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A Mini Review on the Effects of Bases, Catalyst Loadings, Temperatures and Solvents in the Stille Cross-Coupling Reaction using Pd(II), Cu(I, II) and Ni(II) Complexes as Homogeneous Catalysts

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Stille reaction is one of the most common, efficient and selective Pd-catalyzed cross-coupling reactions for the construction of C-C bonds in organic synthesis. It was initially achieved and reported in 1978 by J. K. Stille and D. Milstein. This reaction is based on organotin compounds in the presence of palladium(II) complex as catalyst which can be performed in mild reaction conditions. This review solely focused on the transition of innovation from palladium to other transition metals i.e. copper(I, II) and nickel(II), and emphasized on their catalytic capacity and mechanistic details. The optimization of reaction conditions is also reviewed in this paper by varying the types of bases, amounts of catalysts, temperatures and types of solvents. The catalytic optimization is essential because optimum reaction conditions directly influence the yield of product formed. This review also focused on the effect of aryl halides towards Stille reaction in which electron-withdrawing and electron-donating substituted aryl halides were converted to their corresponding biphenyl products by Stille reaction.

Keywords: Stille reaction; palladium; copper; nickel; catalyst; optimization

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The palladium-catalyzed cross-coupling of aryl halides or pseudo-halides with organostannanes, known as the Stille coupling, is one of the most powerful methods for the straightforward construction of carbon–carbon bonds in synthetic chemistry [1]. Significant progress in the preparation and characterization of variety of ligands and catalysts has been made to avoid protection and deprotection procedures, which therefore allow syntheses to be carried out in fewer steps [2]. Transition metal-catalyzed reactions involve catalytic cycles which are a succession of elemental steps in which the metal is present as different catalytic species. John Kenneth Stille developed his work in 1980s on the synthesis of a multitude of ketones using this versatile mild process and suggested a mechanism for the transformation [3].

Scheme 1 demonstrates the general reaction of Stille reaction and the well-established Stille reaction mechanism [4]. The reaction is between an organostannane also called organotin and an organic electrophile in the presence of palladium catalyst to generate a new C–C single bond [5]. The active Pd(0) species may be generated from Pd(II) precursor that is reduced by the organostannane before entering the catalytic cycle. Three key basic steps involved in the catalytic cycle are oxidative addition, transmetallation and reductive elimination. The mechanism begins with oxidative addition of the organohalide to Pd(0) to form a Pd(II) complex. In the following transmetallation with the organostannane, the R group of the organostannane reagent replaces the halide anion on the palladium complex. Reductive elimination then gives the final coupled product, regenerates the palladium catalyst, thus the catalytic cycle can begin again. Theoretical studies indicate that the steric and electronic properties of ligands are both significant in catalysis to control catalytic performance [6]. In general, oxidative addition is controlled by electronic factors, while a combination of electronic and steric effects regulates the transmetallation and reductive elimination processes [7].

Palladium complexes are mostly used to catalyze this coupling reaction as they offer high product yields, high regioselectivity, high stereoselectivity and compatibility with many functional moieties. The activity of other transition metal catalysts such as nickel and copper has also been investigated [8]. However, the scope and functional group tolerance of the palladium catalysts are far wider than those of any other metal species [9]. The reaction of triorganostannyl ions as nucleophiles with haloarenes has long been known, with the products obtained depending on the nucleophile, solvent, base, and the amount of catalyst used in the reaction [10]. However, the separation and

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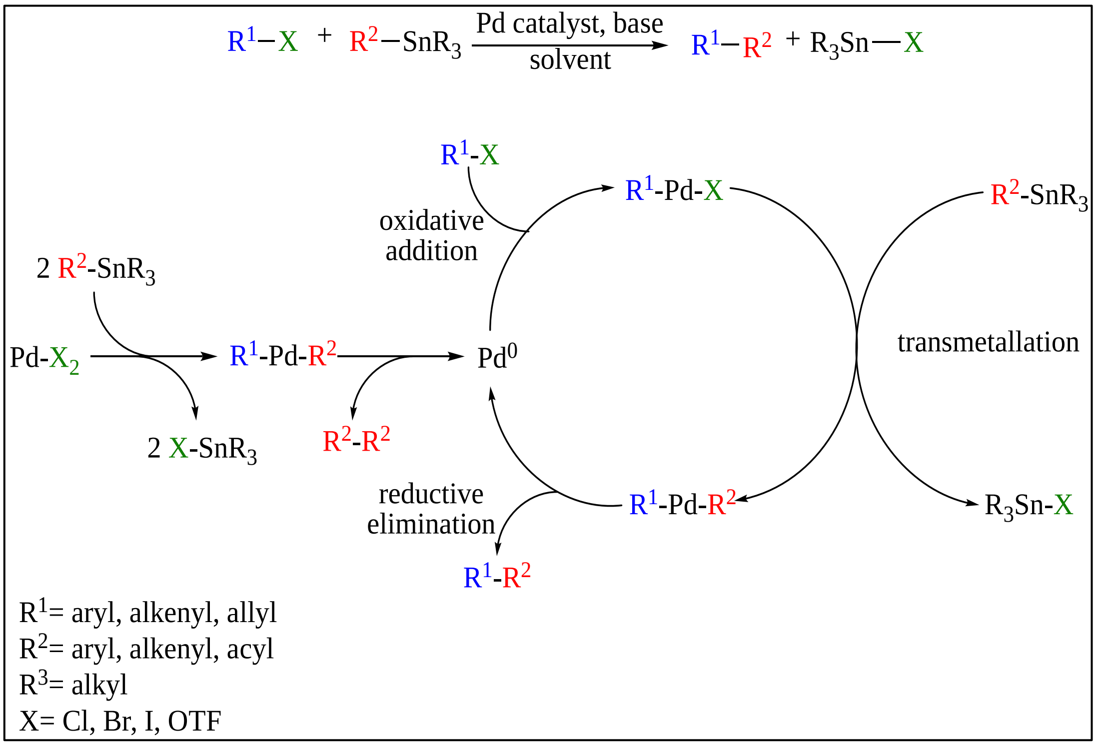
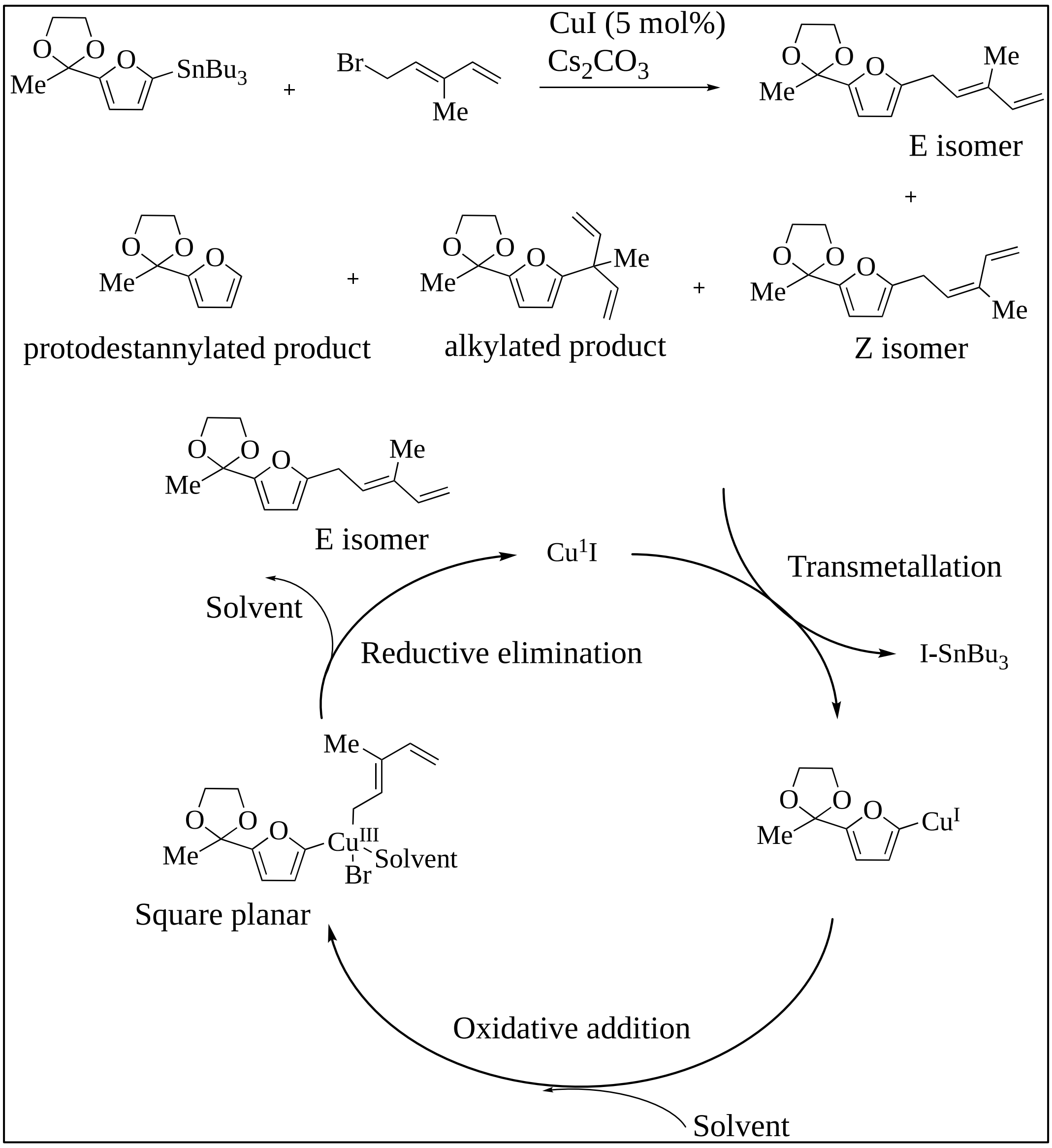
recovery of the catalyst represent major concerns for sustainable development. Generally, homogeneous palladium catalysts are popular for their high selectivity, activity, and resistance towards poisons, while heterogeneous catalysis offers the advantage of simplified product separation and recyclability of the catalyst [11].

Despite the great advances in utilizing palladium as catalyst, copper is still very much used as one of the important catalysts; being a non-noble metal, copper is cheap and available in many organic synthetic laboratories globally [12]. Nickel catalyzed cross-coupling of electrophiles (organic halides and pseudohalides) with carbon nucleophiles (organometallic compounds) has had a prominent impact on organic synthesis [13]. The selection of ligands has made it possible to utilize a variety of reagents with very simple and inexpensive catalyst precursors. Diverse reactivity and cost efficiency have been the valuable driving force behind the remarkable progress of Nickel catalysts in this area, with more challenges in the modern design of process equipment [14]. Nickel has a significant cost advantage compared to palladium [15]. Hence, it is important to explore the possibility of using nickel and copper as catalysts for the cross-coupling.

The palladium-free copper catalyzed Stille-like reactions found in the literature are likely to operate via a Cu^I/Cu^{III} cycle similar to the Pd^0/Pd^{II} classic Stille cycle [16]. The detailed investigation on a possible mechanism for CuI along with Cs_2CO_3 additive as the best catalyst for the coupling of allyl bromide and functionalized furanyl stannyl derivative with minimal catalyst loading at ambient temperature was identified by Ghosh and co-workers (Scheme 2) [17]. The improvement of E/Z ratio is presumably due to solvent ligation on the metal center, resulting in a square planar transition state. The proposed Cu(III) η3 allyl complexation prompted the Z-isomer or the γ-alkylated intermediate to be less stable or to not form, thus resulting in the major (E)-isomer. The E-isomer was obtained in an excellent yield of up to 94%. The significance of this reaction lies in the applicability of the E-isomer in the synthesis of anticancer therapeutic, spliceostatin derivatives.



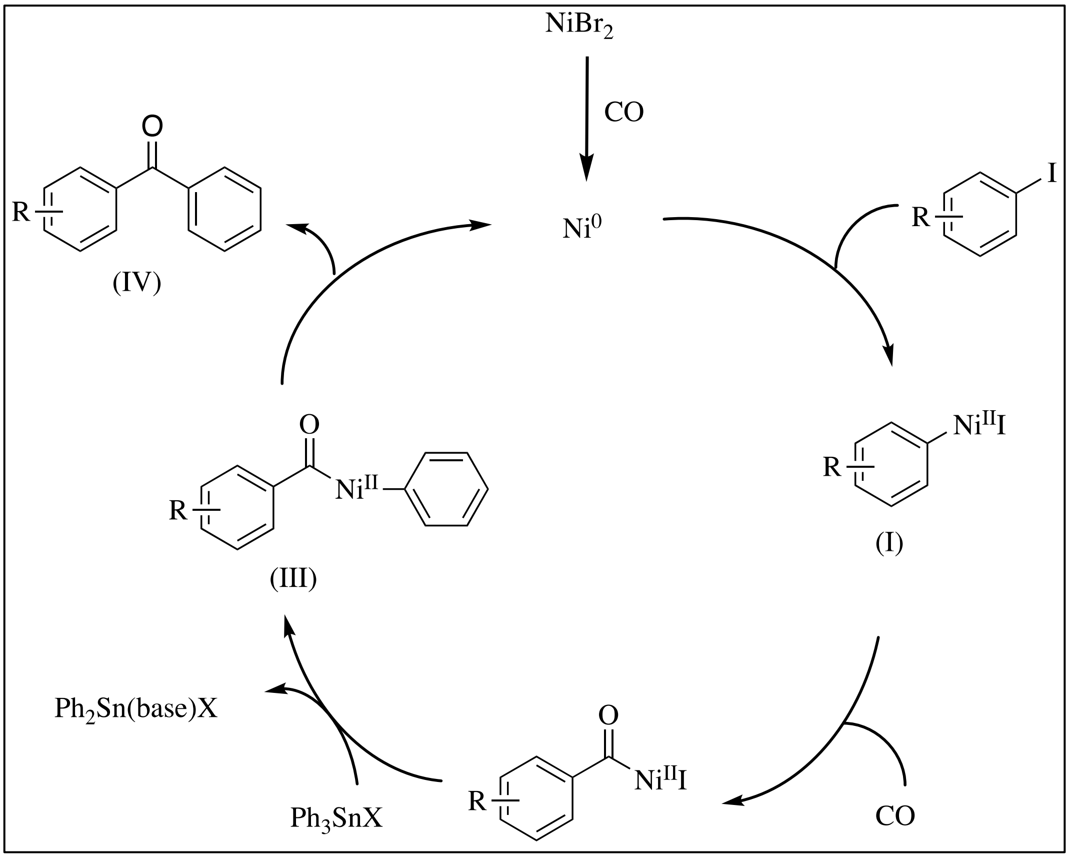
Scheme 1. General reaction and mechanism of Pd-catalyzed cross-coupling Stille reaction



Scheme 2. Plausible mechanistic pathway for the CuI catalyzed E-selective Stille coupling

The plausible mechanism of Ni-catalyzed Stille carbonylative coupling of aryl halides with metal carbonyls as solid source of CO is outlined in Scheme 3 [18]. Carbonylative Stille reaction is a three-component reaction of diverse organostannanes with aryl or vinyl electrophiles which have been applied in the presence of carbon monoxide to give unsymmetrical diaryl ketones. The mechanism begins with Ni(II) pre-catalyst being reduced by the generated CO to Ni(0). Oxidative addition of the carbon-iodide bond to the generated Ni(0) generates the intermediate (I) which followed by CO insertion to generate the intermediate (II). The attack of base to Ph_3SnX followed by migration of a phenyl group generates the intermediate (III). Eventually, after reductive elimination, the corresponding unsymmetrical diaryl ketones and Ni(0) are produced. In addition, a base such as K_2CO_3 or OH^- is able to react with Ph_3SnCl to migrate the Ph group.

The main advantages of the Stille coupling reaction include the stability and functional group tolerance of stannanes, the broad reaction scope of aryl halides and pseudo-halides, and its chemo-selectivity [19]. The optimization could be done by varying parameters such as solvents, reaction time, bases, catalyst loadings and temperature. The synthesis is compatible with the electronic effects and the steric effects exerted by the substituents on the aryl halides. Therefore, this reaction has been widely applied in natural product synthesis, biological research, and for pharmaceutical purposes.



Scheme 3. The plausible mechanism for the carbonylative Stille reaction of aryl iodides

Catalytic Optimization of Stille Cross-Coupling Reaction between Organostannane and Aryl Halides using Palladium Catalyst

Stille coupling rection can be initiated by reacting an aryl halide with organostannane. The palladium-catalyzed Stille cross-coupling of aryl halides (or halide equivalents) with organotin reagents has been widely applied in natural product synthesis [20], carbohydrate chemistry [21] and biological research [22]. The popularity is due, in part, to the ease of handling of organotin reagents and their excellent functional group tolerance [23]. The effect of bases, different amounts of catalysts, temperatures and types of solvents were observed to find optimum reaction conditions. There are many substrates reported in the literature but the most common are aryl iodides and tributylphenylstannane [24][25][26]. However, the optimum reaction conditions for certain substrates cannot be determined easily, thus optimization need to be carried out [27]. In addition, the optimization is essential because optimum reaction conditions directly influence the yield of product formed but there are no specific protocols for different kinds of reaction. This needs to be carried out prior to the catalytic testing of the synthesized complexes in the reaction [28]. The optimization could be done by varying parameters such as solvents, reaction time, bases, catalyst loadings and temperatures. To narrow down the scope of this research, the optimum reaction conditions compiled below are focused on the types of bases, catalyst loadings, reaction temperatures and effect of solvents to produce biphenyl as the main products (Table 1).

Types of Bases

The effect of bases needs to be examined as these bases play a crucial role in Stille reaction. A base is important in palladacycle formation as it facilitates the reaction forward by removing a proton from the coordination of organostannane to the metal in the mechanism of the Stille reaction [29]. Usually, there are two types of bases used in optimization reactions namely organic and inorganic bases [30]. Common organic bases such as amine is generally used in the Stille reaction, for inorganic bases, bicarbonate and hydroxide bases are prevalent. Table 1 shows various optimum bases commonly used which include K_2CO_3, $NaHCO_3$, CsF, NaOAc and Na_2CO_3. These are all inorganic bases. Hence, this shows that inorganic bases are prevalent to be used to achieve optimum reaction conditions with good yields. Since majority of current catalytic systems utilize inorganic bases, modern amination methods suffer from restrictions with regard to functional group compatibility or other operational limitations such as insolubility [31]. As an alternative, inorganic bases are frequently employed, but due to their insolubility, reactions often require a phase transfer agent or high catalyst loadings, as well as elevated reaction temperatures.

Amount of Catalysts

Catalyst loading is one of the parameters used to find the optimum reaction conditions for Stille coupling reaction. The reaction is best run with as low amount of catalyst as possible in order to a get high turnover number (TON) [9]. If the amount of catalyst used is too high, it results in a low turnover number (TON). Utilizing a high catalyst loading has always been unacceptable even though a high product yield could be obtained from the reaction. Since remarkable results could be achieved with less catalyst, it would be a tremendous advantage to optimize the reaction as well as to find pathways to reduce costs simultaneously [32]. Lowering the catalyst load could affect the reaction course [33]. Table 1 displays the amount of catalyst of 0.1 mol% to 5 mol%.

Reaction Temperatures

Other than type of bases and catalyst loadings, optimum reaction temperature for Stille coupling reaction must also be set. An increase in temperature promotes higher percentage of yield of the coupling reaction, thus, the temperature is to be in direct proportion with the yield, and this was proven statistically [34]. Optimum reaction temperature for Stille reaction can go as low as 60 ºC and as high as 120 ºC as displayed in Table 1. With regards to Table 1, it can be concluded that reactions with higher temperatures achieved good yields. The reactions that proceeded at high temperature usually took placed in DMF and $NaHCO_3$. The decomposition of catalyst will occur if too high of a temperature is used. In contrast, using too low of a temperature, the catalyst cannot start or continue the reaction due to insufficient energy. In order to find the most suitable temperature for the catalyst, it is crucial to find the range of temperatures to obtain the best yield of result.

Types of Solvents

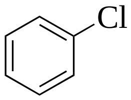
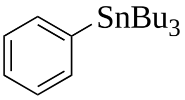
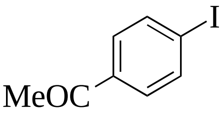
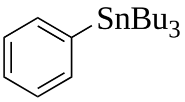
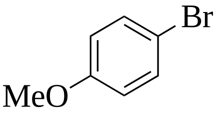
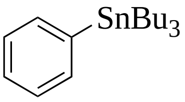
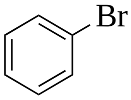
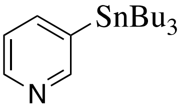
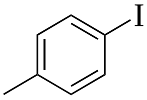
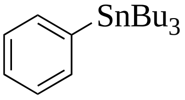
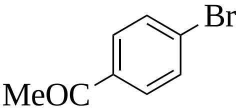
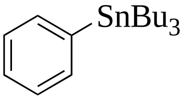
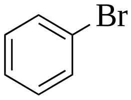
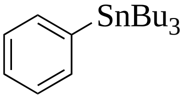
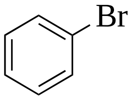
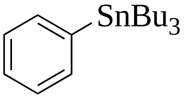
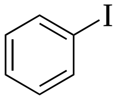
Solvent is also an important component in catalysis. Solvents are used in the analysis of catalysts and/or products, as well as spectroscopy [35]. Since there are many different solvents to choose from, selecting the right ones for a catalytic process can improve the outcome of the reaction considerably [36]. The solvent properties that strongly influence catalysis include dipolarity or polarity, hydrogen-bond donating ability (proticity) and hydrogen-bond accepting ability (basicity) [37]. The performance of a catalyst is strongly influenced by these parameters and therefore finding the right solvent may affect the reaction. Among the reported solvents, DMF, toluene, and PEG led to the corresponding biphenyl products as depicted in Table 1. However, less polar (dioxane, $PhCH_3$) and low-boiling (Et_2O) solvents resulted in lower yields of the biphenyl product [38].

Effects of Aryl Halides Towards the Stille Reaction

A wide range of electron-withdrawing and electron-donating substituted aryl halides are converted to their corresponding biphenyl products by Stille reaction and all biphenyls are prepared in good to excellent yields [39]. To expand the scope of the reaction substrate, various organohalides are used in the Stille cross-coupling reaction as listed in Table 1. The reaction rate of different halides follows the conventional trend of ArI > ArBr > ArCl [39]. The reactions of organohalides bearing both electron-donating and electron-withdrawing substituents, such as $-OCH_3$, $COCH_3$ and $-CH_3$ with organostannane give the corresponding products in good yields. The strengths of the vinyl analogue are $COCH_3 > OCH_3 > CH_3$ [40]. When 4-iodoacetophenone and 4-bromo-acetophenone, which are aryl halides of iodide and bromide with an electron-withdrawing group (-COMe) at the *para-position* are coupled with tributyl-phenylstannane under 1 mol% [41] and 5 mol% [42] catalyst loading, their corresponding Stille coupling products are obtained in 98% and 97% yields, respectively. The yield of 4-iodoacetophenone is slightly higher than the yield of 4-bromoacetophenone with a shorter reaction time of 3 hours compared to 20 hours for 4-bromoacetophenone. Thus, as expected, aryl halides bearing electron-withdrawing groups show a better reactivity and give the higher yields of the biphenyl products.

Iodobenzene and bromobenzene show a slightly lower rate compared with those having electron-withdrawing substituents, but still resulted in excellent yields by prolonging the reaction time [43]. Conversely, aryl halides bearing an electron-donating group at the para-position which is $-CH_3$ yielded a lower yield of 86% even with a long reaction time (15 h). Therefore, it can be concluded that the presence of electron-withdrawing moieties improve the product yields and take shorter reaction times compared to those with electron-donating ones [44]. As listed in Table 1, the temperatures used in the Stille cross-coupling reactions that yielded high yields of products are in the range of 100-120 ºC.

Table 1. The Catalytic Activities of Palladium in Stille Reaction between various Aryl Halide and Tributylphenylstannane

Aryl Halide	Organostannane	Reaction conditions	Catalyst	% GC Yield	Ref.
		DMF, K_2CO_3, 120 ºC, 48 h	Pd/Al(OH)$_3$ (0.7 mol%)	80	[45]
		H_2O, $NaHCO_3$, 110 ºC, 3 h	$PdCl_2(NH_3)_2$/L (1 mol%)	98	[41]
		Toluene, CsF, 60 ºC, 10 h	$Pd_2(dba)_3$/pyrazolyl tethered phosphine ligand (1:1) (2 mol%)	90	[46]
		DMF, CsF, CuI, 110 ºC, 16 h	Cyclopalladated ferrocenylimines (1 mol%)	99	[47]
		NMP/DMF, 120 ºC, 15 h	Pd NCs (0.1 mol%)	86	[48]
		DMF, LiCl, 100 °C, 20 h	Pd(0)-MCM-41 (5 mol%)	97	[42]
		DMF/H_2O, 60 ºC, 6 h	MCM-41-2P-Pd(0) (0.5 mol%)	86	[49]
		THF, NMP, 80 ºC, 12 h	$Pd_2(dba)_3$/iminophosphine-*n*-butyl-lithium ligand (1:1) (5 mol%)	92	[50]
	Ph_3SnCl	PEG, NA_2CO_3, 80 ºC, 1h	BNP@Cur-Pd (0.05 mol%)	96	[44]

Ref: References

Catalytic Optimization of Stille Cross-Coupling Reaction using Copper and Nickel as Catalysts

The use of transition metals in cross-coupling reactions has been verified as a powerful tool in synthetic organic chemistry to access valuable pharmaceutical intermediates and functional organic molecules [51]. Palladium-catalyzed cross-coupling reactions of aryl halides for the formation of new carbon–carbon bonds have huge potential in fine organic synthesis, with particular emphasis [52]. The activity of other transition metal catalysts such as nickel and copper has also been investigated. Copper compounds are described to be a significant tool in building a variety of carbon-carbon and carbon-heteroatom bonds more than a century ago [53]. Whereas nickel catalyst cross-coupling had emerged in 1972 [54]. The catalytic optimization for Stille reaction using copper and nickel catalysts follow similar optimization as that of palladium catalyst i.e. types of bases, catalyst loadings, temperatures and solvents as shown in Table 2. Copper and nickel catalysts cross-coupling reactions of different electrophiles and nucleophiles or two types of nucleophiles are alternative synthetic procedures to Pd(II)-based processes to access functional organic molecules and heterocycles [55]. Furthermore, various proposed reaction mechanisms covering radical path or through the involvement of metal complexes in different oxidation states are highlighted and discussed.

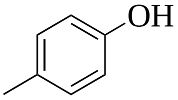
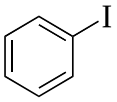
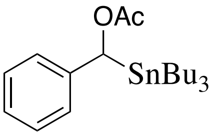
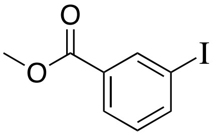
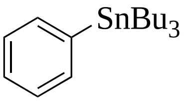
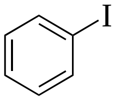
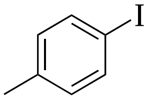
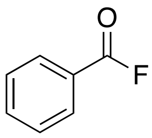
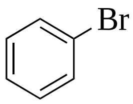
Copper-Catalyzed Stille Coupling

Copper has been explored as both a promoting transition metal and a catalyst over years in conducting stereospecific Stille couplings [56]. The preliminary efforts towards such a process focused on optimizing the reaction of Ph_3SnCl and 4-methylphenol which has reported to have a low yield of 62% in 60 ºC using $Cu(OAc)_2$ as the catalyst for 30 h in Et_3N and Et_2O as the solvent (Table 2, entry 1). The use of low-boiling (Et_2O) solvents resulted in lower yields of biphenyl product. Thapa and co-workers described that a CuCN-catalyzed coupling between α-heteroatom-substituted alkyltributylstannanes and iodobenzene in THF and less polar solvent, $PhCH_3$ in 60 ºC for 48 h yielded a product in low yield of 50% (Table 2, entry 2). This proved that less polar solvent produced low product yields. An earlier study on Cu(I)-catalyzed Stille cross-coupling and carbonylative coupling using hypervalent iodide as the electrophile and tributyl-phenylstannane with NaCl as the additive in N-methyl-2-pyrrolidone (NMP) for 20 h in 100 ºC gave 89% of the product yield, as reported by Kang and co-workers (Table 2, entry 3). A novel Schiff base-alumoxane reinforced mesoporous Cu nano-catalyst (SBA-Cu^{2+}) has been synthesized and well-characterized. It catalyzed the coupling of triphenyltin chloride with aryl/heteroaryl halides in a medium of polyethylene glycol (PEG) and Na_2CO_3 as the base within a short time, as reported by Ghorbani-Choghamarani and co-workers (Table 2, entry 4). The desired biphenyls are acquired in moderate to excellent yields with minor loadings of nano-copper catalyst (0.379 mol%) at high temperatures of about 80 ºC.

Nickel-Catalyzed Stille Coupling

Carbonylative Stille reaction is a three-component reaction of diverse organostannanes with aryl or vinyl electrophiles in the presence of carbon monoxide to give unsymmetrical diaryl ketones [57]. Iranpoor *et. al.* reported that the reaction of 4-iodotoluene, $NiBr_2$, $Cr(CO)_6$, K_2CO_3 as the base and Ph_3SnCl in DMF as the solvent at 100 ºC yielded 89% of the desired product (Table 2, entry 5). The reaction between aryl fluoride and tributylstannyltrimethylsilane in the presence of 10 mol% $NiCl_2$ catalyst and CsF as the base in toluene as the solvent at 140 °C yielded 94% of the product (Table 2, entry 6). Coupling triphenyltin chloride with bromobenzene in H_2O as the solvent and CsF as the base for 60 ºC for 2 h afforded the desired biaryls in decent to excellent yields of 99% (Table 2, entry 7).

Table 2. The Catalytic Activities of Copper and Nickel transition metal catalysts used in Stille Reaction

Entry	Aryl Halide	Organostannane	Reaction conditions	Catalyst	% GC Yield	Ref.
1		Ph_3SnCl	Et_3N, Et_2O, 60 ºC, 30 h	$Cu(OAc)_2$ (40 mol%)	62	[58]
2			THF, $PhCH_3$, 60 ºC, 48 h	CuCN (8 mol%)	50	[59]
3			NMP, NaCl, 100 ºC, 20 h	CuI (10 mol%)	89	[60]
4		Ph_3SnCl	Na_2CO_3, PEG, 80 ºC, 20 min	SBA-Cu^{2+} (0.379 mol %)	93	[61]
5		Ph_3SnCl	DMF, K_2CO_3, 100 ºC, 2.7 h	$NiBr_2$ (16 mol%)	89	[18]
6		Bu_3Sn-$SiMe_3$	CsF, toluene, 140 ºC, 24 h	$NiCl_2$ (10 mol%)	94	[62]
7		Ph_3SnCl	CsF, H_2O, 60 ºC, 2h	G_3DenP-Ni (2 mol%)	99	[63]

Ref: References

CONCLUSION

The present review provides insight into the optimum reaction parameters using Pd(II), Cu(I, II) and Ni(II) as catalysts in the Stille cross-coupling reaction. Pd(II) catalysts are popular to catalyze coupling reactions as they offer high product yields and have good compatibility with many functional moieties. Here in this review, several reports on Stille coupling incorporating transition metal catalysts (copper and nickel) are highlighted, in which they could be viable alternatives to the conventional palladium catalysts. The metal catalysts of copper and nickel serve as inexpensive, less toxic and easily available substitutes. This review also provides an outlook for reaction parameters which include the effect of different amount or types of bases, catalyst loadings, temperatures and solvents. From this review, the number of reports on non-palladium transition metals is much less compared to that on Pd(II) catalyst. In future, it is highly necessary for researchers to focus more on conducting the Stille reactions with non-palladium transition metals. In addition, incorporating computational study in the Stille cross-coupling reactions will provide an interesting insight to achieve greener processes. For example, such combination of theoretical and experimental studies could give a new understanding on the optimal solvent, such as using a water-based condition, to perform a reaction.

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