaryl diselenides resulted in the formation of corresponding diaryl selenides in good yields.²⁷ It is noted that the same authors also was able to



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Scheme 2 Plausible mechanism for the formation of diaryl selenides **3**.

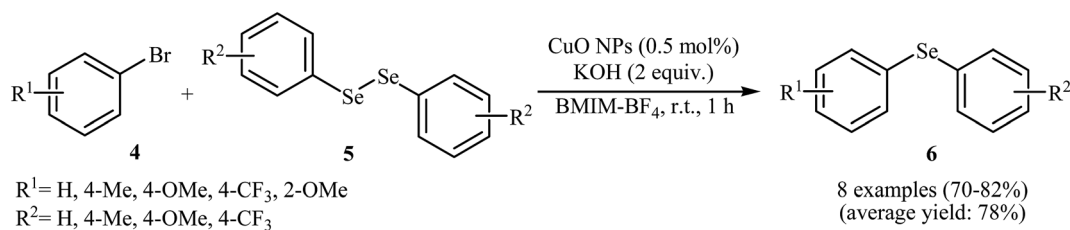
synthesis a series of functionalized selenophenes by CuO NPs catalyzed reaction of KSeCN with 1,3-dienyl bromides.²⁸

Nanosized copper ferrite (CuFe₂O₄ NPs) was also found to be an efficient catalyst for the carbon–selenium heterocoupling of aryl halides (Ar–I and Ar–Br) and diaryl diselenides in DMSO at 120 °C. Yields were good to almost quantitative (60–98% for 27 examples). The magnetic properties of CuFe₂O₄ NPs allow them to be separated from the reaction mixture and recovered with the simple use of an external magnet. The authors showed that this heterogeneous catalyst can be reused at least three times without significant loss in catalytic activity.²⁹

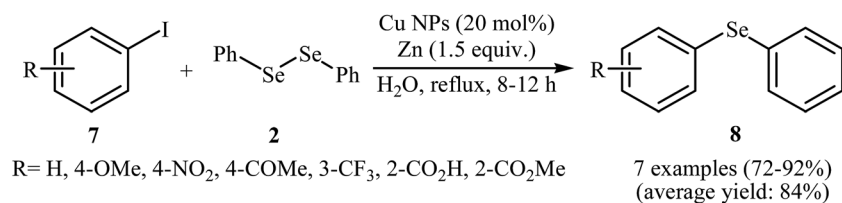
3. C–Se coupling of aryl boronic acids with diorganyl diselenides

Nanostructured copper-based catalysts have recently attracted more and more attention because of their potential as viable alternatives to the expensive rare-earth metals used in many conventional commercial chemical processes.^{30,31} Interestingly, all works on the C–Se heterocoupling reactions between boronic acids and diorganyl diselenides catalyzed by nano-sized metal systems are based on the copper nanoparticles. In this section we have discussed the most important contributions toward the synthesis of aryl selenide derivatives from aryl boronic acids and diorganyl diselenides where copper or copper-based nanoparticles have been used as a catalyst.

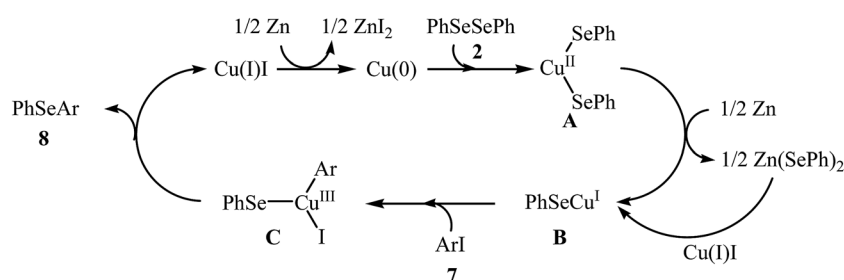
In 2009, Alves and co-workers reported for the first time the usefulness of Cu-based nanocatalysts for the heterocoupling reactions of boronic acids and diorganyl diselenides. Thus, in the presence of a catalytic amount of CuO nanoparticles (CuO NPs) as a recyclable catalyst in DMSO under air atmosphere, Se-arylation reactions of aryl and alkyl diselenides **9** with aryl boronic acids **10** furnished the corresponding selenides **11**. High yields (75–98%) were achieved in reactions with both electron-rich and electron-poor boronic acids using only 3 mol% of the catalyst (Scheme 6). The scope of this ligand-free



Scheme 3 Eco-friendly cross-coupling of aryl bromides **4** with diaryl diselenides **5** in ionic liquid.

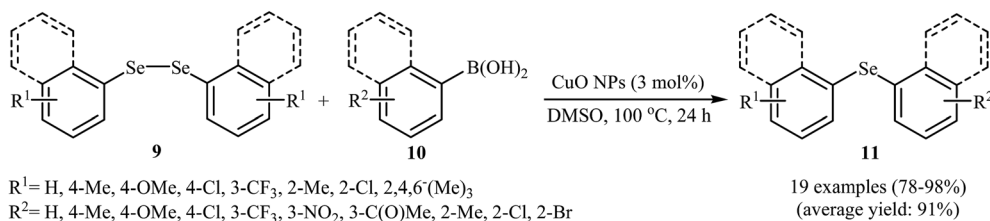


Scheme 4 Nano-Cu catalyzed synthesis of diaryl selenides **8** reported by Ranu.



Scheme 5 Mechanistic proposal for the reaction in Scheme 4.



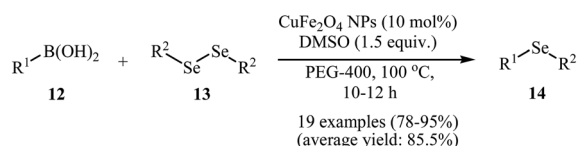


Scheme 6 Nano-CuO catalyzed Se-arylation of aryl and alkyl diselenides **9** with aryl boronic acids **10**.

procedure was also extended to diphenyl ditelluride and resulted in 94% yield.³²

Shortly afterwards, the group of Nageswar found that the C–Se cross-coupling reactions of various boronic acids **12** and diorganyl diselenides **13** using magnetically separable CuFe_2O_4 nanocatalyst can lead to the synthesis of symmetrical and asymmetrical selenides **14** in high yields (Scheme 7). Ten organic solvents were examined and eco-friendly polyethylene glycol-400 (PEG-400) was found to be optimal for this reaction. Recyclability experiments showed that the catalytic efficiency decreased slightly during repeat runs and that this decrease correlated with a progressive increase in the size of nanoparticles due to their inherent agglomeration tendency (from 20 nm to 78 nm for the first and eighth runs, respectively).³³ Similarly, copper nanoparticles $[\text{Cu}_3(\text{BTC})_2]$ (BTC = benzene-1,3,5-tricarboxylate) immobilized onto activated charcoal (AC) furnished the formation of C–Se bonds in a reaction involving boronic acids (aryl, vinyl, and alkenyl boronic acids) and diorganyl (phenyl and benzyl) diselenides. The reaction was run in DMSO and gave good to quantitative yields (61–100%).³⁴

In 2014, Bhaumik and Islam along with their co-workers designed a novel reusable and non-leaching organo-copper catalyst (Cu^{II} -CIN-1), based on loading of bivalent $\text{Cu}(\text{II})$ over the surface of a nitrogen-rich porous covalent imine network material (CIN-1). This novel heterogeneous copper catalyst was



Scheme 7 Synthesis of selenides **14** through nano- CuFe_2O_4 catalyzed Se-arylation of diorganyl diselenides **13** with boronic acids **12** in PEG-400.

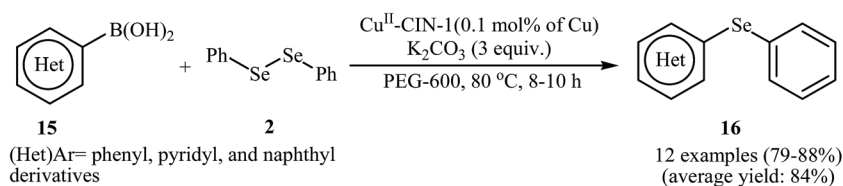
successfully used for the synthesis of a series of organoselenides **16** via C–Se bond forming cross-coupling reaction between aryl boronic acids **15** and diphenyl diselenide **2** in PEG-600. This procedure furnished the desired selenides with use of a very low amount of Cu (0.1 mol%) in high yields (Scheme 8). The protocol showed excellent functional group tolerance, including alkoxy, bromo, cyano, nitro, formyl, and ester functionalities that would allow further elaboration of the products.³⁵

Recently, the same group synthesized a novel heterogeneous copper catalyst Cu@PS-TSC by immobilizing $\text{Cu}(\text{OAc})_2$ onto the surface of a pyridine thiosemicarbazone functionalized polystyrene. The prepared catalyst was applied to the green and highly efficient synthesis of aryl selenides **18** through the reaction of aryl boronic acids **17** with diphenyl diselenide **2** in the presence of 3.0 equiv. of K_2CO_3 as a base in water (Scheme 9). The same catalysts have been also used to promote the phenyl tellurylation of aryl boronic acids with diphenylditelluride in PEG-600.³⁶

4. C–Se coupling of inactive arene C–H bonds with diorganyl diselenides

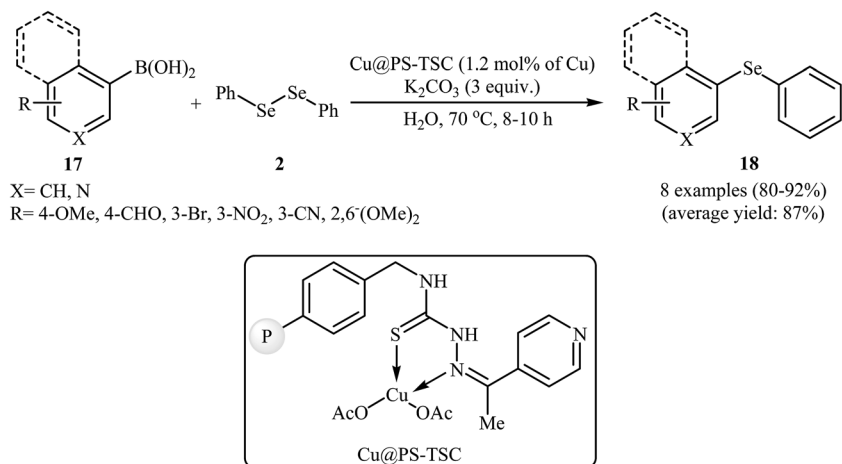
Transition metal-catalyzed direct C–H bond functionalization for the carbon–carbon and carbon–heteroatom bonds formation has emerged as a promising area in organic synthesis.³⁷ In these sets of cross-coupling reactions, the inert C–H bonds can be treated as a functional group, similar to the traditionally used C-halide/pseudohalide bonds.⁹ In recent years, several progress has been made in the construction of new C–Se bonds according to this strategy.³⁸

The possibility of transition metal nanoparticles catalyzed selenylation of (hetero) arene C–H bonds with selenylating reagents was first realized by Rosario and co-workers, who synthesized a variety of 2-(organoselenenyl)benzothiazole derivatives **21** from the reaction of unsubstituted benzothiazole **19** with diaryl diselenides **20** as nucleophilic partners in the



Scheme 8 Cu^{II} -CIN-1 catalyzed synthesis of organoselenides **16**.





Scheme 9 C–Se cross-coupling reaction between aryl boronic acids **17** with $(\text{PhSe})_2$ using Cu@PS-TSC as catalyst in water.

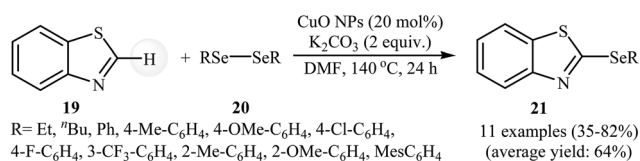
presence of 20 mol% of CuO NPs and 1–2 equiv. of K_2CO_3 in DMF under an inert atmosphere. The reaction tolerated both aryl- and alkyl-diselenides and provided 2-(organoselenyl)benzothiazoles in moderate to high yields (Scheme 10). However, the reaction does not work well for benzyl diselenides. It is noted that the same reaction conditions were also successfully applied in the synthesis of 2-(organothio)benzothiazoles *via* coupling of benzothiazole with diorganyl disulfides.³⁹

Very recently, Lin and co-workers reported the hydrothermal synthesis of ultrasmall Ru–RuO₂ nanocrystals. The resulting material was employed as an efficient catalyst for the selenylation of heterocycles in a binary solvent MeOH/DCM under ambient conditions. Various indoles **22** and diaryl diselenides **23** could be used successfully in this protocol to afford the corresponding 3-(arylselanyl)indoles **24** in almost quantitative yields (Scheme 11). Extension to benzofuran and benzothiophene were attempted, but the corresponding 3-(phenylselanyl)benzofuran and 3-(phenylselanyl)benzothiophene were isolated in less than 5% yields. It is interesting to note that neither Ru

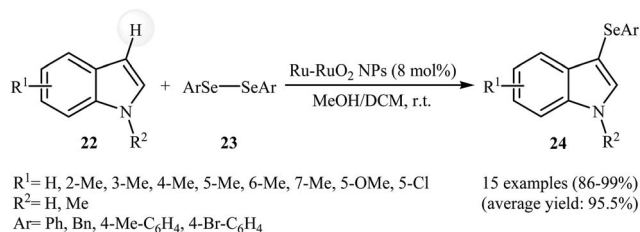
powder nor RuO₂ exhibited catalytic activity in the selenylation reaction. Thus, density functional theory (DFT) calculations were carried out to understanding the synergistic effect of metallic Ru and RuO₂. The results revealed that a diaryl diselenide can initially be adsorbed on metallic Ru sites and cleaved into two ArSe* species, which then migrate to RuO₂ sites and react with the nucleophilic partner to achieve the selenylation of heterocycles.⁴⁰

5. C–Se coupling of alkynes with diorganyl diselenides

Alkynyl selenides as an important framework in organic synthesis^{41–44} have been synthesized, among various methods, by reaction of alkynyl halides with nucleophilic species of selenium generated from a metal;⁴⁵ and selenodecarboxylation of arylpropionic and cinnamic acid promoted by iodosobenzene diacetate.⁴⁶ These various methods are of a limited application as in some of these procedures, the reaction conditions are harsh, while some procedures needs toxic metals or moisture sensitive organometallic reagents. These compounds can also be conveniently synthesized through the metal-catalyzed coupling of terminal alkynes with diselenides.⁴⁷ Copper is the most popular metal for this reaction. In 2012, the group of Braga demonstrated for the first time the usefulness of nano-scale catalysts for the C–Se cross-coupling of terminal alkynes with diorganyl diselenides to obtain alkynyl selenides. Thus, in the presence of CuO nanopowder as a recyclable catalyst and K_2CO_3 as a base in DMSO at 80 °C, C–Se cross-coupling reaction between terminal alkynes **25** and diorganyl diselenides **26** furnished corresponding alkynyl selenides **27**. The reaction tolerated both aromatic and aliphatic alkynes and selenides and gave final products in good to high yields (Scheme 12). Catalyst recycling for this system demonstrated very good yields of 71–79% over four cycles. In Scheme 13, a reasonable mechanism for this transformation is suggested. Terminal alkyne **25** reacts with the catalyst to give the [alkynylCu] cluster **A**, which reacts with diorganyl diselenide **26** to produce the intermediate **B**.

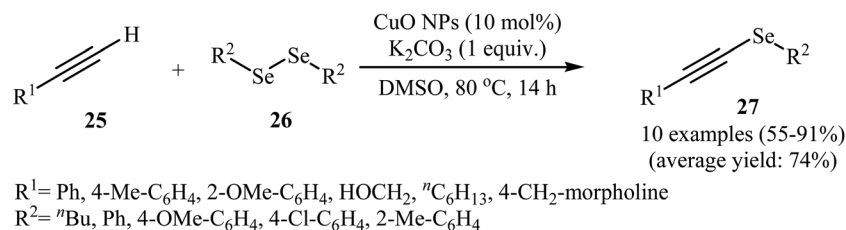


Scheme 10 Zeni's synthesis of 2-(organoselenyl)benzothiazoles **21**.

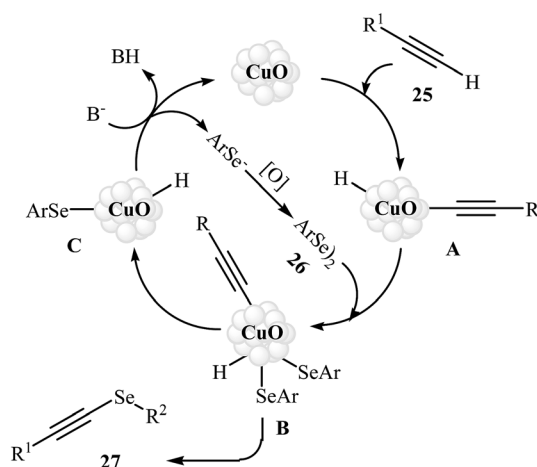


Scheme 11 Nano-Ru–RuO₂ catalyzed direct selenylation of indoles.





Scheme 12 Synthesis of alkynyl selenides **27** via nano-CuO catalyzed C–Se cross coupling of terminal alkynes **25** with diorganyl diselenides **26**.



Scheme 13 Mechanism that accounts for the formation of alkynyl selenides **27**.

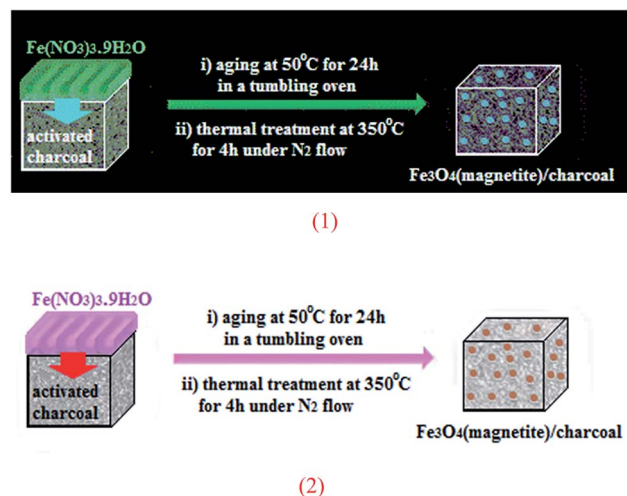


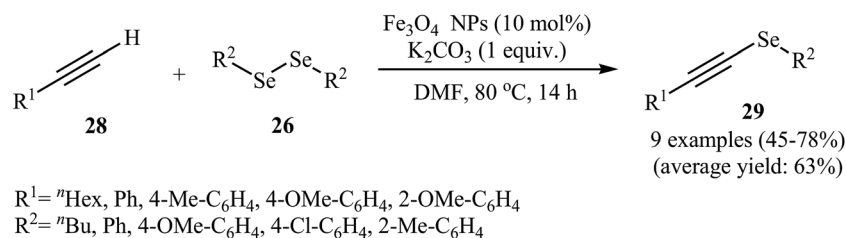
Fig. 2 Schematic diagram showing the formation of nano-Fe₃O₄/C.

Subsequently, reductive elimination of this intermediate affords the observed alkynyl selenides **27** and the species **C**. The last step of the transformation involves the regeneration of the copper catalyst by reaction of **C** with base. It is noted that the authors also successfully extended this procedure to the synthesis of alkynyl telluride derivatives through the reaction of corresponding alkynes with diorganyl ditellurides.⁴⁸

In another attempt, the same research team introduced magnetite ferroferric oxide (Fe₃O₄) nanoparticles as a novel catalyst for this transformation. The authors studied the reaction variables such as base, solvent, and temperature and found that performing the reaction in the presence of a stoichiometric amount of K₂CO₃ in DMF at 80 °C was the optimum reaction condition. Using optimum reaction condition the generality of the reaction was studied (Scheme 14). The results indicated that aromatic alkynes gave higher yields than aliphatic alkynes and

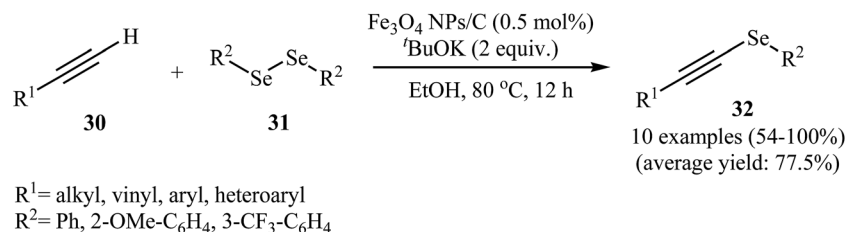
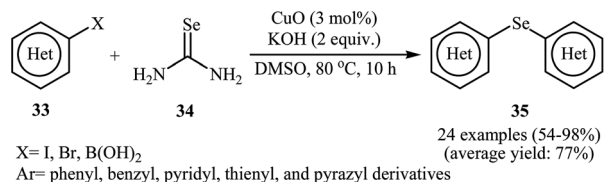
the diorganyl diselenides reacted in the order of electron-poor aromatic diselenides > electron-rich aromatic diselenides > aliphatic diselenides. The broad substrate scope, high reactivity, the simplicity of catalyst separation (using external magnets), and excellent reusability (up to four reaction runs) of the catalyst were the merits of this protocol.⁴⁹

Using solid-state grinding method, Park *et al.* supported Fe₃O₄ nanoparticles on charcoal (Fig. 2). From high-resolution transmission electron microscopy (HRTEM) images, it is noted that the average size of the magnetite nanoparticles is around 13 nm. The porous-charcoal-based Fe₃O₄ catalyst was successfully used for C–Se cross-coupling reaction of terminal alkynes **30** with diorganyl diselenide **31**. The reaction took place in refluxing ethanol in the presence of very low loading of catalyst (0.5 mol%) and generally provided corresponding



Scheme 14 Nano-Fe₃O₄ catalyzed synthesis of alkynyl selenides **29** reported by Braga.



Scheme 15 Park's synthesis of alkynyl selenides **32**.

For ArB(OH)_2 , reaction at 100 °C and prolongation of the reaction time was performed.

Scheme 16 Nano-CuO catalyzed synthesis of symmetrical diaryl selenides **35** from aryl halides/boronic acids **33** and selenourea **34**.

alkynyl selenides **32** in good to quantitative yields (Scheme 15). Noteworthy, the catalyst could be reused for five reaction runs with only slight loss of the catalytic performance.⁵⁰

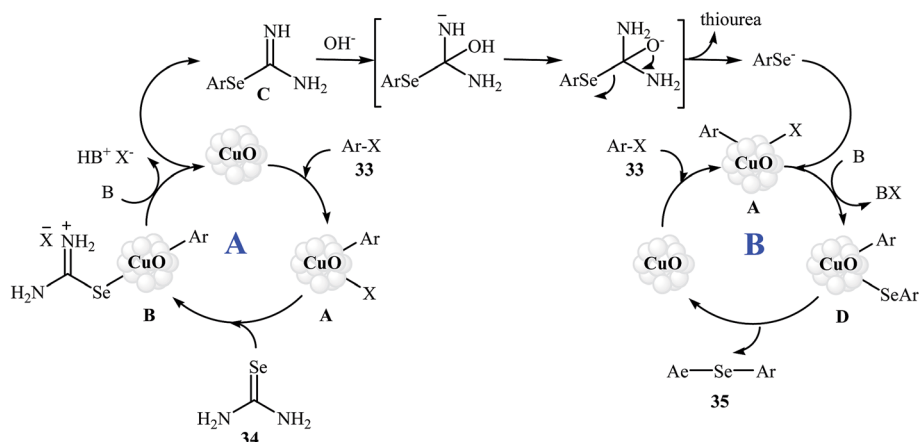
6. C–Se coupling of aryl halides/boronic acids with selenourea

In 2010, Reddy and co-workers reported an elegant copper nanoparticles catalyzed C–Se cross-coupling reaction of aryl halides/boronic acids **33** with selenourea **34** into symmetrical diaryl selenides **35** employing CuO nanoparticles as the catalyst, KOH as the base, and DMSO as the solvent. The reaction was carried out under a nitrogen atmosphere at 80 °C and provided expected selenides in moderate to excellent yields (Scheme 16). The results established that the aryl halides reacted in the order of $\text{Ar-I} > \text{Ar-Br} \gg \text{Ar-Cl}$. The results also showed that aryl iodides gave better results than aryl boronic acids. The authors

assume that the mechanism of this process involves the initial formation of the intermediate **A** through the oxidative addition of aryl halide **33** to the CuO nanoparticles. The reaction of this intermediate with selenourea **34** gives the intermediate **B**, with undergoes reductive elimination to produce intermediate **C**. Subsequently, hydrolysis of this intermediate in the reaction mixture gives a benzeneselenate moiety and urea. Next, oxidative addition of aryl iodide **33** to CuO nanoparticles affords the intermediate **A** which undergoes reaction with benzeneselenate anion to give intermediate **D**. Finally, reductive elimination of this intermediate produces the observed diaryl selenides **35** (Scheme 17).⁵¹

7. C–Se coupling of acyl chlorides with diorganyl diselenides

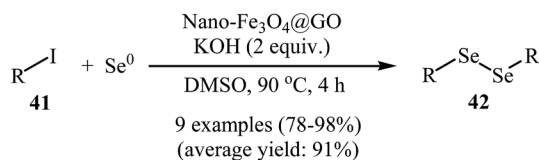
Nanoparticle catalyzed C–Se cross-coupling of acyl chlorides and diorganyl diselenides has been scarcely studied; in fact, only one example of such a reaction was reported in the literature. In this report, Braga's research team synthesized a series of synthetically important selenoesters **38** through treatment of acyl chlorides **36** with diaryl diselenides **37** using 5 mol% of inexpensive nanocrystalline CuO as the catalyst in BMIM-PF₆ ionic liquid as a recyclable solvent. The reaction was run at 80 °C and generally provided the desired selenoesters **38** in moderate to high yields (Scheme 18). This heterogeneous catalyst was chemically stable and could be recovered and reused at least four times without a decrease in the catalytic activity and selectivity. Moreover, the ionic liquid was reusable



Scheme 17 Mechanistic proposal for the reaction in Scheme 16.

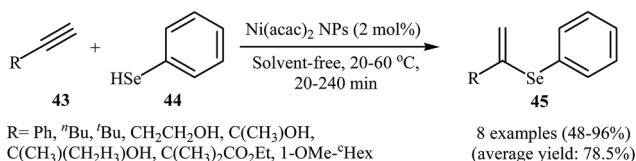






R = Ph, 4-Me-C₆H₄, 4-OMe-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄, 4-NO₂-C₆H₄, 4-CHO-C₆H₄, 3-OMe-C₆H₄, 2-thienyl

Scheme 22 Nano-Fe₃O₄@GO catalyzed cross coupling of aryl iodides **41** with Se(0).

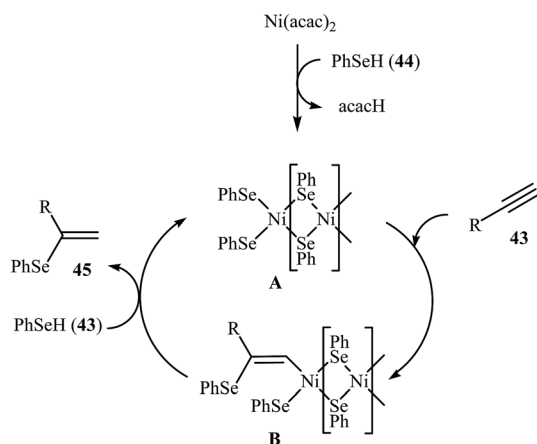


Scheme 23 Regioselective hydroselenation of terminal alkynes **43** with benzeneselenol **44** reported by Ananikov.

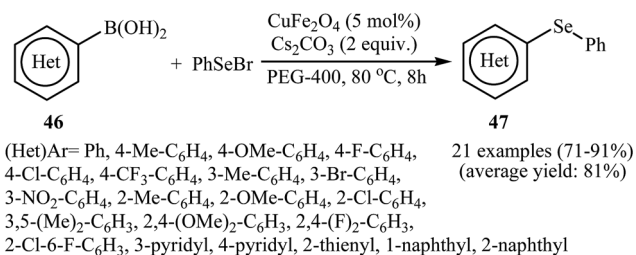
with Se⁰. Various organic solvents were examined and DMSO was found to be optimal for this reaction. Under optimized conditions [nano-Fe₃O₄@GO (7 mol%), KOH (2 equiv.), DMSO, 90 °C, 4 h], the corresponding symmetrical diorganyl diselenides **42** were obtained in high to almost quantitative yields (Scheme 22). Noteworthy, the catalyst was reusable and preserved its catalytic activity after recycling for four runs of reaction.⁵⁴

9. Miscellaneous reactions

Due to the scarce availability and air instability of arylselenols (ArSeH), there are fewer reports on cross-coupling reactions of this type of reagent as compared to other selenium reagents. Consequently, nanoparticles catalyzed C–Se cross-coupling reactions employing arylselenols as electrophilic partners have been very limitedly studied. In 2007, a simple heterogeneous Ni-based nanocatalyst was successfully used by Ananikov, Orlov, and Beletskaya in regioselective hydroselenation of terminal



Scheme 24 Mechanistic proposal for the reaction in Scheme 23.



Scheme 25 Nano-CuFe₂O₄ catalyzed C–Se cross coupling organoboranes **46** with PhSeBr.

alkynes **43** with benzeneselenol **44**. The reaction was performed at room temperature under solvent-free conditions and provided *syn*-addition products **45** in good yields (Scheme 23). However, in the case of methyl propiolate corresponding *trans*-alkene was observed as the main product. The nanostructured Ni catalyst also showed high activity and excellent *syn*-selectivity for a range of internal alkynes. The author proposed mechanism for this reaction is depicted in Scheme 24.⁵⁸

In 2012, the group of Nageswar described a nano-sized bimetallic-catalyzed C–Se cross-coupling of organoboranes **46** with phenylselenenyl bromide (PhSeBr) into unsymmetrical diorganyl selenides **47** employing CuFe₂O₄ as the catalyst in PEG-400. The reaction is noteworthy in that both aryl and heteroaryl boronic acids are tolerated (Scheme 25). The results demonstrated that this heterogeneous catalyst can be easily separated and be used several times with the only slight loss of the catalytic activity.⁵⁹

10. Conclusion

Organic selenides are of great importance in medicinal and organic chemistry, which not only found as skeleton units in biologically active molecules and therapeutic products, but also serves as building blocks in organic synthesis, and play a prominent role as organocatalysts for asymmetric synthesis. Thus a number of methods have been developed for their synthesis. Among various preparation methods of titled compounds, metal catalyzed C–Se cross-coupling reaction is considered one of the most interesting approaches due to the production of various type of selenides with high atom and step economy under environmentally friendly conditions. As illustrated, the use of nano-sized metal catalysts in C–Se cross-coupling reactions due to their high surface to volume ratio, allows for rapid transformations under mild conditions, with the benefits of high product yield and ease of catalyst separation. Despite the significant achievements during the past few years in this field, many challenges still remain to be overcome: (a) almost all of the nanoparticle catalyzed C–Se cross-coupling reactions are limited to the use of mono-metallic catalysts. Thus the exploration of bi-metallic, tri-metallic, and multi-metallic nanoparticles are highly desirable in term of the cost of preparation of the catalysts;⁶⁰ (b) the number of reported examples in some reactions such as coupling of acyl chlorides with diorganyl diselenides and



coupling of aryl halides/boronic acids with selenourea are narrow and there is an urgent need to study the scope and limitations of these reactions; and (c) other reactions such as coupling of diaryliodonium salts with various selenium surrogates should be explored. We conclude this review by hoping that it will stimulate researchers to further research in this interesting field.

Conflicts of interest

There are no conflicts to declare.

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