

Transition-Metal-Catalyzed C—S, C—Se, and C—Te Bond Formation via Cross-Coupling and Atom-Economic Addition Reactions

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1. INTRODUCTION

Transition metal catalysis has dramatically changed the face of modern organic chemistry by introducing a range of novel synthetic methods. A number of outstanding catalytic systems have been developed in recent years. These are applicable to stereo-, regio-, chemo-, and enantioselective transformations of all classes of organic compounds. Of particular interest are the fascinating catalytic achievements made in the field of carbon—heteroatom bond formation. Several very efficient catalytic systems have been developed for the formation of C—N, C—O, and C—P bonds as well as many other carbon—element bonds (Si, B, Sn, Ge, etc.).^{1–8}

Until recently, the efficient and selective construction of C—S bonds in transition-metal-catalyzed transformations remained relatively rare compared to methods developed for other carbon—heteroatom bonds such as those mentioned above. Catalyst poisoning by sulfur species, in particular by thiols and disulfides (RSH and R₂S₂), was one of the serious limiting factors in this area. Indeed, it has been reported that even very low concentrations of these sulfur species can rapidly and irreversibly deactivate the catalyst.^{9,10} This problem has been successfully overcome, and in recent decades, several excellent catalytic systems have been found for C—S bond formation, leading to the development of practical procedures for organic synthesis. Applications were further expanded to include catalytic C—Se bond formation as well as some examples of C—Te bonds.

Catalytic methods for C—S and C—Se bond formation are of great demand in general organic synthesis as well as in the pharmaceutical industry and in material science application.^{11–13}

In the pharmaceutical field, for example, relevant syntheses include selective M2 muscarinic receptor antagonists, COX-2 inhibitors (nonsteroidal anti-inflammatory drugs study), MAP kinase p38 (intracellular signal transduction cascade) inhibitors, human immunodeficiency virus type 1 (HIV-1) protease inhibitors, leukocyte function-associated antigen-1 antagonists, hypoxia-directed bioreductive cytotoxins, ATPase activity of human papillomavirus E1 helicase inhibitors, folate-synthesizing enzymes of cell cultures of *Candida albicans* inhibitors, antitumor agents, and folate-dependent enzyme inhibitors in cancer cells.¹² Without doubt, many future pharmaceutical applications will require the development of C—S and C—Se bond-based synthesis to fulfill the increasing demand and practical requirements.

Toward achieving this aim, two general methods were developed for transition-metal-catalyzed reactions. The first method involves the cross-coupling of organic halides with RZH or R₂Z₂ (Z = S, Se, Te). Cross-coupling chemistry is a widely recognized approach for the construction of new C—C and C—Z bonds. The general mechanistic framework shown in Scheme 1 is well-known. Low valent metal complexes are used as catalysts, and the catalytic cycle includes the following stages: (i) oxidative addition of an organic halide R—X, (ii) transmetalation, and (iii) C—heteroatom reductive elimination. Cross-coupling transformations are substitution reactions, and they produce a salt as a byproduct (or HX, which is trapped by a suitable base).

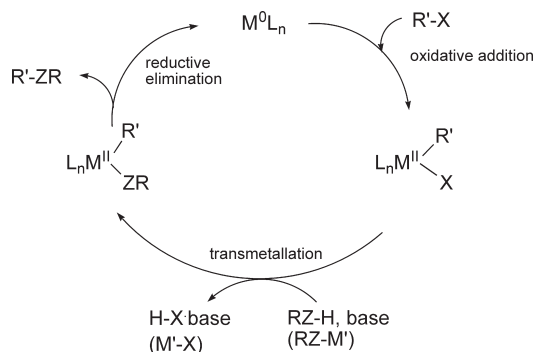
Another important approach to the formation of C—Z bonds involves the addition reaction of Z—Z and Z—H bonds to the triple bond of alkynes (Scheme 2). The catalytic cycle of these addition reactions includes the following stages: (i) oxidative addition; (ii) alkyne coordination and insertion; and (iii) C—Z reductive elimination to form the carbon—heteroatom bond (or protonolysis to form a C—H bond). It should be noted that compared with the cross-coupling reactions discussed above, one important difference in the second stage of the catalytic cycle is that alkyne insertion occurs instead of transmetalation. Such a mechanistic change leads to substantial practical advantages in terms of Green Chemistry. This is due to the fact that addition reactions are characterized by 100% atom efficiency (no other products like HX, salt, etc.).

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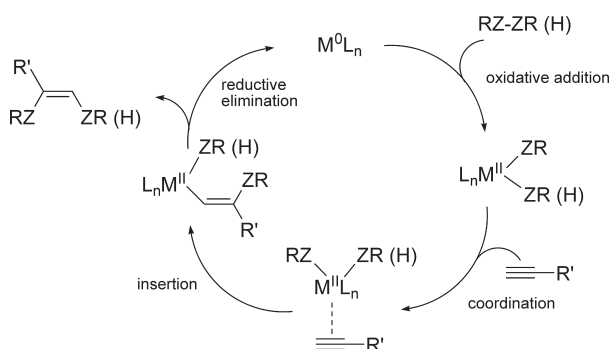
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Scheme 1



Scheme 2



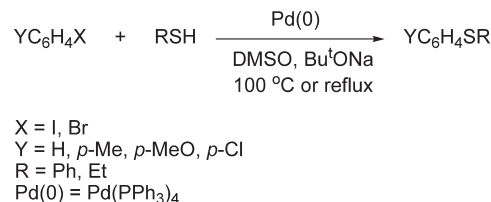
In this review, we describe C–S and C–Se bond formation utilizing both the transition-metal-catalyzed cross-coupling and the addition reaction approach. C–Te bond formation reactions will also be considered, although this chemistry is still in the early stages of development. It should be pointed out that metal-catalyzed reactions are the most efficient for the formation of Csp²–Z and Csp–Z bonds, because nucleophilic substitution on the Csp³ atoms occurs readily and usually does not require a metal catalyst.¹⁴ Noncatalytic reactions in the absence of transition metal catalysts are beyond the scope of the present review. Some relevant aspects of the title topic have been partially addressed in a range of previous reviews on Pd-catalyzed reactions,^{15–17} Cu-catalyzed reactions,^{16,18–21} f-element catalysis,²² catalytic C–S bond formation,^{23,24} the synthesis of organic sulfides and selenides,^{25–28} and catalytic addition reactions.^{29–31} Here we will focus on a discussion of state-of-the-art development of the most significant C–S, C–Se, and C–Te bond-formation research involving cross-coupling and addition reactions.

2. CATALYTIC CROSS-COUPLING REACTIONS (Z = S, SE, TE)

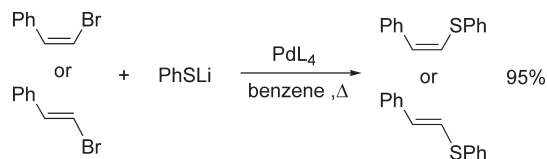
2.1. Pd-Catalyzed Transformations

The first successful reaction of an aromatic–heteroatom bond formation, that of a C–S bond, was demonstrated in 1978 by the Japanese chemists Kosugi, Shimizu, and Migita.³² Diaryl sulfides and arylalkyl sulfides were obtained from thiols and ArX derivatives in moderate to good yields (Scheme 3). High yields were obtained from the reaction with thiolate anions in EtOH or DMSO solutions.³³

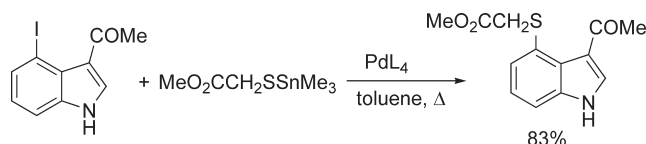
Scheme 3



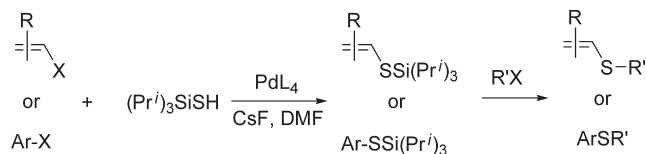
Scheme 4



Scheme 5



Scheme 6

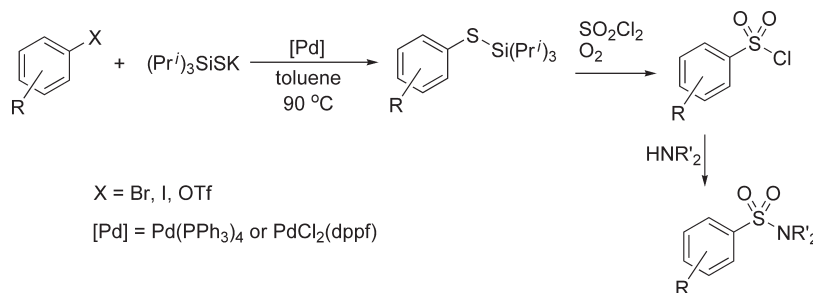


This reaction was further extended to encompass vinyl halides and was found to proceed in a stereospecific manner with retention of the C=C double-bond geometry. The result was overall high product yields (Scheme 4).³⁴

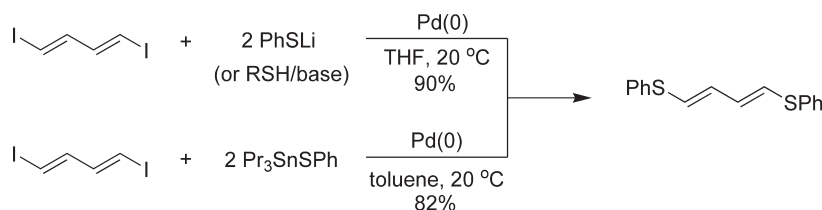
Reactions with tin derivatives such as Bu₃SnSR or Me₃SnSR, in the absence of base, are characterized by quantitative yields. In the case of vinylhalcogenides, high stereospecificity is also a feature.^{35–38} A representative example of such a reaction involving Me₃SnSR is shown in Scheme 5.³⁹ The scope of Pd-catalyzed coupling reactions of organotin sulfides for heteroaryl halides was also studied.⁴⁰

The cross-coupling of the silyl derivatives of the thiols R₃SiSH led to the formation of either vinyl (or aryl) silylsubstituted sulfides (Scheme 6).^{41,42} Further transformation of the products using alkylation or Pd-catalyzed alkenylation reactions was reported as a route to making unsymmetrical RSR' sulfides as the final products. This stepwise synthetic approach allowed for avoiding usage of some scarcely available Ar(Het)SH, which otherwise would be required to prepare the same final products in a single step utilizing cross-coupling.^{41,42} This method has also been used for the preparation of bispyrimidine thioethers.⁴³ An optimized protocol (5 mol % of Pd(OAc)₂ and 22 mol % of

Scheme 7



Scheme 8



PPh_3) has also been reported for the synthesis of silyl-protected aryl thiols via a C–S cross-coupling of aryl halides or triflates with Pr^i_3SiSH .⁴⁴

A series of aromatic and aliphatic triisopropylsilylthiols was prepared from aryl and alkyl halides in a Pd-catalyzed reaction (Scheme 7).⁴⁵ Further transformations involved the preparation of sulfonyl chlorides and sulfonamides.

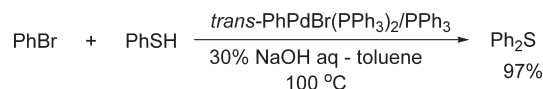
Cross-coupling of E,E -1,4-diiodobuta-1,3-diene⁴⁶ was carried out using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst under mild conditions in tetrahydrofuran (THF) or toluene at 20°C (Scheme 8).⁴⁷ Replacement of both iodide atoms was performed with total retention of the double-bond geometry.

Benzene thiol arylation with bromobenzene utilizing a biphasic aqueous–toluene system was reported by Foa and co-workers (Scheme 9).⁴⁸

Arylation of amino acid derivatives with the thiol group was carried out in the Pd_2dba_3 – dppf – NMP – Et_3N system.^{49,50} It should be mentioned that even in the early development stages of this catalytic methodology, nickel⁵¹ and copper⁵⁵ complexes were considered as potentially useful replacements for Pd catalysts. However, in both cases, high temperatures were required to carry out the reactions.

An important point clarifying the mechanistic picture of this reaction was reported by Hartwig and co-workers.^{17,53,54} Investigation of the stoichiometric C–S reductive elimination reaction on Pd complexes with bidentate ligands indicated the need for extra amounts of phosphine ligand (Scheme 10). This finding clearly emphasizes the noticeable difference between cross-coupling reactions involving the formation of C–heteroatom as opposed to C–C bonds. In addition, it was reported that coupling reactions involving aryl- and vinyl thiol derivatives are easier compared to their alkyl analogues. For ArS groups with electron-donating substituents, the reductive elimination step was faster compared to those bearing electron-withdrawing substituents.^{53,54} The importance of the C–S reductive elimination step in cross-coupling reactions was addressed in the detailed mechanistic study reported by Jutand and co-workers.⁵⁵

Scheme 9



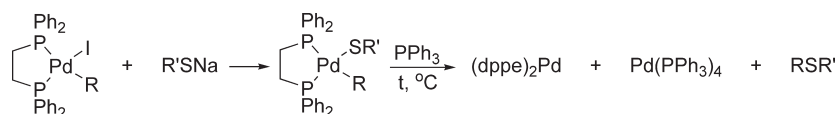
It should be noted that an interest in the detailed study of these cross-coupling reactions leading to the formation of C–S and C–Se bonds was greatly facilitated after the discovery of the amination reaction 17 years after Kosugi and Migita's landmark paper. As in the case of amination reactions, the study of C–S cross-coupling catalytic procedures was devoted to the development of new catalytic systems. These studies focused particularly on finding new ligands, which would extend the scope of the arylation reagents to include aryl triflates, aryl tosylates, unactivated aryl bromides, and aryl chlorides. Another important goal is the need to carry out reactions under mild conditions.

In 1998, after screening the available ligands, Zheng and co-workers found that $\text{Pd}(\text{OAc})_2$ – BINAP – LiCl and in particular the $\text{Pd}(\text{OAc})_2$ – Tol-BINAP system can catalyze cross-coupling reactions of various triflates.⁵⁶ However, a relatively large amount of the catalyst was required for the reaction to occur (Scheme 11). Various ArS^nBu^n products were synthesized using the $\text{Pd}(\text{OAc})_2$ – Tol-BINAP system with $\text{NaN}(\text{SiMe}_3)_2$ as the base.⁵⁷

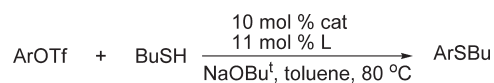
Surprisingly, the phosphine oxide $\text{Bu}^t_2\text{P}(\text{O})\text{H}$, proposed by Li and co-workers, was found to be an efficient ligand for C–S cross-coupling reactions. Its use made it possible to carry out the reaction at 110°C even using unactivated aryl chlorides (Scheme 12).^{58,59} This catalytic system has been used in the reaction of 1-chloro-1-cyclopentene (Scheme 13).⁶⁰

Unsymmetrical aromatic and heteroaromatic thioethers were obtained from $\text{Ar}(\text{Py})\text{I}$ and $\text{Ar}(\text{Het})\text{SH}$ using the Pd_2dba_3 /DPE-phos/ Bu^tOK system in toluene at 100°C in high yields.⁶¹ A series of mono- and bidentate ligands were studied in reactions involving p - $\text{MeOC}_6\text{H}_4\text{Br}$ by Murata and Buchwald. Two

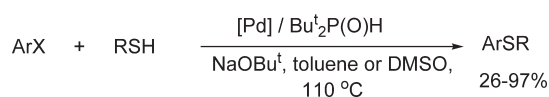
Scheme 10



Scheme 11

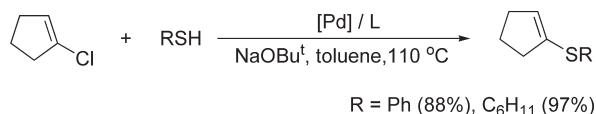


Scheme 12



ArX = PhCl, PhBr, *p*-MeC₆H₄Cl, *p*-MeOC₆H₄Cl, Pyr-Cl
R = *s*-Bu, *tr*-Bu, Hex, Ph

Scheme 13

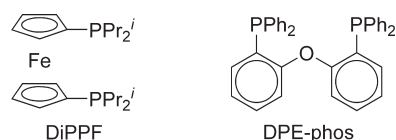


efficient ligands were selected for the reaction with benzene thiol—DiPPF and DPE-phos, but only one ligand was active in the reaction with Bu^tSH—DiPPF (2 mol % cat, Pd/P = 1:1.2, Bu^tONa, dioxane, 100 °C).⁶² The catalytic system using a DiPPF ligand was also employed in the reaction of various alkyl thiols with ArBr (including *o*-substituted), and also with unactivated aryl chlorides (Chart 1).

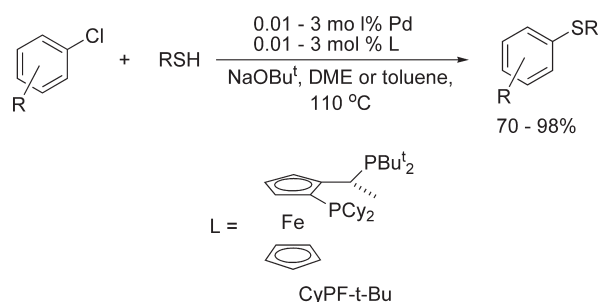
Another excellent example of an efficient bisphosphine ligand is CyPF-Bu^t. It was developed by Hartwig and co-workers. Using this ligand made it possible to carry out the cross-coupling of ArCl and ArOTf with thiols (Scheme 14).⁶³ This bisphosphine ligand possesses a high coordination ability with metal species and it is well balanced, which allows both oxidative addition and reductive elimination stages. This catalytic system showed high efficiency in the reaction with *p*-MeC₆H₄I and *p*-MeC₆H₄Br, thus making it possible to utilize very low concentrations of the catalyst (up to 0.001 mol %).^{64,65} A one-pot synthesis for unsymmetrical diaryl thioethers was developed using the Pd-(OAc)₂/CyPF-Bu^t catalytic system (0.5 mol %) with triisopropylsulfanethiol as the thiol surrogate^{66a} as well as coupling with potassium thioacetate.^{66b}

An interesting reaction using the Josiphos-type (*R*)-(*S*)-PPF-Bu₂ ligand with Pd₂dba₃ as the metal precursor was reported. This reaction leads to the enantioselective synthesis of aryl sulfoxides, which was carried out via arylation of sulfenate anions obtained from the corresponding β-sulfinyl esters (Scheme 15).⁶⁷ Good yields of between 67 and 99% and

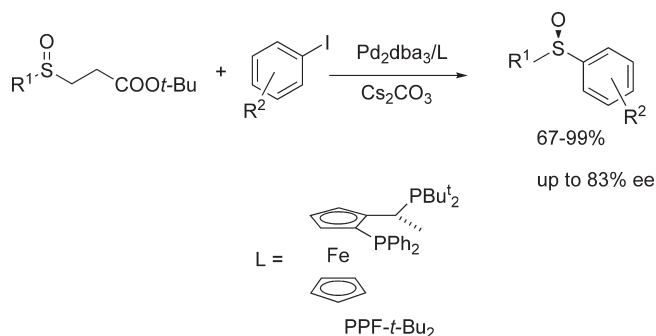
Chart 1



Scheme 14



Scheme 15

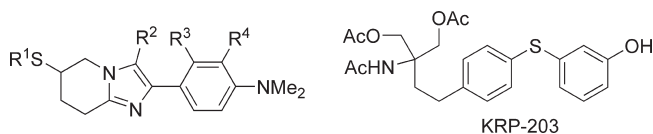


moderate to good enantioselectivities (up to 83% ee) were observed. The same coupling reaction using the achiral ligand Xantphos has also been reported.⁶⁸

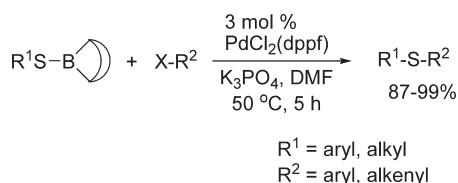
It was reported that using catalytic amounts of ZnCl₂ in a combination with a palladium catalyst allowed the cross-coupling of aryl and alkyl thiols with aryl bromides. Using 0.5 mol % of [Pd(μ-Br)(PBu₃)₂] gave high yields.⁶⁹

A good efficiency was reported for the Pd₂dba₃—Xantphos catalytic system. It was successfully used to carry out the cross-coupling reaction of ArBr, ArOTf, and *p*-NO₂C₆H₄Cl with alkyl- and aryl thiols.^{70,71} Pd complexes with Xantphos and BINAP ligands were utilized for introducing aryl sulfide and alkyl sulfonyl groups into the meso-position of porphyrins, leading to the formation of mono- and disubstituted derivatives.⁷² Special

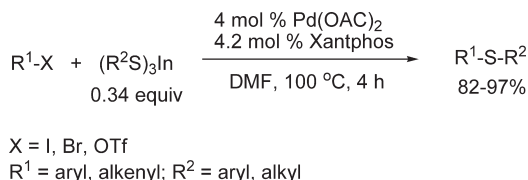
Chart 2



Scheme 16



Scheme 17



reagents for tomography applications were synthesized via the reaction of 6-iodo-2-(4'-*N,N*-dimethylamino) phenylimidazo-[1,2-*a*]pyridine with RSSnMe_3 ; DiPPF and Tol-BINAP were the ligands of choice for the reaction.⁷³ The key step in the synthesis of the immunomodulator KRP-203 was carried out using the Xantphos ligand (Chart 2).⁷⁴

The Suzuki–Miyaura cross-coupling of organic halides with boronic derivatives is a well-known methodology for C–C bond formation.⁷⁵ The cross-coupling of 9-organothio-9-borabicyclo-[3.3.1]nonanes with aryl iodides, alkenyl iodides, and carbonates have all been successfully carried out as a route to organic sulfides (Scheme 16).⁷⁶ High yields of the unsymmetrical sulfides were reported using relatively mild conditions at 50 °C.

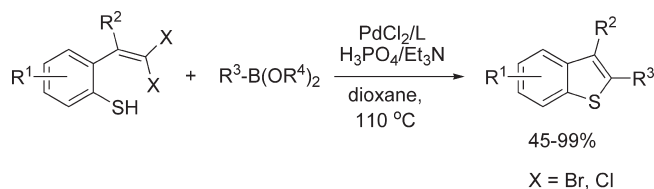
A Pd-catalyzed C–S bond formation reaction was carried out using indium tri(organosulfide) as the nucleophilic coupling partner (Scheme 17).⁷⁷ Using this procedure, a wide range of aryl–aryl, aryl–alkyl, aryl–vinyl, and alkyl–vinyl sulfides were prepared in good to excellent yields. In the reactions involving alkenyl halides, retention of the double-bond geometry was observed.

The synthesis of functionalized benzothiophenes has also been carried out using a cascade reaction of *gem*-dihalovinyl thiophenol for consecutive C–S and C–C bond formation via intramolecular *S*-thiophenylation and cross-coupling (Scheme 18).⁷⁸

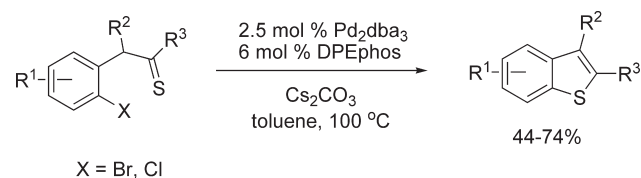
Substituted benzothiophenes were also prepared through the use of the intramolecular thio-enolate *S*-arylation reaction (Scheme 19) using DPE-phos ligand (Chart 1).⁷⁹ The enolates derived from *o*-haloaryl-substituted thio-ketones underwent a cascade sequence under Pd-catalyzed conditions, and the products were formed in moderate to good yields.

Arylation and vinylation of some cysteine derivatives were carried out using the $\text{Pd}_2\text{dba}_3/\text{dppf}$ system with aryl iodides and alkenyl iodides/bromides, respectively (Scheme 20).⁸⁰ This

Scheme 18



Scheme 19



study is of interest because it makes access to biologically active molecules containing the cysteine core possible.^{80,81} The same catalytic system was utilized to carry out the key step in the synthesis of Isoaloin, which is the main cysteine sulfoxide found in onions *Allium cepa* (Scheme 21)^{82a} and for cross-coupling under mild conditions.^{82b} The mechanism of the cross-coupling reaction of cysteine derivative was studied using both ³¹P NMR and electrochemistry.⁵⁵

A three-component reaction of *o*-bromothiophenol and *o*-iodobromobenzene with amines led to the formation of a C–S and two C–N bonds in the $\text{Pd}_2\text{dba}_3/\text{dppf}/\text{NaOBu}^t$ system.⁸³ The reaction was carried out using microwave heating and resulted in good to high yields of products.

Bu^nONa or Bu^tONa are most frequently used for carrying out the cross-coupling reactions of ArX and RSH . Krief and co-workers showed that NaH or CsOH can be a more convenient choice, although the reaction may require higher temperatures (Scheme 22).⁸⁴ It was reported that, for the synthesis of thioethers, the Pd^0L_4 complexes can be replaced with the more stable $\text{Pd}(\text{II})$ analogues.⁸⁵

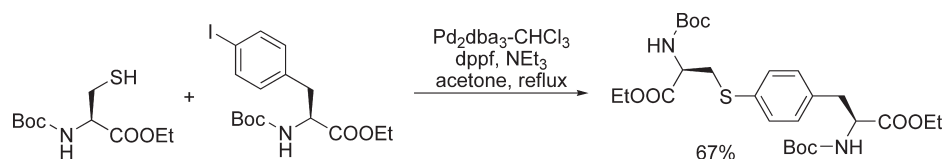
A combinatorial technique was employed for the construction of a library of *m*-(HOCH_2) $\text{C}_6\text{H}_4\text{SR}$ products (Scheme 23).^{86,87} High yields were achieved (93–96%), although significant loadings of the Pd_2dba_3 catalyst (0.2 equiv) and dppf ligand (0.8 equiv) were required.⁸⁷

Synthesis of diaryl selenides via the cross-coupling reaction of $\text{Ar}'\text{SeH}$ is a more challenging task due to the scarce availability of this type of reagent in addition to their facile oxidation in air. The reaction with the tin derivative $\text{Ar}'\text{SeSnBu}_3$ (readily available from $\text{Ar}'_2\text{Se}_2$ and $\text{Bu}_3\text{SnSnBu}_3$) was proposed as an alternative route to unsymmetrical $\text{Ar}'\text{SeAr}$ under Pd-catalyzed conditions (Scheme 24).^{88,89} However, the reaction with ArBr required a higher temperature and the concomitant risk of the facile disproportionation of $\text{R}_3\text{SnSeAr}'$ to $(\text{R}_3\text{Sn})_2\text{Se}$ and $\text{Ar}'_2\text{Se}$.^{88–90}

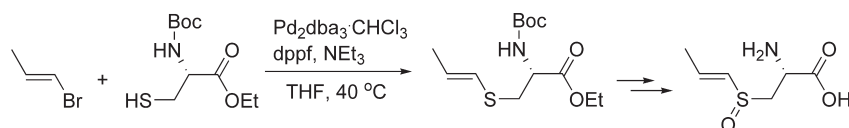
Aryl thiocyanates were used as a source for the ArS moieties through reduction by SmI_2 followed by Pd-catalyzed cross-coupling with aryl halides.⁹¹ The proposed mechanism involves the formation of the samarium thiolate $(\text{ArS})\text{SmI}_2$, transmetalation with $\text{Ar}-\text{Pd}-\text{X}$, and finally C–S reductive elimination. Moderate to good product yields were observed using 10 mol % of the $\text{PdCl}_2(\text{PPh}_3)_2/\text{dppe}$ catalyst.

Diaryl diselenides can serve as a source of ArSe groups. In addition, diaryl disulfides can be considered as a source of ArS

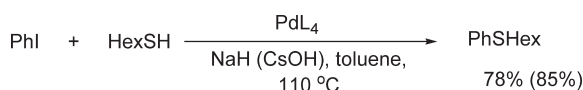
Scheme 20



Scheme 21



Scheme 22



groups. To form PhSeAr, a one-pot procedure involving the reduction of Ph₂Se₂ by Na/NH₃ followed by further transformation into the tin derivative and cross-coupling was developed.⁹² Reduction of the PhZZPh by Zn (Z = S, Se) was used as a first step in the cross-coupling reaction with ArBr (Scheme 25).⁹³ The ArSR disulfides were obtained in high yields, while a lower yield was observed for the ArSeR derivative. It should be mentioned that a convenient procedure was recently reported for the quantitative reduction of diselenides to form selenols (Zn in acidic media).⁹⁴

In(I) has been reported as a good reducing agent for the Z–Z bond. The anions formed can be easily alkylated under non-catalytic conditions.^{95,96} They can also be arylated and vinylated under Pd-catalyzed conditions (Scheme 26).⁹⁷ Although the reaction is stereospecific for the *E*-isomer in the case of the *Z*-isomer, a mixture of isomers was detected. It should be pointed out that, for the reduction of PhSSPh, other reducing agents like NaH or Na₂SO₃ may also be used.⁹⁸ In some cases, the InI-promoted reaction of Ph₂Se₂ and Ar₂S₂ with organic halides was carried out in CH₂Cl₂ at room temperature without using a transition metal catalyst.⁹⁹ For Z = Te, the reaction with alkenylboranes was reported in the synthesis of vinyltellurides.¹⁰⁰

In addition to –SAr groups, the scope of cross-coupling reactions was extended to –SO₂Ar and –S–COOMe groups. The reaction of sulfonium acid salts with aryl- and vinyl halides or triflates (Xantphos, Cs₂CO₃, Bu₄NCl, PhMe, 80 °C for ArI or 120 °C for ArBr and ArOTf) made it possible to synthesize various sulfones (Scheme 27).^{101,102} Cross-coupling of arylsulfonyl chlorides (ArSO₂Cl) with boronic acids was carried out under surprisingly mild conditions (0–25 °C) using a simple PdCl₂ catalyst. Reaction led to unsymmetrical diaryl sulfones with 80–98% yields.¹⁰³

On the basis of the catalytic cross-coupling reaction between *p*-MeC₆H₄SO₂Na and *p*-BrC₆H₄I, followed by reaction with piperidine, a target compound containing a β-3 adrenergic receptor agonist motif was prepared in 81% yield (Chart 3).¹⁰¹ A similar Pd-catalyzed reaction involving vinyl tosylates and

arylsulfonate salts coupling and a Xantphos ligand has also been reported.¹⁰⁴

The Pd-catalyzed C–S cross-coupling reaction shown in Scheme 28 was carried out starting with aryl bromides and aryl triflates and potassium thioacetate.^{105,66b} Various sulfur compounds (such as ArSH, ArSR, ArSCl, ArSOCl) are obtainable from these products in a single step.

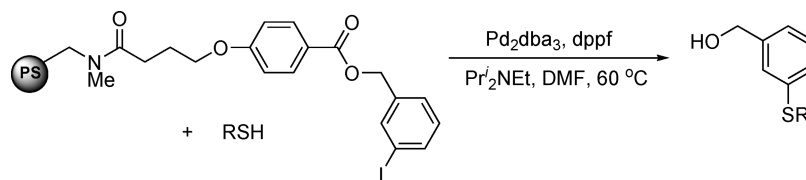
This method has been used for the synthesis of the pyrrolidine-constrained phenethylamine DPP-IV inhibitor (Scheme 29).¹⁰⁵ An example of the preparation of another biologically active compound, (±)-chuangxinmycin, with intramolecular C–S bond-formation reaction using the Pd(PPh₃)₄/Et₃N system has been described.¹⁰⁶

It is worth noting that the method described above in Scheme 28 is a useful alternative for carrying out the reaction between ArSM and RCOCl. This was previously employed for the formation of PhCOSePh using PhSeSnBu₃ as a starting material. This reaction, as well as the alkylation reaction leading to ArCOCH₂SePh,¹⁰⁷ were carried out under Pd-catalytic conditions, although both reactions easily occur under noncatalytic conditions as well.^{88,108}

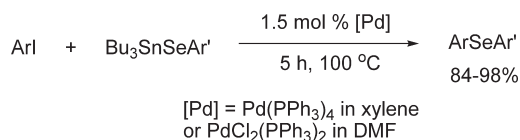
Intramolecular oxidative C–H bond functionalization using the Pd(PPh₃)₄/MnO₂ catalytic system was followed by C–S bond formation to produce 2-aminobenzothiazoles in good yields (66–96%) (Scheme 30).¹⁰⁹ An interesting reaction mechanism involving molecular oxygen and the formation of H₂O₂ was proposed.¹⁰⁹ Another synthetic pathway leading to benzothiazoles was developed starting from 2-bromoanilides and reacting with alkyl thiolate and a Pd catalyst.¹¹⁰ The Pd/Cu catalytic system containing 10 mol % of PdX₂ and 50 mol % of CuI was reported for the preparation of benzothiazoles via C–H functionalization and intramolecular C–S bond formation,¹¹¹ whereas one-pot synthesis of benzo[*b*]thiophenes from thioenols was achieved by using 10 mol % of PdX₂ catalyst.¹¹² An example of Pd-catalyzed C–H bond activation and functionalization with arylsulfonyl chlorides was described with 10 mol % of Pd(CH₃CN)₂Cl₂ as a catalyst.¹¹³

A majority of the Pd-catalyzed transformations discussed in this section were carried out using different phosphine ligands. *N*-Neterocyclic carbene (NHC) ligands have also been shown to be useful for Pd-catalyzed cross-coupling reaction using mixed [(NHC)Pd(PPh₃)Cl₂] complexes.¹¹⁴ Good yields were reported for the reaction of aryl iodides and aryl bromides with aryl thiols (45–99%) in refluxing toluene, whereas alkyl and benzyl thiols were significantly less reactive.

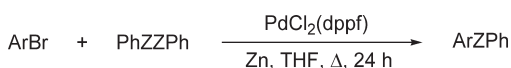
Scheme 23



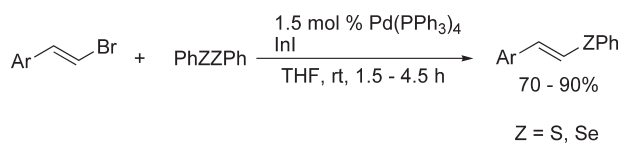
Scheme 24



Scheme 25



Scheme 26



Ligand-free Pd-catalyzed C–S cross-coupling of aryl halides with aryl thiols was developed in water under microwave heating.¹¹⁵ In the Pd(OAc)₂/NaF/TBAB catalytic system, good product yields were shown after 20 min at 150 °C.

A catalytic decarboxylative cross-coupling reaction was carried out in the Pd/Cu system under relatively harsh conditions (Scheme 31).¹¹⁶ Alkyl thiols, aryl thiols, and disulfides were involved in the reaction with varying product yields (25–90%). In the case of *o*-nitrobenzoic acid, the cross-coupling reaction was accompanied by reduction of the NO₂ group. The transformation of benzyl thiol led to formation of benzothiazoles.¹¹⁶ Synthesis of allyl phenyl selenides was achieved via a Pd-catalyzed decarboxylation of selenocarbonates.¹¹⁷ Interestingly, the Pd-catalyzed reaction of cyclic thioamides with boronic acids in the presence of stoichiometric amounts of Cu(I) gave rise to the desulfurative C–C bond-formation reaction.¹¹⁸

A heterogeneous catalytic system using a Pd/charcoal catalyst was developed for the cross-coupling of aryl- and alkyl thiols with aryl halides.¹¹⁹ High yields were observed in the case of aryl iodides (63–96%), and moderate yields were observed with activated aryl (heteroaryl) bromides and chlorides (53–75%). Catalyst recycling for this system demonstrated very good yields of 93–96% over five cycles.¹¹⁹ A comparative study of the activity of several commercially available Pd/charcoal catalysts was reported for cross-coupling reactions, including C–S cross-coupling.¹²⁰

2.2. Ni-Catalyzed Transformations

Under carefully optimized conditions, nickel complexes have shown excellent performance in catalytic cross-coupling

Scheme 27

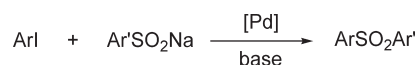
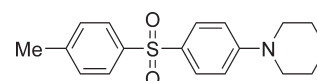
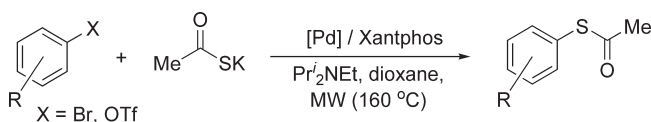


Chart 3



Scheme 28



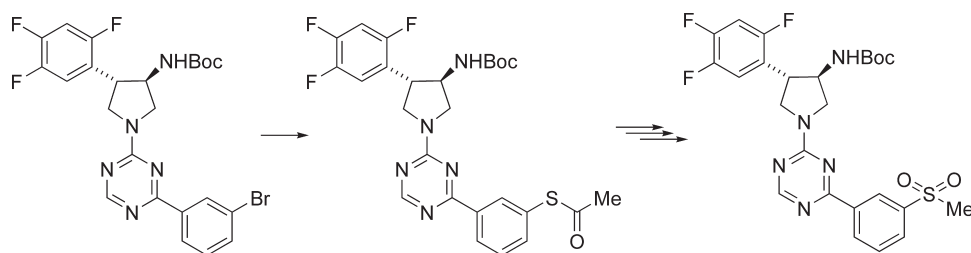
reactions. The possibility of Ni catalysis being used for Csp²–S bond formation was first demonstrated by Cristau and co-workers in 1981.⁵¹ The reaction leading to Ar₂S formation was carried out with NiBr₂ as the catalyst precursor and *o*-(Ph₂P)₂C₆H₄ as the ligand.⁵¹ A reaction involving PhSeNa was developed for the preparation of ArSePh derivatives using the NiBr₂/bpy catalytic system.¹²¹ The same authors extended the application of this cross-coupling reaction to vinyl halides (Scheme 32).¹²² Phenyl mesylate was utilized as a coupling partner in the NiCl₂(dppf)-catalyzed reaction with PhSNa (94%). However, the protocol proved of limited scope because of byproduct formation with substituted mesylates.¹²³ It was also shown that Ni(II) could replace the more expensive PdL₄ complexes as precatalyst.⁸⁵

Cross-coupling reactions of *E*-alkenyl halides and thiols were carried out with retention of double-bond geometry in the Ni/P(OEt)₃ catalytic system.¹²⁴ However, under the same conditions, the transformation of *Z*-alkenyl halides resulted in the formation of alkynes.

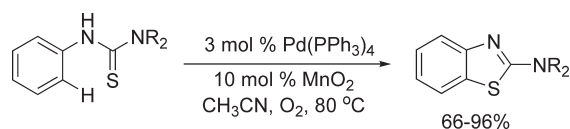
Diaryl sulfides were synthesized under mild conditions (rt–60 °C) through the reaction of XC₆H₄SH (X = H, *p*-Me, *p*-MeO) and YC₆H₄X (X = I, Br; Y = H, Me, MeCO, etc.) using the catalytic system based on NiBr₂/Zn/dppf (Scheme 33).¹²⁵

The NiBr₂(bpy) complex was found to be an efficient catalyst precursor not only for the synthesis of ArSar' derivatives but also for the catalytic formation of ArSeAr' compounds (via the cross-coupling reaction of aryl selenols). Polymer-supported borohydride was used as a reducing agent, and polymer-supported aryl iodide was used as the reagent. The reaction gave high yields as

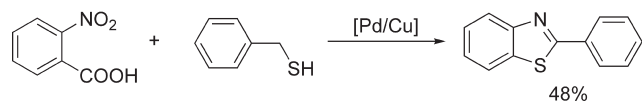
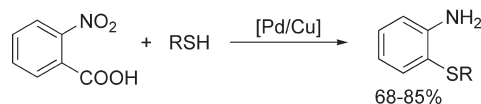
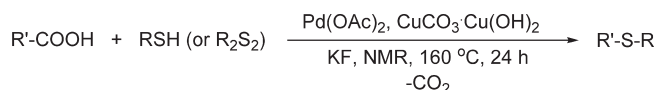
Scheme 29



Scheme 30



Scheme 31



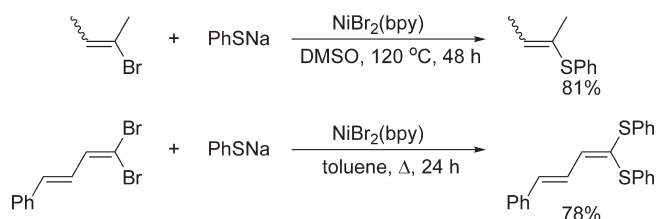
well as good product purity, which led to the construction of a library of supported species (Scheme 34).¹²⁶

Using different reducing agents, disulfides and diselenides can be involved in the cross-coupling reaction. The in situ reduction of diselenides with polymer-supported borohydride and the same Ni catalyst gave moderate to high yields in the reaction with Ar(Het)I (Scheme 35).¹²⁷

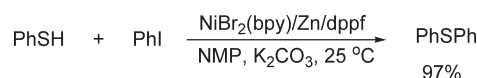
When disulfides R₂S₂ were used in the reaction, the reduction step was carried out using Zn and the same Ni catalyst precursor (Scheme 36).¹²⁸

Nickel pincer complexes (PCP)NiCl were reported as acting as efficient catalysts for C–S cross-coupling reactions (Scheme 37). With R = Bu^t the only exception, high product yields were observed.¹²⁹ The involvement of Ni(I) and Ni(III) complexes in the mechanism of the catalytic cycle was proposed for this particular case.¹²⁹ A mechanistic study of the C–S cross-coupling reaction catalyzed by nickel bis(phosphinite) pincer complexes was carried out by Guan and co-workers.¹³⁰ Surprisingly, it was found that the pincer ligand framework was destroyed to generate an active form of the catalyst. A simple Ni(COD)₂/Ph₂P(O)H catalytic system was found to be more efficient for this transformation.¹³⁰

Scheme 32



Scheme 33



Nickel complexes incorporating NNN nitrogen pincer ligands showed good efficiency in the both allyl- and aryl thiolation of iodobenzene (Chart 4).^{131,132}

It was reported recently that ligand-free nickel compounds such as NiCl₂·6H₂O can also act as efficient catalysts for the reaction of ArI and RSH in ionic liquid media. The product PhSR was formed in high yields.¹³³ Using the model reaction between *p*-MeC₆H₄SH and *p*-NO₂C₆H₄I, it was demonstrated that 5 recyclings, without noticeable loss of catalytic activity, was achievable.

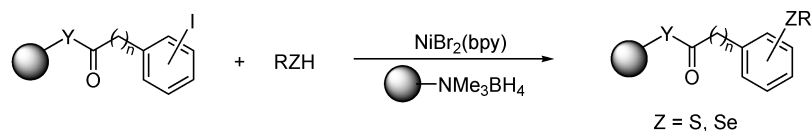
Nickel complexes with N-heterocyclic carbene ligands (NHC) were found to be efficient catalysts for the C–S coupling of aryl iodides and bromides with aryl thiols.¹³⁴ The best results, yields of 87–99%, were achieved with Ni/NHC = 1:2 ratio. The reaction with cyclohexyl thiol was also possible but gave a somewhat lower product yield (78%). It was demonstrated that for activated aryl chlorides the rate of the nucleophilic substitution pathway was competitive or even higher when compared to the metal-mediated transformation.^{134,135}

Surprisingly, the reaction of aryl thiols with ArMgBr in the presence of NiCl₂(PPh₃)₂ resulted in desulfurative C–C bond formation rather than C–S cross-coupling (Scheme 38).¹³⁶ A similar transformation was observed using the Pd/Cu catalytic system discussed above (see section 2.1).¹¹⁸

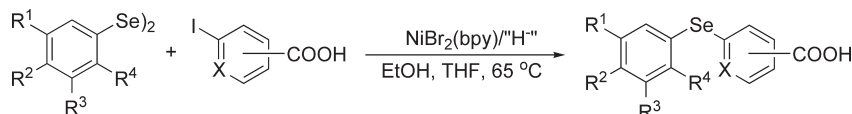
The preparation of aryl sulfides by reacting aryl bromides with thiols was carried out using the NiBr₂/Zn/PEG400 catalyst.¹³⁷ The procedure was carried out under basic conditions (NaOH) in the absence of solvent at 120 °C. Moderate to high product yields were observed with aryl and alkyl thiols (46–90%).¹³⁷

When Ni nanoparticles (15–18 nm) were used, an interesting cross-coupling reaction was found.¹³⁸ The formation of thio-

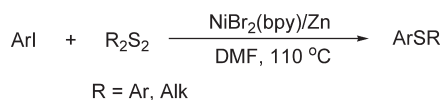
Scheme 34



Scheme 35



Scheme 36



Scheme 37



ethers from thiols and alcohols at room temperature under mild conditions has also been reported (Scheme 39). The reaction involved various aryl thiols and alkyl thiols with a wide range of alcohols and gave high yields (except for $\text{R}' = \text{alkyl}$).

2.3. Cu-Catalyzed Transformations

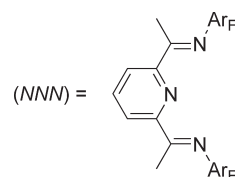
The recent renaissance in Ullmann chemistry has opened up new opportunities for the successful implementation of novel cross-coupling approaches to synthesis. These have proven especially useful for copper compounds in carbon–heteroatom bond formation under mild conditions. Numerous publications have appeared dealing with the thiolation and selenation of aryl- and alkenyl halides using various catalytic Cu complexes. The high reaction temperatures of 200–300 °C¹³⁹ were significantly reduced to 100 °C and less. This leads to several advantages: simplified synthetic reaction techniques, cheaper solvents, and greatly reduced side reactions due to the lower temperatures.

However, some of the difficulties encountered in the field of Cu-catalyzed cross-coupling reactions are due to the absence of a clear understanding of the mechanism involved. This is essential for efficient catalyst design and the selection of suitable ligands. A good understanding of the mechanism is also required for the classification of all the available data on Cu-catalyzed cross-coupling reactions.

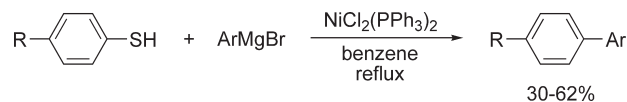
The possibility of a reaction between unactivated aryl iodides and aryl thiols was first demonstrated by H. Suzuki and co-workers using CuI in hexamethylphosphoramide (HMPA).¹⁴⁰ Corresponding aryl sulfides were also obtained in good yields (60–77%) after 1 h at 70–80 °C.

Various Ar(Het)Br compounds were prepared in good to high yields in a cross-coupling reaction using tin derivatives of the type

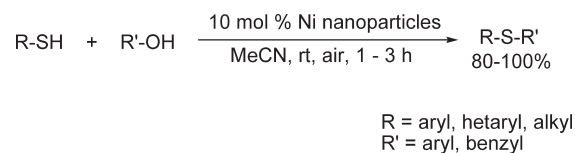
Chart 4



Scheme 38



Scheme 39

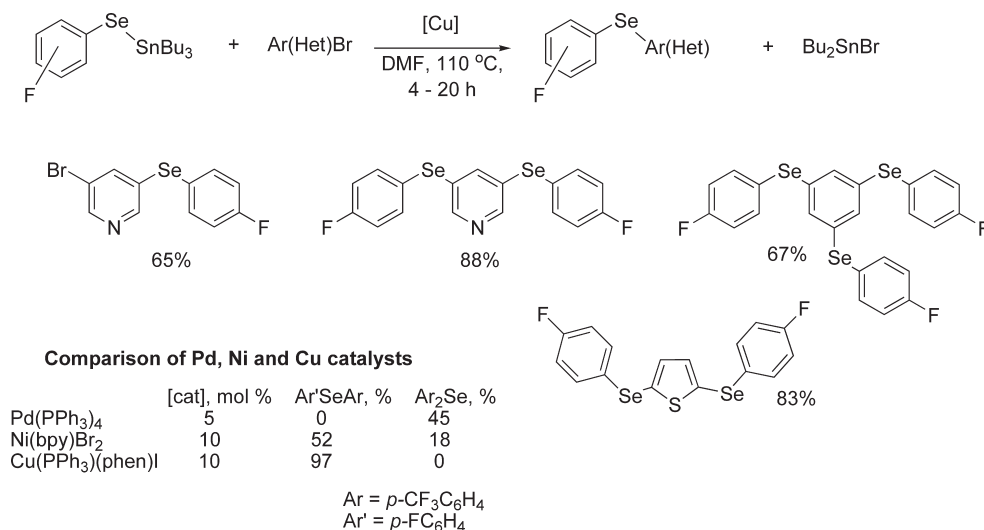


$\text{Ar}'\text{SeSnBu}_3$ and Cu(I) complexes (Scheme 40).¹⁴¹ The copper catalyst demonstrated a much better performance than the Pd and Ni systems in terms of higher product yields and the absence of the disproportionation product Ar_2Se (Scheme 40).

Under microwave irradiation, the reaction of trialkyltin arylselenides with aryl bromides was carried out using $[(\text{phen})\text{CuI}]_2$ as catalyst. Unsymmetrical diaryl selenides were produced in high to excellent yields.¹⁴² The key intermediate of this catalytic reaction—dinuclear copper(I) arylselenoate complex—was isolated and characterized using X-ray analysis (Chart 5). It was found that the catalytic activity of the isolated dinuclear complex and $[(\text{phen})\text{CuI}]_2$ were identical in the cross-coupling reaction studied.

The catalytic system incorporating the $\text{CuPF}_6(\text{MeCN})_4$ complex has been successfully applied to the synthesis of *o*-substituted aryl iodides and aryl thiols (Scheme 41).¹⁴³ An intramolecular version of the reaction leading to the formation of diaryl thioethers has also been reported.

Scheme 40



Diaryl sulfides in high yields were obtained from the reaction of aryl iodides and activated aryl bromides under CuBr-catalyzed conditions using Schwesinger's phosphazene base. Most likely, the base was also coordinated as a ligand (Scheme 42).¹⁴⁴ Similar results, but requiring longer reaction times, were observed when DBU (1,8-diazabicyclo[5.4.0]undec-7-en) was used.

Venkataraman and co-workers suggested using neocuproin as a ligand. This significantly extended the scope of the reaction to include aryl(hetaryl) iodides with both electron-donating and electron-accepting substituents as well as various alkyl and aryl thiols such as *o,o*-Me₂C₆H₃SH (Scheme 43).¹⁴⁵

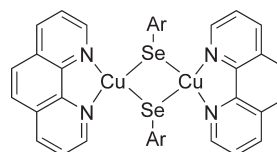
The CuI–neocuproin (1:1) complex was used in the arylation of 8-mercaptoadenine (Scheme 44). This catalytic system was utilized for the synthesis of a series of 8-arylsulfanyl adenine derivatives.¹⁴⁶ The synthesis of diaryl selenides was also reported using the 10 mol % CuI/neocuproin catalyst. Starting from aryl iodides and phenyl selenol, yields were from 60 to 90% (toluene, 110 °C, 24 h).¹⁴⁷

A soluble Cu(I) complex was successfully used by Venkataraman and co-workers in a C–S cross-coupling if more reactive vinyl iodides were utilized as a reagent (Scheme 45).¹⁴⁸ Stereo- and regiospecific reactions of vinyl iodides with thiols were performed using CuI as catalyst with *cis*-1,2-cyclohexanediol as the ligand and K₃PO₄ as base.^{149,150} The synthesis was carried out under mild conditions at 30–50 °C (0.5–4 h) and resulted in high product yields. Electron-rich vinyl iodides, such as 3,5-dimethoxyphenyl vinyl iodide, reacted smoothly with this catalytic system (96%).¹⁴⁹ The CuI/phenanthroline catalytic system was also employed for the preparation of 2-sulfide carbapenems.¹⁵¹ A single example of a reaction of a vinyl bromide with *o*-methylbenzenethiol has also been reported using the CuCl catalyst.¹⁵²

Kwong and Buchwald suggested using a simpler ligand, ethylene glycol, to carry out cross-coupling reactions with alkyl and aryl thiols using a smaller amount of CuI and lower temperatures (Scheme 46).¹⁵³ This catalytic system was successful in the cross-coupling reaction of aryl thiols with 6-halogenoimidazo[1,2-*a*]pyridines.¹⁵⁴

Even better results were achieved using the tridentate oxygen ligand—1,1,1-tris(hydroxymethyl)ethane (Scheme 47).

Chart 5

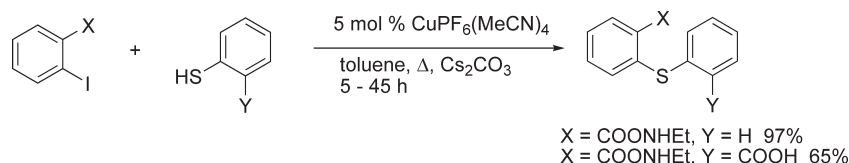


Near-quantitative yields were obtained for the reaction involving various aryl iodides (including *o*-MeO-substituted) with aryl thiols and alkyl thiols.¹⁵⁵

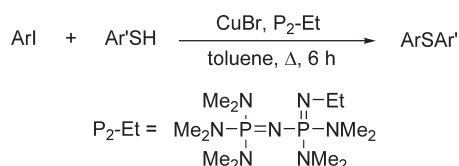
Another efficient copper catalytic system was developed to encompass not only aryl iodides but also aryl bromides.¹⁵⁶ Using the CuI/tris-(2-aminoethyl)amine catalyst in dioxane, good yields of the corresponding diaryl sulfides were reported (Scheme 48).

A protocol for the copper-catalyzed synthesis of diaryl sulfides was described using CuCl/*trans*-1,2-diaminocyclohexane system in water.¹⁵⁷ An aqueous solution of the copper complex was recycled in 3 runs without loss of activity. However, a further fourth recycling led to degradation of catalytic activity. Surprisingly, the amount of water played a critical role in catalytic behavior: either a decrease or an increase in water content resulted in lower product yields.¹⁵⁷ Another diamine ligand—BINAM (1,10-bisnaphthyl-2,2'-diamine)—has also been used for the cross-coupling of aryl iodides and aromatic/aliphatic thiols (Chart 6).^{158,159} Using 20 mol % of the Cu(OTf)₂ catalyst, 88–97% product yields were obtained. It is interesting to point out that CuI and CuBr were both less efficient catalysts with the BINAM ligand.¹⁵⁸ The CuCl₂/BINAM catalytic system was applied to the intramolecular coupling of *N*-(2-chlorophenyl)benzothioamides with benzothiazoles as the products.¹⁵⁹ An efficient and functional-group-tolerant catalytic system was reported for the Cu-catalyzed *S*-arylation of thiols with aryl halides using both unsubstituted¹⁶⁰ and substituted quinolines as ligands (Chart 6).¹⁶¹ The nitrogen ligand, 9-azajulolidine, has been used for a C–S bond formation reaction with the CuI catalyst.¹⁶² Other nitrogen ligands have also been used.¹⁶³ Various diamine ligands for use in Cu-catalyzed transformations have been recently reviewed.¹⁶⁴

Scheme 41



Scheme 42



To carry out the reaction with aryl iodides, including *o*- $\text{HOC}_6\text{H}_4\text{I}$, a Cu catalyst with a new ligand bearing oxime and phosphine oxide groups had to be developed (Scheme 49).¹⁶⁵ The products were obtained in good to high yields. It was shown that CuI could be replaced by the readily available and air-stable Cu_2O . It should be noted that when Cu_2O is without additives it requires stoichiometric amounts and high temperatures (160 °C).^{23,166} In spite of this limitation, ligand-free Cu_2O -catalyzed C–S bond formation was possible in the dimethylsulfoxide (DMSO)/ H_2O /KOH system. Good to high product yields for various aryl iodides and aryl thiols were achieved.¹⁶⁷ The catalytic system was further developed to establish a more efficient C–S cross-coupling protocol using the 2-oxocyclohexanecarboxylate ligand, and the role of water was also addressed.¹⁶⁸

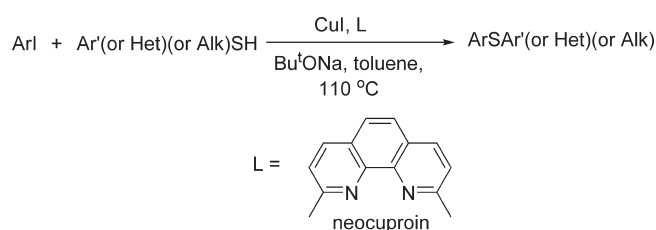
Small *p*-phenylene sulfide oligomers were prepared from the corresponding aryl halides using Cu_2O -mediated Ar–S coupling with thiols (Scheme 50)¹⁶⁹ or a CuI catalytic system.¹⁷⁰ The resulting products were studied because of possible applications in material science.

Significant progress has been achieved using amino acids as ligands in the Cu-catalyzed reaction. Not only aryl iodides but also aryl bromides (but without electron-donating substituents) were used as starting materials and led to yields of 90–98% and 72–85%, respectively (Scheme 51).¹⁷¹ This catalytic system was found to be very sensitive to the nature of both the solvent and the base. A plausible mechanism was reported, and the involvement of a Cu(I)/Cu(III) species was proposed (Scheme 52). Using *L*-proline as the ligand, it was possible to carry out the reaction under milder conditions and a concomitant high functional group tolerance.^{171–173}

The Cu/*L*-proline catalytic system was found to be very efficient in the synthesis of vinyl sulfides in the reaction of 3-iodocyclohexanone with Ar(Het)SH (Scheme 53).¹⁷⁴ Good to high product yields were reported for the cross-coupling reaction carried out in 95% ethanol.

A very efficient CuI–benzotriazol catalytic system was reported by Verma and co-workers. They used a range of aryl bromides in the cross-coupling reactions (Scheme 54).¹⁶⁶ High yields were achieved in reactions with both alkyl and aryl thiols using only small amounts of catalyst and ligand (high turnover number (TON) values). It should be noted that, for the reactions with alkyl thiols, the temperature could be decreased from 100 to 80 °C. For ArX compounds bearing COOH and CHO groups,

Scheme 43



Cs_2CO_3 was added instead of Bu^tOK . It was suggested that the mechanism of this catalytic cycle involved the Cu(I)/Cu(III) species (Scheme 55).

The C–S cross-coupling of aryl(hetaryl) iodides and bromides, activated aryl chlorides, and vinyl iodides with thiols was carried out with good to high yields using the CuI catalytic system. The unusual ligands catechol violet¹⁷⁵ and *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol were used¹⁷⁶ (Chart 7). In the case of the activated aryl chlorides, the possibility of noncatalytic transformation was not studied under these experimental conditions.

In the particular case of the substrate *o*-bromobenzoic acid, a binary Cu/ Cu_2O catalyst was employed with 2-ethoxyethanol as both solvent and ligand (Scheme 56).¹⁷⁷ It was reported that in this particular catalytic system the formation of the C–S bond was observed to be faster than formation of the C–O and C–N bonds.

Catalytic cross-coupling reactions were shown to be particularly favorable for the preparation of several important compounds. For example, triazene-substituted arylthioglycosides were readily synthesized in MeCN via the reaction of the corresponding thiols with aryl iodides using the CuI/Py catalytic system (Scheme 57).¹⁷⁸

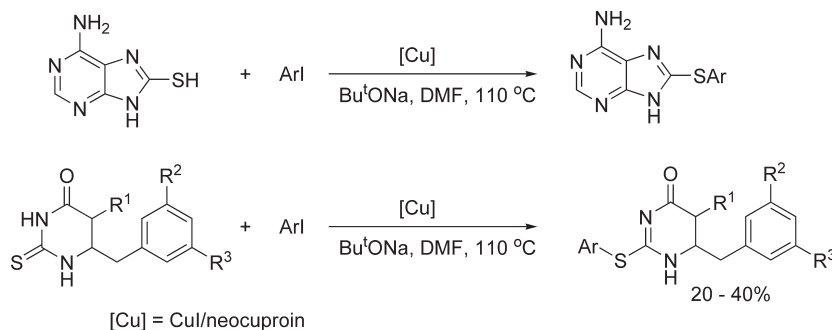
Using Buchwald's catalytic system, highly hindered sulfides were prepared in moderate to good yields (Scheme 58).¹⁷⁹ However, the reaction was not catalytic and required 1 equiv of CuI. The Cu-mediated synthesis of highly hindered *o*-substituted sulfides has also been reported much earlier.¹⁸⁰

In the synthesis of VX-745 (the P38 α MAPK inhibitor), the Cu-catalyzed reaction proved better than the Pd-catalyzed transformation (Scheme 59).^{181,182} In both catalytic systems, microwave heating (MW) facilitated the procedure and shortened the reaction times.

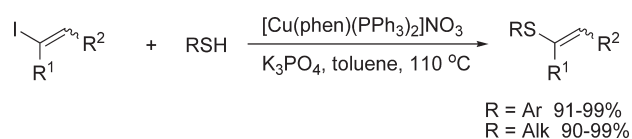
Applying MW to the reaction of ArI and ArBr with RSH in the CuI/NMP/ Cs_2CO_3 /195 °C catalytic system made it possible to shorten the reaction time to 2–6 h while maintaining good yields of 64–89%.¹⁸³ The cross-coupling of aryl iodides with aryl thiols was also performed using a β -keto ester as a CuBr ligand in the Cs_2CO_3 /DMSO/60–75 °C system.¹⁸⁴

An example of the catalytic cross-coupling reaction of aryl bromides with thiols in ionic liquids has been reported ([BMIM]-[BF₄]/ K_2CO_3 /CuI/*L*-proline/110–120 °C).¹⁸⁵ High yields and

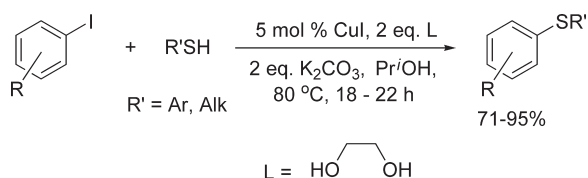
Scheme 44



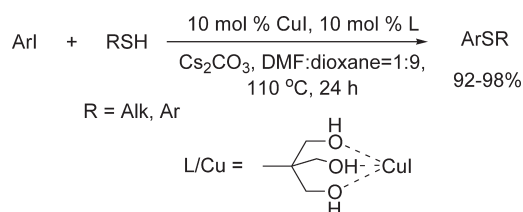
Scheme 45



Scheme 46



Scheme 47



high *E/Z*-selectivity were found, although catalyst recycling led to significant loss in activity. Using activated aryl chlorides, the reaction in water was shown to proceed in the CuI/ethylenediamine/120 °C system. In most cases, it gave moderate to high product yields (50–95%).¹⁸⁶ Unfortunately, the authors did not report the yields in the absence of copper or comment on the possibility of hydrolysis under the experimental conditions used.¹⁸⁵

One topic of special interest is the development of cross-coupling methodologies to carry out the reaction between ArX and RSH in water in the absence of organic ligands. CuI, without additional ligands, was used as a catalyst in the reaction of thiols with iodoalkenes to give products in moderate to good yields.¹⁸⁷ Recently, it was reported that thiophenol reacts with phenyl halides in water in the presence of Bu₄NBr (TBAB) at 80 °C (Scheme 60).¹⁸⁸ Product yields for the reaction involving

Scheme 48

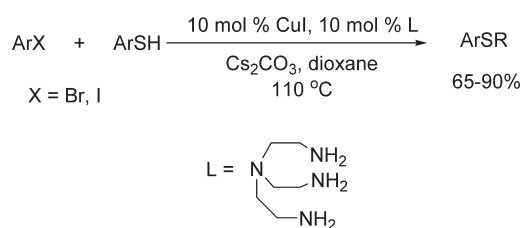
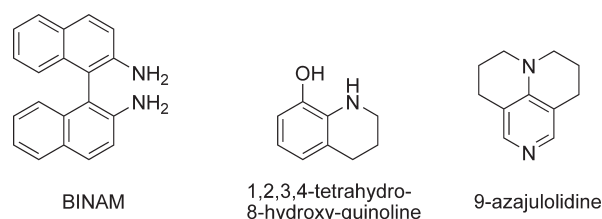
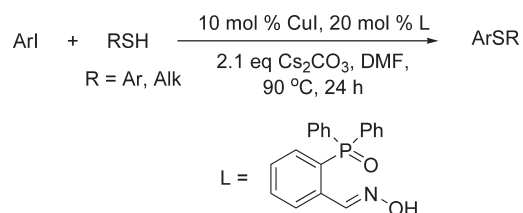


Chart 6



Scheme 49

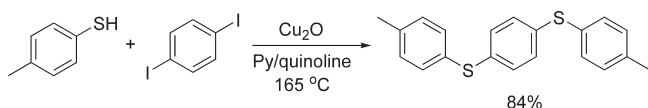


ArSH and PhCH₂SH were as high as 91–99%, whereas with BuSH the yield dropped to 15%. A ligand-free reaction was also carried out in toluene solution in the presence of NaOH and TBAB.¹⁸⁹

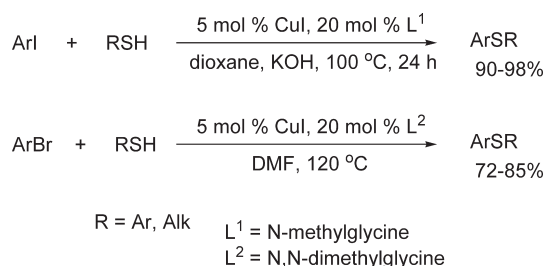
van Koten and co-workers reported a ligand-free catalytic system using 1–2.5 mol % of CuI, 2 equiv of NMP, and 1.1 equiv of K₂CO₃ (6 h, 100 °C).¹⁹⁰ Except for 1-naphthyl iodide (46%), high yields were observed (78–96%) for reactions of benzenethiol and aryl iodides. Various aryl thiols reacted smoothly with iodobenzene (85–95%). Yields were lower in the case of electron-withdrawing substituents and alkyl thiols (54–60%).¹⁹⁰

Ligand-free CuI-catalyzed intramolecular S-vinylation of thiols with vinyl chlorides (dioxane as a solvent) and bromides

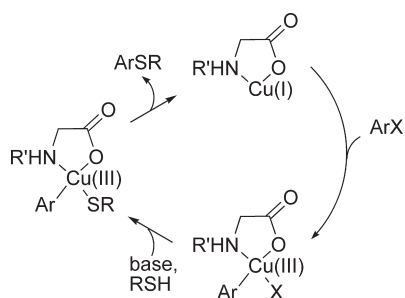
Scheme 50



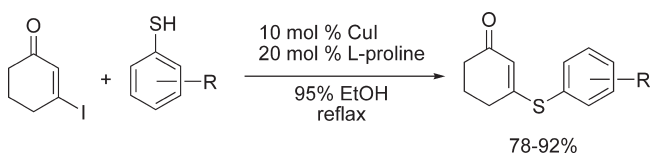
Scheme 51



Scheme 52



Scheme 53

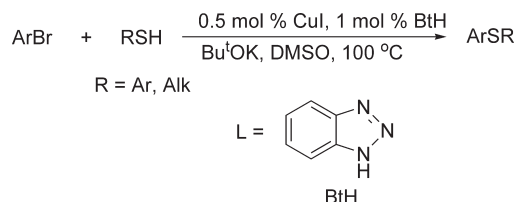


(acetonitrile) using K_3PO_4 as a base (Scheme 61) have all been reported.¹⁹¹ The cyclization took place preferably via the 4-*exo* route (Scheme 61).

A ligand-free reaction was reported for the CuS/Fe catalytic system in reactions of aryl iodides and bromides with diaryl diselenides (Scheme 62).¹⁹² An important role of the iron additive was not only to reduce the CuS to the active form Cu_2S but also to provide a support to prevent catalyst agglomeration (scanning electron microscopy–energy-dispersive X-ray (SEM-EDX) catalyst characterization was reported). It proved possible to recycle the catalytic system with a loss of catalytic activity from 99% in the first run to 87% in the fourth run.

An interesting approach toward C–S bond formation was developed on a solid support based on a Cu(I) -mediated coupling reaction.¹⁹³ Immobilized aryl halides were reacted with thiols to produce thioethers including sterically hindered

Scheme 54



Scheme 55

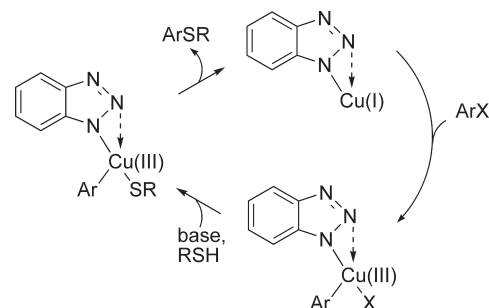
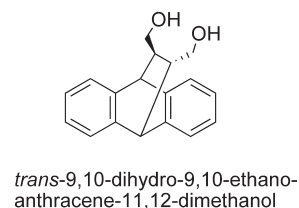
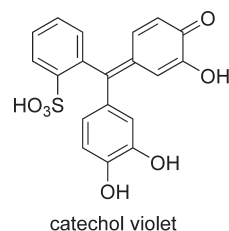
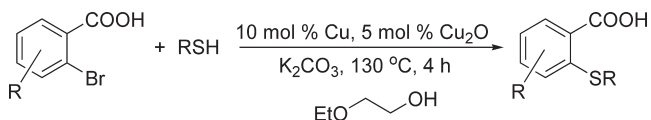


Chart 7



Scheme 56

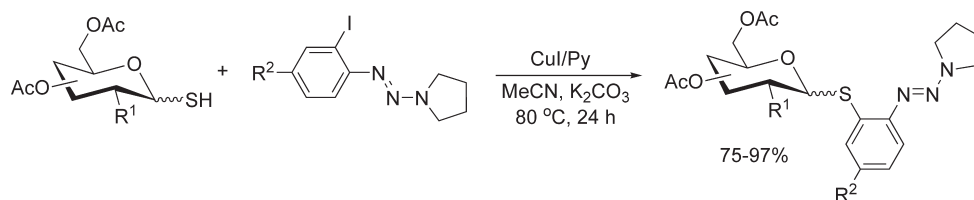


and electronically deactivated aryl moieties. After C–S cross-coupling, the products were cleaved from the resin support.

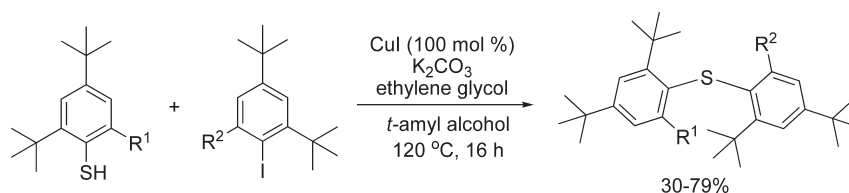
A simple protocol was developed for the C–S coupling of aryl iodides with aryl thiols and alkyl thiols using $\text{CuI}/\text{PEG}/\text{H}_2\text{O}$ catalytic systems in the absence of additional ligands.¹⁹⁴ The products were easily separated using extraction techniques, and high isolated yields were obtained (85–98%). The catalyst was recycled over six runs without significant loss of activity (95–98% yield over all runs). The proposed reaction mechanism involved the reduction of the CuI precursor and the participation of a $\text{Cu(0)}/\text{Cu(II)}$ species in the catalytic cycle (Scheme 63).¹⁹⁴ Ligand-free C–S cross-coupling has also been described using $\text{KF}/\text{Al}_2\text{O}_3$ as the base.¹⁹⁵

Copper nanoparticles were shown to be an efficient catalyst for cross-coupling reactions under ligand-free conditions.

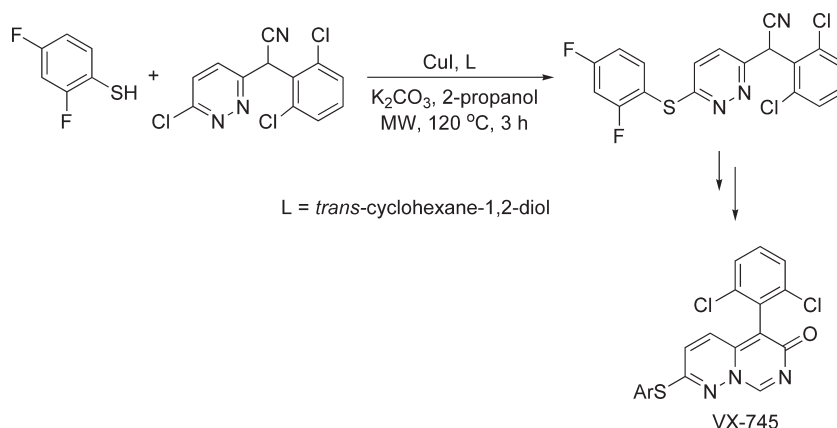
Scheme 57



Scheme 58



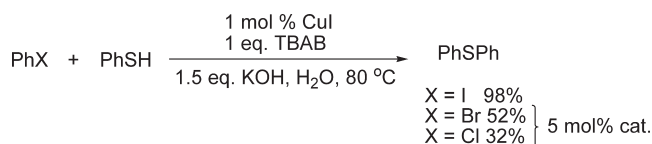
Scheme 59



Sustainable procedures were developed to achieve the phenyl selenation of aryl iodides and vinyl bromides in water using 20 mol % of Cu nanoparticles.¹⁹⁶ The possibility for catalyst recycling was demonstrated, although the activity of the catalyst did decrease after each cycle. Retention of stereochemistry was observed for *E*-vinyl bromides, whereas in the case of the *Z*-vinyl bromides resulted there was a loss in stereoselectivity.¹⁹⁶

A high catalytic activity of Cu nanoparticles was observed in the reaction between aryl iodides and thiols under MW heating at 120 °C (Scheme 64).¹⁹⁷ The reaction was completed in minutes, which is much faster compared to CuI-catalyzed transformation in the absence of the nanoparticles.¹⁸³ In the case of ArSH, high product yields of 82–98% were found, whereas in the case of AlkSH, significantly lower yields were observed due to a side reaction leading to the formation of Alk₂S₂. The authors noticed that using copper powder under the same conditions led to yields of only 25–40%.¹⁹⁷ Copper nanoparticles supported on hexagonal microporous silica were shown to catalyze the *S*-arylation of activated aryl iodides with high yields (up to 99%) under MW heating.¹⁹⁸ The yields and selectivities observed for aryl iodides

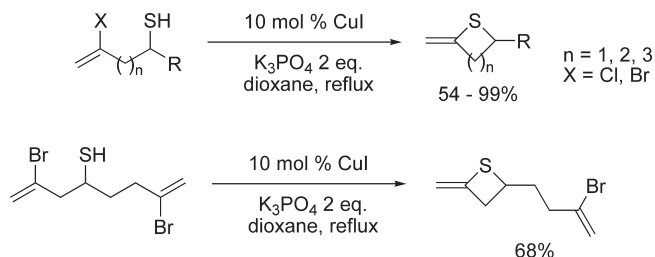
Scheme 60



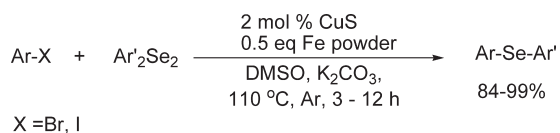
bearing electron-donating groups were lower (69% for benzenethiol and *p*-tolyl iodide). This was attributed to homocoupling of the thiols leading to ArSSAr. Catalyst recyclization has been shown to lead to a slow decrease in activity from a 99% yield in the first run to 93% in the fourth run (MW, 80–100 °C, 10–20 min).¹⁹⁸

Nanosized CuO was also found to be an efficient catalyst for the reaction of ArI and RSH (for both ArSH and AlkSH) in DMSO at 80 °C (Scheme 65).¹⁹⁹ Yields were almost quantitative (85–99%). Catalyst recycling was possible for three successive cycles, although the yield of the reaction decreased. Introducing electron-donating groups into the ArI significantly decreased product yields.

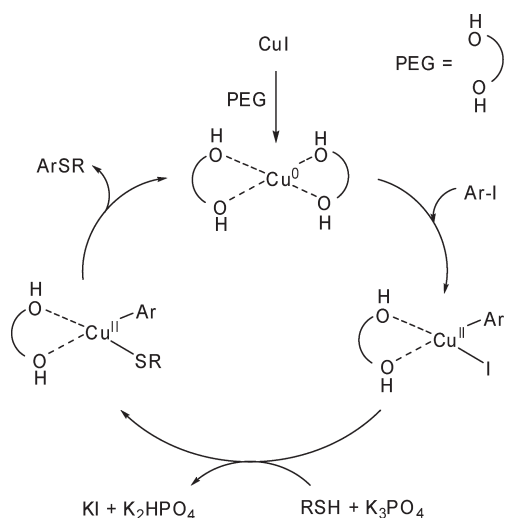
Scheme 61



Scheme 62

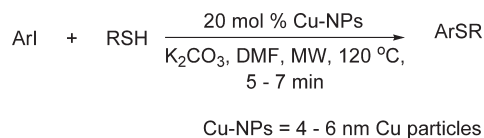


Scheme 63

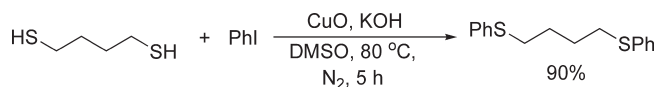


CuO nanoparticles in the KOH/DMSO system catalyzed the coupling of diaryl diselenides with aryl halides and gave high (ArI) to good (ArBr) product yields at 110 °C.²⁰⁰ It was found that various metal oxide nanoparticles—Fe₂O₃, Bi₂O₃, In₂O₃, NiO, and ZnO—can all catalyze the reaction of iodobenzene and diphenyl diselenide in 65–72% yields, whereas CuO has shown the best performance (94%). Catalyst recycling was demonstrated in three cycles and led to similar product yields (91–94%). Although the proposed reaction mechanism was suggested to start from Cu^{II}O and involve Cu(IV) intermediates (Scheme 66),²⁰⁰ an alternative mechanism could involve a reduction of Cu^{II} to Cu^I and subsequent participation within the Cu^I/Cu^{III} catalytic cycle.²⁰¹ This CuO/DMSO/KOH system was also used in an efficient preparation of vinyl sulfides.²⁰² It is interesting to note that the above-mentioned metal oxide nanoparticles have also shown substantial catalytic activity.²⁰² Same groups reported the nano-In₂O₃ catalyzed²⁰³ C–S cross-coupling of thiols and aryl halides, as well as application of Ln₂O₃ to the preparation of both diaryl

Scheme 64



Scheme 65



chalcogenides²⁰⁴ and vinyl chalcogenides.²⁰⁵ Other examples of C–S bond formation using the Cu-cat/KOH system have been also reported.^{206–208}

Using 1–5 mol % catalyst loadings, CuO on mesoporous silica was applied to C–S bond formation between aryl iodides and various aromatic and aliphatic thiols (66–97% yields).²⁰⁹ An attempt of catalyst reuse showed small but noticeable loss of catalytic activity from 85% in the first run to 78% in the fourth run.²⁰⁹ A heterogeneous copper catalyst supported on Al₂O₃ was utilized for the selective coupling of iodobenzene with thiols in the presence of K₂CO₃ as well as the coupling of bromobenzene with thiols in the presence of Cs₂CO₃ (dimethylformamide (DMF), 110 °C).²¹⁰ The reaction for aromatic, heteroaromatic, and aliphatic thiols resulted in 70–98% product yields. The important role of the support was demonstrated in this reaction. The yield of Ph₂S increased from 35% with no support to 97% for supported catalyst.²¹⁰

CuO nanoparticles in ionic liquids have been used to develop a synthesis of selenoesters from acyl chlorides and diselenides (Scheme 67).^{211,212} The [BMIM][PF₆] ionic liquid proved most efficient affording yields of 61–91%.²¹² The potential of recycling was demonstrated with catalyst activity decreasing from 89% to 74% for the first and fourth runs, respectively.²¹²

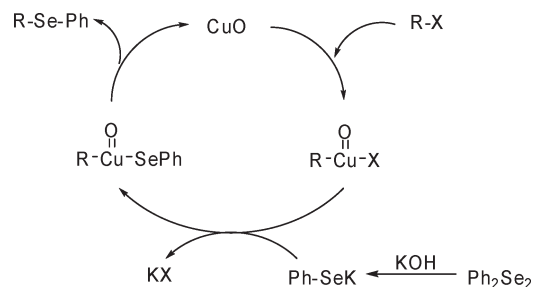
As has already been discussed in the section on Pd-catalyzed transformations, disulfides and diselenides can also be used as a source of ArZ groups in Cu-catalyzed reactions. This is particularly important in the latter case, since ArSeH selenols are unstable and hence less available than the corresponding Ar₂Se₂ diselenides. The reduction of Ar₂Z₂ to give ArZ groups was carried out by the addition of Mg or Zn metals. An example of the [Cu]/bpy/Mg catalytic system developed by Taniguchi and Onami is shown in Scheme 68.^{213,214}

Similarly, the CuI/imidazole catalytic system furnished the formation of C–Se and C–Te bonds in a reaction involving alkynyl bromides and dichalcogenides (Scheme 69).²¹⁵ The reaction required Mg turnings and gave moderate to high yields (51–89%).

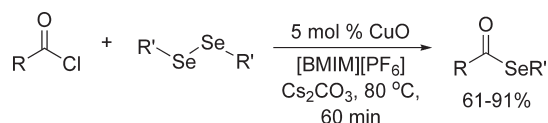
Under MW heating (160–200 °C) and using the CuI/bipyridil/Mg catalytic system, a wide range of dichalcogenides, including tellurium derivatives, and ArBr with electron-donating groups (*p*-HOC₆H₄Br, *p*-Me₂NC₆H₄Br), were successfully reacted to form cross-coupled products in good to high yields.²¹⁶ Alkenyl derivatives of selenium were synthesized in ionic liquids (65–91%) using Zn as the reducing agent (Scheme 70).²¹⁷ The route to Z-vinyl chalcogenides has also been described.²¹⁸

The use of thiourea as a thiol surrogate was reported in the CuI-catalyzed synthesis of thioethers from aryl halides and alkyl

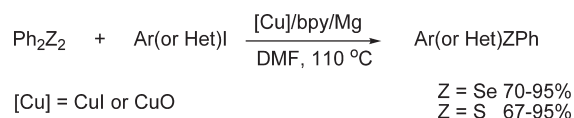
Scheme 66



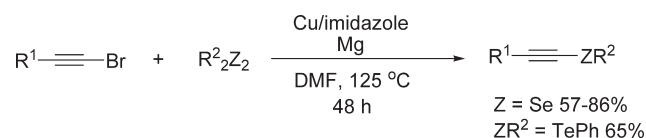
Scheme 67



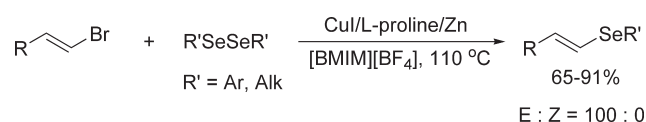
Scheme 68



Scheme 69



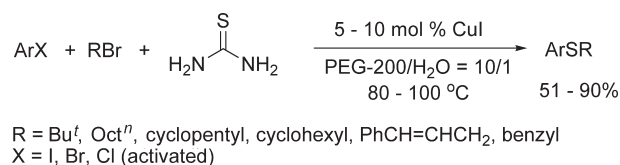
Scheme 70



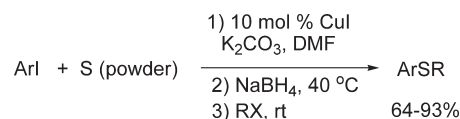
bromides (Scheme 71).²¹⁹ The reaction was carried out in wet PEG-200 at 80–100 °C under an inert atmosphere. This thioetherification synthesis protocol could benefit from a variety of readily available alkylbromides.²¹⁹ Thiourea in wet PEG-200 was also used as a sulfur donor in addition reactions involving various organyl halides and electron-deficient alkenes.²²⁰ Both intra- and intermolecular reactions with substituted thiourea derivatives have been reported in the C–S cross-coupling synthesis of 2-(arythio)arylcyanamides^{221a} as well as CuO-mediated reaction involving selenourea.^{221b}

DMSO was used as the source of the MeS group to carry out a Cu-mediated methyl thiolation of the C–H bond in arylpyridines.²²² The reaction was carried out in the presence of $\text{CuF}_2/\text{K}_2\text{S}_2\text{O}_8$ and afforded monomethylated products

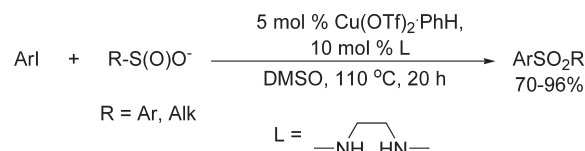
Scheme 71



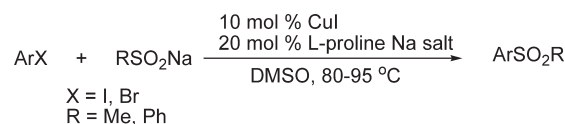
Scheme 72



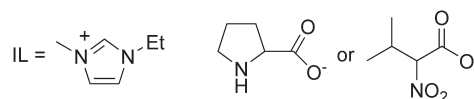
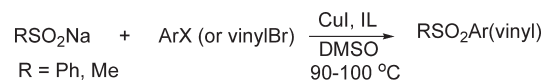
Scheme 73



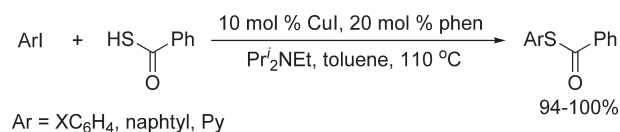
Scheme 74



Scheme 75

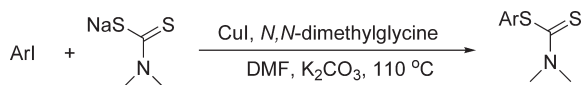


Scheme 76

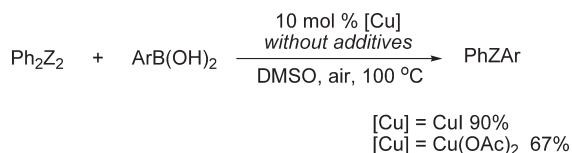


in 54–72% yield (125 °C, 72 h). However, the reaction required an excess of the copper salt (1.6 mmol of CuF_2 to 0.4 mmol of the substrate).²²² Improving the reaction to catalytic conditions and enlarging the scope of the substrates would be of great interest, because DMSO is a widely available reagent.

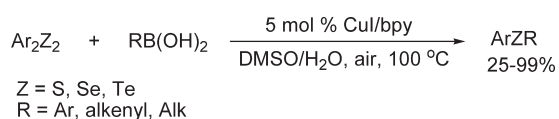
Scheme 77



Scheme 78



Scheme 79



Taniguchi has developed a CuI/bpy catalytic system for the reaction of aryl iodides with sulfur or selenium powder in the presence of aluminum for the preparation of diaryl chalcogenides.²²³ The procedure was further developed to form arylalkyl disulfide derivatives using NaBH₄ as the reducing agent (Scheme 72).²²⁴ This procedure also proved to be suitable for the preparation of aryl thiols²²⁴ and diaryl dichalcogenides.²²³ Sodium sulfide and 3-mercaptopropionic acid were used as the sulfur source in the Cu-catalyzed synthesis of symmetrical diaryl sulfides from aryl iodides.^{225,223}

Cu complexes were found to be suitable catalysts for C–S bond formation starting from ArX and sulfonic acid salts. Reaction led to the formation of ArSO₂R sulfones (Scheme 73).²²⁶ The reaction was limited to aryl iodides, however, since aryl bromides did not react.²²⁶ C–S bond formation in aryl halides with 3-methoxy-3-oxopropane-1-sulfinate was carried out in the presence of 3 equiv of CuI.²²⁷

It is interesting to note that, if the CuI catalyst was used in combination with a sodium salt of L-proline, both ArI and ArBr, either with electron-donating or electron-accepting substituents, gave sulfones even at lower temperatures (Scheme 74).²²⁸ Both types of sulfones were formed in good to high yields.

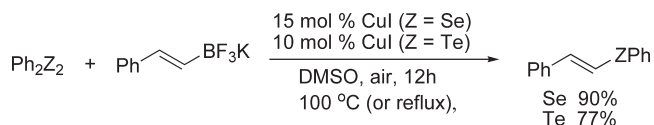
The reaction of RSO₂Na with ArX or vinyl bromide was carried out in a mixture of solvents consisting of DMSO and anion-functionalized ionic liquids with a CuI catalyst (Scheme 75).^{229,230} High yields were observed for aryl iodides (71–91%). Acceptable to high yields were observed for aryl bromides (48–92%).

Cu complexes with the 1,10-phenanthroline (phen) ligand catalyzed the arylation of thiobenzoic acid in high yields (Scheme 76).²³¹ In contrast to ArI, which readily reacted with the thiobenzoic acid, only traces of products were observed for the reaction with PhBr.

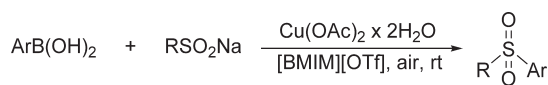
A catalytic system based on CuI and the *N,N*-dimethylglycine ligand was found to catalyze the C–S cross-coupling of aryl iodides and vinyl bromides with sodium dithiocarbamates (Scheme 77).²³² As in the previous case, PhBr did not react in this catalytic system.

The oxidative cross-coupling of aryl boronic acids with alkyl thiols (including cysteine), in the Cu(OAc)₂/Py-DMF system under heating, gave good yields.²³³ This protocol was also

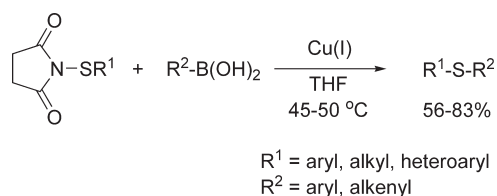
Scheme 80



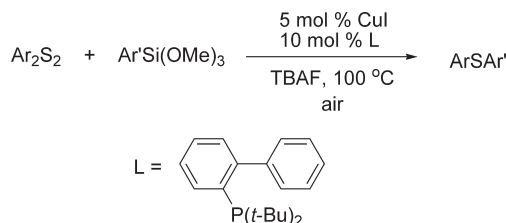
Scheme 81



Scheme 82



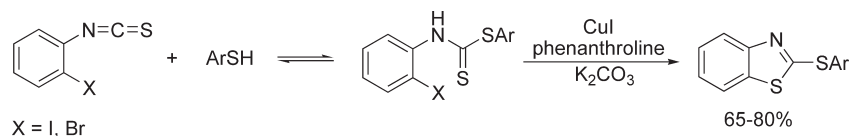
Scheme 83



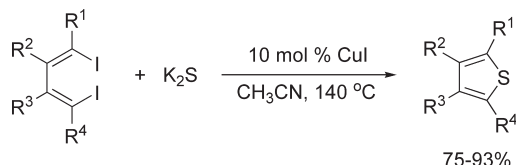
utilized for the synthesis of *N*-benzyloxycarbonyl-(*S*-phenyl)-L-cysteine, which is the key intermediate for the preparation of the HIV protease inhibitor Nelfinavir.²³³ The procedure for the synthesis of *N*-acetyl-S-aryl cysteines using S-arylation and of *N*, *N'*-diacetylcysteine has been reported.²³⁴ Both thiols and disulfides were used as reagents with a copper catalyst. However, the use of disulfides with a CuOAc catalyst demonstrated a better performance. The proposed reaction mechanism involves a bimetallic copper intermediate species.²³⁴ Historically, the first example of a Cu-catalyzed C–S bond formation involving cysteine derivatives (30% yield) was reported by White and co-workers already in 1985.²³⁵

In the case of Cu-catalyzed reactions, organic boronic derivatives were often used as the cross-coupling partner, together with either disulfide, diselenide, or ditelluride as the ArZ-group donor. An example, the Cu-catalyzed reaction without ligands, is shown in Scheme 78.²³⁶ Under similar conditions, the reaction with the CuI/bpy catalytic system was also carried out (Scheme 79).^{237,238} However, for R = Bu, the yield was much lower, and for Z = Te, the reaction only occurred with PhB(OH)₂.²³⁷ The selective coupling of substituted pyrazolyl disulfides and arylboronic acids in the CuI/phenanthroline/O₂ catalytic system was developed for the synthesis of pyrazolyl derivatives, including fipronil analogues, all with the NH₂ group.²³⁹

Scheme 84



Scheme 85



CuO nanoparticles were also reported as an effective catalyst for the coupling of aryl and alkyl diselenides with boronic acids with high yields of 75–98%.²⁴⁰ Catalyst recycling was possible, although the yield decreased from 97% in the first run to 83% in the fourth run. The scope of the procedure was also extended to Ph_2Te_2 and resulted in 94% yield.²⁴⁰

Selenium and tellurium alkenyl derivatives were synthesized using the reaction of diphenyl dichalcogenides and potassium vinyltrifluoroborates. Good yields were obtained in the case of Ar_2Z_2 , but only 45–53% yields were obtained for Alk_2Se_2 (Scheme 80).²⁴¹ This catalytic reaction did not require the addition of base.

It was possible to carry out the oxidative coupling of aryl boronic acid with the sodium salt of sulfonic acid in an ionic liquid (Scheme 81).²⁴²

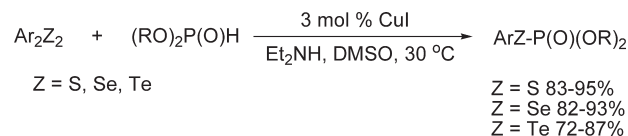
N-Thio(alkyl, aryl, heteroaryl) imides were used as the RS group donor in the Cu-catalyzed reaction with boronic acids (Scheme 82).²⁴³ Moderate to good yields were observed for reaction under relatively mild conditions. The proposed reaction mechanism involved the oxidative addition of the S–N bond to form the Cu(III) species followed by transmetalation from boron to copper and subsequent C–S reductive elimination. It is interesting to note that, although $\text{Cu}^{\text{I}}\text{SR}$ was found to be inactive during this transformation,²⁴³ it was in fact involved in C–S bond formation under other conditions.²³⁸

Aryl silanes have been shown to successfully replace boronic acids as cross-coupling partners in C–S bond formation.²⁴⁴ Originally, the cross-coupling of Si derivatives with ArX was demonstrated by Hatanaka and Hiyama for C–C bond formation, and this approach was then extended to other reactions.²⁴⁵ In the reaction between aryltrimethoxysilanes and diaryl disulfides, moderate to good yields were observed (36–87%) using the $\text{CuI}/2\text{-(di-}t\text{-tert-butylphosphino)biphenyl}$ catalytic system in air (Scheme 83).²⁴⁴

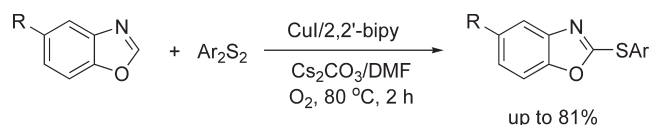
A copper-catalyzed cascade reaction was developed to prepare 1,3-benzothiazoles from 2-haloaryl isothiocyanates and aryl thiols (Scheme 84).²⁴⁶ The best yields were achieved using the $\text{CuI}/\text{phenanthroline}$ catalytic system. Earlier, a similar cyclization procedure had been used for the reaction of aryl isothiocyanates and *o*-iodophenols, leading to 2-imino-1,3-benzothiazoles under Cu(I) catalytic conditions.²⁴⁷

An efficient procedure for accessing substituted benzothiazoles based on a cross-coupling/condensation of 2-haloanilides

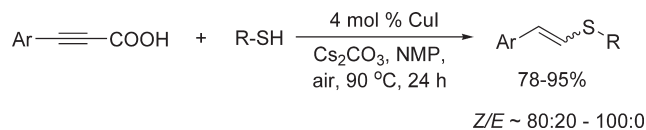
Scheme 86



Scheme 87



Scheme 88

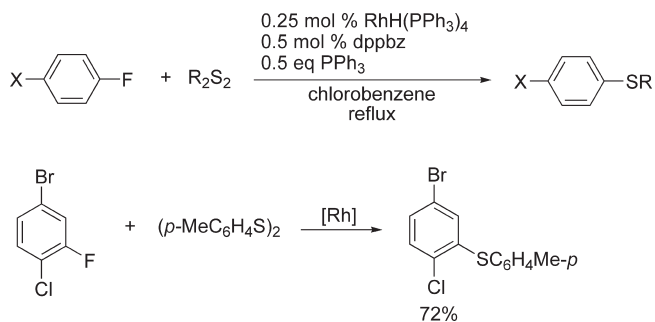


and metal sulfides (Na_2S or K_2S) was reported.²⁴⁸ The use of easily available metal sulfides as coupling partners is of much interest as a means to develop cost-efficient S-arylation procedures.²⁴⁸ Intramolecular Cu-catalyzed thiolation annulations, using Na_2S or NaHS as the sulfur source, were reported for the preparation of benzothiazoles and benzothiophenes bearing trifluoromethyl substituents.²⁴⁹ Another synthetic approach to making arylthiobenzothiazoles using a one-pot procedure of sequential intra- and intermolecular C–S bond formation with $\text{CuI}/1,2\text{-diaminocyclohexane}$ catalyst has also been reported.²⁵⁰ It should be pointed out that the direct C–H functionalization in the Pd system discussed earlier (Scheme 30)¹⁰⁹ eliminates the need for *ortho*-halo-substituted precursors for the synthesis of benzothiazoles.

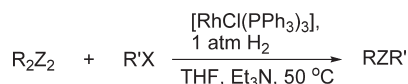
An elegant transformation for the synthesis of substituted thiophenes via a Cu-catalyzed double S-alkenylation of K_2S (Scheme 85) was reported by Xi and co-workers.²⁵¹ This methodology was successfully applied to access di-, tri-, and tetrasubstituted thiophenes in high yields and good substitution group tolerance. A series of 1,4-diiodo-1,3-dienes, which were the starting compounds, have been shown to be very useful reagents in organic synthesis.²⁵² An efficient procedure for C–S bond formation in aqueous solution was developed using KSCN as a sulfur source.²⁵³

Cross-coupling involving diaryl dichalcogenide and H–phosphonate was performed under copper catalysis and led to chalcogen–phosphorus bond formation under mild conditions (Scheme 86).²⁵⁴

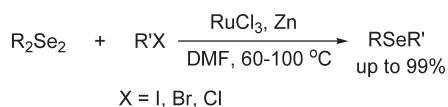
Scheme 89



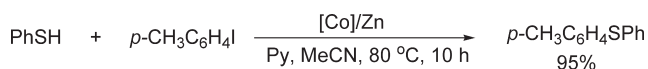
Scheme 90



Scheme 91



Scheme 92



The important role of copper catalysis not only in the area of cross-coupling chemistry but also in the rapidly growing C–H activation/heterofunctionalization field should be emphasized. Fukuzawa and co-workers first demonstrated the direct thiolation of benzoxazole using aryl thiols and diaryl disulfides (Scheme 87).²⁵⁵ They proposed a catalytic cycle involving Ar–H activation and the formation of an intermediate Ar–Cu–SAr' species. The reaction was carried out in DMF at 80 °C under oxygen.²⁵⁵

The Cu-catalyzed thiolation of the C–H bond of di- and trimethoxybenzenes using dichalcogenides in the presence of oxygen has been achieved.²⁵⁶ The ligand-free reaction was carried out with 20 mol % of CuI and gave yields of 40–98% (DMF, 120 °C, 24–48 h).²⁵⁶ Thiolation of C–H bond using PhSH and Me₂S₂ sulfur group precursors was also reported.²⁵⁷

Vinyl sulfides were prepared by reacting arylpropionic acids with thiols under copper-catalytic conditions (Scheme 88).²⁵⁸ The authors classified the transformation as a “decarboxylative C–S cross-coupling”. To our knowledge, an alternative reaction mechanism should also be considered involving decarboxylation leading to aryl acetylene Ar–C≡CH followed by addition of the S–H bond to the triple bond of the alkyne (without an actual cross-coupling pathway). The S–H bond addition to alkynes will be discussed in section 3 of this review. Another decarboxylative

Scheme 93



Scheme 94

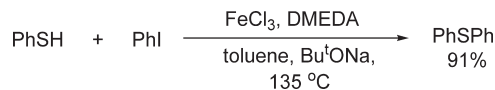
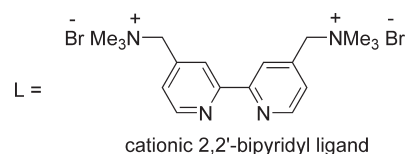


Chart 8



reaction has been already considered earlier for the Pd/Cu catalytic system (Scheme 31).¹¹⁶

2.4. Other Transition Metals As Catalysts

Catalytic reactions aimed at the formation of Csp²–S and Csp²–Se bonds are known to take place with rhodium, ruthenium, and cobalt complexes. One particularly promising research area that has attracted much attention in recent years is the development of applications for iron-based catalysts.

A rhodium hydride complex in the presence of 1,2-bis-(diphenylphosphino)benzene (dppbz) and an excess of triphenylphosphine was found to catalyze the reaction between aryl fluorides containing electron-withdrawing groups and disulfides (Scheme 89).²⁵⁹ Unsubstituted fluorobenzene was found to be inert under these conditions. However, in the presence of electron-withdrawing groups, the reactivity of aryl fluoride was higher than that of either bromide or chloride (Scheme 89). Clearly, the mechanistic nature of this interesting catalytic reaction merits further investigation. Polyaryl thiolation was observed with polyfluorobenzenes, leading to the preferential formation of *p*-difluorides.²⁵⁹ Recently, a combined experimental and theoretical study was published concerning aromatic C–F bond activation by platinum sulfur complexes within the S_NAr mechanistic framework.²⁶⁰

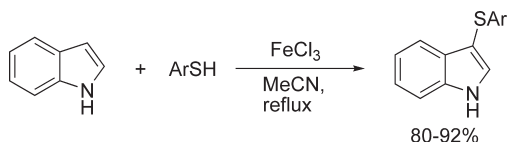
A Wilkinson complex was reported as being able to catalyze both alkylation and arylation reactions of thiols and selenols formed after the reduction of R₂Z₂ by hydrogen (Scheme 90).²⁶¹

Similarly, the reaction with various alkylation reagents took place with RuCl₃ as catalyst and diselenide reduction with Zn (Scheme 91).²⁶²

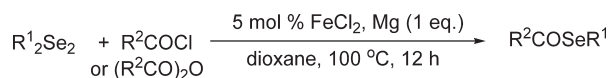
Cross-coupling reactions leading to the formation of Csp²–S bonds was made possible using a cobalt catalyst. The best results were achieved using the CoI₂(dppe)/Zn catalytic system (Scheme 92).²⁶³ This new cross-coupling reaction is of great interest because it complements the other known transition-metal-catalyzed reactions with Pd, Ni, and Cu catalysts very well.

The reaction was successfully carried out with various aryl-(hetaryl) iodides and bromides and involved different aryl thiols and alkyl thiols. A plausible catalytic cycle includes the reduction of the Co(II) complex to Co(I) and substitution of the iodide

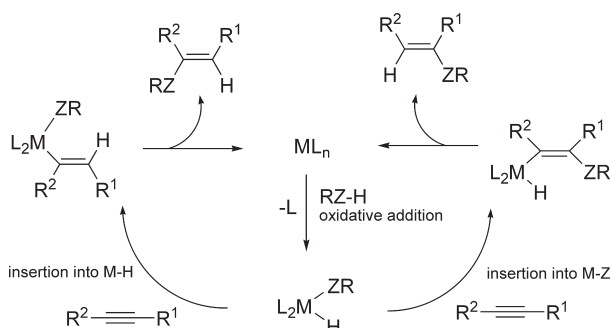
Scheme 95



Scheme 96



Scheme 97



Scheme 98

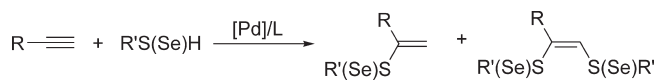


ligand by SR, which in turn leads to the formation of ArSCo(I) . Subsequent oxidative addition of ArX to this cobalt complex with concomitant formation of a Co(III) derivative, followed by reductive elimination (Scheme 93), results in formation of the product and regeneration of the Co(I) catalyst.

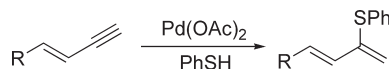
Recently, Bolm and co-workers showed that such a cross-coupling reaction is possible with an iron catalyst. Starting from the corresponding thiols, it leads to the formation of Ar(Het)SAr' (Scheme 94).²⁶⁴ The reaction proved successful only with the Ar(Het)SH thiols because the alkyl thiols AlkSH did not react. Undoubtedly, there is the potential to further develop cheap and efficient iron catalysts to carry out various C-Z bond-formation reactions.

In a subsequent study, this reaction was further extended to include ArI and Ar(Het)SH with high selectivity and good yields in the $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ /cationic 2,2'-bipyridyl (L) system in water (with an exception of PhCH_2SH).²⁶⁵ The catalyst with the cationic ligand L preserved its activity over several cycles in aqueous solutions (Chart 8).²⁶⁵ A series of bidentate phosphine ligands were studied for the Fe-catalyzed thioetherification of thiols with aryl iodides.²⁶⁶ An efficient catalytic system using BINAP and Xantphos ligands (10 mol % FeCl_3 and 10 mol % of ligand) was developed for the coupling reaction involving alkyl thiols (64–99% yield; 135°C , 24 h).²⁶⁶

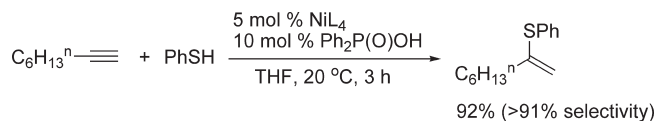
Scheme 99



Scheme 100



Scheme 101



A ligand-free iron-catalyzed cross-coupling reaction of aryl iodides with aromatic and aliphatic thiols was reported by Rao and co-workers. It involved an Fe/graphite system.²⁶⁷ The reaction was carried out in DMSO/KOH under an inert atmosphere (125°C , 24 h) and gave yields of 67–98%. The loss in catalytic activity caused the yield to decrease from 97% in the first cycle to 67% in the seventh cycle.²⁶⁷

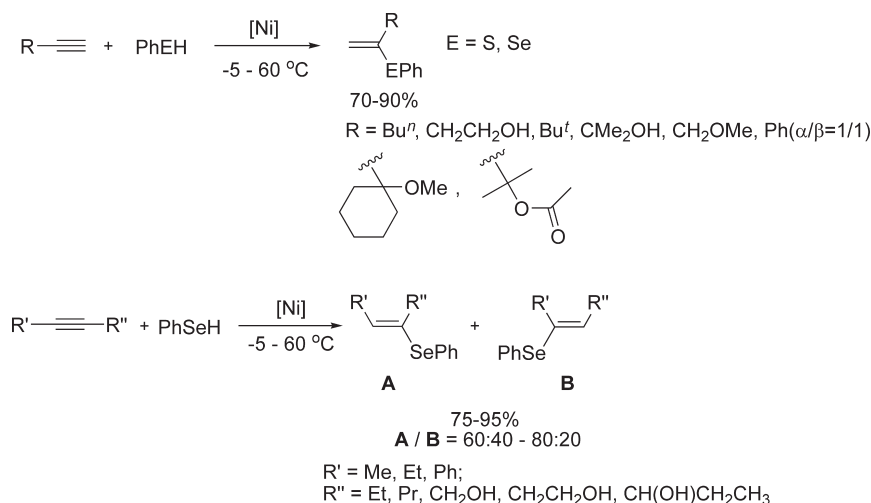
The direct sulfenylation of indoles and its derivatives was carried out by Yadav and co-workers using aromatic thiols in the presence of FeCl_3 as a Lewis acid.²⁶⁸ High selectivity, as well as good yields, in the synthesis of 3-arylthioindoles was observed (Scheme 95).²⁶⁸ Site-specific sulfenylation of indoles with disulfides was performed under Fe(III) -catalyzed reaction.²⁶⁹

The cross-coupling of arylboronic acids with ditellurides and diselenides was mediated with the use of 10 mol % of iron catalyst in the absence of a ligand.²⁷⁰ Various Fe(II) and Fe(III) salts, as well as Fe powder, were used in a series of reactions in DMSO at 130°C . Although a rather questionable mechanism was proposed, the synthetic application of the reaction is of interest because it gave high yields of 62–98%. The same authors also reported C-Se bond formation via the reaction of diselenides and acyl chlorides or benzoic anhydride (Scheme 96).²⁷¹ The reaction required 1 equiv of Mg dust for the product to form (no product was observed without magnesium).

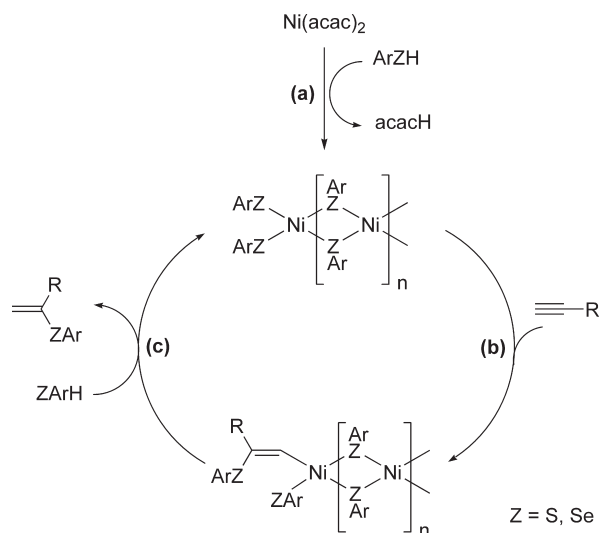
Although much interest has been shown recently in the possible application of various iron catalysts, some caution is advised in trying to understand the nature of the active species involved in the catalytic cycle. A recent study by Buchwald and Bolm raised the question of the role of trace amounts of other metals, particularly Cu.²⁷²

In addition to the indium oxides nanoparticles discussed above^{200,202,203} where their ability to promote C-Z cross-coupling was demonstrated, it has been shown that indium metal,^{273,274} InI ,²⁷⁵ and the Lewis acid $\text{In(OTf)}_3/\text{TMEDA}$ also exhibit the desired catalytic activity.²⁷⁶ The reaction with indium triflate was performed for aryl and alkyl thiols with aryl halides in KOH/DMSO at 135°C (51–96% yields).²⁷⁶ It would be interesting to establish the mechanism of catalysis in the indium system and, hence, to understand to what extent the nature of the

Scheme 102



Scheme 103



catalytic species depends on the metal precursor. The Lewis acid InBr_3 -catalyzed arylation of diselenides and ditellurides with boronic acid was achieved without the need for any additives.²⁷⁷ High product yields of 71–99% were observed with 5 mol % of the indium bromide in DMSO at 130 °C. A possible reaction mechanism involving $\text{ArSeIn}^{\text{III}}(\text{Br})\text{Ar}$ intermediate has been proposed.²⁷⁷

A gold-catalyzed C–S bond formation involving thiols that was reported used 10 mol % of the $\text{PPh}_3\text{AuCl}/\text{AgOTf}$ system and unusual alkylating agents—*o*-alkynylbenzoic acid alkyl esters.²⁷⁸ The reaction was carried out in 1,2-dichloroethane (80 °C, 15 h), and the corresponding thioethers were obtained in moderate to high yields (42–99%).

The La_2O_3 /TMEDA-catalyzed cross-coupling of vinyl iodides and vinyl bromides with thiols and diphenyl diselenide was developed (anhydrous DMSO, KOH, 90 °C).²⁷⁹ The lanthanum-catalyzed transformation was carried out with retention of the double-bond stereochemistry, high yields for vinyl iodides

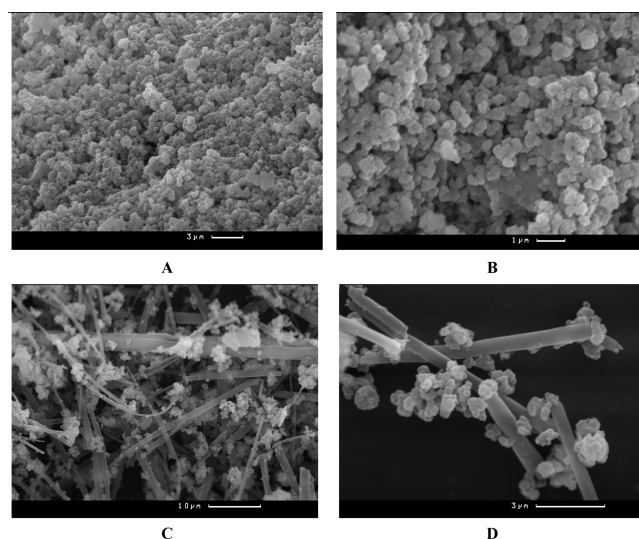


Figure 1. SEM images of catalyst particles prepared from $\text{Ni}(\text{acac})_2$ (A, 4 000 \times ; B, 10 000 \times) and $\text{NiCl}_2/\text{Et}_3\text{N}$ system (C, 2 000 \times ; D, 9 000 \times). Reproduced with permission from ref 300. Copyright 2007 American Chemical Society.

(81–96%), and moderate yields for vinyl bromides (41–55%). The possibility of catalyst recycling was demonstrated with the product yield decreasing from 95% in the first cycle to 84% in the fourth cycle.²⁷⁹

3. CATALYTIC ADDITION OF RZ–H DERIVATIVES TO ALKYNES AND ALLENES (Z = S, SE)

Vinyl chalcogenides can be prepared not only by substitution reactions as discussed in the previous section but also by addition reactions to the triple bond of alkynes. Aryl chalcogenides, on the other hand, can only be prepared by substitution reactions. Because of high atom efficiency and the absence of byproduct, addition reactions show great potential in terms of Green Chemistry requirements.

It is important to understand the mechanistic differences between these two approaches for C–Z bond formation. Chemical selectivity is the main concern in the design of cross-coupling

Chart 12

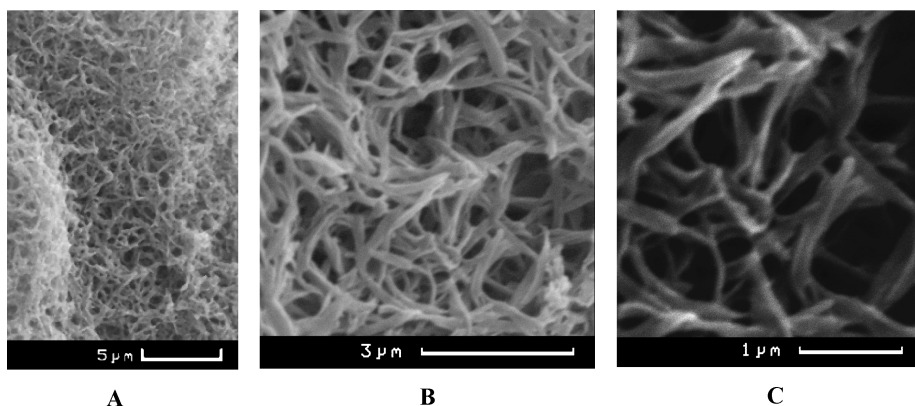
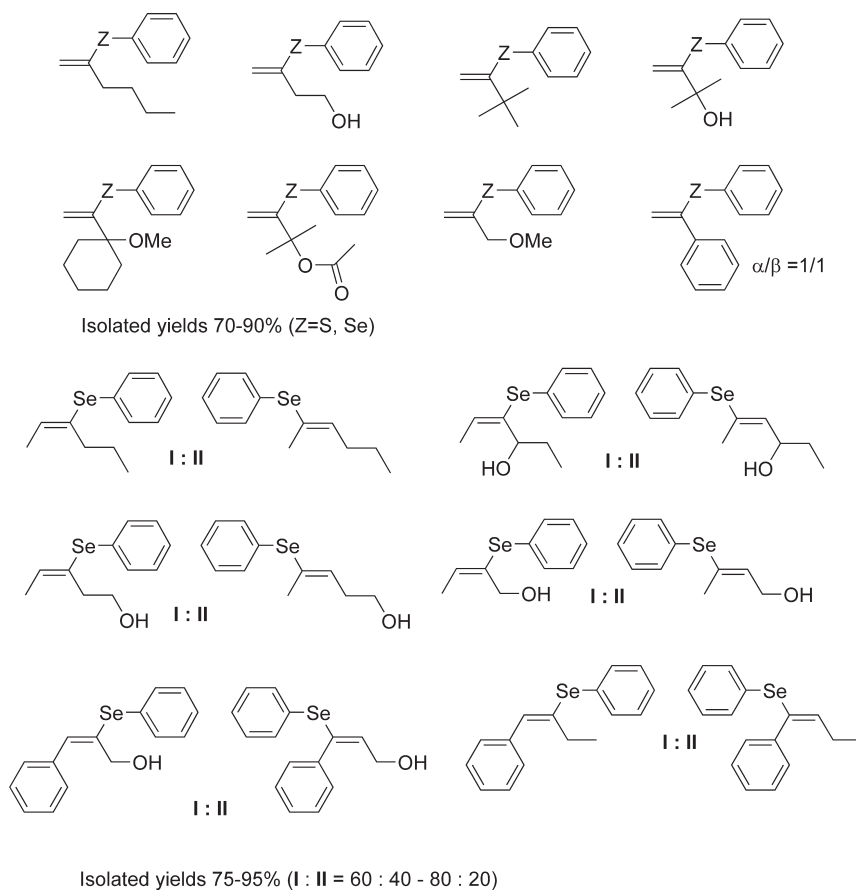


Figure 2. Low magnification (A, 1 000 \times) and high magnification (B, 8 000 \times ; C, 16 000 \times) SEM images of $[\text{Pd}(\text{SCy})_2]_n$. Reproduced with permission from 302. Copyright 2007 American Chemical Society.

reactions to improve the ratio of hetero-/homocoupling products and to avoid reduction of the C–halogen bond. However, an examination of the addition reactions raises other important problems—stereoselectivity in the case of addition of dichalcogenides and regioselectivity in the case of the addition of thiols and selenols.

In the present section, we shall describe the available literature on the addition reaction of thiols and selenols RZH ($\text{Z} = \text{S}, \text{Se}$) to multiple carbon–carbon bonds leading to carbon–heteroatom bond formation in the vinyl–chalcogenide products. Pd- and Ni-

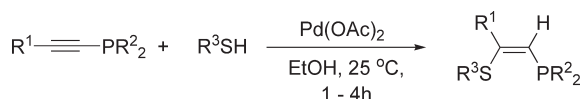
catalyzed transformations will be considered first, followed by Rh, Ir, Pt, and other metal-catalyzed addition reactions involving alkynes. Finally, the reactions involving allenes will be summarized at the end of the section.

Noncatalytic addition reactions carried out without transition metal catalysts are beyond the scope of this review, and this topic has already been addressed in several publications (see refs 28, 280–283, 352, and references therein). It was shown that the noncatalytic reactions lead to different outcomes: in the addition of RZH to alkynes, the anti-Markovnikov

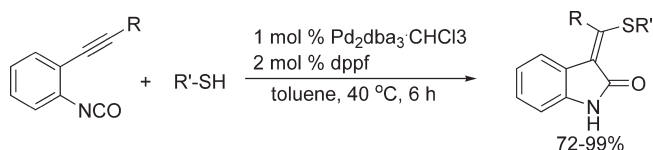
Table 1. Pd-Nanoparticle-Catalyzed Regioselective RSH Addition to Alkynes under Microwave Heating (Both NMR Estimated and Isolated Yields Are Given)

Entry	Alkyne	Thiol	Product	Yield	Selectivity
1		CySH		99(92)	>99:1
2		CySH		98(88)	>99:1
3		CySH		98(75)	95:5
4		CySH		96(87)	91:9
5		CySH		98(77)	84:16
6		BnSH		88(74)	>99:1
7		BnSH		68(57)	97:3

Scheme 104



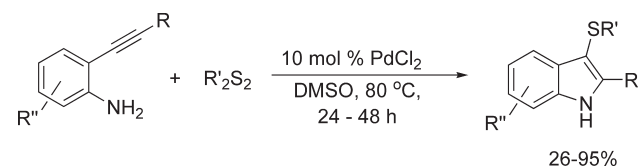
Scheme 105



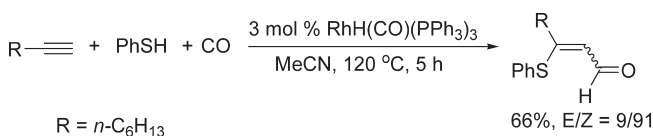
products are formed. Our goal is to concentrate on the selective formation of the relatively unavailable Markovnikov-type isomers by RZH addition to the triple bond of alkynes.

Starting with terminal alkynes, Markovnikov-type products can be formed following alkyne insertion into the M–Z bond and C–H reductive elimination (Scheme 2). However, the general mechanistic framework of the catalytic cycle appears to be more complicated because insertion into both the M–Z and M–H bonds can take place and subsequently lead to different products (Scheme 97). Both of these transformations are stereoselective and proceed via a *syn*-addition. However, the regioselectivity of the reaction may change and depends on the metal

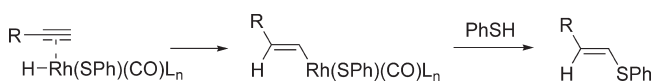
Scheme 106



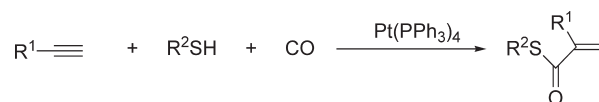
Scheme 107



Scheme 108



Scheme 109



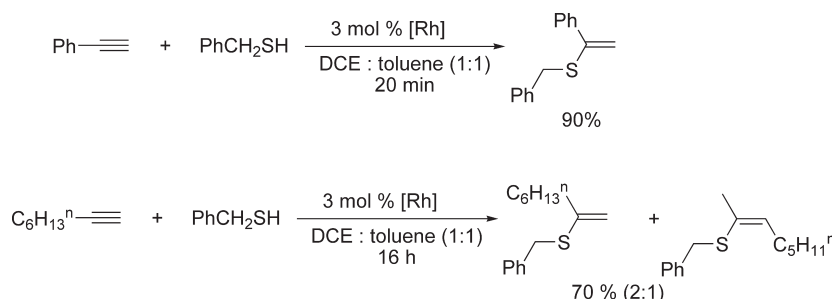
complex, the type of the alkyne (terminal or internal), and the nature of substituents R^1 and R^2 .^{29–31} Recent theoretical studies at various levels (B3LYP, B3PW91, BLYP, MP2, and ONIOM) have shown that, in the H–M–Z hydride complexes, insertion into the M–H bond is much more facile compared to the insertion into M–Z bond.²⁸⁴

Ishii and co-workers carried out an excellent mechanistic study of alkyne hydroselenation and were able to isolate a (hydrido) (selenolato) platinum complex, which resulted after oxidative addition of Se–H bond to the metal.²⁸⁵ It was demonstrated that the isolated complex can serve as a catalyst for the hydroselenation of dimethyl acetylenedicarboxylate. Dissociation of the phosphine ligand prior to alkyne coordination was found to be a key step in the catalytic reaction.²⁸⁵ Intermediate σ -vinyl complexes formed after alkyne insertion into the M–Z bond were isolated and structurally characterized.^{286,287}

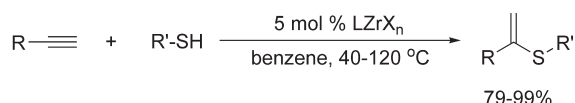
The first catalytic addition of thiols to an acetylenic triple bond was described by Newton and co-workers in 1976 using molybdenum complexes.²⁸⁸ Their study involved only highly activated dimethyl acetylenedicarboxylate, which can also readily react with thiols under both radical and nucleophilic conditions. For synthetic purposes, the Mo catalyst was not efficient enough and produced a mixture of isomers.²⁸⁸

In 1992, Ogawa, Sonoda, and co-workers carried out the selective catalytic addition of aromatic thiols²⁸⁹ and selenols²⁹⁰ to alkynes using $Pd(OAc)_2$. Although the Markovnikov isomer was the major product, the yields were not very high.³¹ The catalytic reaction was accompanied by noncatalytic addition, leading to

Scheme 110

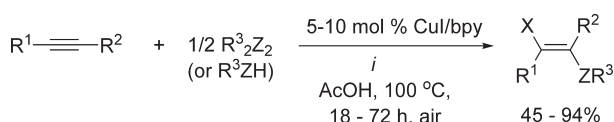


Scheme 111



R, R' = alkyl, benzyl, aryl
 L = Me₂SiCMe₂NCMe₃, C₅Me₅
 X = Me, benzyl, Cl, NMe₂

Scheme 112



Z = S, Se; X = Cl, Br, I, SCN

R¹, R² = Alk, Ph, AcOCH₂

R³ = Alk, Ar

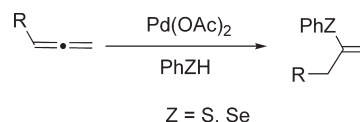
i = Buⁿ₄NBr, Buⁿ₄Nl, CsCl, NH₄SCN

the anti-Markovnikov isomers (free-radical or nucleophilic reactions) as well as double-bond isomerization in the case of the thiols (THF, 67 °C) and selenols (benzene, 80 °C).^{289,290} The isomerization reaction was especially pronounced with the Pd-(PhCN)₂Cl₂ catalyst.²⁹¹ It is interesting to note that the intermediate metal complex taking part in the catalytic reaction was denoted as Pd(SPh)₂L_n.²⁹¹ Regioselective hydroselenation of terminal alkynes with benzeneselenol followed by double-bond isomerization was efficiently catalyzed by Pd(PPh₃)₂Cl₂.²⁹²

The mechanism of the catalytic hydrothiolation and hydroselenation reactions differs from the bisthiolation and bis-selenation reactions at the product formation stage. For the Z-H bond addition to alkynes, the last stage of the catalytic cycle is protonolysis or C-H reductive elimination. It was found that, independently of the catalyst precursor (either Pd⁰ or Pd^{II} derivatives), the same catalytically active species [Pd(ZR)₂]_n were formed (Scheme 98).^{293,294}

It is interesting to compare the catalytic activity of Pd-chalcogenide species in Z-Z and Z-H addition reactions.²⁹ The [Pd(ZR)₂]_n complexes proved totally inactive in the disulfide and diselenide addition to alkynes. A C-Z reductive elimination constituted the final product-forming step (see discussion in section 5). However, using a [Pd(ZR)₂]_n catalyst, in the presence of phosphine ligands, significant amounts of bisthiolation and bis-selenation products, with a Z-geometry, were detected. This was in addition

Scheme 113



to the expected Markovnikov product (Scheme 99).²⁹³⁻²⁹⁵ It can be concluded, therefore, that in the presence of PR₃ ligands Pd catalyst used for the addition of Z-H bonds to alkynes also demonstrated some activity as well as high selectivity in Z-Z bond-addition reactions. The mechanistic changes occurring under these reaction conditions were initiated by catalyst leaching.²⁹⁶

Using pyridine as a solvent for Pd(OAc)₂-catalyzed phenyl selenol additions to alkynes resulted in better regioselectivities and yields (although in some cases the yields were not very high).²⁹⁷ Most likely, in this catalytic system, pyridine facilitated the formation of soluble Pd complexes, but without promoting C-S reductive elimination.

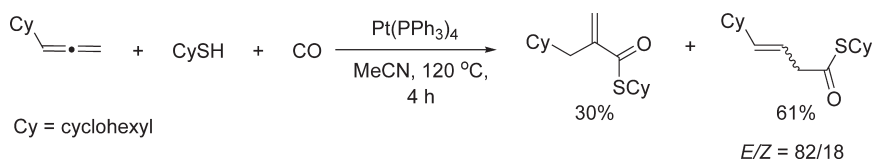
The hydrothiolation of conjugated enynes with PhSH was carried out using a Pd(OAc)₂ catalyst in THF at 50 °C and led to the formation of a 1,3-diene in 41-75% yield after 14-18 h (Scheme 100).

Han and co-workers showed that the reaction between PhSH and 1-octyne can be catalyzed by a Ni(PPh₂Me)₄ complex with high selectivity in the presence of catalytic amounts of Ph₂P-(O)OH acid (Scheme 101). However, the role of the Ph₂P-(O)OH additive in this reaction remains unclear.

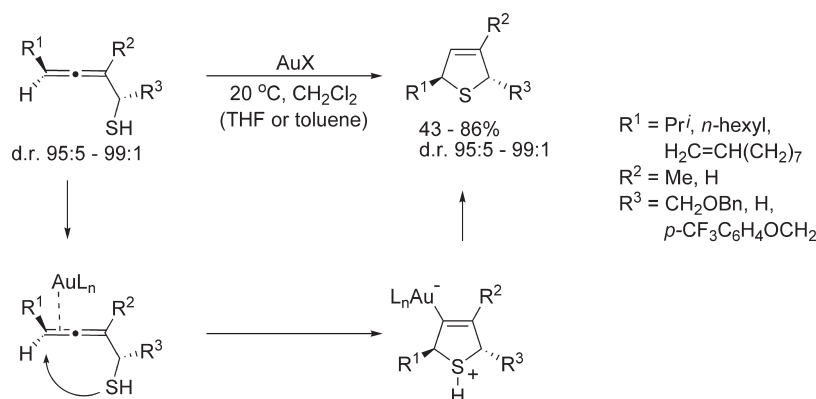
An even simpler NiCl₂/Et₃N catalytic system resulted in high selectivity and good yields in hydrothiolation reactions in the presence of a radical trap, which suppressed the side reaction.²⁹⁵ For activated alkynes with R = Ph and COOMe, significant amounts of anti-Markovnikov products were obtained. The overall regioselectivity of the reaction depended on the alkyne/RZH ratio, and much better yields were achieved utilizing Ni(acac)₂ as a catalyst precursor.²⁹⁸

Further research into the higher activity of the Ni complexes compared to their Pd analogues led to the discovery of a novel nanosized catalytic system. It showed a superior performance in the hydrothiolation and hydroselenation reactions of alkynes.^{299,300} Furthermore, it was found that with Ni(acac)₂ as a simple catalyst precursor the reaction produced excellent yields and selectivity even at room temperature. Both terminal and internal alkynes were successfully used in these additions. This catalytic system proved tolerant to various functional groups in the alkynes and was easily scaled up for the synthesis of up to 50 g

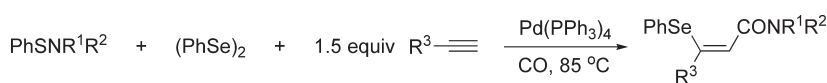
Scheme 114



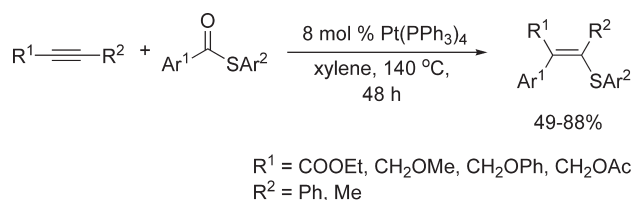
Scheme 115



Scheme 116



Scheme 117



of product (Scheme 102).^{299,300} The proposed mechanism of the catalytic reaction involved (a) catalyst self-organization with nanosized particles formation, (b) alkyne insertion into the Ni–Z bond, and (c) protonolysis with RZH (Scheme 103).

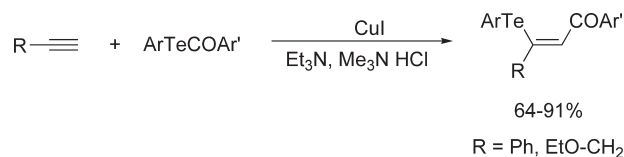
According to elemental analysis, the same nickel complex $[\text{Ni}(\text{ZPh})_2]_n$ was formed irrespective of the precursor under different reaction conditions. However, catalytic activity and selectivity of the catalyst were found to differ dramatically. A SEM study of the catalyst morphology (Figure 1) revealed round shaped particles of 300 ± 90 nm size in the case of $\text{Ni}(\text{acac})_2$ catalyst precursor, which had in fact shown the best performance.²⁹⁹ Another type of catalyst was formed in the $\text{NiCl}_2/\text{Et}_3\text{N}$ system, where the $[\text{Et}_3\text{NH}][\text{Cl}]$ salt served as a support for the $[\text{Ni}(\text{ZPh})_2]_n$ particles (the salt was formed upon reaction of PhZH with the NiCl_2 in the presence of the amine).³⁰⁰ Comparative kinetic measurements revealed a linear dependence

between the catalytic activity and the particle size in the μm range of sizes. An exponential increase in catalytic activity was observed with decreasing particle sizes into the nm region.^{299,300} The nanostructured Ni catalyst showed high activity and excellent *syn*-selectivity for a broad range of terminal and internal alkynes (Chart 12).

The heterogeneous hydrothiolation reaction carried out with $[\text{Ni}(\text{ZAr})_2]_n$ catalyst particles was compared with the homogeneous reaction based on the $\text{CpNi}(\text{NHC})\text{SAr}$ catalyst (NHC, *N*-heterocyclic carbene ligand).³⁰¹ Since only one SAr group was present in this catalyst, the formation of bithiolation product could be avoided. These homogeneous catalysts, especially in the case with NHC = *N,N'*-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes), showed good performance in the hydrothiolation reaction with yields of 61–87%. However, compared to the heterogeneous reaction, a higher temperature of 80 °C was required and only terminal alkynes were suitable for the reaction.³⁰¹

The challenging problem of achieving regioselective alkyl thiol addition to alkynes was solved by developing a nanosized $[\text{Pd}(\text{SALK})_2]_n$ catalyst. This in turn was formed in situ in a self-organized manner from the $\text{Pd}(\text{OAc})_2$ precursor in the thiol/alkyne mixture (Figure 2).³⁰² Catalyst particles size and morphology proved to be of crucial importance for achieving high activity and selectivity in these addition reactions (Table 1). It is interesting to note that $[\text{M}(\text{ZAr})_2]_n$ catalysts with $\text{M} = \text{Ni}$ were superior for the addition of aryl chalcogenides, whereas with $\text{M} = \text{Pd}$ they were superior for the alkyl derivatives.

Scheme 118



Scheme 119

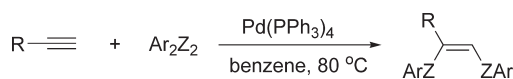
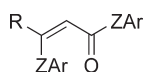
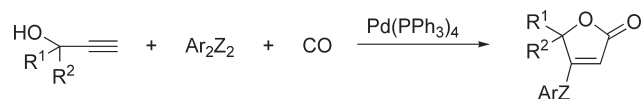


Chart 9



Scheme 120



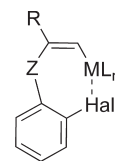
The hydrothiolation of 1-alkynylphosphines was catalyzed by Pd(OAc)₂ in EtOH and gave the Z-1-phosphino-2-thio-1-alkene as the product (Scheme 104).³⁰³ Surprisingly, the addition reaction took place in an anti-fashion. This probably means that an external nucleophilic attack on the coordinated triple bond is a key step rather than alkyne insertion as observed in the other examples.

The reaction of 2-(alkynyl) aryl isocyanates with thiols was carried out under Pd-catalyzed conditions and resulted in C–S bond formation accompanied by cyclization (Scheme 105).³⁰⁴ High product yields and very good selectivities were observed in the reactions. Although the reaction formally belongs to this section, further studies are required to reveal whether the catalytic cycle contains a hydrothiolation step or proceeds via an alternative pathway.³⁰⁴

Using disulfides as the source of the R'S group, a Pd-catalyzed addition/cyclization reaction was shown to be successful for 2-(alkynyl)benzenamines (Scheme 106).³⁰⁵ The reaction was carried out in DMSO at 80 °C in air. The yields of the 3-sulfenylindoles were between 26 and 95%. The catalytic system required significant Pd loadings (10 mol %). As in the previous example, the mechanism of this catalytic transformation warrants further investigation.

Concerning the regioselectivity of the thioformylation reaction in the presence of CO (Scheme 107), somewhat contradictory data was published in 1995³⁰⁶ and later in 2003.³⁰⁷ Using the RhH(CO)(PPh₃)₃ catalyst, the Markovnikov derivatives were obtained after alkyne and CO insertion steps. However, the major product formed with the Wilkinson complex in the hydroformylation reaction (Scheme 108) was the anti-Markovnikov isomer.²⁹¹ The same regiochemistry was found in the reaction of AlkSH.³⁰⁸

Chart 10



If a Pt(PPh₃)₄ catalyst was utilized, the α,β-unsaturated thioether was formed as the major product (Scheme 109).³⁰⁹ The formation of *trans*-[PtH(SPh)(PPh₃)₂] in the catalytic cycle was proposed.³¹⁰

Love and co-workers reported that a pyrazolyl–borate complex of rhodium (Tp*Rh(PPh₃)₂, Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) is active in hydrothiolation not only with ArSH but also with AlkSH. Good to high yields of the Markovnikov isomer were obtained at room temperature (Scheme 110).^{311,312} However, the reaction of 1-octyne gave a mixture of isomers with a yield of 70%. In addition to the double-bond isomerization, a Markovnikov/anti-Markovnikov ratio of 12:1 was found for the 1-octyne reaction. Further development and improvement of this Rh system has recently been described.^{313,314}

The catalytic activity of Ir complexes in the hydrothiolation of alkynes has been demonstrated by Messerle and co-workers.^{315,316} Formation of the anti-Markovnikov products as a mixture of *E/Z* isomers was observed. The reaction of benzene thiol with phenyl acetylene gave a yield of 93% but poor 26/74 selectivity under mild room-temperature conditions.³¹⁵ Achieving a high selectivity in such a case is a rather difficult task due to the noncatalytic addition reaction, which leads to the same products (a mixture of *E/Z* isomers).

Marks and co-workers recently reported an actinide- and lanthanide-mediated selective hydrothiolation of terminal alkynes with aliphatic, aromatic, and benzylic thiols.^{317,318} The topic was recently reviewed in the framework of organo-f-element catalysts for hydroalkoxylation and hydrothiolation.²² An efficient procedure for Markovnikov-selective hydrothiolation of terminal alkynes has also been reported. It used organozirconium complexes as the catalysts (Scheme 111).³¹⁹ High selectivity and good yields of the products were observed for a broad range of thiols. A detailed kinetic study of the reaction mechanism provided evidence for the possible involvement of a zirconium–thiolate dimeric species and protonolysis step.

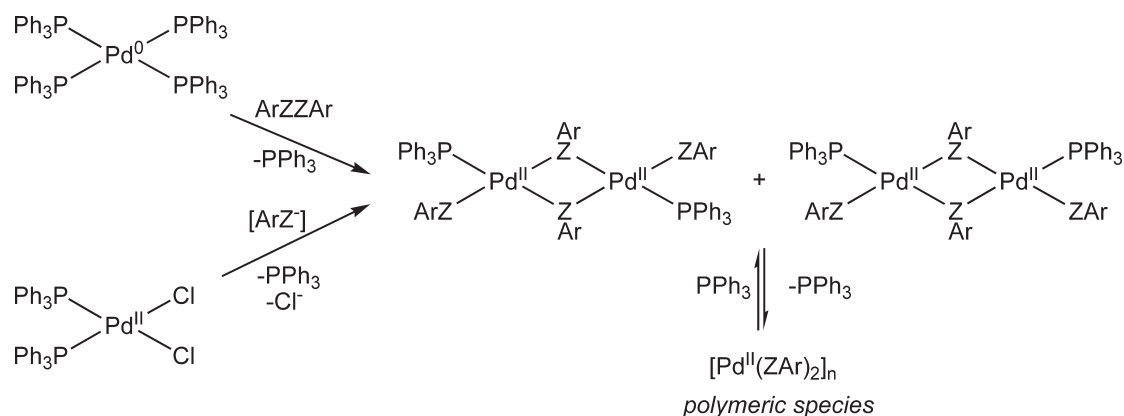
The Cu-catalyzed addition reaction of dichalcogenides to internal alkynes was developed for the preparation of β-substituted alkenyl chalcogenides (Scheme 112).³²⁰ The reaction was anti-stereoselective and allowed the introduction of either a halogen or a SCN group into the *trans*-position of the SR³ and SeR³ substituents.

Some other recent protocols of interest, because they are related to the theme of this review, include the CeCl₃-catalyzed hydrochalcogenation of propargylic alcohols and amines,³²¹ the Cs-catalyzed addition of dichalcogenides to alkynes,³²² and GaCl₃-mediated disulfidation.³²³

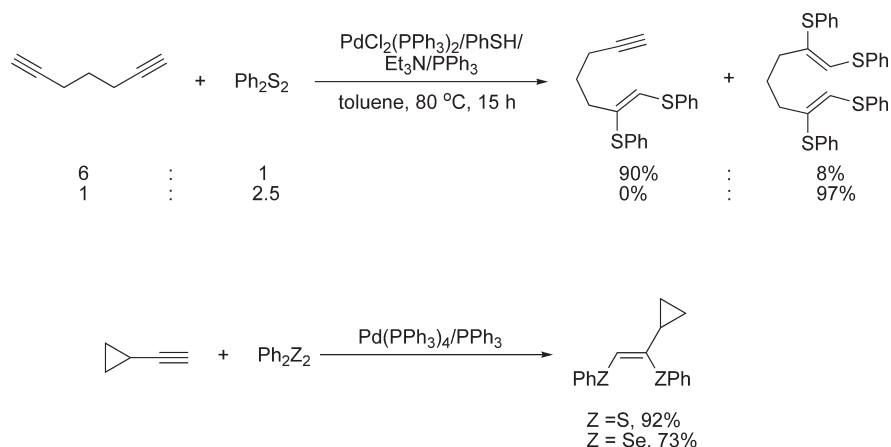
In a Pd(OAc)₂-catalyzed reaction, the products of the PhSH and PhSeH addition to the internal double bond of a series of allenes were formed in good to high yields (Scheme 113).^{324,325}

The reaction of allenes with cyclohexyl thiol in the presence of CO depends on the nature of transition metal complex.³²⁶ Pd complexes did not catalyze this transformation. Rh complexes resulted in copolymerization products of allene and CO. However, good yields, but with low

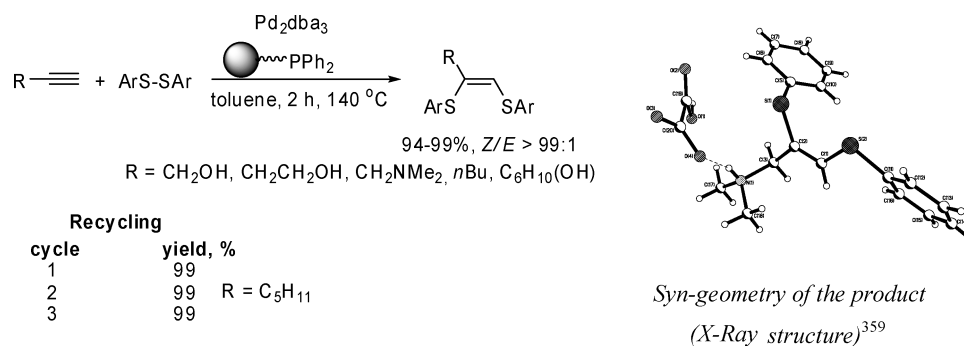
Scheme 121



Scheme 122



Scheme 123



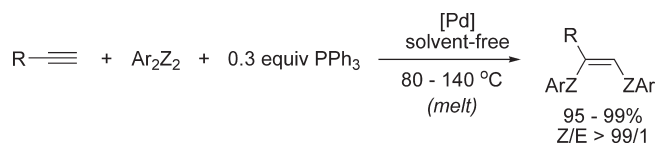
regio- and stereoselectivities, were the result when the addition reaction was carried out using a $\text{Pt}(\text{PPh}_3)_4$ catalyst (Scheme 114).

A gold-catalyzed intramolecular addition reaction was reported by Morita and Krause for the preparation of 2,5-dihydrothiophenes from α -thioallenes (Scheme 115).³²⁷ An efficient and stereoselective procedure was developed using either AuCl or AuI as the catalyst precursor. The proposed reaction

mechanism involves an intramolecular nucleophilic attack of the thiol group followed by transformation into the heterocyclic product. The reaction proceeds with an axis-to-center chirality transfer.³²⁷

The hydrothiolation of alkynes was developed by Iglesias, Sánchez, and co-workers using soluble and heterogenized gold catalysts. They were able to prepare anti-Markovnikov products with high stereo- and regioselectivity.³²⁸ The reaction was carried

Scheme 124



out in toluene at 40 °C with only 0.1 mol % of the Au catalyst and resulted in yields of 90–97%. The heterogenized catalyst was recovered and reused for three further cycles without noticeable loss of activity.³²⁸ Yamamoto and co-workers have reported the gold-catalyzed regioselective intermolecular hydrothiolation of aromatic allenes by aromatic thiols, leading to the formation of the corresponding dithioacetals in good yields (0 °C, 5 min, 5 mol % AuBr₃).³²⁹

4. CATALYTIC ADDITION OF Z–X AND Z–C BONDS TO ALKYNES AND ALLENES (Z = S, SE, TE)

A new Csp²–S or Csp²–Se bond can be formed using an addition reaction of substrates with S–B, S(Se)–P, or S–Si bonds to alkynes. A Pd(PPh₃)₄ catalyst was found to be active in thioboration,³³⁰ thiophosphorylation,³³¹ thioselenation,³³² thiosilylation,³³³ and thiogermanylation³³⁴ reactions. In all of the cases studied, the regioselectivity of the addition reaction was preferably to form the R(R′)C=CHX products (X = B, P, Si, Ge).

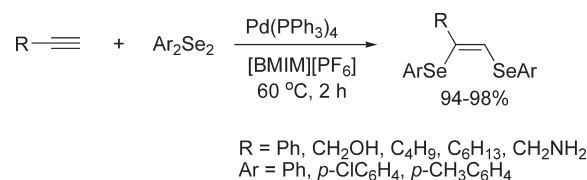
The same mechanism was proposed for the cyanothiolation of alkynes with PhSCN in a Pd(PPh₃)₄-catalyzed reaction (120 °C, 66 h, PhH).³³⁵ The intermediate *trans*-Pd(SPh)(CN)(PPh₃)₂ complex was isolated from the corresponding stoichiometric reaction, and it was found that the complex led to the same product—Z-(PhS)RC=CH(CN)—as the catalytic reaction. The stereochemical results of the reaction with PhSCN depended on the nature of the alkyne, whereas it was found that the reaction with AlkSCN did not take place.

A theoretical study (CCSD(T), MP2, and B3LYP levels) of the reaction mechanism showed that alkyne insertion into the NC–Pd–SH model complex is easier for the Pd–S bond than for the Pd–C bond.³³⁶ For alkynes with electron-donating substituents (Me and NH₂), the insertion into the Pd–S bond was found to be more favorable than for the alkynes with electron-withdrawing substituent (CN).³³⁶ A theoretical study at B3LYP and ONIOM (B3LYP:HF) levels indicated that PhS–CN bond cleavage at the Pd(0) center is kinetically and thermodynamically favored compared to Ph–SCN bond cleavage. In the same study, the question of regioselectivity of alkyne insertion was also addressed.³³⁷

The Csp²–Se bond was formed in the Pd-catalyzed alkynylselenation of acetylenedicarboxylates leading to enyne selenides.³³⁸ The reaction was carried out using the Pd(OAc)₂/P(*o*-tol)₃/K₂CO₃ catalytic system in toluene/water at 115 °C. The resulting enyne selenides underwent an intramolecular cycloaddition reaction to form multisubstituted aryl selenides.³³⁸

The Csp²–Se bond was also formed in a multicomponent reaction of the sulfonylamine, diphenyldisulfide, alkyne, and CO under Pd(PPh₃)₄-catalyzed conditions (Scheme 116).^{339,340} It was proposed that the intermediate Pd complex formed after the carbonylation reaction underwent a nucleophile attack of the amide instead of reductive elimination. Other pathways leading to the same product are also possible.^{339,340}

Scheme 125



Kuniyasu, Kambe, and co-workers considered the mechanistic aspects of the carbochalcogenation of alkynes and addressed its possible implementation in synthetic procedures.^{341–343} They found that, in particular, unsymmetrical alkynes underwent decarbonylative aryl thiolation by thioethers under Pt-catalyzed conditions (Scheme 117).³⁴² The proposed mechanism involved alkyne insertion into the M–S bond followed by reductive elimination as the key steps of the catalytic cycle. In a similar way, the Pt-catalyzed furyl thiolation,³⁴³ thienyl thiolation,³⁴⁴ and pyridyl thiolation³⁴⁵ of alkynes were described. One interesting development resulting from this methodology is the Pd-catalyzed regioselective iminothiolation of alkynes.³⁴⁶

The selenoacylation of allenes was carried out under Pd-catalyzed conditions and led to the regioselective formation of functionalized allylselenides (55–90% yields).³⁴⁷ Interestingly, the theoretical study at B3LYP level showed that reductive elimination, which is the last step in the catalytic cycle, could be reversible and hence responsible for Z/E isomerization of the product.³⁴⁷

An example of a Cu-catalyzed addition of telluroesters to terminal alkynes was reported by Meng and co-workers. There was stereoselective formation of the *syn*-addition products (Scheme 118).³⁴⁸ The transformation was also regioselective with the ArTe group attached to the same carbon atom as the R group of the alkyne. A multistage reaction mechanism was proposed. It involves the formation of a R–C≡C–COAr′ derivative followed by addition of an in situ generated ArTeH.³⁴⁸

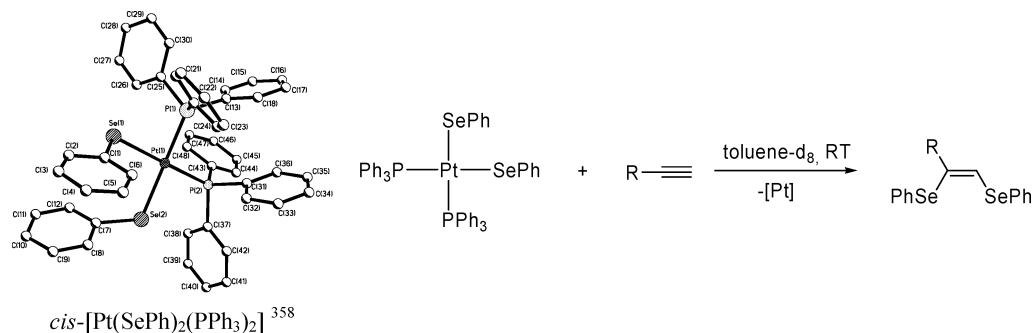
It should be pointed out that the C–Te bond undergoes oxidative addition to the metal center easier compared to either the C–Se or C–S bond.³⁴⁹ It appears, therefore, that the metal-mediated formation of vinyl tellurides involving a catalytic cycle with C–Te reductive elimination as the product formation step (see Scheme 1 and 2) might be less favorable.

5. CATALYTIC ADDITION OF RZ–ZR DERIVATIVES TO ALKYNES AND ALLENES (Z = S, SE)

In the present section, we describe the current literature on addition reactions using dichalcogenides RZ–ZR as the reagent. These lead to the formation of two carbon–heteroatom bonds in a one-pot procedure. The Pd- and Ni-catalyzed catalytic reactions are discussed first. This is followed by applications of the Rh catalysts. Finally, examples for addition reactions involving allenes will be covered at the end of the section.

Noncatalytic addition reactions carried out without transition metal catalysts will not be presented because this topic has been already addressed in several publications (see refs 28 and 350–352 and references therein). It was shown that the noncatalytic reactions led to different products. A mixture of *E*–/*Z*-isomers is very often formed in the addition of RZZR to alkynes. Our goal is to concentrate on the selective formation of the *Z*-isomers in the catalytic addition of RZZR to the triple bond of alkynes.

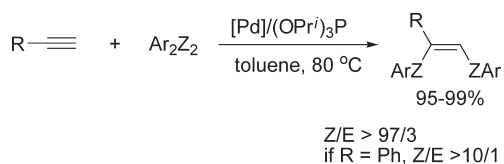
Scheme 126

Table 2. Ligand Effect in the Palladium-Catalyzed Ph_2S_2 Addition to 3-Butyn-1-ol^a 368

entry	ligand	yield, %
1	PPh_3	90
2	$P(p-FC_6H_4)_3$	88
3	PCy_3	15
4	PBu_3	2
5	DPPB	2
6	DPPE	0
7	$P(OPh)_3$	4
8	$P(OBu)_3$	99
9	$P(OiPr)_3$	99

^a Conditions: toluene, 80 °C, 15 h, 1.5 mol % of Pd_2dba_3 and 30 mol % of the ligand.

Scheme 127



In the pioneering study of Ogawa, Sonoda, and co-workers published in 1991, it was shown that under $Pd(PPh_3)_4$ -catalyzed conditions, Ph_2S_2 and Ar_2Se_2 can add to terminal alkynes (benzene, 80 °C), giving good yields (54–98%) with high selectivity toward the Z -isomer formation (Scheme 119).³⁵³ The exception is phenylacetylene, however, which readily underwent a thermal side reaction and resulted in the formation of significant amounts of the E -isomer.³⁵³ This catalytic reaction was not suitable for Alk_2Z_2 (only 24% yield and $E/Z = 25/75$ selectivity with Bu_2Se_2 ; 6% yield with $(PhCH_2)_2S_2$). The internal alkynes were not involved in the reaction.

The catalytic cycle proposed for this reaction involved oxidative addition of Ar_2Z_2 to $Pd(0)$ with formation of a Pd disulfide or diselenide. This is followed by alkyne coordination and insertion into the $Pd-Z$ bond and finally reductive elimination (Scheme 2). It should be pointed out that the mechanism of the $Z-Z$ bond addition to alkynes in terms of alkyne insertion is somewhat simpler compared to the $Z-H$ bond addition, where two types of insertion pathways are possible (cf. Scheme 97). The stereoselectivity of the addition reactions of symmetrical dichalcogenides to alkynes is a major concern.

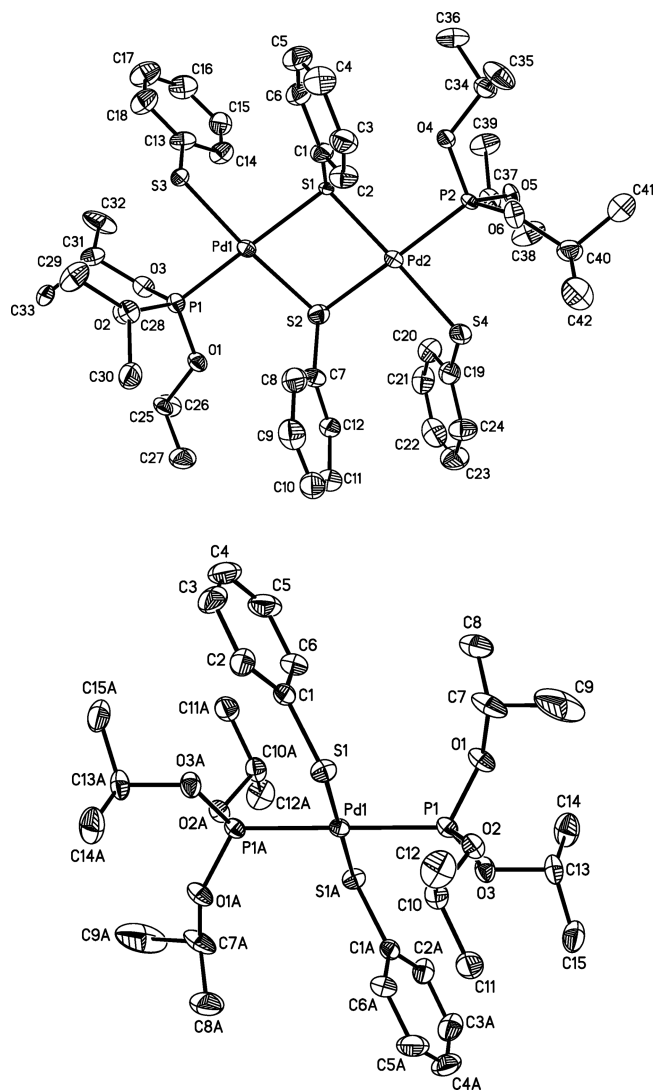
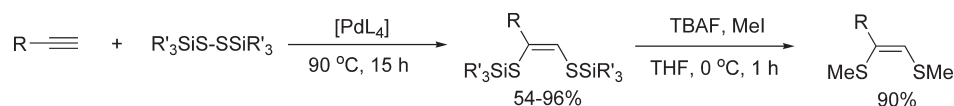


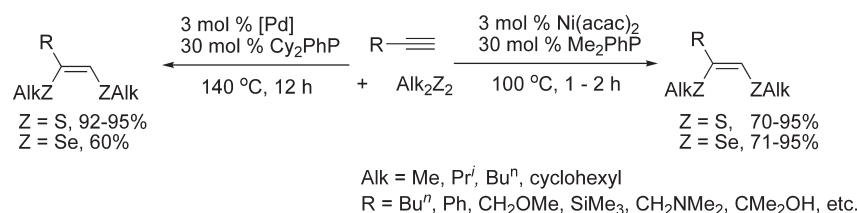
Figure 3. Molecular structures of the dinuclear complex $trans-[Pd_2(SPh)_4(P(OPr^i)_3)_2]$ (top) and mononuclear complex $trans-[Pd(SPh)_2(P(OPr^i)_3)_2]$ (bottom) complexes. Reproduced with permission from ref 368. Copyright 2005 American Chemical Society.

Important mechanistic data was provided from the study of carbonylative addition reactions. It was proven that alkyne insertion is both stereo- and regioselective, that the Pd atom is

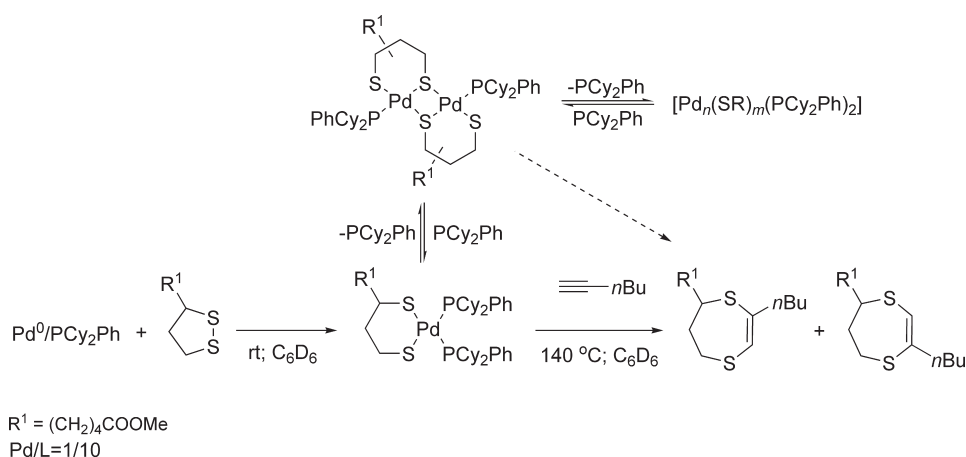
Scheme 128



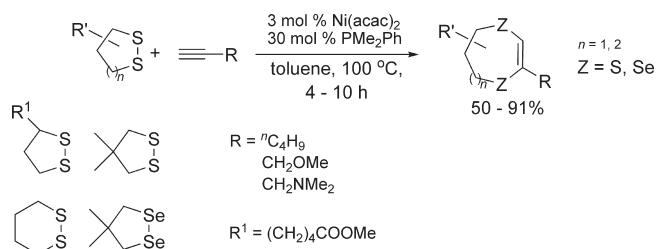
Scheme 129



Scheme 130



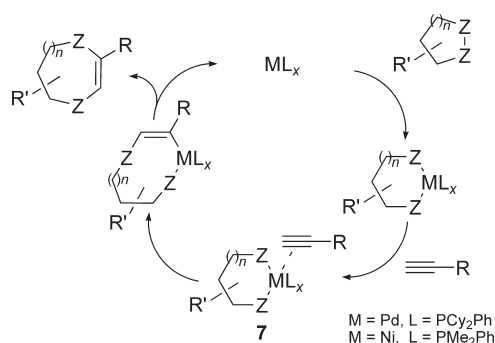
Scheme 131



attached to the β -position, and that the substituent R is in the α -position of the alkyne unit.^{354,341} Carbonylation of this intermediate Pd alkenyl complex led to the formation of a single product (Chart 9). If propargylic alcohols were employed in the carbonylative addition, the reaction resulted in the formation of a lactonization product with moderate to good yields (Scheme 120).³⁵⁴

The presence of a halogen substituent in the *o*-position of the phenyl ring substantially facilitated the reaction as a result of coordination with the Pd atom in a *syn*-fashion.³⁵⁵ This was confirmed in a study of alkyne insertion into the Pt–S bond (Chart 10).³⁵⁶

Scheme 132



Wang, Wu, and co-workers reported an excellent mechanistic study of a methylacetylene biselenation on a Pd catalyst using theoretical calculations at the B3LYP level.³⁵⁷ Several possible pathways were studied, and the overall mechanism was shown to involve oxidative addition, insertion, and reductive elimination (Scheme 2). In addition, it was reported that, in the presence of carbon monoxide, alkyne coordination

and insertion into the Pd–Se was followed by reaction with CO.³⁵⁷

The attempts to carry out a synthetic procedure with Pd(PPh₃)₄ as catalyst (Scheme 119) gave product yields lower than 65%.^{358,359} The reasons were revealed in a study of the nature of the intermediate Pd complexes involved in the reaction. It was found that dinuclear and polymeric Pd species, formed after oxidative addition or halogen substitution in the catalyst precursors, play an important role in the catalytic cycle (Scheme 121).^{360,361}

Dinuclear complexes with *trans*- and *cis*-geometries (*trans*-complexes are more thermodynamically stable) have the ArZ–Pd–ZAr structural unit, which is needed to operate in the catalytic cycle. The observed rate constant of the addition reaction of Ph₂Se₂ to an alkyne was linearly dependent on the concentration of the dinuclear complexes [Pd(SePh)₄(PPh₃)₂].³⁵⁸ A theoretical study at density functional theory level has shown that alkyne insertion into the dinuclear complex preferably involves the terminal ZAr group rather than the bridging ZAr group, which is coordinated in η^2 mode.³⁰ Deficient amounts of the phosphine ligand under catalytic conditions resulted in the rapid formation of polymeric species and catalyst deactivation (Scheme 121). This observation suggests that the catalytic reaction should be carried out in the presence of at least some excess of the phosphine ligand. Indeed, an additional amount of the ligand (2–4 equiv) improved the performance of the catalytic reaction and resulted in high product yields easily reproducible for various alkynes and dichalcogenides.^{358,359}

Addition reactions carried out with 1,6-heptadiyne as the reagent and different amounts of Ph₂S₂ have been shown to proceed via a stepwise pathway (Scheme 122).³⁵⁹ From the mechanistic point of view, the product structure indicates that the Pd center binds to the terminal position of the alkyne. If this were not the case, then the formation of a cyclic compound as a product would be expected (see also the carbonylative addition reaction discussed above). Independent confirmation of the regioselectivity of the insertion step was provided by carrying out the addition reaction with cyclopropylacetylene, as shown in Scheme 122 (i.e., the absence of the homoallylic rearrangement product).

For synthetic purposes, the Pd catalyst was developed on a polymeric support. The subsequent addition reaction was carried out with both excellent yields of 94–99% and stereoselectivity >99:1 (Scheme 123).³⁶² After completion of the reaction, the catalyst was easily isolated by filtration and a pure product was obtained after solvent evaporation (>98% purity without any additional purification procedures). Unfortunately, it was found

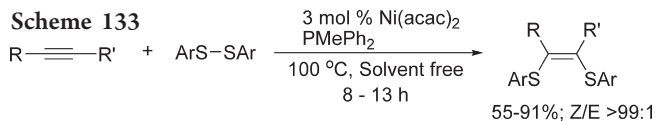
that this synthetic approach was not applicable in the Ph₂Se₂ addition to alkynes. At 140 °C the triphenylphosphine bound to the polymer reacted with Ph₂Se₂ and resulted in selenium atom transfer to the phosphorus (Se=PR₃) with the formation of Ph₂Se as a byproduct. The mechanism of this side reaction was addressed in a joint experimental and theoretical study, which revealed the relationship between the C–Z and Z–Z bonds, which involved activation by the Pd complexes.³⁶³

These difficulties were overcome by developing a synthetic procedure using solvent-free molten-state conditions. At 80–140 °C the (PPh₃)₃ ligand and the dichalcogenide R₂Z₂ formed a melt, in which the alkyne and the catalyst readily dissolved (Scheme 124).³⁶⁴ Under these catalytic conditions, the reaction with Ph₂S₂ was completed after 5 min using 1 mol % of catalyst, and at 140 °C the reaction was completed after 1 h with only 0.01 mol % of the catalyst. Reactions involving both Ar₂S₂ and Ar₂Se₂ were carried out with excellent yields and selectivity. A kinetic study showed that the solvent-free reaction in the melt is much faster than the corresponding reaction in solution. In addition, the catalyst can be easily isolated by rapid flash chromatography and reused in the catalytic reaction without noticeable loss of catalytic activity. Recycling of the homogeneous catalyst from the solvent was not possible because of decomposition of the Pd species. The reaction was successfully scaled up for the preparation of addition products on a gram-scale. A mechanistic study confirmed the presence of dinuclear Pd intermediate complexes in the reaction.³⁶⁴

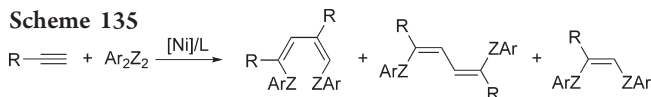
By using microwave irradiation, the reaction time was shortened to 10 min and the amount of catalyst decreased to 0.1 mol % of Pd content.³⁶³ Even various simple species such as Pd(PPh₃)₄, Pd(OAc)₂, or PdCl₂ in the presence of PPh₃ could be utilized as the catalyst precursors. To study catalytic reactions in molten-state systems, a special NMR technique was developed.³⁶⁵ Using this technique, intermediate dinuclear Pd complexes with the same *trans*–*cis*-isomers ratio were detected in the solvent-free/melt systems after both conventional and microwave heating.³⁶⁵

The Pd(PPh₃)₄-catalyzed addition of diaryl diselenides to terminal alkynes was carried out in ionic liquids with high yields and selectivity at 60 °C (Scheme 125).³⁶⁶ The possibility of catalyst recycling was shown for these catalytic conditions.

In contrast to Pd catalysts, Pt complexes were found to be inactive in catalytic reactions between Ar₂Z₂ compounds and alkynes.³⁵⁸ It was shown that Pt(PPh₃)₄ undergoes oxidative addition of diaryl dichalcogenides with the ultimate formation of *trans*–[Pt(ZAr)₂(PPh₃)₂]. A mechanistic study at lower temperatures showed that, after the oxidative addition step, the *cis*–[Pt(ZAr)₂(PPh₃)₂] complex was formed first. At room temperature, this complex underwent irreversible isomerization to form the *trans*-derivative.³⁵⁸ It is known that *cis*–PtCl₂(PPh₃)₂



R = Me, Et, Pr, Ph
R' = Et, Pr, Ph, CH₂NMe₂, CH₂OMe
Ar = Ph, *p*-MeC₆H₄, *p*-ClC₆H₄, *p*-MeOC₆H₄



Scheme 134

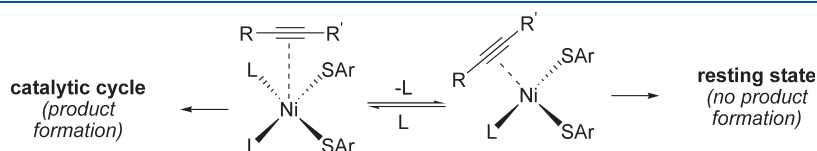
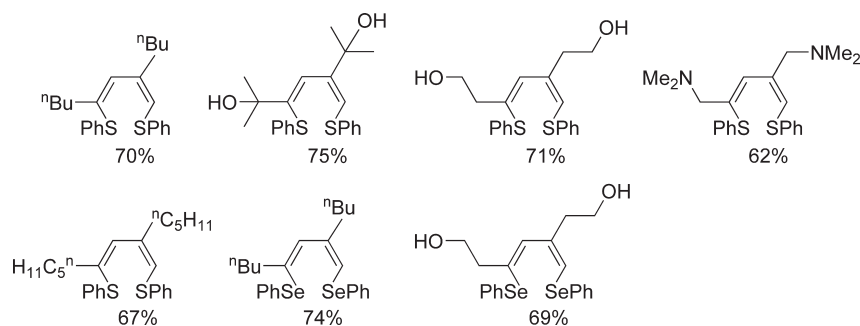
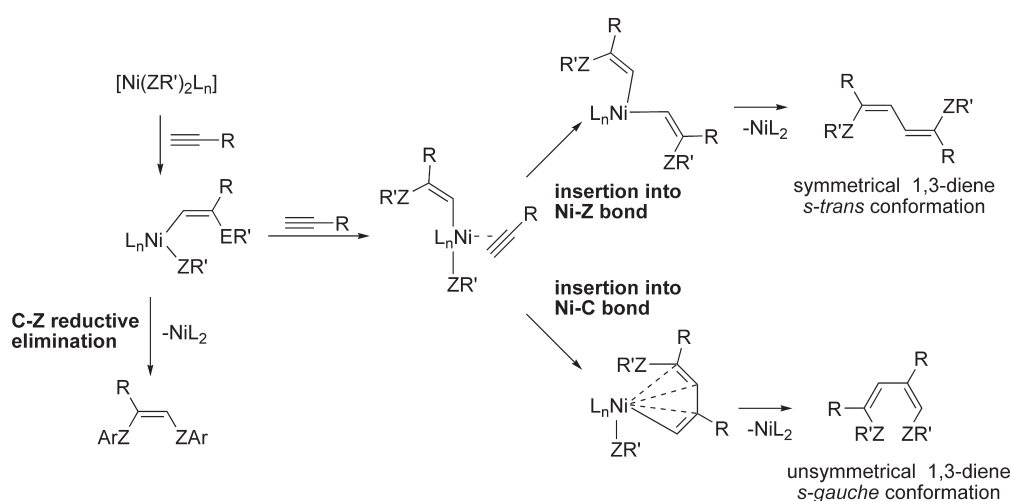


Chart 11



Scheme 136



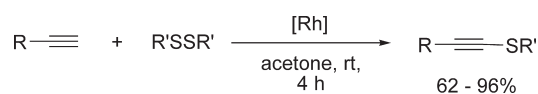
and *cis*-PtCl(SPh)(PPh₃)₂ complexes also undergo isomerization into the corresponding *trans*-isomers. In the case of the latter complex, the isomerization took place in the presence of pyridine.³⁶⁷

The *cis*-[Pt(SePh)₂(PPh₃)₂] complex was isolated and its structure was characterized using X-ray analysis. It was found that this complex does in fact mediate the addition of the Se-Se bond to alkynes (Scheme 126).³⁵⁸

The question of the influence of the various phosphine ligands was addressed in a study of the Pd-catalyzed reaction of Ph₂S₂ addition to alkynes (Table 2).³⁶⁸ Good catalytic activity was observed with Ar₃P ligands (entries 1, 2; Table 2). Interestingly, trialkylphosphite ligands (AlkO)₃P (Alk = Buⁿ, Prⁱ) were even more active in these catalytic reactions (entries 8, 9; Table 2). On the other hand, P(OPh)₃ led only to trace amounts of the product. This finding was implemented into the Pd₂dba₃/((OPrⁱ)₃P) catalytic system, which aimed for and resulted in high selectivity Z/E > 97/3 for typical alkynes and good selectivity Z/E > 10/1 for activated alkynes (Scheme 127).

The P(OPrⁱ)₃ ligand was found to be very convenient not only for synthetic purposes but also for mechanistic study. In the ¹H NMR spectra of the [Pd]/Ar₂Z₂/((OPrⁱ)₃P) catalytic system, the signals of the ligand (both free and coordinated) were clearly distinguishable with no overlap of the Ar₂Z₂ reagent and ArZ-Pd-ZAr species spectral lines.³⁶⁸ This is in sharp contrast with traditional [Pd]/

Scheme 137



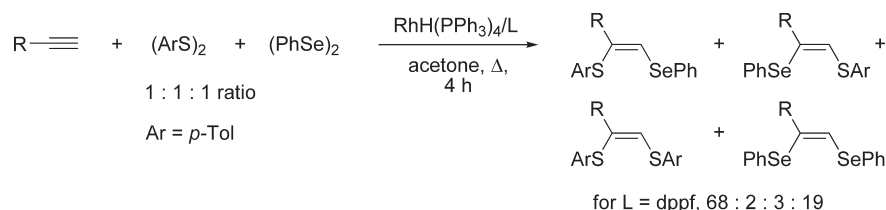
Ar₂Z₂/Ar₃P catalytic systems, where signal overlap of the Ar/Ar' groups made the ¹H NMR spectra barely interpretable.

Using ¹H and ³¹P NMR for the model [Pd]/Ph₂S₂/((OPrⁱ)₃P) catalytic system, *trans*- and *cis*-mononuclear and dinuclear metal complexes were detected. The equilibrium constant of the dinuclear metal complex dissociation was measured, K = 0.066 ± 0.007 M at 30 °C.³⁶⁸ Although the equilibrium is shifted toward the dinuclear complex, with an excess of the (OPrⁱ)₃P ligand, the mononuclear *trans*-[Pd(SPh)₂((OPrⁱ)₃P)₂] complex was isolated and characterized using X-ray analysis (Figure 3).

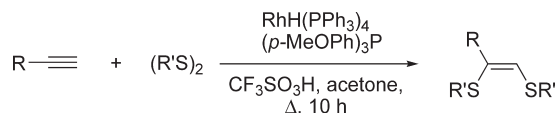
Until recently, transition-metal-catalyzed additions of the Alk₂Z₂ moiety to alkynes remained a challenging problem. The only available synthetic route to such products involved the stepwise reaction of R'₃Si-S-SiR'₃ and alkynes, followed by alkylation (Scheme 128).^{369,370}

The nature of the organic group in the dichalcogenide plays an important role in the reactivity of such compounds with metal complexes. In fact, the S-S bond-dissociation energy in Alk₂S₂ is

Scheme 138



Scheme 139



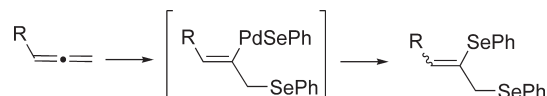
higher compared to Ph_2S_2 : 74 kcal/mol versus 55 kcal/mol, respectively.³⁷¹ This could be one of the reasons why different ligands are required to promote the oxidative addition step with these dichalcogenides. Indeed, it was found that a Pd catalyst with the Cy_2PhP ligand did catalyze the stereoselective Alk_2Z_2 addition to the triple bond of alkynes (Scheme 129).³⁷¹ The reaction was carried out at 140 °C for 12 h and gave high yields for $\text{Z} = \text{S}$ and good yields for $\text{Z} = \text{Se}$. The lower yields obtained in the case of the diselenides were attributed to the side reaction where Alk_2Se_2 converted to Alk_2S .

A much more efficient catalytic system based on Ni complexes was designed. Using 3 mol % of a simple catalyst precursor $\text{Ni}(\text{acac})_2$ and 30 mol % of the Me_2PhP ligand, a highly stereoselective addition of Alk_2Z_2 ($\text{Alk} = \text{Me}, \text{Bu}^i, \text{Pr}^i, \text{Cy}$) to alkynes was performed under solvent-free conditions (Scheme 129). The ligand was found to play a dramatic role in these catalytic reactions. For both metals, R_2PhP -based ligands were found to be the ones of choice: $\text{R} = \text{Cy}$ for Pd and $\text{R} = \text{Me}$ for Ni.³⁷¹ In spite of trying out a range of alkynes, only terminal alkynes were found to be successful in the reaction; internal alkynes remained inactive.

A comparative theoretical study of the Pd- and Ni-mediated reactions carried out at the B3LYP level has shown that (i) NiL_2 complexes are more reactive in oxidative additions of the $\text{Z} \text{--} \text{Z}$ bond than PdL_2 ; (ii) for both Ni and Pd complexes, the $\text{Z} \text{--} \text{Z}$ bond oxidative addition is energetically more favorable than that for the $\text{C} \text{--} \text{Z}$ bond; and (iii) the activation of the $\text{C} \text{--} \text{Z}$ bond by the metal complex should be easier for $\text{Z} = \text{Se}$ than $\text{Z} = \text{S}$.³⁷¹

Cyclic vinyl chalcogenides were successfully synthesized via the addition reaction of terminal alkynes to cyclic disulfides and diselenides.²⁹⁶ In the Pd/ Cy_2PhP catalytic system ($\text{L}/\text{Pd} = 10/1$), the reaction of 1-hexyne with methyl(\pm)- α -lipoate led to formation of the product with a yield of 67% after 2 h and 99% after 8 h. As in the case discussed above for the acyclic Alk_2Z_2 , the ligand effect had a crucial influence on the performance of the catalytic reaction. For example, using Cy_2PhP and CyPh_2P resulted in 99% and 19% yields, respectively. It was found that the ligand effect is important not only from the point of view of performance in the catalytic cycle but also for avoiding catalytic polymerization. It is also involved in initiating formation of active species via the "leaching" process (Scheme 130).²⁹⁶ Stoichiometric oxidative addition (40 °C) and alkyne insertion reactions (140 °C) were studied using NMR monitoring. Mononuclear and

Scheme 140



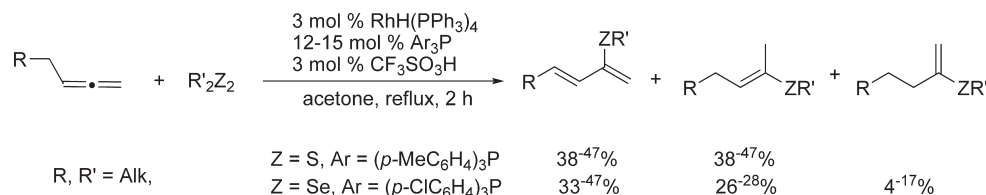
polynuclear Pd complexes were detected with ^{31}P and $2\text{D } ^1\text{H} \text{--} ^{31}\text{P}$ HMQC NMR. The catalytic activity of the $[\text{Pd}_n(\text{ZR})_m(\text{Cy}_2\text{PhP})_2]$ species was found to be significantly decreased when the value of n was increased. The most likely explanation is that both factors, lower solubility and a decreased number of the terminal ZR groups (the terminal groups are more reactive toward alkyne insertion compared to the η^2 -coordinated bridging ZR groups), are responsible for the observed diminishing of the catalytic activity.²⁹⁶

The Ni-based catalytic system was found to be synthetically superior to the Pd system (100 °C for Ni instead of 140 °C for Pd).²⁹⁶ Five-membered and six-membered dichalcogenides reacted smoothly with alkynes and resulted in yields of 50–91% (Scheme 131). A ligand excess was required to maintain a high activity of the catalyst ($\text{L}/\text{Ni} = 10/1$). The same effect has also been reported for the Ni-catalyzed reaction of the acyclic analogues.³⁷¹ Without the ligand excess, the formation of insoluble metal species was observed. These were isolated and studied using scanning electron microscopy (SEM). According to the SEM study, the isolated solid possessed a flaky structure. The smallest structural units were 100–500 nm in size and had a thickness of 40–90 nm.²⁹⁶ This solid was dissolved in toluene in the presence of an excess of the ligand and subsequently showed the desired catalytic activity in the addition reaction. Without the phosphine ligand, the solid proved to be inactive in the catalytic reaction.

A plausible mechanism for the catalytic cycle involves the oxidative addition of the cyclic dichalcogenide to the ML_x species. This is followed by alkyne coordination and insertion into the $\text{M} \text{--} \text{Z}$ bond and finally reductive elimination (Scheme 132).²⁹⁶ Although only mononuclear metal complexes are shown in Scheme 132, dinuclear and polynuclear metal species may also contribute to product formation.

Using the Ni catalyst made it possible to solve the problem of $\text{Z} \text{--} \text{Z}$ bond addition to internal alkynes.³⁷² In the $\text{Ni}(\text{acac})_2/\text{PMePh}_2$ catalytic system, addition of Ar_2S_2 to internal alkynes led to the formation of vinyl sulfides in 55–91% isolated yields as well as >99:1 stereoselectivity (Scheme 133). The reaction was carried out at 100 °C under solvent-free conditions. A combined experimental and theoretical (PBE level) mechanistic study has shown that Ni complexes may bind to the alkyne by the apical site of a five-coordinated intermediate and subsequent successful mediation of the addition reaction. A classical four-coordinated complex would most likely lead to a resting state (Scheme 134).

Scheme 141



The study of the ligand effect in the Ni-catalyzed addition of diaryl dichalcogenides to terminal alkynes revealed that in several cases a mixture of alkenes and 1,3-dienes was formed (Scheme 135).³⁷³ The most selective reaction for the formation of dienes was observed for $\text{L} = \text{Cy}_2\text{PhP}$ and Cy_3P . These ligands completely suppressed formation of the alkenes and gave a $\sim 75:25$ ratio in favor of the asymmetric diene.

Under optimized conditions (MeCN , 40°C , 5 h, 3 mol % $\text{Ni}(\text{acac})_2$, 30 mol % PPhCy_2), the synthetic procedure produced good yields and the asymmetric dienes were isolated in pure form using flash chromatography (Chart 11).

According to solution-phase NMR analysis as well as solid state X-ray analysis, the structures possess a *s-gauche* configuration of the central C—C bond in contrast to the *s-trans* configuration reported for the majority of known 1,3-dienes. It is the first example of the application of this synthetic procedure to this type of dienes, which cannot be accessed by any other method with similar efficiency.

The results have suggested that an intermediate Ni—vinyl complex formed after reaction with the first molecule of alkyne may subsequently undergo different pathways (Scheme 136). One of the options is a very well-known pathway involving an intramolecular C—Z reductive elimination, which leads to the formation of the alkene. If the intermediate vinyl complex is stable enough, it may react with the second alkyne molecule via an insertion into the Ni—Z or Ni—C bonds, leading to symmetrical or unsymmetrical 1,3-dienes, respectively. According to theoretical calculations at the B3LYP level, the formation of the unsymmetrical diene is preferable from an energy point of view. This is in agreement with experimental findings.³⁷³

The reaction of terminal alkynes with disulfides in the presence of a $\text{RhH}(\text{PPh}_3)_4/\text{dppf}$ catalyst resulted in C—H bond cleavage and formation of a Csp—S bond (Scheme 137).³⁷⁴ Other examples of these Rh-catalyzed σ -bond metathesis reactions involving sulfur groups have also been reported.³⁷⁵ However, the Rh complex catalyzed the stereoselective addition reaction in the mixture of alkyne with diaryl disulfide and diphenyl diselenide (Scheme 138).³⁷⁶

The *syn*-addition of dialkyl disulfides was catalyzed with the same Rh complex in the presence of 3 mol % of trifluoromethanesulfonic acid (Scheme 139).³⁷⁷ The reaction was found to be very sensitive to the ligand effect. The best performance was found for 3 mol % of $\text{RhH}(\text{PPh}_3)_4$ and 12 mol % of tris(*p*-methoxyphenyl)phosphine. In some cases, the Rh complex with the dppf ligand also showed good catalytic activity.

Vinyl chalcogenides were also prepared using transition-metal-catalyzed RZZR addition to the double bond of allenes. Ogawa and co-workers reported allene bisseleination with Ph_2Se_2 and a $\text{Pd}(\text{PPh}_3)_4$ catalyst (Scheme 140).³⁷⁸ The product was obtained in good to high yields, but with poor stereoselectivity. Only in the case of cyclohexyl allene was a good yield combined with high selectivity $E/Z = 93/7$. A detailed computational study (B3LYP level) of the regioselective bisseleination of allenes catalyzed by

palladium complexes was carried out by Wu and co-workers.³⁷⁹ The study revealed the ligand effect (PH_3 and PMe_3 ligands) on the reaction mechanism and showed that reductive elimination is the rate-determining step in the case of bulkier ligands.

The $\text{RhH}(\text{PPh}_3)_4$ complex discussed above was also found to be a suitable catalyst for the addition of disulfides to allenes (Scheme 141).³⁸⁰ In contrast to the reaction with alkynes (Scheme 139), the reaction with allenes was accompanied by hydride transfer and resulted in poor selectivity with $\sim 1:1$ ratio of the diene and alkenes.

6. CONCLUSIONS

The advent of palladium-catalyzed cross-coupling reactions has resulted in tremendous advancement in modern organic chemistry. This has been highlighted by numerous landmarks including the recognition of its importance by the awarding of the Nobel Prize to Heck, Negishi, and Suzuki in 2010.³⁸¹ Although first developed for $\text{Csp}^2\text{—Csp}^2$, $\text{Csp}^2\text{—Csp}$, etc. bond formation, the cross-coupling methodology was further expanded to include numerous reactions for constructing carbon—heteroatomic bonds. Attention to the even more complicated case of carbon—chalcogen bond synthesis (S, Se) has resulted in outstanding progress and found widespread synthesis applications.

Currently we are experiencing another breakthrough due to the possibility of replacing palladium by other metals, in particular by copper and iron. The groundbreaking renaissance of Ullmann chemistry has led to the development of several very efficient catalysts, which in some cases replace the more traditional palladium systems. Copper catalysts have proven not only cheaper and more readily available but also superior in terms of efficiency and functional group tolerance. One important advantage of copper systems concerns the involvement of less toxic nitrogen or oxygen ligands. Palladium-based catalytic systems usually require phosphines. The explosion of interest in Cu-catalysis for C—S and C—Se bond formation has taken place only in recent years, and we have tried to reflect this in the present review.

Another fascinating opportunity for making $\text{Csp}^2\text{—Z}$ bonds is to carry out the hydrochalcogenation or bischalcogenation reactions via the addition of Z—H or Z—Z bonds to alkynes. Catalyst design for this transformation is a rather difficult task: in addition to efficiency, the question of selectivity is of vital importance. High stereoselectivity is required for bischalcogenation, and regioselectivity is a critical issue in hydrochalcogenation. The full atom-economic potential of this catalytic chemistry will be realized only after a solution to the selectivity issue is found. As was the case for cross-coupling reactions, palladium catalysts were first developed for use in the Z—H and Z—Z bond-addition reactions. In recent years, it was demonstrated that nickel complexes exhibit superior activity for these transformations and in some cases even outperform the palladium analogues.

The next challenge in carbon—heteroatom cross-coupling chemistry is to develop recyclable catalytic systems, which can

be easily isolated from the products and reused many times without loss of catalyst or activity. In the case of cross-coupling reactions (section 2), it is significant that heterogeneous systems with the possibility of recycling are more commonly found for copper. This is in contrast to palladium, where only a few recyclable catalytic systems have been developed. It appears to be more likely that the copper particles suffer less from the problem of leaching. It is well-known that this is the situation for palladium.^{382,383} In addition reactions (sections 3–5), the degree of leaching and the nature of the catalytic system can be efficiently controlled by the use of phosphine ligands. This phenomenon provides a convenient tool to control Pd- or Ni-mediated transformations in homogeneous or solid-state catalysis. The dependence of the catalytic activity on the size and shape of the nanostructured particles is of particular interest in heterogeneous systems.

Finally, we anticipate further development of traditional Pd systems as well as the exploitation of other metals (Cu, Ni, Fe, Zr, Ln, An) as catalysts for C–S and C–Se bond formation. In addition, there is potential to use this chemistry in the search for more reliable approaches for the construction of C–Te bonds. There is a definite need to design and develop highly efficient, selective, and recyclable catalysts of industrial importance in the near future.

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BIOGRAPHIES

Valentine Ananikov received his Ph.D. degree in 1999 and his Habilitation in 2003, and in 2005 he was appointed Professor and Laboratory Head of the ND Zelinsky Institute of Organic Chemistry, The Russian Academy of Sciences. In 2008 he was elected as a Corresponding Member of Russian Academy of Sciences. He was a recipient of the Russian State Prize for Outstanding Achievements in Science and Technology (2004), an Award of the Science Support Foundation (2005), a Medal of the Russian Academy of Sciences (2000), and Liebig Lecturer by German Chemical Society (2010). His research has been supported by grants from the President of Russia (2004, 2007). He is a member of the International Advisory Boards of Organometallics and Chemistry An Asian Journal. His scientific interests are focused on (i) transition metal catalyzed reactions, (ii) development of new NMR methods, and (iii) mechanistic studies of catalytic reactions.



Irina Beletskaya received her Diploma degree in 1955, her Ph.D. degree in 1958, and her Doctor of Chemistry degree in 1963 from Moscow State University. The subject for the latter was Electrophilic Substitution at Saturated Carbon. She became a Full Professor at Moscow State University in 1970, and in 1974 she became a Corresponding Member of the Academy of Sciences (USSR), of which she became a full member (Academician) in 1992. She is currently Head of the Laboratory of Organoelement Compounds, Department of Chemistry, Moscow State University. Irina Beletskaya is Chief Editor of the Russian Journal of Organic Chemistry. She was President of the Organic Chemistry Division of IUPAC from 1989 to 1991. She was a recipient of the Lomonosov Prize (1979), the Mendeleev Prize (1982), The Nesmeyanov Prize (1991), the Demidov Prize (2003), and the State Prize (2004). She is the author of more 600 articles and 4 monographs. Her current scientific interests are focused on (i) transition metal catalysis in organic synthesis, (ii) organic derivatives of lanthanides, and (iii) carbanions and nucleophilic aromatic substitution.



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NOTE ADDED IN PROOF

During preparation of the present article for publication, new studies have appeared dealing with usage of sodium thiosulfate as a mercapto surrogate in Pd-catalyzed reactions.³⁸⁴ Pd-catalyzed C—S cross-coupling with indium tri(organothiolates),³⁸⁵ Fe-catalyzed³⁸⁶ and Cu-catalyzed³⁸⁷ synthesis of benzothiazoles, Cu-catalyzed preparation of benzoselenazoles,³⁸⁸ Cu/Fe-catalyzed coupling of aryl thiols and aryl iodides,³⁸⁹ Cu-catalyzed coupling reaction using resin-bound organic bases,³⁹⁰ and utilization of Cu catalysis in the synthesis of sulfonamides.³⁹¹