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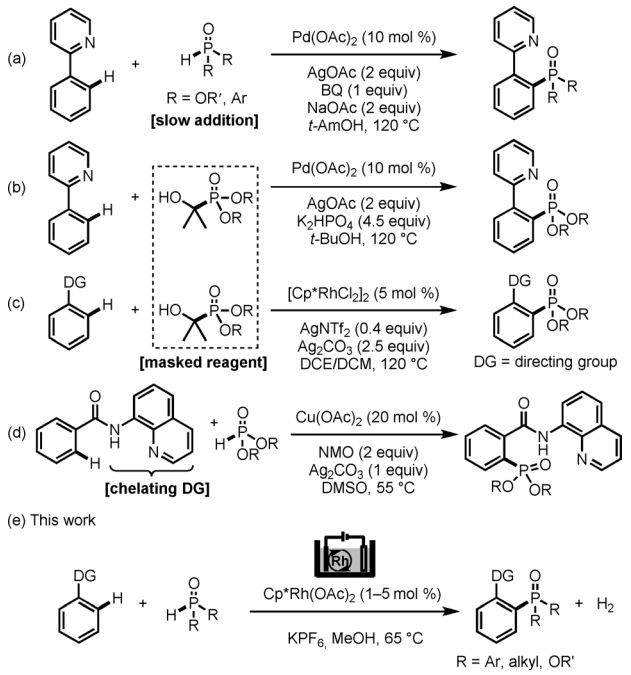
Scalable Rhodium(III)-Catalyzed Aryl C–H Phosphorylation Enabled by Anodic Oxidation Induced Reductive Elimination

Zheng-Jian Wu[+], Feng Su[+], Weidong Lin, Jinshuai Song, Ting-Bin Wen, Hui-Jun Zhang,* and Hai-Chao Xu**

Abstract: *Transition metal catalyzed C–H phosphorylation remains an unsolved challenge. Reported methods are generally limited in scope and require stoichiometric silver salts as oxidants. Reported here is an electrochemically driven Rh^{III}-catalyzed aryl C–H phosphorylation reaction that proceeds through H_2 evolution, obviating the need for stoichiometric metal oxidants. The method is compatible with a variety of aryl C–H and P–H coupling partners and particularly useful for synthesizing triarylphosphine oxides from diarylphosphine oxides, which are often difficult coupling partners for transition metal catalyzed C–H phosphorylation reactions. Experimental results suggest that the mechanism responsible for the C–P bond formation involves an oxidation-induced reductive elimination process.*

Organophosphorus compounds are widely utilized in medicinal chemistry, materials science, and catalysis.[1] Although transition metal catalyzed C–H phosphorylation is a straightforward and attractive approach for the construction of C–P bonds, it is difficult to execute in practice because of the strong propensity of phosphorus reagents to induce catalyst poisoning through coordination.[2] Deactivation can be avoided by either adding the phosphorus reagent slowly to the reaction mixture (Scheme 1 a)[3] or employing α-hydroxyalkylphosphonate as a masked, slow-releasing phosphonating reactant (Scheme 1 b,c).[4,5] In addition, the installation of a chelating directing group on benzoic acid derived substrates has been shown to enable the use of H-phosphonates directly in Cu-catalyzed reactions (Scheme 1 d).[6] Despite these significant advances,[7] the reported methods (Scheme 1 a–d) require stoichiometric amounts of silver salts as oxidants and are inefficient in converting diarylphosphine oxides into triarylphosphine oxides, which are precursors to triarylphosphine ligands.[8]



Scheme 1. Reaction design.

Organic electrochemistry is increasingly viewed as an attractive, environmentally friendly synthetic strategy as it requires no sacrificial oxidizing or reducing reagents and instead uses electricity to promote redox transformations.[9] In this context, the merger of electrochemistry with transition metal catalyzed C–H activation provides a powerful tool for the development of sustainable C–H functionalization reactions.[10] Recently, many elegant examples of electrochemically driven transition metal catalyzed C–H functionalizations have been reported,[11,12] including a Pd-catalyzed C–H phosphorylation reaction[11i] and a few Rh^{III}-catalyzed C–C cross-coupling reactions.[12] Herein, we describe an unprecedented Rh^{III}-catalyzed electrochemical phosphorylation of aryl C–H bonds that can be used to efficiently synthesize triarylphosphine oxides from diarylphosphine oxides. Experimental results suggest that the mechanism of the C–P bond formation in our method involves oxidation-induced reductive elimination rather than the Rh^{III}/Rh^{I} catalytic cycle that has previously been proposed for similar transformations with chemical oxidants.[5]

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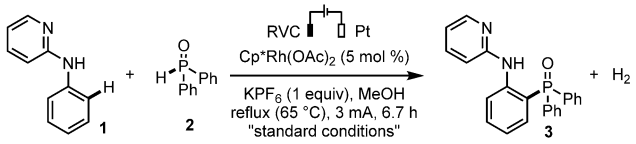
We began our studies by first optimizing electrochemical conditions for the phosphorylation of *N*-(2-pyridyl)aniline (**1**) with diphenylphosphine oxide (**2**), a reaction which has not been reported previously. The electrosynthesis was performed in an undivided cell (a three-necked round-bottomed flask) equipped with a reticulated vitreous carbon (RVC) anode and a platinum plate cathode. The optimal results were obtained at reflux (65 °C) and a constant current of 3 mA, with a reaction mixture consisting of $Cp^*Rh(OAc)_2$ (5 mol %) as the catalyst, KPF_6 (1 equiv) as the supporting salt, and MeOH as the solvent (Table 1). Under these reaction

Table 1: Optimization of reaction conditions.[a]



Entry	Deviation from standard conditions	Yield [%][b]
1	none	75 (9)
2	under argon	71 (12)
3	reaction at RT	0 (62)
4	no [Rh] catalyst	0 (< 5)
5	no electricity	0 (97)[c]
6	$[Cp^*RhCl_2]_2$ (2.5 mol %), KOAc (2 equiv)	< 5 (54)
7	$[Cp^*IrCl_2]_2$ (2.5 mol %), KOAc (2 equiv)	0 (30)
8	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5 mol %)	69
9	EtOH as the solvent	18 (54)
10	*t*AmOH/H_2O (3:1) as the solvent	43 (37)[c]
11	5 mA	68 (10)
12	10 mA	57 (12)
13	Pt plate anode (1 cm × 1 cm)	< 5 (69)
14	graphite rod anode	< 5 (20)
15	1.2 equiv of **2**	69 (5)

[a] Reaction conditions: undivided cell, **1** (0.3 mmol), **2** (0.54 mmol), MeOH (6 mL), air, 2.5 F mol^{-1} (based on **1**). [b] Yield of isolated product. Recovered unreacted **1** is shown within parentheses. [c] Yield determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

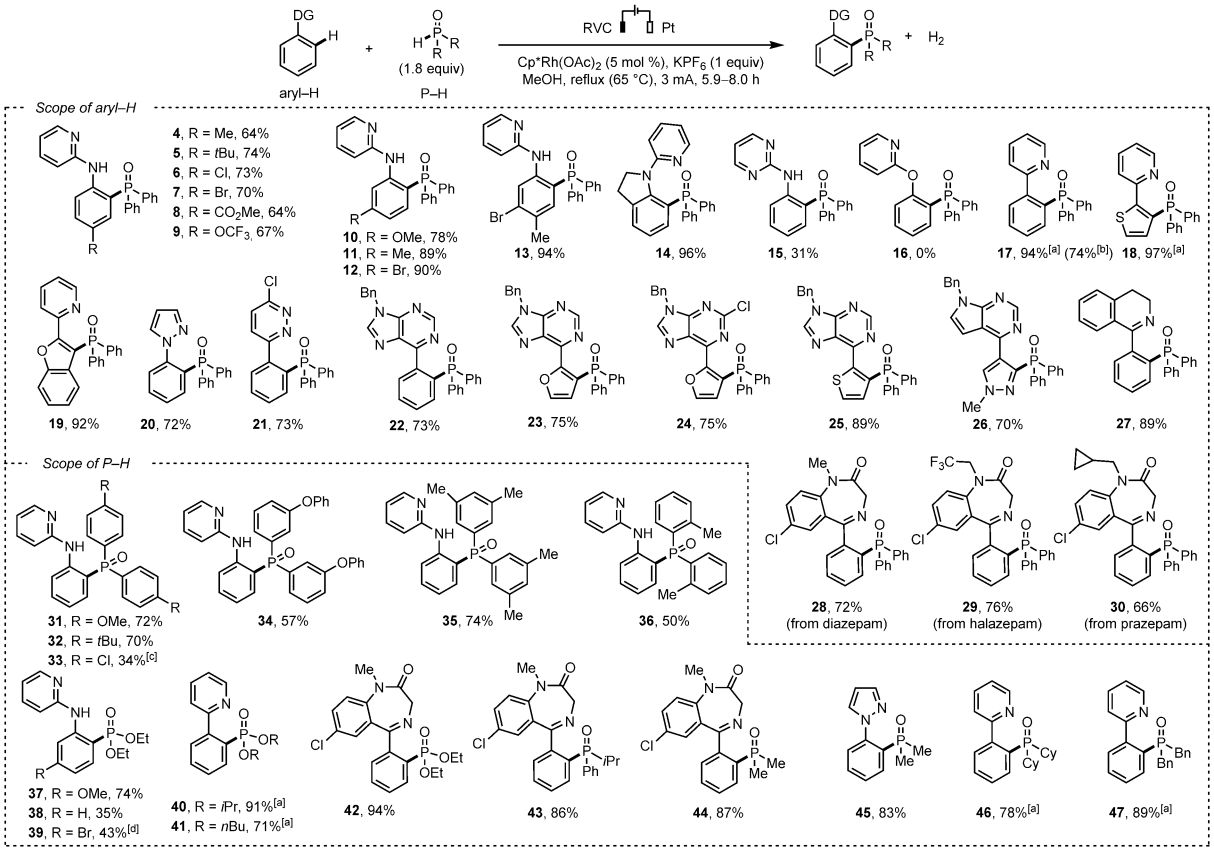
conditions, the desired phosphorylation product **3** was isolated in 75 % yield (entry 1). Similar results were obtained when the reaction was conducted under argon (entry 2). Heating (entry 3), the Rh catalyst (entry 4) and electricity (entry 5) are all indispensable for the C–H phosphorylation of **1**. Further evaluation of different catalysts revealed that $Cp^*Rh(OAc)_2$ can be replaced with $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (entry 8) but not with $[Cp^*RhCl_2]_2$ (entry 6) or $[Cp^*IrCl_2]_2$ (entry 7), suggesting that the acetate ligands were not required. Meanwhile, decreased formation of **3** was observed when the reaction was conducted in another solvent such as EtOH (entry 9) or *t*AmOH/H_2O (entry 10), at a higher current density (entries 11 and 12),[13] or with a different type of anode such as Pt plate (entry 13) or graphite rod (entry 14). Reducing the amount of **2** to 1.2 equivalents (entry 15) only led to a slight decline in the yield of **3** (69 %).

We next evaluated the coupling of **2** with various aryl substrates (Scheme 2). The results demonstrated that the phenyl ring of *N*-(2-pyridyl)aniline can be substituted at its *para*-position with a wide range of electronically diverse functional groups, including Me (**4**), *t*Bu (**5**), Cl (**6**), Br (**7**), CO_2Me (**8**), and OCF_3 (**9**). *meta*-Substitution resulted in regioselective phosphorylation at the sterically less hindered site (**10**–**13**). Other aryl systems, such as *N*-(2-pyridyl)indoline (see product **14**) and *N*-(2-pyrimidyl)aniline (**15**) were also tolerated, but *O*-(2-pyridyl)phenol bearing a weaker coordinating directing group failed to react (**16**) because **2** inhibited C–H activation. Pyridine itself was found to be an excellent directing group for the C–H phosphorylation of benzene ring (**17**), thiophene (**18**) and benzofuran (**19**). In fact, 2-phenylpyridine could react at room temperature to afford **17** in 74 % yield. In addition to pyridine, many other heterocyclic moieties commonly present in bioactive compounds, such as pyrazole (**20**), pyridazine (**21**), purines (**22**–**25**), and pyrrolopyrimidine (**26**), were also effective DGs. Notably, a cyclic ketimine was also effective in directing *ortho* C–H phosphorylation (**27**), and it enabled convenience functionalization of benzodiazepine drugs such as diazepam (**28**), halazepam (**29**), and prazepam (**30**).

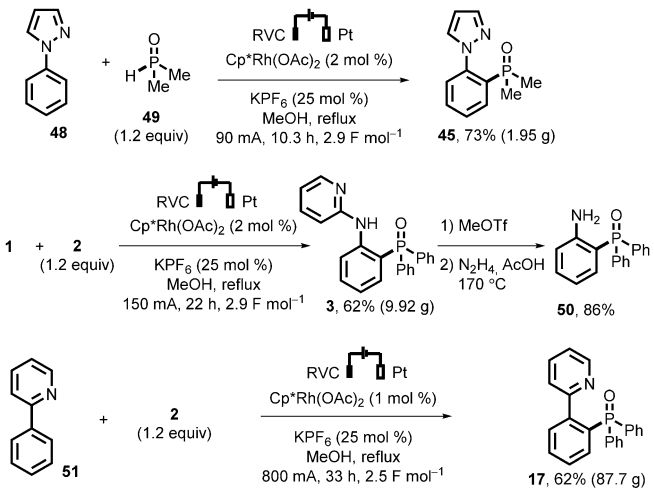
The scope with respect to the phosphorus coupling partner was next examined (Scheme 2). With **1** as the C–H donor, the reaction tolerated a diverse array of diphenylphosphine oxides bearing two functionalized aryl groups, each with an OMe (**31**), *t*Bu (**32**), or Cl (**33**) at the *para*-position, an OPh (**34**) at the *meta*-position, or with Me groups at the *meta*- or *ortho*-positions (**35**, **36**). The NH-linked pyridine was a less efficient DG for the synthesis of arylphosphonates employing *H*-phosphonates as the phosphorus reagent. While the *N*-(2-pyridyl)aniline substrate bearing an electron-donating OMe afforded the corresponding product **37** in 74 % yield, the reaction of an *N*-(2-pyridyl)aniline derivative carrying an unsubstituted (**38**) or Br-substituted (**39**) phenyl group at the same position proceeded with substantially lower efficiency. In contrast, aryl substrates bearing a more effective DG could be efficiently phosphorylated by *H*-phosphonates (**40**–**42**), isopropyl(phenyl)phosphine oxide (**43**), and even the challenging dialkylphosphine oxides (**44**–**47**).

The electrochemical C–H phosphorylation reaction could be easily scaled up to gram and decagram scales as demonstrated with the synthesis of **45**, **50**, and **17** (Scheme 3). The amounts of Rh catalyst, phosphorus reagents, and KPF_6 were decreased to reduce cost and facilitate product isolation. The pyridyl group in **3** could be removed by methylating the pyridyl nitrogen with MeOTf, followed by nucleophilic replacement with hydrazine, to furnish the corresponding free aniline **50**.

Our mechanistic studies indicated that **1** underwent rapid H–D exchange in CD_3OD in the presence of the Rh^{III}-catalyst, even at room temperature, without the need for electric current (Scheme 4 a). Furthermore, the reaction of **1** with **2** in CD_3OD resulted in the formation of deuterated **1** and **3**, both of which were deuterated at the *ortho*-position. These findings suggested that activation of the *ortho* C–H bond in the aryl substrate was reversible under the reaction conditions that we employed. Competition experiments (**52** vs. **53**) found the phosphorylative coupling reaction to favor electron-rich aryl substrate over electron-poor ones, and **2**



Scheme 2. Scope of the electrochemical aryl C–H phosphorylation. Reaction conditions: same as those used in Table 1, entry 1. Yields of isolated products are reported. [a] Reaction with 10 mA. [b] Reaction at RT. [c] Reaction for 10 h (3.7 F mol^{-1}). [d] [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5 mol %) as catalyst.

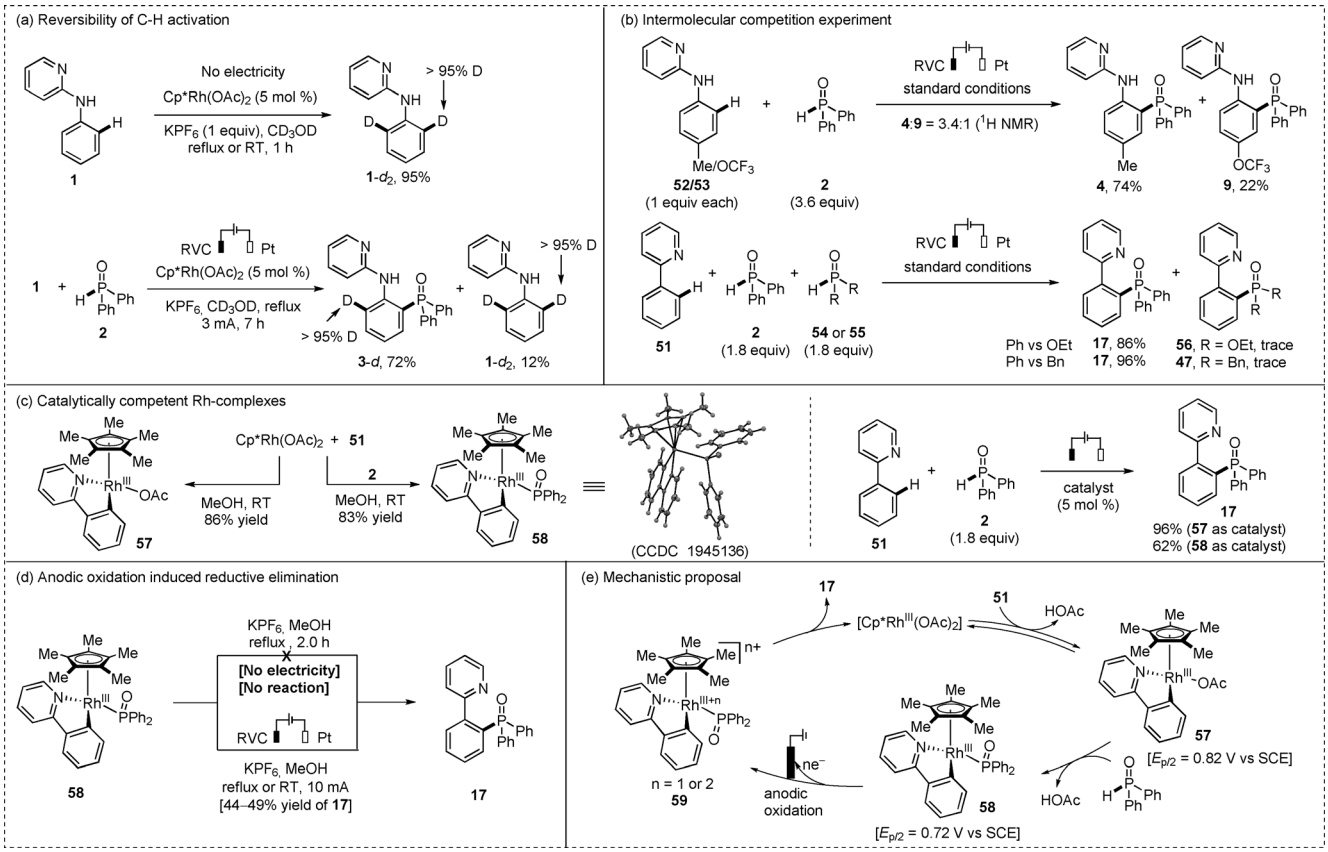


Scheme 3. Reaction scale up.

over diethylphosphite (**54**) and dibenzylphosphine oxide (**55**; Scheme 4b). To probe the mechanism for C–P bond formation, we prepared, under stoichiometric conditions, the organometallic complexes **57** and **58**, which were effective catalysts for the coupling reaction of **51** with **2** (Scheme 4c). Though stable in refluxing methanol, **58** reacted to afford the phosphine oxide **17** when electrolyzed, even at room temperature (Scheme 4d). These results provided compelling evidence that the C–P bond was formed through oxidation-induced reductive elimination.[14]

A possible mechanism for the electrochemical C–H phosphorylation reaction is shown in Scheme 4e using the synthesis of **17** as an example. The *ortho* C–H bond of 2-phenylpyridine undergoes facile and reversible cyclorhodation to afford the rhodacycle **57**. Ligand exchange between **57** and **2** affords the more oxidizable organometallic complex **58**,[15] which then undergoes oxidation-induced reductive elimination to generate the C–H phosphorylation product **17** and either a Rh^{III} or Rh^{II} complex depending on the oxidation state of **59**. It is currently unclear how many electrons **58** loses prior to the reductive elimination. At the cathode, protons are reduced to generate H_2, obviating the need for external electron or proton acceptors.

In summary, we have developed an electricity-powered, Rh^{III}-catalyzed aryl C–H phosphorylation reaction. The electrochemical reactions are flexibly scalable and proceed through H_2 evolution. The method is compatible with a diverse range of arenes and phosphorous reagents, and allows facile access to various triarylphosphine oxide derivatives. Anodic oxidation effectively promotes reductive elimination of a Rh-complex to form the C–P bond. Such a mechanistic paradigm should be useful in developing new Rh-catalyzed oxidative transformations.



Scheme 4. Mechanistic studies and proposal.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H activation · electrochemistry · oxidation · phosphorylation · rhodium

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[15] See the Supporting Information for cyclic voltammetry studies.

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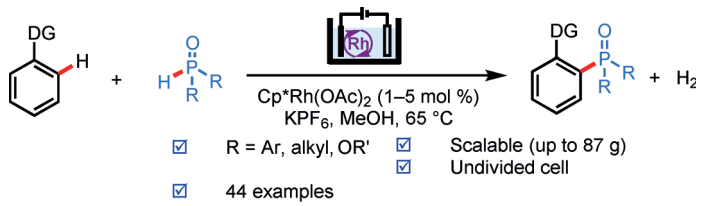
Communications

Electrochemistry

Z.-J. Wu, F. Su, W. Lin, J. Song, T.-B. Wen,* H.-J. Zhang,* H.-C. Xu* ——— ■■■■–■■■■

Scalable Rhodium(III)-Catalyzed Aryl C–H Phosphorylation Enabled by Anodic Oxidation Induced Reductive Elimination



Electric cell: Reported herein is an electrochemically driven Rh^{III}-catalyzed aryl C–H phosphorylation reaction which proceeds through H_2 evolution. The method is compatible with a variety of aryl C–H and P–H coupling partners and particularly useful for synthesizing triarylphosphine oxides from diarylphosphine oxides. Experimental results suggest that the mechanism responsible for the C–P bond formation involves an oxidation-induced reductive elimination process. DG = directing group.

