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C–S Coupling Using a Mixed-Ligand Pd Catalyst: A Highly Effective Strategy for Synthesizing Arylthio-Substituted Heterocycles

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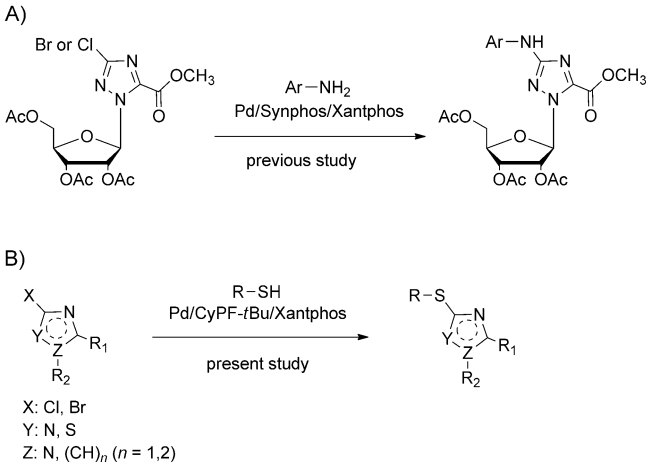
Pd-catalyzed cross-coupling reactions that form C–S bonds have recently emerged as a powerful synthetic approach for synthesizing various sulfur-containing compounds or structural motifs in both medicinal chemistry and material sciences.[1] Pd-catalyzed C–S coupling reactions remain relatively underdeveloped compared to other carbon–heteroatom bond-forming reactions. Indeed, many Pd catalysts are highly sensitive to substrates containing the reactive sulfur moieties and some sulfur-containing compounds may function as ligands, thus forming complexes that impair the catalytic reaction.[2] In addition, the yields of products of such reactions are highly dependent on the electronic features and steric environments of the thiol substrates. To overcome these issues, judicious choice of the ligands for the Pd catalysts is crucial.[2] However, the screening of ligands often requires trial and error, making it a time-consuming process. One rewarding way to circumvent this problem is the inventive combination of ligands with complementary features for transition-metal catalysis.[3] For instance, the mixed-ligand catalyst recently developed by Buchwald and co-workers has been successfully implemented in C–N coupling of both primary and secondary amine substrates.[4] The reported results clearly demonstrate the compelling advantages of combining and harnessing the properties of each individual ligand, thus promoting catalytic activity and dramatically broadening the substrate scope. Taking into account these aspects, our research group has extended this concept of mixed-ligand catalysis towards the synthesis of various arylamine-substituted triazole nucleosides, which were indeed obtained in high yields (Scheme 1A).[5] These remarkable results have encouraged us to further expand the scope of this approach to other



Scheme 1. Mixed-ligand Pd catalysts to promote cross-coupling reactions for synthesizing triazole nucleoside analogues and heterocycles.

cross-coupling reactions and in particular those involving the formation of C–S bonds. Indeed, to the best of our knowledge, there is no report in the literature referring to the use of mixed-ligand catalysis for C–S coupling. Hence, we disclose herein the first mixed-ligand Pd catalyst for such coupling reactions based on $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu (dba = *trans*,*trans*-dibenzylideneacetone). This new mixed-ligand catalytic system proved to be extremely effective for the synthesis of myriad arylthio-substituted triazole nucleosides (Scheme 1B). In addition, the effectiveness of this catalytic system for the activation of C–Cl bonds on heteroaryl rings and its versatility for use in coupling reactions involving both aryl and alkyl thiols was demonstrated.

We were motivated to develop Pd-catalyzed C–S coupling by our discovery of the appealing biological activities of aryl-appended triazole nucleosides and by our desire to synthesize their *S*-arylthiotriazole nucleoside analogues, as part of our general search for novel antiviral and anticancer drug candidates and efforts to better understand structure–activity relationships.[6] Throughout our studies, the synthesis of the arylthio-substituted triazole nucleosides has proven challenging. Indeed, our first attempt to achieve direct thiolation employed the conventional nucleophilic aromatic substitution reaction (S_NAr), which showed very limited nucleoside substrate scope: only the 5-bromotriazole nucleoside **1′** was able to afford the corresponding target (Scheme 2A),[6b] and

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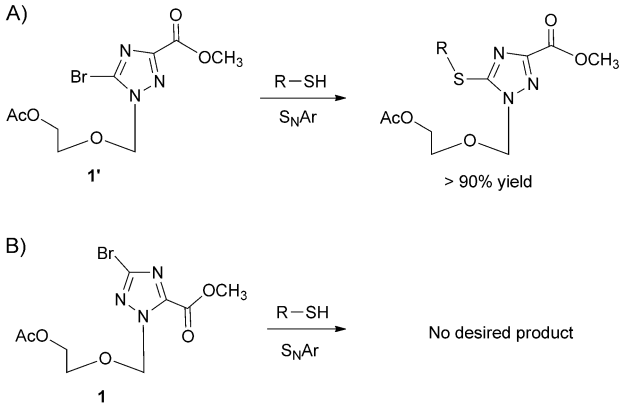


Scheme 2. Nucleophilic aromatic substitution for synthesizing arylthiol-substituted triazole nucleosides.

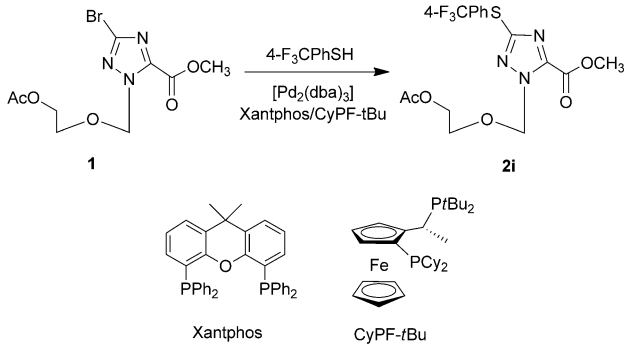
no product could be achieved with the isomeric substrate **1** (Scheme 2B).[7] Therefore, we turned our attention to the Pd-catalyzed C–S coupling reaction. However, only a few reaction conditions based on single-ligand Pd catalysts could promote the corresponding C–S bond formation with low yields (see the Supporting Information, Table S1); triazole heterocyclic aromatic rings are notoriously uncooperative for Pd catalysis.[6a]

To address this issue, we aimed to develop mixed-ligand Pd catalysts (Table 1). It has been reported that the Josiphos-type ligand CyPF-*t*Bu is an extremely active ligand in Pd-catalyzed thiolation.[8] Xantphos, on the other hand, is one of the rare ligands that has been reported for the C–S coupling of aryl halides with electron-deficient thiols.[9] Taking this into consideration, we tried the first attempt of C–S coupling with a mixed-ligand system using Xantphos and CyPF-*t*Bu in a 1:1 molar ratio, successfully obtaining the product in an extremely encouraging yield of 68% (Table 1, entry 3). This dramatically improved yield was indeed the direct consequence of the mixed-ligand Pd catalytic system because neither the single-ligand systems, $[Pd_2(dba)_3]$/CyPF-*t*Bu and $[Pd_2(dba)_3]$/Xantphos, could afford the corresponding product with acceptable yields (Table 1, entries 1 and 2). By systematically varying the ligand ratio, we found that the best yield was obtained with Xantphos and CyPF-*t*Bu at a ratio of 3:1 (Table 1, entries 3–7). Moreover, we further examined several bases and solvents as both base and solvent often impact the course of the reaction (see the Supporting Information, Tables S2 and S3). The best combination turned out to be Et_3N as base and toluene as solvent for the mixed-ligand system, $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu.

This mixed-ligand system was successfully amenable to a wide range of aryl thiols (Scheme 3), leading to excellent product yields with aryl thiols bearing both electron-deficient and electron-rich substituents at various positions. Furthermore, reactions with alkyl thiols led to very high yields (Scheme 3, **2h** and **2l**) and even the extremely sterically hindered substrate, 2-methyl-2-propanethiol, could be transformed into product (Scheme 3, **2m**). Therefore, the mixed-ligand catalyst $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu appears particularly effective with an exceptionally broad thiol substrate scope.

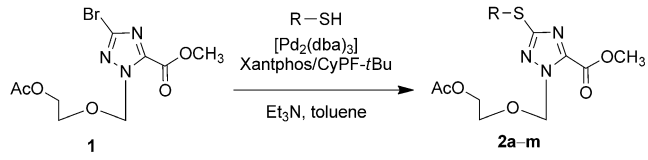
We further examined the substrate scope using different triazole nucleoside analogues. Interestingly, we found that aryl thiolation was also effective with sterically hindered 3-

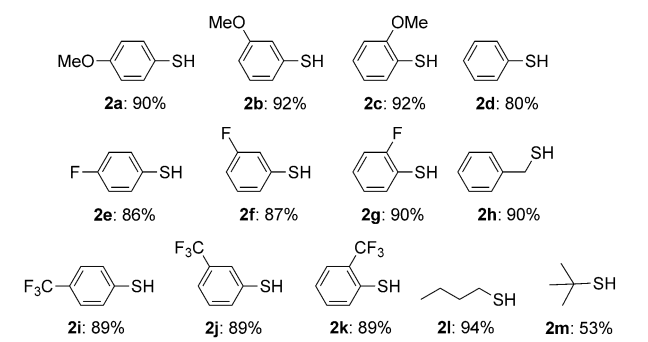
Table 1. Evaluation of Pd/Xantphos/CyPF-*t*Bu systems for C–S coupling by using the triazole nucleoside **1** and 4-(trifluoromethyl)thiophenol.[a]



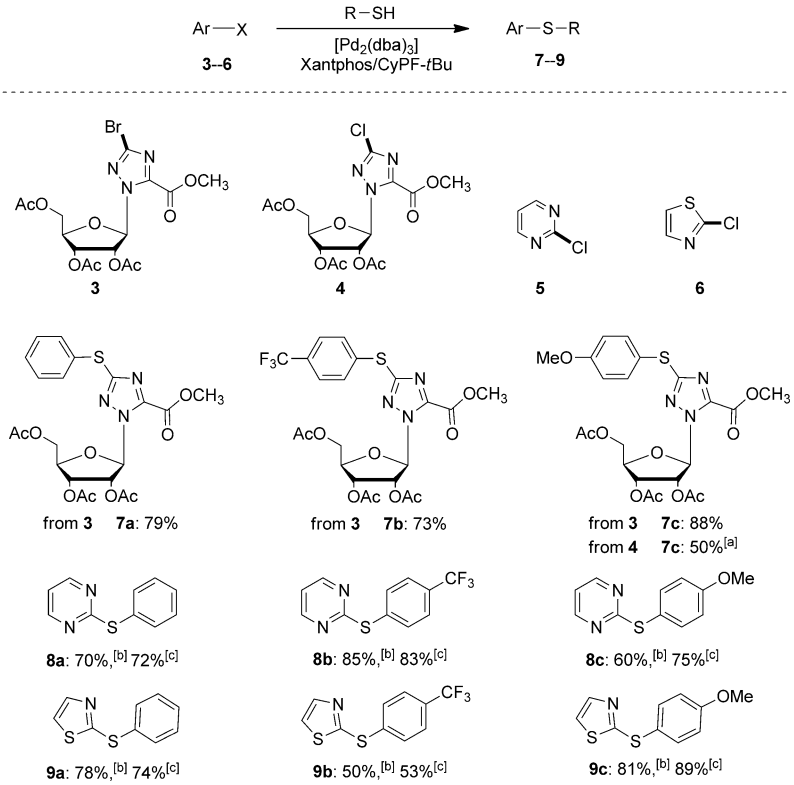
Entry	Xantphos/CyPF-*t*Bu[b]	Yield of **2i** [%][c]	Recovery of **1** [%][c]
1	1:0	17	59
2	0:1	5	0
3	1:1	68	19
4	1:2	51	16
5	2:1	71	8
6	3:1	89	0
7	4:1	53	27

[a] Reaction conditions: **1** (0.10 mmol), 4-(trifluoromethyl)thiophenol (0.12 mmol), $[Pd_2(dba)_3]$ (0.010 mmol), [Pd]/[ligand] = 1:1.1, K_2CO_3 (0.26 mmol), toluene (2.0 mL), reflux at 115 °C, 3 h. [b] Molar ratio. [c] Yield of isolated product.





Scheme 3. Synthesis of arylthio-substituted triazole nucleosides by using the Pd/Xantphos/CyPF-*t*Bu system with **1** and various thiols. Reaction conditions: **1** (0.10 mmol), thiol (0.12 mmol), $[Pd_2(dba)_3]$ (0.0050 mmol), [Pd]/[ligand] = 1:1.1, [Xantphos]/[CyPF-*t*Bu] = 3:1, Et_3N (0.70 mmol), toluene (2.0 mL), reflux at 115 °C, 4 h.



Scheme 4. Aryl thiolation of heteroaryl substrates using the Pd/Xantphos/CyPF-*t*Bu mixed-ligand system. Reaction conditions (exceptions, see below): aryl halide (0.10 mmol), thiol (0.12 mmol), $[Pd_2(dba)_3]$ (0.0050 mmol), [Pd]/[ligand] = 1:1.1, [Xantphos]/[CyPF-*t*Bu] = 3:1, Et_3N (0.70 mmol), toluene (2.0 mL), reflux at 115 °C, 4 h. [a] Double the catalyst loading, 20 h. [b] *N*,*N*-Diethylmethylamine (1.0 mmol) instead of Et_3N, 16 h. [c] Scale-up synthesis with aryl halide (0.50 mmol), thiol (0.60 mmol), $[Pd_2(dba)_3]$ (0.025 mmol), [Pd]/[ligand] = 1:1.1, [Xantphos]/[CyPF-*t*Bu] = 3:1, Et_3N (3.5 mmol), toluene (10 mL), reflux at 115 °C, 24 h.

bromotriazole ribonucleoside **3** (Scheme 4, **7a–c**). Additionally, and more importantly, the exceedingly challenging chlorinated heteroaryl substrates **4–6** could also afford the corresponding products in good to excellent yields (Scheme 4, **7c**, **8a–c**, **9a–c**).[10] Collectively, these data demonstrate the extraordinary power of this mixed-ligand catalyst for C–S coupling in general.

To gain more insight into how the two ligands work in harmony to boost the catalytic activity, we undertook ^{31}P NMR analysis to investigate the different catalytic systems based on the knowledge that both Xantphos and CyPF-*t*Bu are phosphine ligands and have characteristic signals in ^{31}P NMR spectra. We found that considerable amounts of free CyPF-*t*Bu remained in the single-ligand system of $[Pd_2(dba)_3]$/CyPF-*t*Bu, as shown by the intense NMR signals corresponding to free CyPF-*t*Bu (Figure 1 A, III). Consequentially, only a small amount of the catalytic complex [(CyPF-*t*Bu)Pd(dba)] could form in the $[Pd_2(dba)_3]$/CyPF-*t*Bu system, a behavior that was revealed by the weak NMR signals corresponding to [(CyPF-*t*Bu)Pd(dba)].[11] Clearly, these data reflect that the Pd complex formation with CyPF-*t*Bu alone was not efficient. Unlike CyPF-*t*Bu, no NMR signal for free Xantphos was observed in the spectrum of the $[Pd_2(dba)_3]$/Xantphos system; only those signals corresponding to the complex [(Xantphos)Pd(dba)] were observed (Figure 1 A, IV). Clearly, these results indicate that Xantphos is a highly efficient ligand in forming the complex with $[Pd_2(dba)_3]$ compared with CyPF-*t*Bu. Most interestingly, free CyPF-*t*Bu was no longer detected in the mixed-ligand system (Figure 1 A, V), thus suggesting that Xantphos promoted the ligation of CyPF-*t*Bu to Pd, probably through rapid ligand exchange.

Further ^{31}P NMR studies were carried out on the oxidative-addition step after adding the substrate **1** into solutions of both the two individual single-ligand systems and into a solution of the mixed-ligand system (Figure 1 B). In the single-ligand system of $[Pd_2(dba)_3]$/Xantphos/**1** (Figure 1 B, II), we observed that the NMR signals for the [(Xantphos)Pd(dba)] complex disappeared, whereas a new signal corresponding to the oxidative complex [(Xantphos)Pd(**1**)] emerged. Notably, the NMR signal of free Xantphos also reappeared, thus suggesting that free Xantphos was released from Pd complexes upon the addition of **1**. This conclusion was further supported by the large amount of free Xantphos observed in the mixed-ligand system (Figure 1 B, III). On the contrary, there was no free CyPF-*t*Bu observed in the mixed-ligand system, thus highlighting that **1** preferentially reacts to form the oxidative-addition intermediate with the [(CyPF-*t*Bu)Pd(dba)] complex rather than with the [(Xantphos)Pd(dba)] complex. This result implies that ligand exchange at the level of Pd complexes involved in the oxidative-addition steps also favors the formation of an adduct containing CyPF-*t*Bu, and consequently enhances the whole reaction. Notably, oxidative addition of a substrate onto [(CyPF-*t*Bu)Pd(dba)] is usually fast.[2a] Taking all arguments together, we postulate a general mechanism for this C-S cross coupling reaction catalyzed by the mixed-ligand Pd catalyst where Xantphos favorably promotes the formation of the active Pd catalyst while CyPF-*t*Bu plays a major role in the catalytic reaction (Figure 2).

To support the above hypothesis, we performed cyclic voltammetry (CV) studies on both the single-ligand and mixed-ligand catalytic systems.[12] CV allows a more precise and descriptive investigation of the mechanistic features because unlike NMR spectroscopy, it can routinely be used to detect

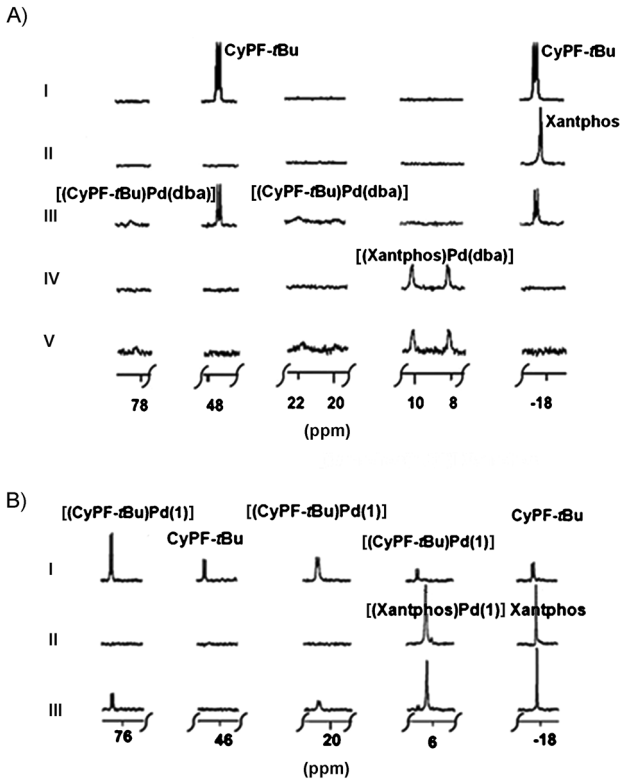


Figure 1. ^{31}P NMR study on single-ligand and mixed-ligand systems. A) ^{31}P NMR spectra of the systems containing (I) free CyPF-*t*Bu, (II) free Xantphos, (III) $[Pd_2(dba)_3]$/CyPF-*t*Bu, (IV) $[Pd_2(dba)_3]$/Xantphos, and (V) $[Pd_2(dba)_3]$/CyPF-*t*Bu/Xantphos. B) ^{31}P NMR spectra of the systems containing (I) $[Pd_2(dba)_3]$/CyPF-*t*Bu/**1**, (II) $[Pd_2(dba)_3]$/Xantphos/**1** and (III) $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu/**1**.

reactive species with short lifetimes.[13] Cyclic voltammograms of the free ligands (Figure 3A, I) revealed an irreversible one-electron redox system ($\mathbf{O_1}$) corresponding to the formation of the radical cation for Xantphos together with two irreversible waves and one reversible wave ($\mathbf{O_2}$, $\mathbf{O_3}$, and $\mathbf{O_4}$) for CyPF-*t*Bu (Figure 3A, II).[14] When CV was carried out on the $[Pd_2(dba)_3]$/Xantphos system (Figure 3A, III), a new oxidation peak, $\mathbf{O_5}$, at a lower potential than that of free Xantphos ($\mathbf{O_1}$) was observed, corresponding to the formation of the [(Xantphos)Pd(dba)] complex. The concomitant disappearance of the Xantphos oxidation peak ($\mathbf{O_1}$) implies that the formation of the [(Xantphos)Pd(dba)] complex is really fast and efficient. On the contrary, a different feature was observed in the case of the $[Pd_2(dba)_3]$/CyPF-*t*Bu system (Figure 3A, IV). The three oxidation peaks of free CyPF-*t*Bu ($\mathbf{O_2}$, $\mathbf{O_3}$, and $\mathbf{O_4}$) remained mainly unchanged except for their decreased intensity. Nevertheless, a new weak oxidation potential peak $\mathbf{O_6}$, corresponding to the [(CyPF-*t*Bu)Pd(dba)] complex appeared.[14] The weak current intensity of $\mathbf{O_6}$ in the cyclic voltammogram of the $[Pd_2(dba)_3]$/CyPF-*t*Bu system highlights that the formation of the [(CyPF-*t*Bu)Pd(dba)] complex is much slower and less efficient than that of the kinetically favored [(Xantphos)Pd(dba)] complex. In addition, the oxidation potential of the [(CyPF-*t*Bu)Pd(dba)] complex ($\mathbf{O_6}$) was lower than that of the [(Xantphos)Pd(dba)] complex ($\mathbf{O_5}$), consistent with a more electron rich complex for [(CyPF-*t*Bu)Pd(dba)]. Most importantly, all the oxidation peaks ($\mathbf{O_2}$, $\mathbf{O_3}$, $\mathbf{O_4}$, $\mathbf{O_5}$, $\mathbf{O_6}$) were presented in the mixed-ligand system of $[Pd_2(dba)_3]$/CyPF-*t*Bu/Xantphos (Figure 3A, V), and no new oxidation peak was detected (as confirmed by the deconvoluted CV). This result implies that no new catalytic species was formed in the mixed-ligand system. Moreover, the current intensity of the oxidation peak of [(CyPF-*t*Bu)Pd(dba)] was stronger in the mixed-ligand system than in the single-ligand system, thus highlighting that the formation of the [(CyPF-*t*Bu)Pd(dba)] complex was effectively promoted by Xantphos in the mixed-ligand system (confirmed by the deconvoluted CV). Altogether, these data are in perfect agreement with the ^{31}P NMR results and support our hypothesis that the presence of Xantphos favors the formation of the [(CyPF-*t*Bu)Pd(dba)] complex in the mixed-ligand system. Furthermore, the corresponding cyclic-voltammetry investigation on the oxidative addition of the substrate **1** to the two single-ligand systems of $[Pd_2(dba)_3]$/Xantphos and $[Pd_2(dba)_3]$/CyPF-*t*Bu and the mixed-ligand system $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu (Figure 3B), unveiled that all the oxidation potentials observed in the single-ligand systems were observed in the mixed-ligand system. This fur-

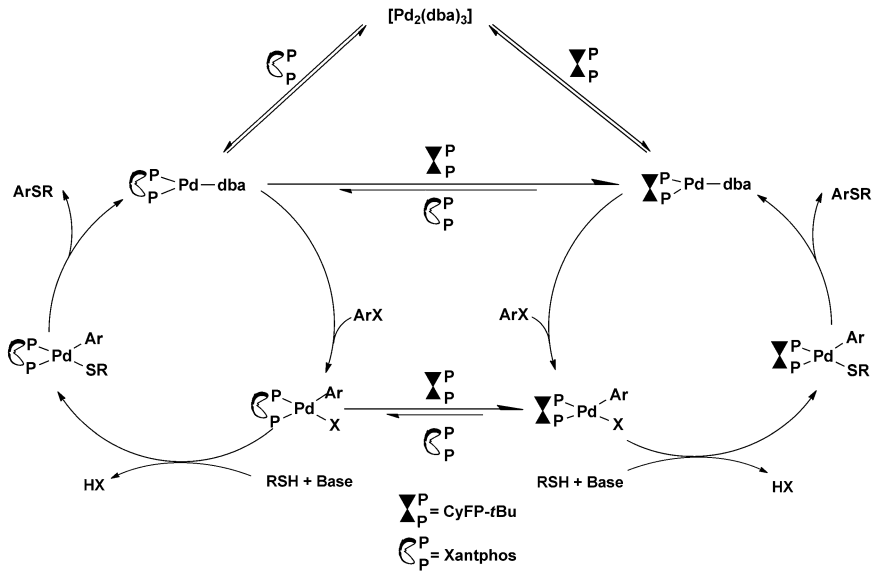


Figure 2. Proposed mechanism used by the $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu mixed-ligand catalytic system to promote C–S coupling reaction.

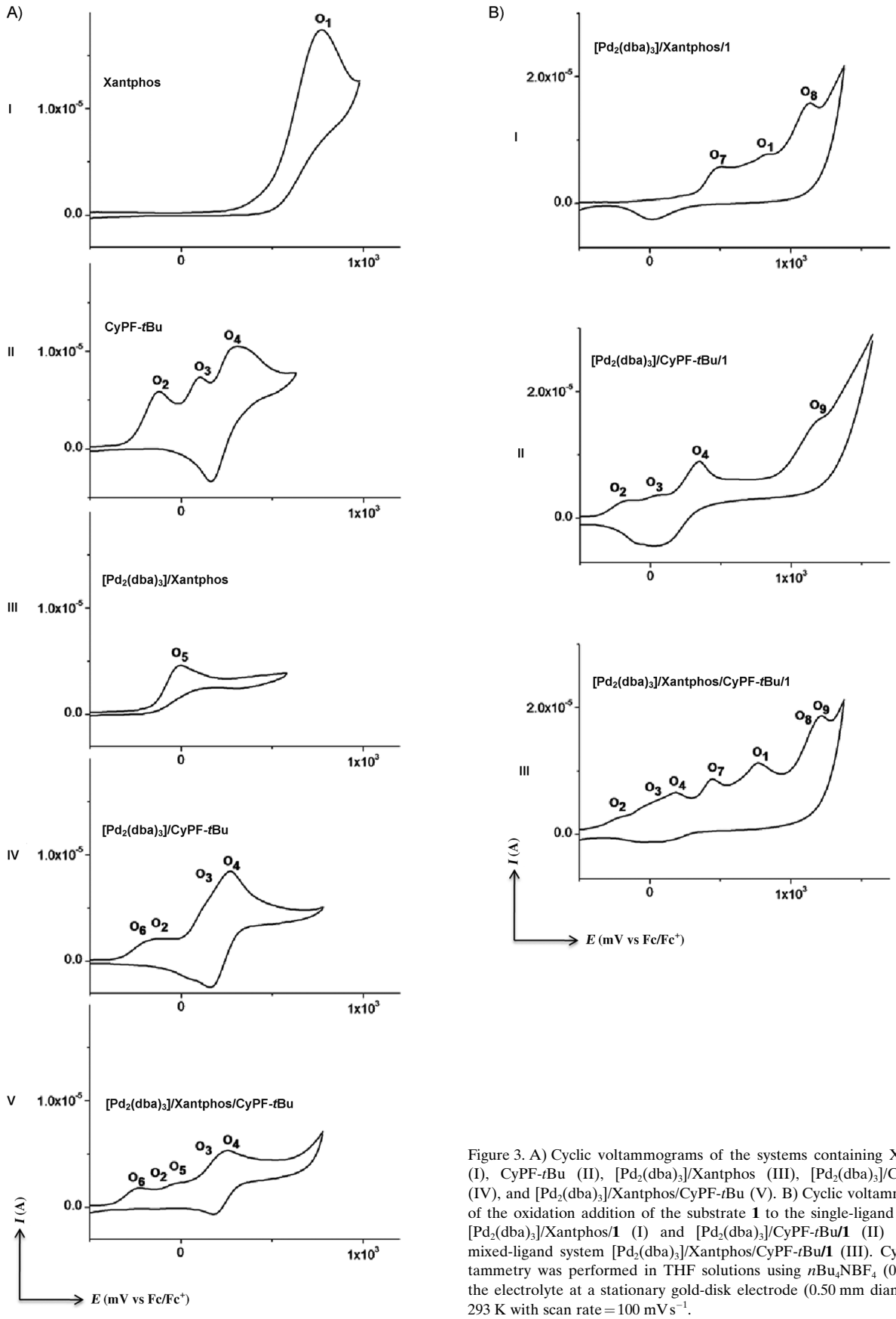


Figure 3. A) Cyclic voltammograms of the systems containing Xantphos (I), CyPF-*t*Bu (II), $[Pd_2(dba)_3]$/Xantphos (III), $[Pd_2(dba)_3]$/CyPF-*t*Bu (IV), and $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu (V). B) Cyclic voltammograms of the oxidation addition of the substrate **1** to the single-ligand systems, $[Pd_2(dba)_3]$/Xantphos/**1** (I) and $[Pd_2(dba)_3]$/CyPF-*t*Bu/**1** (II) and the mixed-ligand system $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu/**1** (III). Cyclic voltammetry was performed in THF solutions using nBu$_4$NBF$_4$ (0.30 M) as the electrolyte at a stationary gold-disk electrode (0.50 mm diameter) at 293 K with scan rate = 100 mV s^{-1}.

ther endorses the proposed mechanism relying on the coexistence and interplay of two catalytic cycles mediated by two individual ligands, between which Pd is shuttled to promote the catalysis (Figure 2). This mechanism matches that proposed for C–N coupling reaction,[4–5] thus suggesting that it may be generally applicable across many mixed-ligand catalytic systems, opening new opportunities and perspectives for challenging and otherwise difficult-to-achieve reactions.

In summary, we have developed a novel and efficient mixed-ligand catalyst $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu for synthesizing *S*-arylthiotriazole nucleoside analogues with extremely high efficiency. This catalyst boasts unparalleled broad substrate scope with high product outputs including diverse heteroaryl systems and thiols. Moreover, the catalytic system can also strongly activate C–Cl bonds in heteroaryl rings for C–S bond formation. ^{31}P NMR and cyclic-voltammetry investigations revealed a general mechanism for the thiolation as mediated by the $[Pd_2(dba)_3]$/Xantphos/CyPF-*t*Bu catalytic system in which the two mixed ligands cooperate ingeniously and advantageously. To our knowledge, this is the first example of a mixed-ligand system used for a Pd-catalyzed C–S coupling reaction. We now expect to uncover a broad spectrum of applications for mixed-ligand systems in other transition-metal-catalyzed reactions and are working actively in this direction.

Acknowledgements

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Keywords: C–S cross-coupling · cyclic voltammetry · mixed-ligand catalysts · nucleosides · triazoles

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[7] Under the same reaction conditions for S_NAr substitution of substrate **1′**, isomeric 3-bromo-5-methoxycarbonyl (**1**) did not undergo substitution with thiol and over 90% of the starting material **1** was recovered even after 3 days at 80°C in the presence of weak base (K_2CO_3 or triethylamine) in CH_3CN. We also tried numerous other reaction conditions such as those involving stronger bases (DBU, Cs_2CO_3, NaO*t*Bu) and higher temperatures (up to 130°C) as well as those using polar solvents such as DMF and high concentrations of thiols; unfortunately, in all cases, the starting material **1** decomposed after several hours and no thiolation product could be observed or identified.

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[10] We did control experiments with substrates **1** and **3**–**6** under the reaction conditions presented in the manuscript in the absence of $[Pd_2(dba)_3]$. No thiolation product could be identified even after 8 h and over 90% starting material was recovered. Therefore, there was no S_NAr reaction under these reaction conditions with substrates **5** or **6**, neither with **1**, **3**, and **4**.

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[12] All the NMR and CV experiments for investigating the catalytic mechanism were performed under reaction conditions similar to those used for the synthesis. Consequently, all samples for ^{31}P NMR measurement were subjected to reflux at 115°C for 1 h, thus following the same procedure as for the synthetic reaction, then cooled down to 25°C for ^{31}P NMR recording. Likewise, all samples for CV measurement were refluxed at 80°C for 1 h. We could not heat the samples for CV experiments to 110°C owing to the use of THF, toluene being a poor solvent for CV investigation.

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