C–C Coupling

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Decarboxylative Cross-Coupling of Mesylates Catalyzed by Copper/Palladium Systems with Customized Imidazolyl Phosphine Ligands**

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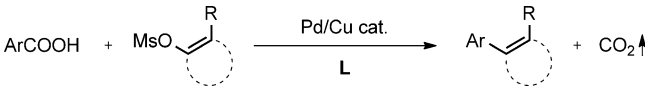
Decarboxylative cross-coupling reactions have recently emerged as a powerful methodology for the regioselective construction of C–C and C–heteroatom bonds.[1] Their key advantage over traditional cross-coupling reactions is that they draw on stable and readily available carboxylate salts as sources of carbon nucleophiles rather than expensive and sensitive organometallic reagents. In the last decade, a rapidly growing number of decarboxylative reactions have been discovered including decarboxylative Heck reactions,[2] allylations,[3] redox-neutral cross-coupling reactions,[4] oxidative coupling reactions,[5] C–H arylations,[6] homocouplings,[7] and Chan–Lam-type reactions.[8]

Redox-neutral decarboxylative cross-couplings mediated by Cu/Pd or Ag/Pd bimetallic catalyst systems proved to have a particularly broad scope with regards to both carboxylates and carbon electrophiles. In this variant, the decarboxylation step is mediated by a Cu^{I}[9] or Ag^{I}[10] catalyst, while a Pd complex catalyzes the coupling with the carbon electrophile. Whereas aryl bromides and iodides can be converted with very simple ligand systems,[11] the activation of aryl chlorides,[12] triflates,[13] and tosylates[14] requires the use of sophisticated catalyst systems containing electron-rich, bulky phosphine ligands. However, all attempts to develop decarboxylative couplings of the notoriously hard-to-activate methanesulfonates (mesylates) have failed so far (Scheme 1).

Aryl and alkenyl mesylates are particularly attractive carbon electrophiles for preparative- and industrial-scale syntheses, since they have the lowest molecular weight of all sulfonate leaving groups. They are easily accessible by esterification of broadly available phenols or enolates with inexpensive mesyl chloride or anhydride, often in substitution patterns different to those of related organohalides.[15]



Scheme 1. Decarboxylative cross-coupling of aryl and alkenyl mesylates.

However, the higher basicity of mesylates in comparison with, for example, triflates or even tosylates results in a particularly stable C–O bond[16] that can only be cleaved with a handful of extremely active cross-coupling catalysts. Among the few catalysts that are capable of activating mesylates are $[NiCl_2(PCy)_2]$[17] and palladium complexes bearing sophisticated ligands of the X-Phos, Brett-Phos, and CM-Phos types (Figure 1).[18] The groups led by Percec, Buchwald, and Kwong demonstrated that mesylates can be used as substrates in traditional cross-couplings including Suzuki–Miyaura,[19] Hiyama,[20] and Stille reactions,[21] as well as in carbonylations and C–heteroatom bond-forming reactions.[22]

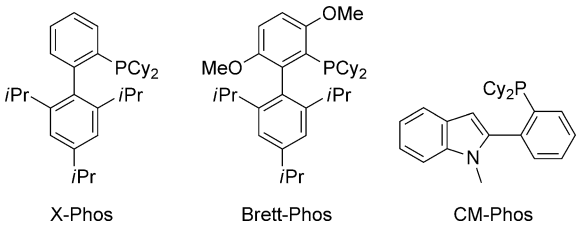


Figure 1. State-of-the-art palladium ligands for mesylate activation.

In decarboxylative couplings, the use of mesylates is a particular challenge because transmetalations are known to proceed from copper or silver only to palladium but not to nickel, precluding the use of this catalyst metal. Moreover, particularly electron-rich ligands, which might promote the oxidative addition of aryl/alkenyl mesylates onto palladium catalysts, tend to interfere with the decarboxylation catalyst.[12,13]

In search for an effective catalyst system for the desired decarboxylative arylation of mesylates, we chose the reaction of potassium *ortho*-nitrobenzoate (**1a**) with 2-naphthyl mesylate (**2a**) as a model. The desired biaryl (**3aa**) was formed only in trace amounts when a phenanthroline/copper decarboxylation catalyst was used in combination with various palladium complexes. Neither Buchwald's S-Phos nor Brett-Phos, nor Kwong's CM-Phos proved to be effective.

In the coupling reaction using the CM-Phos ligand, significant amounts of protodecarboxylation products were observed, indicating that this ligand does not inhibit the decarboxylation step. As its ability to activate aryl mesylates is well-documented, we reasoned that the transmetalation from copper to palladium must be the critical step in the overall catalytic process depicted in Scheme 2.[23]

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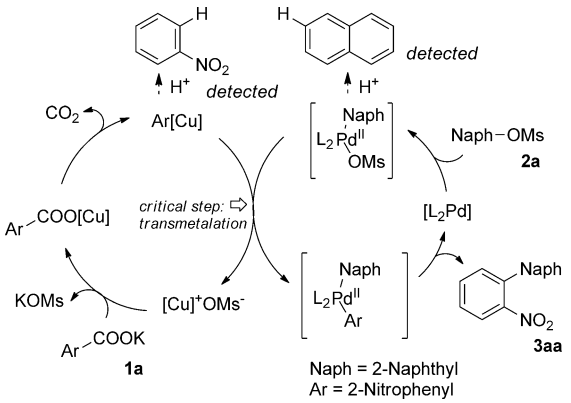
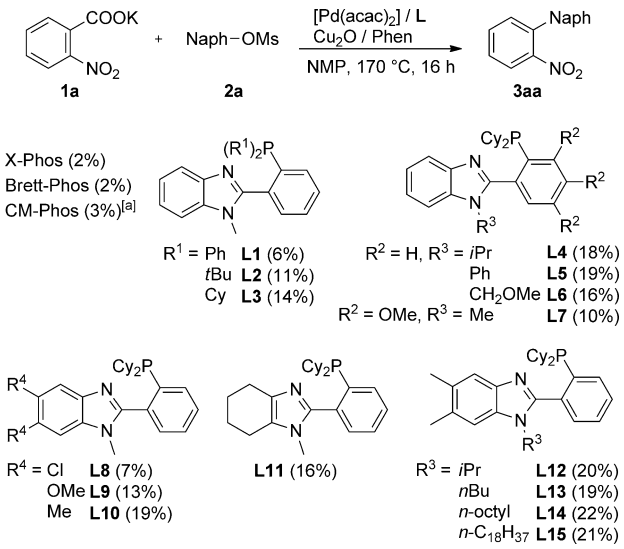


Scheme 2. Decarboxylative cross-coupling of 2-naphthyl mesylate.



Scheme 3. Study of ligand performance in the decarboxylative coupling of aryl mesylates. Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), $[Pd(acac)_2]$ (5.0 mol%), **L** (7.5 mol%), Cu_2O (2.5 mol%), 1,10-phenanthroline (5.0 mol%), NMP (2.0 mL), 170°C, 16 h. Yields determined by GC analysis using *n*-tetradecane as the internal standard. Cy = cyclohexyl, *i*Pr = isopropyl, *t*Bu = *tert*-butyl. [a] 50% yield of protodecarboxylation product was observed.

In the Stille reaction, where the transmetalation step is often limiting, it has been found that the use of tri-2-furylphosphine rather than triphenylphosphine enhances reaction rates by two orders of magnitude.[24,25] This ligand features a potentially coordinating heteroatom in close proximity to the phosphorus, which enhances π-back-donation. It has also been reported that only one phosphine should be present in transmetalations to palladium.[26]

As a lead structure for ligand design, we thus chose a benzimidazolyl skeleton rather than the indolyl system of CM-Phos. This ligand class, which was first reported by Altenbach[27] and has recently been used by Kwong in Suzuki couplings,[28] should have reduced σ-donor strength, offer a weakly coordinating group that may aid an associative transmetalation step, and provide enhanced π-back-donation. We synthesized various imidazolyl phosphines by a sequence of cyclization, alkylation, and phosphonation reactions,[29] and systematically evaluated their activities in decarboxylative cross-couplings of aryl mesylates (Scheme 3).

In the decarboxylative cross-coupling of **1a** with **2a**, the new ligands **L1**–**L15** directly proved to be effective. A clear trend was evident for the influence of the phosphorus substituents (**L1**–**L3**). The moderately bulky, electron-rich dicyclohexyl-substituted phosphine showed the highest activity (**L3**), whereas *tert*-butyl and phenyl groups were less effective. As a substituent on the imidazole nitrogen (R^3), more sterically demanding groups such as isopropyl (**L4**), phenyl (**L5**), and methoxymethyl (**L6**) had a beneficial effect. When the substitution on the phosphorus-bound aryl ring was increased using alkoxy groups in the manner of a Brett-Phos ligand (R^2 = OMe, **L7**), the yields dropped. Increasing the electron density of the benzimidazole nitrogens by methyl substituents (R^4) on the ring improved the yields (**L10**). A tetrahydrobenzimidazole fragment (**L11**), which would also have a high electron density on the nitrogens, was nearly as effective as **L10**. Further optimization of the N-substituents (R^3) on the final ligand core led to another step-up in the yields (**L12**–**L15**), with *n*-octyl being the most effective residue.

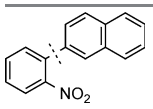
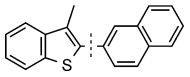
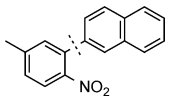
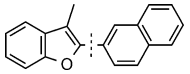
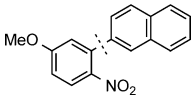
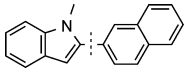
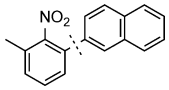
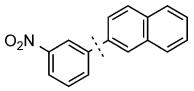
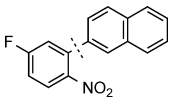
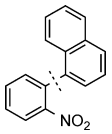
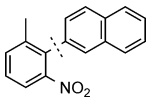
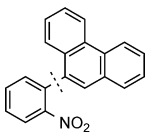
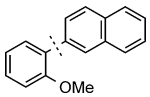
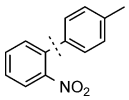
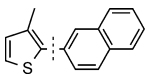
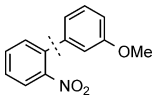
In the crystal structure of the optimal catalyst system (Figure S1 in the Supporting Information),[30] the palladium center is coordinated by both amino and phosphino groups in a distorted square–planar geometry. The Pd–N bond is longer (2.042 Å) than the Pd–C_σ bond in the Pd–CM-Phos complex (1.986 Å),[16] confirming the targeted labile chelating coordination mode.

The reaction conditions were systematically optimized using the solid ligand **L10** (Table S1 in the Supporting Information). A step-up in yields to 68% was achieved by changing the solvent to a 1:3 mixture of NMP and mesitylene and changing to $[Pd(dba)_2]$ as the Pd precursor. Further experiments confirmed that $[Pd(dba)_2]$ and Cu_2O are the most effective precatalysts. Silver decarboxylation co-catalysts can also be used but are less effective. Among the N ligands, the best results were obtained with 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4-phen). Control experiments revealed that the decarboxylative coupling reaction requires both palladium and copper to proceed. Under these optimized conditions, the use of ligand **L14**, a viscous oil, still made a positive difference. Up to 79% yield was obtained with the catalyst generated in the reaction solution and almost quantitative yields were obtained using the preformed $PdCl_2$–**L14** complex. The reaction is easy to perform also in a laboratory microwave reactor.

We next investigated the scope of the new transformation. Various aromatic carboxylate salts were successfully coupled with 2-naphthyl mesylate using a catalyst system generated in situ from $[Pd(dba)_2]$ (5 mol%), **L14** (12 mol%), Cu_2O (2.5 mol%), and 3,4,7,8-tetramethyl-1,10-phenanthroline (5 mol%) within 30 min at 180°C in a laboratory microwave reactor. As illustrated in Table 1, various *ortho*-substituted arenecarboxylate salts were converted into the corresponding biaryls in high yields (**3aa**–**3ea**). Even the highly sterically demanding substrate **1g** gave satisfactory yields. Potassium *ortho*-methoxybenzoate was converted only in low yield, while non-*ortho*-substituted benzoates did not react (**3ha**).

Table 1: Decarboxylative coupling of aryl and heteroaryl carboxylates with aryl mesylates.[a]

1a–1l 2a–2e 3aa–3ae

Product	Yield [%]	Product	Yield [%]
 **3aa**	86	 **3ja**	73
 **3ba**	88	 **3ka**	50
 **3ca**	85	 **3la**	62
 **3da**	84	 **3na**	0
 **3ea**	80[b]	 **3ab**	27
 **3ga**	50[b]	 **3ac**	26[d,e]
 **3ha**	17[c]	 **3ad**	28[d,e]
 **3ia**	45	 **3ae**	35[d,e]

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), $[Pd(dba)_2]$ (5.0 mol%), **L14** (12.0 mol%), Cu_2O (2.5 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (5.0 mol%), NMP (1.0 mL), mesitylene (3.0 mL), μW at 180°C/100 W/30 min; yields of isolated products. [b] **1**/**2** ratio = 2:1. [c] Yield determined by GC. [d] NMP/mesitylene = 1:5. [e] $[Pd(acac)_2]$ was used instead of $[Pd(dba)_2]$.

Control experiments revealed that the phosphine ligand impedes the decarboxylation of these derivatives. Heterocyclic carboxylates were smoothly transformed into biaryls in moderate to high yields (**3ia**–**3la**). Besides 2-naphthyl, other aryl mesylates could also be coupled, albeit in moderate yields (**3ab**–**3ae**).

We considered the cross-coupling of alkenyl mesylates to be of even higher interest than that of aryl mesylates as these compounds are easily accessible by esterification of enolates in substantially greater structural diversity than alkenyl halides. We were pleased to find that only minor adjustments were necessary to extend this reaction concept to this substrate class (Tables S2 and S3). Remarkably, **L8** with electron-withdrawing chloro substituents on the benzimidazolyl backbone was most effective as the ligand for palladium, and 2,2′-bipyridine for copper. With the catalyst system generated in situ from $Pd(OAc)_2$/**L8** and Cu_2O/2,2′-bipyridine, a broad array of arenecarboxylate salts were coupled with various alkenyl mesylates in high yields within only 1 h (Table 2). Among the products are several that would be hard to access otherwise, for example tetrasubstituted olefins and vinyl arenes.

The range of carboxylate salts that were successfully converted includes *ortho*-substituted benzoates and heterocyclic carboxylates. Even sterically demanding derivatives gave good results. The reaction is broadly applicable with regard to the alkenyl mesylates. Sterically hindered vinyl mesylates (**5d**–**f**) generated from highly substituted ketones reacted as well as unsubstituted vinyl mesylates. Even conjugated alkenyl mesylates were converted in moderate yields (**6ah**). No experiments have yet been performed with stereoisomerically pure alkenyl mesylates, but when *E*/*Z* mixtures were used as starting materials, it appears as if the ratio between the *E*- and *Z*-configured products increases slightly in the course of the reaction.

In summary, the use of customized imidazolyl phosphines for the first time allows the use of aryl and alkenyl mesylates in decarboxylative cross-coupling reactions. This is a decisive step in leading this relatively young reaction concept to synthetic maturity. Further optimization of the catalyst system is currently underway in our group.

Experimental Section

An oven-dried, nitrogen-flushed 10 mL microwave vessel was charged with potassium 2-nitrobenzoate (**1a**, 103 mg, 0.50 mmol), bis(dibenzylideneacetone)palladium(0) (14.4 mg, 0.025 mmol, 5.0 mol%), copper(I) oxide (1.81 mg, 0.0125 mmol, 2.5 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (5.9 mg, 0.025 mmol, 5.0 mol%), and 2-naphthyl mesylate (**2a**, 167 mg, 0.75 mmol, 1.5 equiv). A solution of **L14** in NMP (0.06 M, 1 mL, 0.06 mol, 12 mol%) and mesitylene (3 mL) was added by syringe. The mixture was then stirred for 5 min at 50°C, treated with microwave irradiation at 180°C for 30 min at a maximum power of 100 W, and then cooled with air-jet cooling. The mixture was diluted with HCl_{aq} (1N, 20 mL), extracted with ethyl acetate (3 × 20 mL), washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (SiO_2, ethyl acetate/hexane gradient) yielding **3aa** [CAS-No. 94064-83-2] as a yellow solid (214 mg, 86%).

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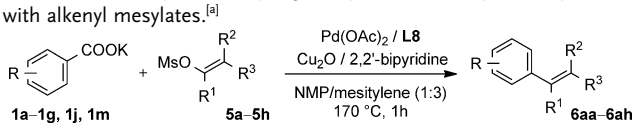
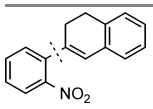
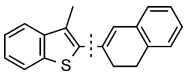
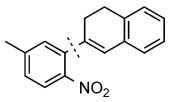
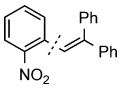
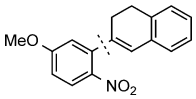
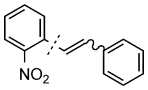
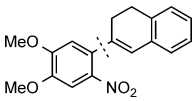
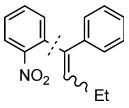
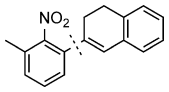
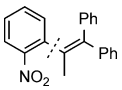
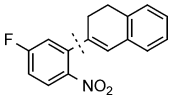
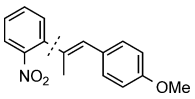
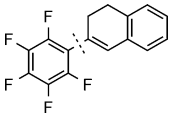
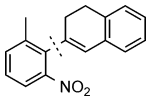
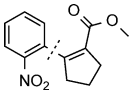
Table 2: Decarboxylative coupling of aryl and heteroaryl carboxylates with alkenyl mesylates.[a]



Product	Yield [%]	Product	Yield [%]
 **6aa**	86	 **6ja**	54
 **6ba**	82	 **6ab**	83
 **6ca**	84	 **6ac**	86[b]
 **6ma**	83	 **6ad**	40[c,d]
 **6da**	85	 **6ae**	63
 **6ea**	80	 **6af**	73
 **6fa**	22	 **6ag**	54[e]
 **6ga**	42	 **6ah**	21[f]

[a] Reaction conditions: **1** (0.5 mmol), **5** (0.75 mmol), $Pd(OAc)_2$ (5.0 mol%), **L8** (12.0 mol%), Cu_2O (2.5 mol%), 2,2′-bipyridine (5.0 mol%), NMP (1.0 mL), mesitylene (3.0 mL), 170°C, 1 h; yields of isolated products. [b] *E*/*Z* isomers = 2.8:1 (*E*/*Z* isomers of starting material = 2.3:1) [c] **1**/**5** ratio = 2:1. [d] *E*/*Z* isomers = 1:2 (*E*/*Z* isomers of starting material = 1:3.2). [e] **1**/**5** ratio = 1:3. [f] **1**/**5** ratio = 1.5:1.

Keywords: carboxylic acids · copper · decarboxylative coupling · mesylates · palladium

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