Decarboxylative Cross-Coupling

International Edition: DOI: 10.1002/anie.201505843
German Edition: DOI: 10.1002/ange.201505843

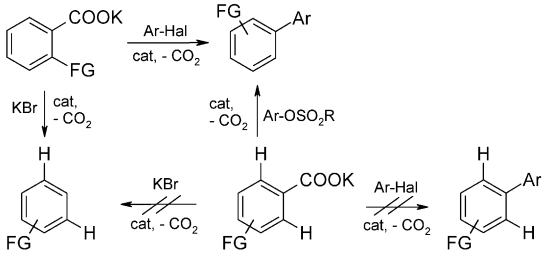
Catalytic Decarboxylative Cross-Coupling of Aryl Chlorides and Benzoates without Activating *ortho* Substituents

*Jie Tang, Agostino Biafora, and Lukas J. Goossen**

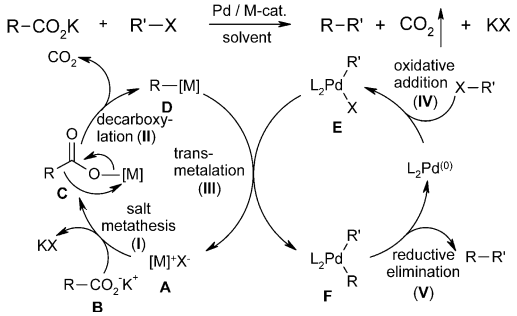
Abstract: *The restriction of decarboxylative cross-coupling reactions to ortho-substituted or heterocyclic carboxylate substrates was overcome by holistic optimization of a bimetallic Cu/Pd catalyst system. The combination of a CuI/Me_4phen decarboxylation catalyst and a [$(MeCN)_4$Pd](OTf)$_2$/XPhos cross-coupling catalyst enables the synthesis of biaryls from inexpensive aryl chlorides and potassium benzoates regardless of their substitution pattern.*

The past decade has witnessed tremendous progress in the development of decarboxylative cross-coupling reactions.[1] The key advantage of this reaction concept is that it is based on inexpensive carboxylate salts as the source of carbon nucleophiles instead of preformed organometallic reagents. Various synthetic transformations have been developed based on this strategy, including decarboxylative Heck-type vinylations,[2] redox-neutral cross-coupling reactions,[3] allylations,[1a,4] oxidative coupling reactions,[5] C–H arylations and acylations,[6] and addition reactions.[7] Whereas aromatic carboxylates are usually coupled through two-electron steps, one-electron steps predominate in the activation of aliphatic carboxylates.[8] A particularly topical development in this field is the implementation of photoredox catalysts that permit decarboxylatively coupling, for example, of aliphatic carboxylic and amino acids.[9]

The discovery of bimetallic Cu/Pd or Ag/Pd catalysts has enabled the efficient coupling of various aromatic and heteroaromatic carboxylates with aryl electrophiles.[3b,10] Initially, the reaction concept appeared to be limited to certain heterocyclic and mono- or di-*ortho*-substituted carboxylates. In protodecarboxylations, improved catalysts soon allowed the energetic barrier to decarboxylation to be surmounted, even for *meta*- and *para*-substituted benzoates.[11] Unfortunately, the addition of halide salts, as they form in cross-coupling reactions with aryl halides, completely suppresses protodecarboxylations of such non-activated benzoates (Scheme 1).[3b] Based on the mechanistic outline depicted in Scheme 2, it was initially hypothesized that the thermodynamically disfavored salt metathesis between copper or silver halides (**A**) and the potassium carboxylate



Scheme 1. Scope and limitations of known decarboxylative coupling reactions. FG = functional group.



Scheme 2. Decarboxylative cross-coupling reaction. M = Cu, Ag; R = (hetero)aryl, vinyl, acyl; R′ = (hetero)aryl; alkenyl.

(**B**) proceeds only when aided by coordinating groups in the *ortho* position. This theory appeared to be supported by the successful coupling of non-*ortho*-substituted carboxylates with carbon electrophiles with noncoordinating sulfonate leaving groups,[10d,e] for which the salt metathesis step (I) should be favorable. Unfortunately, the price and availability of these electrophiles somewhat limit the practical utility of these procedures.

Overcoming the restriction to *ortho*-substituted benzoates for aryl halide substrates remained a prime target in the development of decarboxylative arylations, because *meta*- and *para*-substituted biaryls are otherwise difficult to access from inexpensive precursors, whereas *ortho*-substituted biaryls can be synthesized in increasing diversity through *ortho*-C–H arylation.

In-depth mechanistic studies confirmed the unfavorable position of the upstream salt metathesis equilibrium (I), but surprisingly revealed that it is almost unaffected by the substitution pattern of the benzoates.[12] Instead, the presence of σ-withdrawing groups in the *ortho* position enables decarboxylative coupling reactions by reducing their rate-determining energy span by 4–8 kcal mol^{-1} overall, thus

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505843.

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making them just feasible at manageable reaction temperatures.[13] The transmetalation step (III) was found to have an energy barrier in the same high range as the salt metathesis/decarboxylation process. Improving the decarboxylation catalysts by introducing ligands that strongly stabilize intermediate **D** would facilitate its formation but reduce its reactivity in step III, once again disabling the overall process. Only a holistic optimization of all reaction steps together might enable the desired decarboxylative cross-coupling of non-activated benzoates with aryl halides using metal mediators only in catalytic amounts.

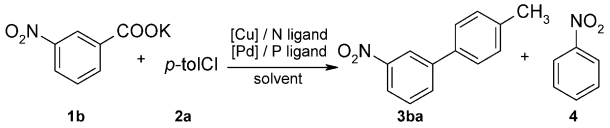
For the development of a decarboxylative arylation of benzoates without activating *ortho* substituents, we set the focus on aryl chloride substrates, the most available and inexpensive of the aryl halides. Thus, we started by investigating the protodecarboxylation of 3-nitrobenzoic acid. At 190 °C, quantitative conversion was observed in the presence of the standard Cu_2O/1,10-phenanthroline catalyst, but when 1 equiv of potassium chloride was added, the yield dropped to 14 %. The addition of other salts, for example, NaCl, nBu$_4$NCl, or CsCl, suppressed the protodecarboxylation to a comparably strong extent, whereas it was unaffected by the presence of potassium salts with weakly coordinating anions such as KOTf. This confirms that it is mostly the anion and not the cation that affects the decarboxylation step. However, after in-depth optimization, a quantitative yield was finally achieved using a 3,4,7,8-tetramethyl-1,10-phenanthroline ligand in quinoline as the solvent (see the Supporting Information). This result demonstrates that the decarboxylation barrier of non-activated carboxylates can be overcome with customized catalysts, even when excess halide salt reduces the availability of copper carboxylate intermediates.

Silver-based catalysts were ineffective under these conditions. The proverbial stability of silver chloride shifts the salt exchange equilibrium away from the silver carboxylates. Furthermore, the influence of *ortho* substituents is particularly strong for silver, which catalyzes the decarboxylation of 2,6-dimethoxybenzoates under very mild conditions but is inactive for non-*ortho*-substituted benzoates.[10a,14]

Encouraged by the protodecarboxylation results, we searched for an effective decarboxylative cross-coupling catalyst for the model reaction of potassium 3-nitrobenzoate (**1b**) with 4-chlorotoluene (**2a**). Using a combination of the optimal protodecarboxylation catalyst (Cu_2O/Me$_4$phen) with a state-of-the-art cross-coupling system (PdBr$_2$/JohnPhos), only 15 % yield of the desired product was detected (Table 1, entry 1). The yield of **3ba** was even lower with other phenanthroline derivatives (entries 2–4). Remarkably, large amounts of protodecarboxylation product **4** were formed. This indicates that the decarboxylation step proceeds efficiently and suggests that the transmetalation step has become limiting. The ratio of **3ba** to **4** improved when shifting to a more polar solvent mixture of quinoline/NMP and to CuI as the copper source (entries 5 and 8).

The key improvement in the overall yield was achieved by optimizing the palladium co-catalyst. Among the electron-rich, bulky phosphines known to activate aryl chlorides, XPhos was by far the most effective (entry 13). Another major improvement resulted from the use of palladium

Table 1: Optimization of the reaction conditions.[a]



1b 2a 3ba 4

Entry	[Cu]	N ligand	[Pd]	P ligand	Yield [%] 3ba	4
1[b]	Cu_2O	Me$_4$phen	PdBr$_2$	JohnPhos	15	70
2[b]	Cu_2O	phen	PdBr$_2$	JohnPhos	4	60
3[b]	Cu_2O	Ph$_2$phen	PdBr$_2$	JohnPhos	5	72
4[b]	Cu_2O	(MeO)$_2$phen	PdBr$_2$	JohnPhos	0	18
5	Cu_2O	Me$_4$phen	PdBr$_2$	JohnPhos	16	40
6	CuBr	Me$_4$phen	PdBr$_2$	JohnPhos	12	42
7	CuCl	Me$_4$phen	PdBr$_2$	JohnPhos	14	38
8	CuI	Me$_4$phen	PdBr$_2$	JohnPhos	19	30
9	CuI	Me$_4$phen	PdBr$_2$	tBu$_3$P·HBF$_4$	17	28
10	CuI	Me$_4$phen	PdBr$_2$	PCy$_3$	8	28
11	CuI	Me$_4$phen	PdBr$_2$	SPhos	14	34
12	CuI	Me$_4$phen	PdBr$_2$	DavePhos	17	25
13	CuI	Me$_4$phen	PdBr$_2$	XPhos	36	23
14	CuI	Me$_4$phen	PdI$_2$	XPhos	37	24
15	CuI	Me$_4$phen	Pd(OAc)$_2$	XPhos	42	40
16	CuI	Me$_4$phen	[Pd$_2$(dba)$_3$]	XPhos	7	25
17	CuI	Me$_4$phen	[Pd(allyl)$_2$Cl$_2$]	XPhos	29	32
18	CuI	Me$_4$phen	XPhos-Pd-G2	XPhos	12	27
19	CuI	Me$_4$phen	[(MeCN)$_4$Pd](OTf)$_2$	XPhos	58	50
20[c]	CuI	Me$_4$phen	[(MeCN)$_4$Pd](OTf)$_2$	XPhos	67	38

[a] Reaction conditions: **1b** (0.6 mmol, 1.2 equiv), **2a** (0.5 mmol), Cu source (10 mol %), N ligand (10 mol %), Pd source (2 mol %), P ligand (5 mol %), 3 mL of solvent (quinoline/NMP = 1:1), 190 °C, 16 h, yields determined by GC analysis using *n*-tetradecane as the internal standard based on **2a**, for abbreviations see Ref. [15]. [b] In quinoline. [c] 5 mL of solvent.

precursors with weakly coordinating counterions, that is, [(MeCN)$_4$Pd](OTf)$_2$ (entry 19). Finally, the cross-coupling catalyst was found to preserve its activity better at greater dilution (entry 20). Control experiments showed that both metals are essential for this transformation and that the yields sharply decrease at lower temperatures (38 % at 180 °C, 30 % at 170 °C, and 0 % at 150 °C; see the Supporting Information for details).

By using the optimal catalyst, a mixture of CuI, Me$_4$phen, [(MeCN)$_4$Pd](OTf)$_2$, and XPhos in 1:1 quinoline/NMP, the desired product **3ba** was obtained in close to 70 % yield after 16 h at 190 °C, along with unreacted aryl chloride and the protodecarboxylation product **4**.

Under these conditions, a wide variety of benzoic acids were coupled with the model substrate 4-chlorotoluene (**2a**) in good yields (Table 2). The yields obtained for *ortho*-substituted carboxylates are significantly higher than those previously reported, thus confirming the superiority of the new procedure. *ortho*-Methyl benzoate and *ortho*-phenyl benzoate (**3uf**, **3vf**), which have never before been converted in decarboxylative coupling reactions, gave reasonable yields. Electron-withdrawing substituents, such as nitro, cyano, fluoride, trifluoromethyl, trifluoromethoxy, sulfonyl, and sulfonamide may be present in any position of the aromatic ring. The catalyst reaches its performance limit for 3-phenoxy

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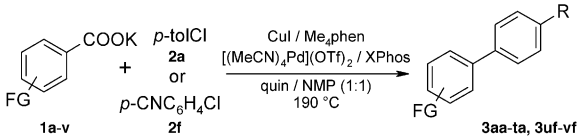
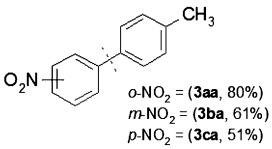
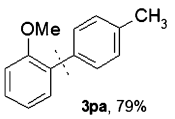
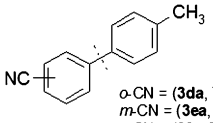
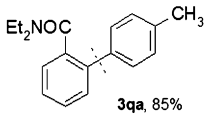
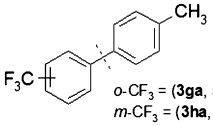
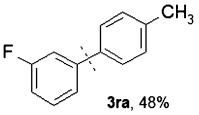
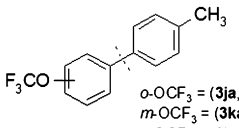
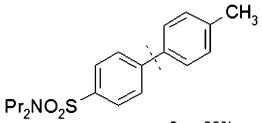
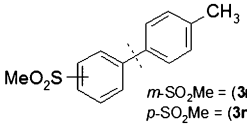
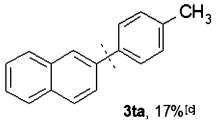
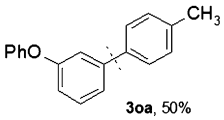
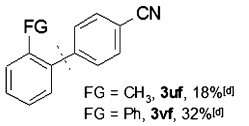
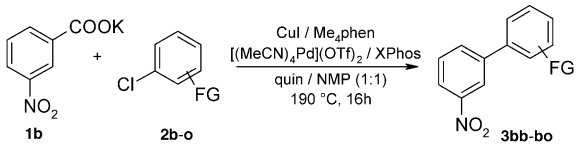
Table 2: Scope with regard to the aromatic carboxylates.[a]



Product	Product
 *o*-NO_2 = (**3aa**, 80%) *m*-NO_2 = (**3ba**, 61%) *p*-NO_2 = (**3ca**, 51%)	 **3pa**, 79%
 *o*-CN = (**3da**, 76%) *m*-CN = (**3ea**, 70%) *p*-CN = (**3fa**, 54%[b])	 **3qa**, 85%
 *o*-CF_3 = (**3ga**, 50%) *m*-CF_3 = (**3ha**, 50%) *p*-CF_3 = (**3ia**, 76%[b])	 **3ra**, 48%
 *o*-OCF_3 = (**3ja**, 80%) *m*-OCF_3 = (**3ka**, 61%) *p*-OCF_3 = (**3la**, 50%)	 **3sa**, 88%
 *m*-SO_2Me = (**3ma**, 60%) *p*-SO_2Me = (**3na**, 88%[b])	 **3ta**, 17%[c]
 **3oa**, 50%	 FG = CH_3, **3uf**, 18%[d] FG = Ph, **3vf**, 32%[d]

[a] Reaction conditions: **1a–v** (0.6–0.75 mmol), **2a** or **2f** (0.5 mmol), CuI (10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (10 mol%), $[(MeCN)_4Pd](OTf)_2$ (2 mol%), XPhos (5 mol%), 5 mL of solvent, 190°C, 16 h. Yields of isolated products. [b] 32 h. [c] GC yield. [d] 4-Chlorobenzonitrile (**2f**) used as coupling partner.

Table 3: Scope with regard to the aryl chlorides.[a]



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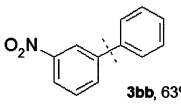
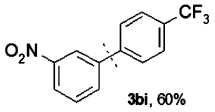
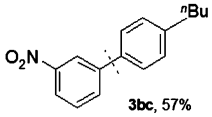
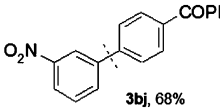
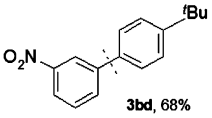
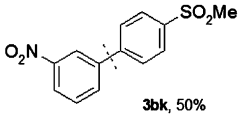
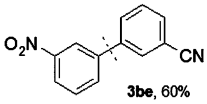
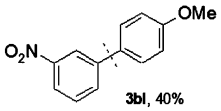
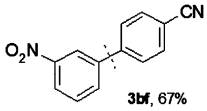
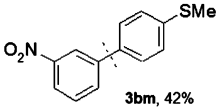
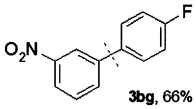
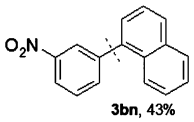
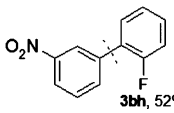
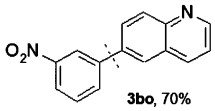
 **3bb**, 63%	 **3bi**, 60%
 **3bc**, 57%	 **3bj**, 68%
 **3bd**, 68%	 **3bk**, 50%
 **3be**, 60%	 **3bl**, 40%
 **3bf**, 67%	 **3bm**, 42%
 **3bg**, 66%	 **3bn**, 43%
 **3bh**, 52%	 **3bo**, 70%

[a] Reaction conditions: **1b** (0.6 mmol), **2b–o** (0.5 mmol), CuI (10 mol%), 3,4,7,8-tetramethyl-1,10-phenanthroline (10 mol%), $[(MeCN)_4Pd](OTf)_2$ (2 mol%), XPhos (5 mol%), 5 mL of solvent, 190°C, 16 h. Yields of isolated products.

benzoate (**3oa**). Substrates that were even more electron rich gave unsatisfactory yields. However, the formation of protodecarboxylation by-products indicates that the decarboxylation step is not limiting for any of the substrates.

The scope with regard to the electrophilic coupling partner was explored with potassium 3-nitrobenzoate (**1b**). As shown in Table 3, various aryl chlorides with common functionalities such as cyano, fluoro, trifluoromethyl, ether, sulfonyl, and ketone groups, as well as heterocyclic derivatives react smoothly. Notably, electron-rich derivatives gave lower ratios of decarboxylative coupling to protodecarboxylation than electron-poor substrates. A rationale for the observation that the oxidative addition becomes the selectivity-determining step can be derived from the energy span model, if one assumes that 1) the transmetalation proceeds via the highest-energy transition state in the reaction profile, 2) the protodecarboxylation always proceeds with the same speed, and 3) the transmetalation is unaffected by the substituent on the Pd-bound aryl group. The oxidative addition equilibrium, which should lie more on the side of the starting materials for electron-rich compared to electron-poor substrates, increases the rate-determining energy span for the former, so that the decarboxylative cross-coupling is more selective for the latter.

In conclusion, a customized bimetallic Pd^{II}/Cu^{I} catalyst system was found to enable the decarboxylative cross-coupling of non-*ortho*-substituted aromatic carboxylates with aryl chlorides. This confirms predictions by DFT studies that the previously observed limitation to certain activated carboxylates is not intrinsic. Since the decarboxylation step is no longer limiting, further studies can now be directed towards the development of a new generation of catalysts with bridging ligands designed to facilitate the transmetalation and allow catalytic turnover at strongly reduced temperatures.

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Acknowledgements

We thank the DFG (SFB/TRR-88, "3MET") and the China Scholarship Council (fellowship to J.T.) for financial support.

Keywords: aryl chlorides · benzoic acids · copper · cross-coupling · palladium

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13130–13133
Angew. Chem. **2015**, *127*, 13324–13327

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[15] dba = dibenzylideneacetone; NMP = *N*-methyl-2-pyrrolidone; phen = 1,10-phenanthroline; Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; $(MeO)_2$phen = 4,7-dimethoxyl-1,10-phenanthroline; JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl; SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; DavePhos = 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl; XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl; XPhos-Pd-G2 = chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II); Ts = 4-toluenesulfonyl; Tf = trifluoromethylsulfonyl.

Received: June 25, 2015
Published online: September 4, 2015

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