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2,2′-Biaryldicarboxylate Synthesis via Electrocatalytic Dehydrogenative C−H/C−H Coupling of Benzoic Acids

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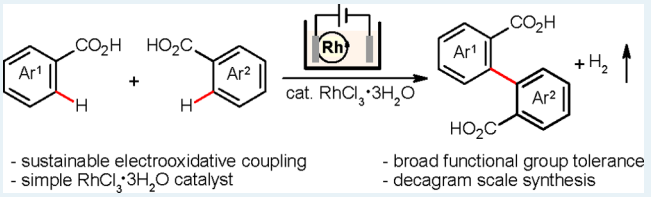
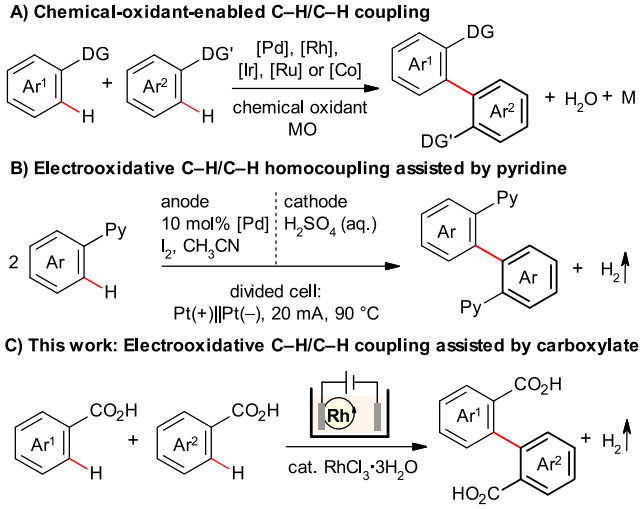
ABSTRACT: 2,2′-Biaryldicarboxylates are important functionalities in bioactive compounds, functional materials, and chiral catalysts. These compounds have been found to be conveniently accessible from benzoic acids via Rh-catalyzed electrooxidative C−H/C−H couplings, giving valuable dihydrogen as the byproduct. In an undivided cell with Pt electrodes, $RhCl_3 \cdot 3H_2O$ catalyzes the oxidative carboxylate-directed *ortho*-homocoupling of various aromatic acids with a current efficiency of 67%. The protocol is operationally simple, tolerates a wide variety of functional groups, and does not require the exclusion of air and moisture. Heterodimerizations via cross-dehydrogenative couplings of naphthyl-1-carboxylic acids with acrylic or benzoic acids were also shown to work.



KEYWORDS: *electrooxidation, rhodium catalysis, C−H/C−H coupling, carboxylic acids, biaryl synthesis*

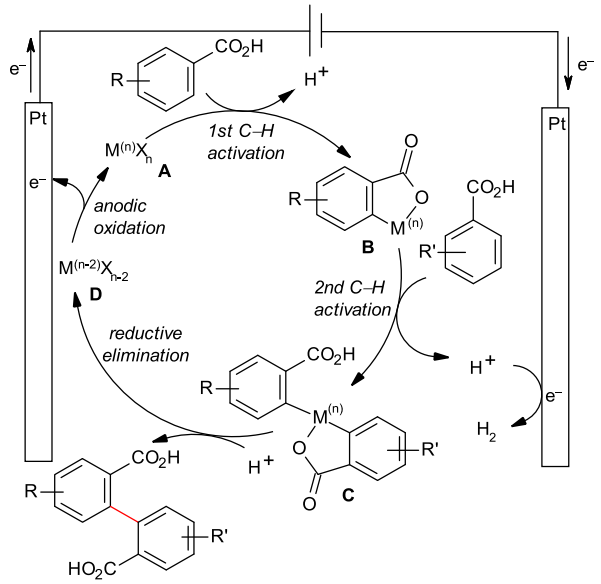
Cross-dehydrogenative couplings involving the activation of two aromatic C−H bonds with release of dihydrogen

Scheme 1. Biaryl Syntheses by C−H/C−H Coupling



are arguably the most desirable synthetic entries to biaryl moieties because no prefunctionalization of aromatic feedstocks is required.[1] However, the high atom and step economy of the coupling step is often offset by a stoichiometric use of metal oxidants, usually Ag, Cu, or Mn salts in combination with elaborate transition metal catalysts. Thus, stoichiometric metal hydroxide waste is released rather than valuable hydrogen. Moreover, regioselective couplings based on

Scheme 2. Mechanistic Blueprint for the Target Reaction



electronic or steric factors alone are possible for only few (hetero)aromatic substrates.[2] Alternatively, strongly coordinat-

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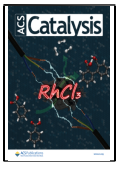

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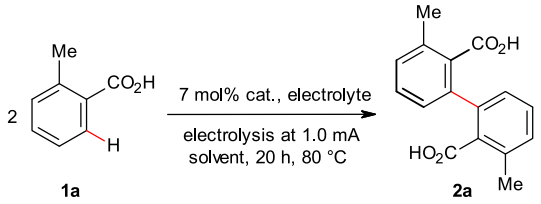
Table 1. Optimization of the C−H/C−H Homocoupling[a]



no.	catalyst	solvent	electrode	conv. (%)	**2a** (%)
1	$[Cp^*IrCl_2]_2$	DMF	Pt(+)‖Pt(−)	46	<5
2	$Pd(OAc)_2$	DMF	Pt(+)‖Pt(−)	35	<5
3	$[RuCl_2(p\text{-cym})]_2$	DMF	Pt(+)‖Pt(−)	60	39
4	$[Rh(cod)Cl]_2$	DMF	Pt(+)‖Pt(−)	>95	81
5	$Rh_2(OAc)_4$	DMF	Pt(+)‖Pt(−)	83	71
6	$Rh(OAc)_3$	DMF	Pt(+)‖Pt(−)	75	69
7	$[Cp^*RhCl_2]_2$	DMF	Pt(+)‖Pt(−)	>95	71
8	**$RhCl_3{\cdot}3H_2O$**	**DMF**	**Pt(+)‖Pt(−)**	**>95**	87 (77)
9	$RhCl_3{\cdot}3H_2O$	DMF	Ni(+)‖Pt(−)	70	6
10	$RhCl_3{\cdot}3H_2O$	DMF	graphite(+)‖Pt(−)	>95	26
11	$RhCl_3{\cdot}3H_2O$	DMF	RVC(+)‖Pt(−)	49	38
12	$RhCl_3{\cdot}3H_2O$	DMF	Pt(+)‖steel(−)	>95	78
13	$RhCl_3{\cdot}3H_2O$	DMAc	Pt(+)‖Pt(−)	77	72
14	$RhCl_3{\cdot}3H_2O$	DMSO	Pt(+)‖Pt(−)	33	18
15	$RhCl_3{\cdot}3H_2O$	^{n}BuOH	Pt(+)‖Pt(−)	42	24
	further variation from optimal condition (entry 8)				
16	3 mol % $RhCl_3{\cdot}3H_2O$			91	74
17	$^n Bu_4NPF_6$ instead of $^n Bu_4NOAc$			9	trace
18	KOAc instead of $^n Bu_4NOAc$			>95	86
19	electrolysis at 3.0 mA			>95	78
20	electrolysis at 0.5 mA			>95	86
21	run at 60 °C			89	66
22	no electricity			18	<5
23	no $RhCl_3{\cdot}3H_2O$			<5	trace
24	O_2 (balloon) instead of electricity			36	15
25	$NaClO_2$ (2 equiv) instead of electricity			42	19
26	Ag_2CO_3 (2 equiv) instead of electricity			>95	65
27	MnO_2 (2 equiv) instead of electricity			>95	60
28	CuO (2 equiv) instead of electricity			53	39

[a]Conditions: 0.50 mmol **1a**, 7 mol % catalyst, 0.5 mmol electrolyte, 8.0 mL solvent, undivided cell with 1 cm × 2 cm electrodes, constant current of 1.0 mA (ca. 1.5 F·mol^{-1}), 80 °C, 20 h. Conversions and yields were determined by GC after esterification with methyl iodide using *n*-tetradecane as an internal standard. Isolated yield of the free acid **2a** in parentheses. Cp*, 1,2,3,4,5-pentamethylcyclopenta-1,3-diene; DMF, *N*,*N*-dimethylformamide; DMAc, dimethylacetamide; DMSO, dimethyl sulfoxide; RVC, reticulated vitreous carbon.

ing mono- or bidentate functional groups are often required to direct transition-metal mediated C−H/C−H coupling into specific positions, usually *ortho* to the directing groups (Scheme 1A).[3]

The use of an electric current as an inexpensive and waste-free oxidant has opened up a window of opportunities for the development of sustainable C−H functionalization reactions.[4] On the basis of pioneering work by Amatore and Jutand, Mei, and others,[5] Kakiuchi et al. showcased the feasibility of electrooxidative biaryl synthesis with a palladium-catalyzed homocoupling of arylpyridines. However, this innovative reaction could be conducted only within a divided cell setup in the presence of stoichiometric iodine (Scheme 1B).[5f] The necessity of using strongly coordinating pyridyl directing groups, which are hard to install and remove, further limits its practical utility.

Carboxylate groups represent some of the most desirable directing groups for C−H functionalization, since carboxylic acids are widely accessible in great structural variety. After acting as directing groups, they can be removed tracelessly by protodecarboxylation or serve as leaving groups in decarboxylative cross-couplings.[6] However, in comparison to pyridyl groups, they coordinate only weakly, which makes the development of catalytic reactions based on directed C−H metalations more difficult. Their use in electrochemical reactions is further complicated by their electrostatic attraction to the anode and tendency to undergo electrodecarboxylative couplings of the Kolbe or Hofer-Moest type.[7] Nevertheless, several *ortho*-C−H functionalizations of carboxylates have been transferred successfully from metallic oxidants to electrooxidative protocols, for example, oxidative annulations[8] and Heck-type reactions.[9] In this context, Ackermann et al. showed that benzoic acids undergo electrochemical alkenylations in the presence of alkyl acrylates.[9]

Our plan was to develop a biaryl synthesis based on a carboxylate-directed electrocatalytic dehydrogenative coupling (Scheme 1C). This reaction is of considerable preparative utility, since 2,2′-biaryldicarboxylates are valuable synthetic

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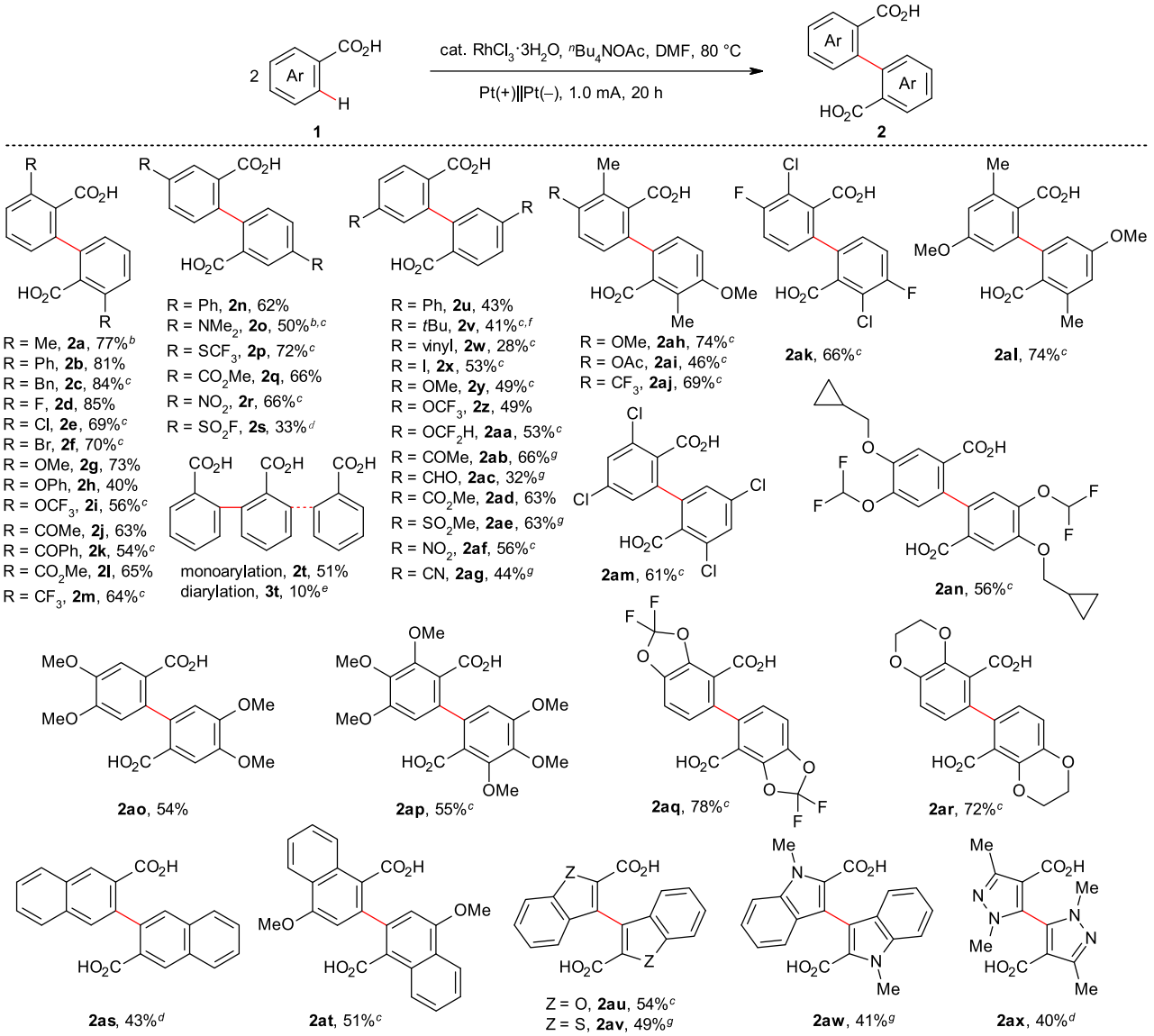
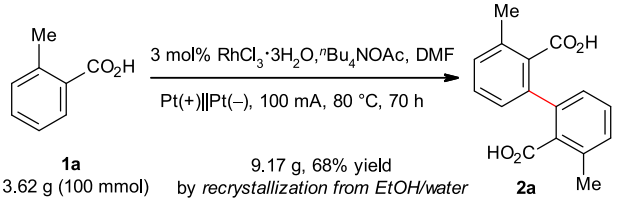
Table 2. Scope of the C−H/C−H Homocoupling[a]



[a]Conditions: 0.50 mmol **1**, 7 mol % $RhCl_3·3H_2O$, 0.5 mmol $^nBu_4NOAc$, 8.0 mL DMF, undivided cell with two Pt electrodes (each 1 × 2 cm^2), constant current of 1.0 mA (ca. 1.5 $F·mol^{-1}$), 80 °C, 20 h under air; isolated yields of methyl esters **2′** after esterification with methyl iodide. [b]Isolated as free acid. [c]10 mol % $RhCl_3·3H_2O$. [d]15 mol % $RhCl_3·3H_2O$. [e]GC yield with *n*-tetradecane as an internal standard. [f]<5% of double arylation. [g]10 mol % $RhCl_3·3H_2O$ at 90 °C.

Scheme 3. Scale-up Reaction



hubs en route to bioactive compounds and natural products,[10] functional materials,[11] as well as C_2-symmetric chiral ligands/catalysts.[12] Our mechanistic blueprint for such a reaction is shown in Scheme 2.

In the first step, one of the carboxylates directs an electrophilic metal catalyst **A** toward its *ortho*-C−H bond, which breaks with formation of metallacycle **B**. This step is documented, for example, for Pd, Ir, and Rh complexes.[13] A follow-up C−H activation of a second carboxylate leading to a diaryl species such as **C** is not unprecedented[3k−n] but still a major challenge, since the first metal−carbon bond reduces its electrophilic reactivity. One possible pathway consists of protonolysis of the M−O bond in the metallacycle by a second carboxylate, followed by its chelation-controlled C−H activation. Alternatively, dinuclear pathways in which carboxylate-bridged complexes exchange bridging carboxylate ligands with formation of **C** also seemed possible.[14] Reductive elimination would liberate the biaryl product from **C**. Reoxidation of the catalyst **D** to **A** would take place at the anode, while at the cathode, the hydrogen byproduct is generated.

In our search for an effective catalyst system for the outlined electrooxidative coupling, we chose the homocoupling of 2-toluic acid (**1a**) as a model reaction (Table 1). Various catalyst

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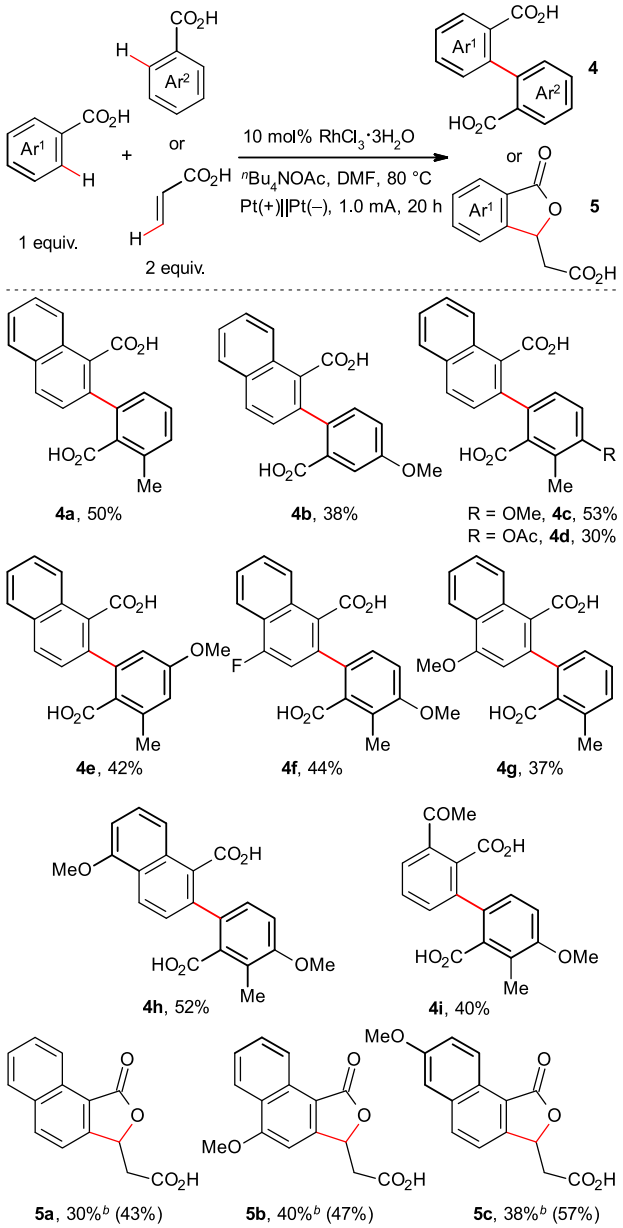
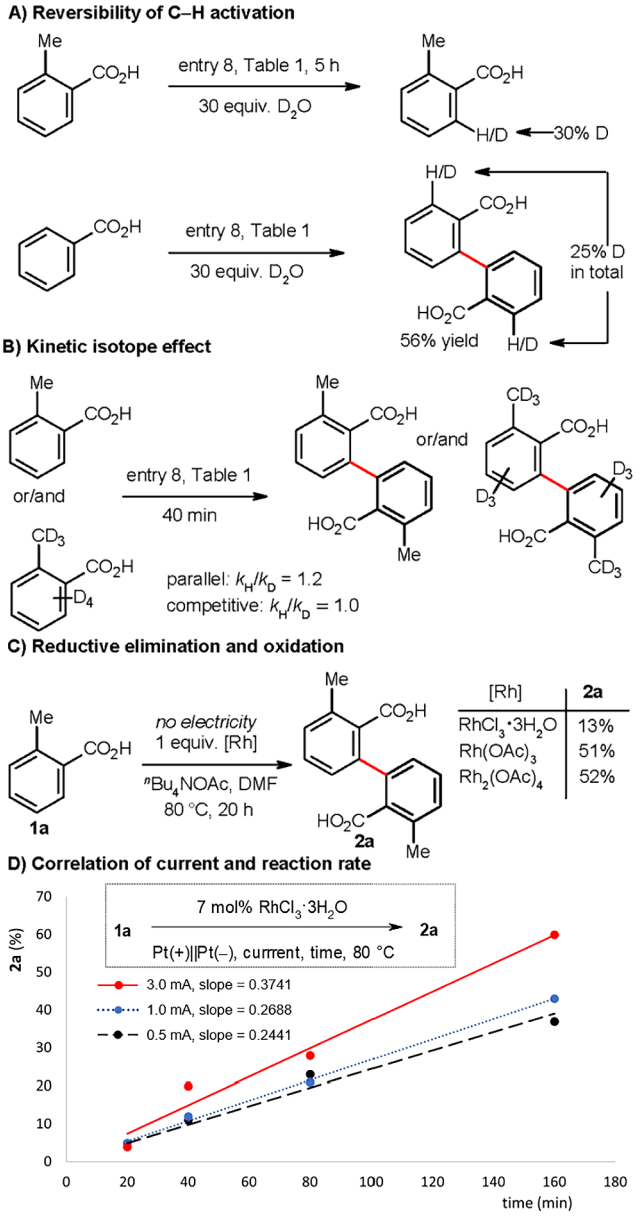
Table 3. Scope of the Cross-Dehydrogenative Coupling[a]



[a]Conditions: see Table 2 with 2.0 equiv of $^{n}Bu_4NOAc$; isolated yields of the corresponding methyl esters **4′** or **5′** after esterification with methyl iodide. [b]1.0 equiv of $^{n}Bu_4NOAc$; yields in parentheses obtained with 5 mol % $[Cp^*RhCl_2]_2$.

Scheme 4. Mechanistic Investigations



metals were investigated in an undivided cell equipped with Pt electrodes. With Ir, Ru, and Pd complexes, unsatisfactory yields were obtained (entries 1–3), while Rh complexes gave promising results (entries 4–8). We were pleased to find that simple $RhCl_3·3H_2O$ was effective even at a loading of 3 mol % (entry 16). This is remarkable, as its use in electrochemical couplings has not yet been reported.[15] Several anode materials, for example, nickel, graphite, and reticulated vitreous carbon (RVC), were investigated, and the best results were obtained with Pt (entries 9–11). As the cathode, Pt and stainless steel worked similarly well (entries 8, 12), while other materials were less effective. Amides, in particular DMF, were found to be the optimal solvents, whereas other common solvents such as DMSO, ^{n}BuOH, HFIP, water, or acetonitrile gave only unsatisfactory yields (entries 13–15 and Table S1).

The presence of acetate in the electrolyte is essential (entries 17, 18). This is in line with findings by Ackermann et al., who propose a base-assisted electrophilic process for carboxylate-directed C–H rhodation.[9a] The reaction proceeds best at a temperature of 80 °C and current densities between 0.5 and 3.0 mA (entries 19–21). Exclusion of air and moisture is not required. Control experiments confirmed that a Rh catalyst is necessary and that oxygen and overstoichiometric oxidants are less effective than electrochemical oxidation. The electro-oxidative process has an excellent current efficiency of 67%, which underlines the sustainability of the overall process.

We next investigated the scope of the optimized protocol. As can be seen from the examples in Table 2, it is widely applicable to both electron-rich and electron-deficient benzoic acids, bearing substituents in the *ortho*, *meta*, or *para* position. The products were isolated after conversion into their esters to simplify chromatographic purification. The functional group

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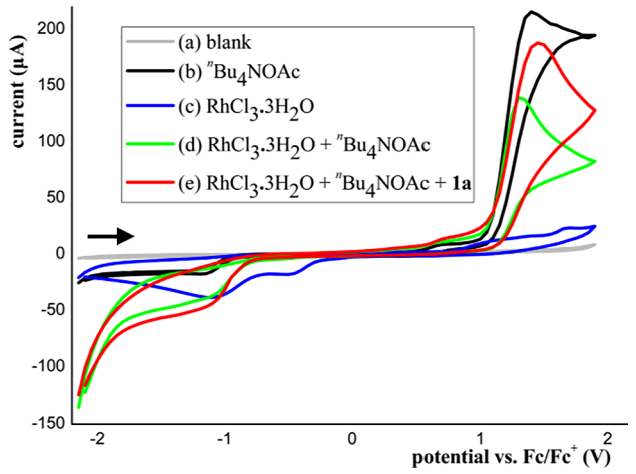

Figure 1. Cyclic voltammograms using glassy carbon electrode, scan rate: 100 mV/s, 10 mM **1a**, 0.1 M $^{n}Bu_4NPF_6$, 0.1 M $^{n}Bu_4NOAc$, 5 mM $RhCl_3{\cdot}3H_2O$.

tolerance of the process is remarkable. It includes ether (**2g**, **2h**, **2y**), ester (**2l**, **2q**, **2ad**, **2ai**), keto (**2j**, **2k**, **2ab**), cyano (**2ag**), sulfonyl (**2ae**), amino (**2o**), fluoroalkyl (**2m**), fluoroalkoxy (**2i**, **2z**, **2aa**), and fluoroalkylthio groups (**2p**). Oxidation-sensitive formyl groups (**2ac**) and easily reduced nitro groups (**2r**, **2af**) are tolerated. Compounds bearing chloro (**2e**), bromo (**2f**), iodo (**2x**), and even SO_2F (**2s**) groups were selectively coupled, demonstrating the orthogonality of this process to traditional cross-couplings.

Competing double arylation was observed in significant amounts only for unsubstituted benzoic acid (product **3t**). Any substituent seems to effectively suppress unwanted double arylation (**2n**−**2ag**). 3-Substituted benzoic acids as well as 2-naphthoic acid underwent selective coupling in the less-hindered position. Multisubstituted and fused benzoic acids were also successfully coupled (**2ah**−**2at**), as were several heterocyclic acids (**2au**−**2ax**). In some cases, for example, **2h**, **2r**, and **2ag**, less than 5% yields of final *ortho*-C−H methoxylated products were observed, which probably result from the *ortho*-C−H hydroxylation[16] of benzoic acids with air and subsequent etherification by reaction with methyl iodide.

The electrooxidative coupling was successfully performed on multigram scale with 3% catalyst loading (Scheme 3). The diacid **2a** was obtained in high purity after recrystallization, which underlines the scalability of the reaction.

We went on to investigate whether selective electrocatalytic dehydrogenative cross-coupling could be achieved for mixtures of two different aromatic carboxylates (Table 3). Since 1-naphthoic acids had reacted rather slowly in homodimerizations, we investigated their cross-coupling with more reactive acids. Indeed, moderate yields and reasonable selectivities were achieved in cross-dimerizations with benzoic acids (**4a**−**4h**). Attempts to achieve selectivity in the coupling of electron-rich with electron-deficient benzoic acids gave close to statistical product mixtures (**4i**). Cross-couplings with vinylcarboxylates resulted in the formation of lactones. The lactonization is a typical follow-up reaction in α-vinylations of benzoic acids (**5a**−**5c**), which itself could result from a C−H alkenylation/oxa-Michael addition sequence, or a cross-dehydrogenative coupling. In this reaction, $[Cp^*RhCl_2]_2$ gave higher yields than $RhCl_3{\cdot}3H_2O$, which points toward a shift in the mechanistic pathway.

To probe the viability of our mechanistic blueprint, we performed a series of mechanistic studies. Conducting the reaction in the presence of D_2O led to deuterated products, which point toward a rapid, reversible C−H metalation step (Scheme 4A). This was not observed for acrylic acids, which support a C−H alkenylation/oxa-Michael addition sequence, and rules out a cross-dehydrogenative coupling route for the acrylate cross-couplings. A negligible isotope effect for deuterated substrate confirmed that neither of the two C−H activation steps is rate determining (Scheme 4B). This explains why it is so difficult to achieve selectivity in cross-couplings. The reaction rates correlate with the electric current densities, showing that the regeneration of the Rh^{III} catalyst is rate-determining (Scheme 4D).

When conducting the reaction in the absence of electricity, the amount of product corresponded to the amount of Rh catalyst (entry 22, Table 1). With $Rh(OAc)_3$, the stoichiometric reaction gave 51% yield (Scheme 4C). This suggests that the reaction starts from Rh^{III} without an upfront oxidation step. In cyclic voltammetry, two reduction peaks of $RhCl_3{\cdot}3H_2O$ were observed at −0.50 and −1.10 V (curve c), which confirms that the Rh^{III} salt is easily reduced to Rh^{II} and/or Rh^{I}, but that an oxidation to Rh^{IV} and/or Rh^{V} is difficult under the reaction conditions (Figure 1). Adding $^{n}Bu_4NOAc$ to $RhCl_3{\cdot}3H_2O$ showed a broad reduction peak, which may result from carboxylate-bridged oligonuclear species (curve d). This system displayed a large oxidation peak at +1.35 V, which may be explained with the oxidation of the acetate (curve b). All findings support the pathway proposed in Scheme 2.

In conclusion, the newly developed electrocatalytic dehydrogenative C−H/C−H coupling allows generating various biaryl dicarboxylates under mild conditions. The reaction is operationally simple and easily scalable, has an excellent functional group compatibility, and is orthogonal to common cross-coupling strategies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01127.

General information, experimental details, spectra data, copies of NMR spectra for all final products (PDF)

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Notes

The authors declare no competing financial interest.

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