Synthetic Methods

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Rhodium-Mediated Decarboxylative Conjugate Addition of Fluorinated Benzoic Acids: Stoichiometric and Catalytic Transformations**

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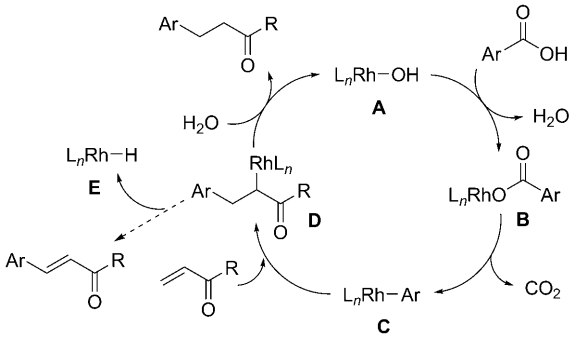
Transition-metal-catalyzed conjugate addition is a powerful strategy for C–C bond formation.[1] In general, a stoichiometric amount of a main-group organometallic reagent is required, and the desired organometallic nucleophile containing a transition metal is generated through transmetalation. Rhodium-catalyzed conjugate addition reactions of organoboron reagents proceed under mild conditions with high regio- and stereoselectivities.[2] To further advance rhodium-catalyzed conjugate addition, it is desirable to find alternatives to the conventional transmetalation method for the formation of organorhodium nucleophiles.[3] We herein report the development of a rhodium-catalyzed decarboxylative conjugate addition of benzoic acids on the basis of mechanistic observations for the corresponding stoichiometric reactions.

Decarboxylative transformations of benzoic acids under the catalysis of late transition metals have generated much interest in the past few years.[4] Typically, reactive aryl metal intermediates were formed by the release of CO_2 from benzoate species.[5c] In this way, benzoic acids could be used as readily available and easy-to-handle building blocks in transition-metal catalysis. Pioneered by the Myers research group in the palladium-catalyzed decarboxylative Heck–Mizoroki reaction,[5] this decarboxylation strategy has been expanded to several new reactions. For example, Gooßen and co-workers developed palladium-catalyzed decarboxylative cross-coupling reactions for the synthesis of biaryl compounds,[6a–e] and similar reactions were reported by a few other research groups.[6f–j] Other important examples include palladium- and copper-catalyzed reductive decarboxylation[7] and rhodium- and iridium-catalyzed decarboxylative alkyne arylation.[8,9]

Our decarboxylative conjugate addition of benzoic acids is based on a proposed catalytic cycle (Scheme 1) that has similarities with the rhodium-catalyzed conjugate addition of aryl boronic acids.[2d,e] In place of transmetalation, the rhodium(I) aryl nucleophile **C** would be generated by decarboxylation from a rhodium(I) benzoate intermediate **B**. Subsequent olefin insertion would form the desired C–C bond at the β position to give a rhodium(I) enolate **D**, and protonolysis would then release the product of conjugate addition and regenerate the rhodium(I) hydroxide catalyst **A**.[2e]



Scheme 1. Proposed catalytic cycle for the rhodium-catalyzed conjugate addition of benzoic acids through decarboxylation.

Besides the typical issues encountered with reported decarboxylative cross-coupling reactions (e.g. reaction temperatures generally above 150 °C, limited substrate scope, and stoichiometric amounts of heavy-metal salts required as additives),[4] the following challenges are expected from a mechanistic viewpoint: First, CO_2 release from rhodium(I) carboxylates may be thermodynamically disfavored, as suggested by observations of CO_2 insertion into rhodium(I) aryl species to generate rhodium(I) benzoates in stoichiometric reactions.[10] In fact, this reverse reactivity has recently been exploited in the rhodium-catalyzed carboxylation of organoboron reagents and in related studies.[11] Second, carboxyl-directed aromatic C–H activation at the *ortho* positions may interfere with decarboxylation, as demonstrated with rhodium and other late transition metals.[5d,6h,12] Third, attack on the olefin by carboxylic acids as oxygen-based nucleophiles may also occur as a competitive pathway.[13] Lastly, the selectivity issue of the desired conjugate-addition products (Michael-type) versus oxidative-arylation products (Heck–Mizoroki-type) may arise if β-hydride elimination occurs after the decarboxylation and olefin insertion steps (Scheme 1, formation of **E**).[5,14]

With these possible obstacles in mind, we began our investigation by the design and preparation of phosphine-ligated rhodium(I) carboxylates and tested their reactivity towards stoichiometric decarboxylative conjugate addition.

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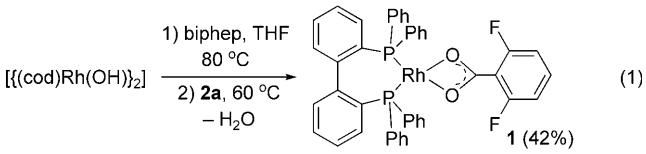
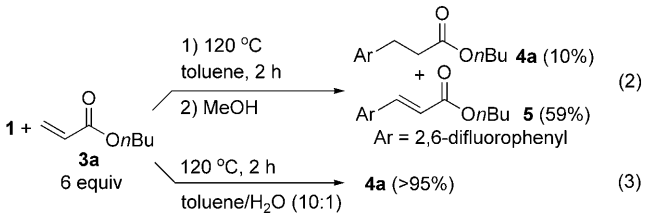
We focused our attention on chelating bisphosphine ligands as a result of their successful application in rhodium-catalyzed conjugate addition reactions of boronic acids.[2] For the benchmark carboxylate group, we chose 2,6-difluorobenzoate for the following reasons: 1) the favorable combination of an electron-deficient fluorinated aryl group and an electron-rich Rh^I center should facilitate decarboxylation from a thermodynamic viewpoint (product stabilization);[15] 2) substitution at both *ortho* positions would prevent the undesirable *ortho* C–H activation pathway; 3) the moderate steric hindrance of *ortho* fluoro substituents would probably promote decarboxylation through ground-state destabilization, but should not significantly hinder subsequent C–C bond formation through olefin insertion. Furthermore, fluorinated aryl groups are themselves highly useful building blocks in biomedical studies.[16]

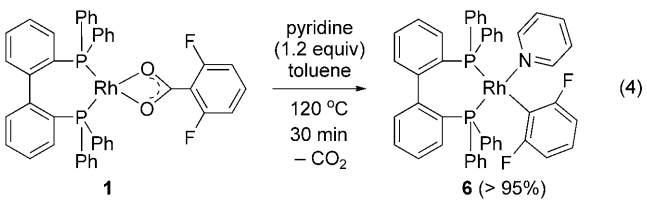
The highest reactivity was observed for a bidentate rhodium(I) carboxylato complex, [(biphep)Rh{κ^2-$O_2C(2,6\text{-}F_2C_6H_3)$}] (**1**; biphep = 2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl), which was prepared from 2,6-difluorobenzoic acid (**2a**) and [{(cod)Rh(OH)}$_2$] [Eq. (1)].[17] The treatment of **1** with excess *n*-butyl acrylate (**3a**, 6 equiv) in dry toluene at 120 °C gave a mixture of the conjugate-addition product **4a** and a Heck–Mizoroki product **5** (1:6) in 69% combined yield [Eq. (2)]. In contrast, when the same mixture of **1** and **3a** was heated in a 10:1 mixture of toluene and H_2O, **4a** was formed selectively in near-quantitative yield [Eq. (3)]. These results suggested that the decarboxylation of **1** did occur to generate an aryl rhodium(I) intermediate; subsequent olefin insertion into the rhodium–aryl linkage, followed by competitive hydrolysis/β-hydride elimination, generated **4a** or **5**, respectively (see Scheme 1).[2c,d]

To further elucidate the decarboxylation step, we sought to identify the rhodium(I) aryl intermediate before the olefin-insertion step. The thermal decomposition of **1** in the absence





of an olefin substrate failed to generate detectable organorhodium complexes, presumably as a result of the instability of the proposed [(biphep)Rh(2,6-$F_2C_6H_3$)] complex as the direct decarboxylation product. However, when **1** was heated at 80 °C with pyridine, clean formation of a discrete aryl rhodium(I) complex, [(biphep)Rh(2,6-$F_2C_6H_3$)(pyridine)] (**6**), was observed [Eq. (4)].[18] Complexes **1** and **6** were



characterized by spectroscopic methods, and both structures were determined by single-crystal X-ray diffraction (Figure 1).[19] In the solid state, the chelating carboxylato ligand forced **1** into a significantly distorted square-planar geometry, as also observed for the related structure of [Rh(κ^2-O_2CCH_3)(P*i*Pr$_3$)$_2$].[19a] Complex **6** adopts a near-square-planar geometry, with apparent π–π stacking between the difluorophenyl plane and a phenyl group on the adjacent phosphorus atom (centroid distance: ca. 3.53 Å; see the Supporting Information).[20]

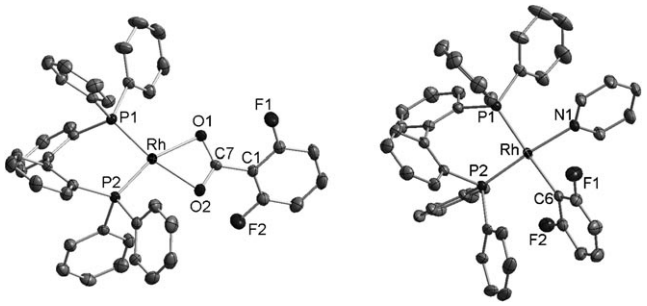
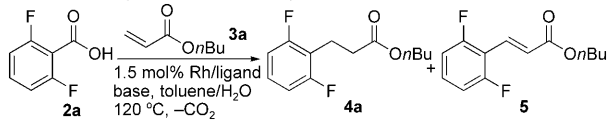


Figure 1. ORTEP diagrams of [Rh(biphep){κ^2-$O_2C(2,6\text{-}F_2C_6H_3)$}] (**1**, left) and [Rh(biphep)(2,6-$F_2C_6H_3$)(pyridine)] (**6**, right). Thermal ellipsoids are set at the 30% probability level; hydrogen atoms are omitted for clarity.

The stoichiometric investigation guided our efforts to develop a catalytic process. Some key results are shown in Table 1. The catalytic decarboxylative conjugate addition of **2a** (1 equiv) to **3a** (1.5 equiv) proceeded smoothly at 120 °C with a catalyst system composed of [{(cod)Rh(OH)}$_2$] (1.5 mol%), the biphep ligand (3 mol%), and NaOH as an additive (1.0 equiv); the desired conjugate-addition product **4a** was formed in near-quantitative yield (Table 1, entry 1). Notably, this reaction occurred in a common solvent system composed of toluene and water (10:1), whereas polar solvents, such as 1-methyl-2-pyrrolidinone, dimethyl sulfoxide, and *N*,*N*-dimethylformamide, which are used in typical palladium-catalyzed decarboxylative Heck–Mizoroki reactions and cross-coupling reactions were not suitable.[4] The less expensive racemic binap ligand gave equally good results (Table 1, entry 2), whereas the use of other phosphine ligands led to a lower yield and lower selectivity for **4a** over the Heck–Mizoroki by-product **5** (Table 1, entries 4–12). As expected, the aqueous reaction medium was beneficial for optimal yield and selectivity (see Table 1, entry 14). The choice of NaOH as an inorganic additive was also critical for satisfactory results, although its role remains unclear at this stage (Table 1, entries 15–20).[21] Interestingly, the ligand (*R*,*R*)-diop[22] promoted the selective formation of **5** over **4a**

Table 1: Development of the catalytic reaction conditions.[a]



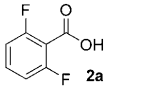
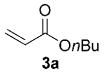
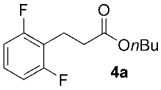
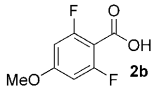
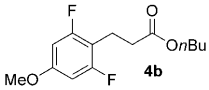
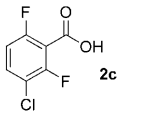
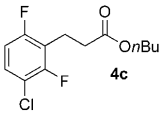
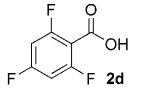
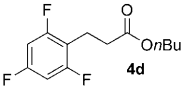
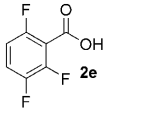
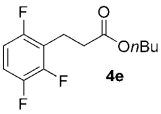
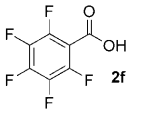
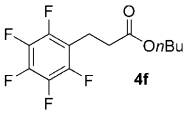
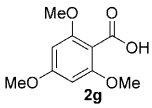
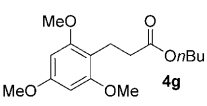
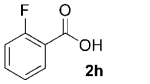
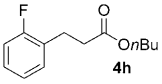
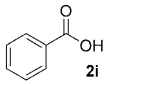
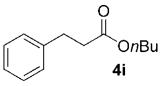
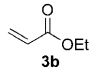
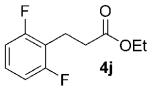
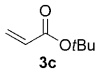
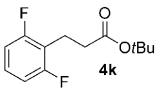
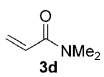
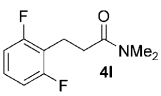
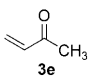
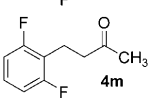
Entry	Ligand	Additive	Yield [%][b] (**4a** and **5**)	**4a**/**5**
1	biphep	NaOH	99	>99:1
2	*rac*-binap	NaOH	99	>99:1
3[c]	(*R*,*R*)-diop	NaOH	96	1:19
4	dpppentane	NaOH	0	–
5	dppb	NaOH	77	1.4:1
6	dppp	NaOH	73	1.3:1
7	diphos	NaOH	53	3:1
8	dppf	NaOH	68	1.2:1
9	xantphos	NaOH	0	–
10	PEt_3	NaOH	0	–
11	PPh_3	NaOH	0	–
12	$PtBu_3$	NaOH	<5	3:1
13	none	NaOH	0	–
14[d]	*rac*-binap	NaOH	72	20:1
15	*rac*-binap	none	<3	10:1
16	*rac*-binap	KOH	83	>99:1
17	*rac*-binap	LiOH	91	>99:1
18	*rac*-binap	Na_2CO_3	95	>99:1
19	*rac*-binap	LiCl	0	–
20	*rac*-binap	pyridine	0	–
21[e]	*rac*-binap	NaOH	62	49:1
22[f]	*rac*-binap	NaOH	95	>99:1

[a] Reaction conditions: **2a** (1 equiv), **3a** (1.5 equiv), [{(cod)Rh(μ-OH)}$_2$] (0.015 equiv), phosphine ligand (0.03 equiv for chelating phosphines, 0.06 equiv for monophosphines), additive (1.0 equiv), toluene/H_2O (10:1), 120°C, 24 h. [b] The combined yield of **4a** and **5** was determined by GC. [c] The reaction was carried out with [{(cod)Rh(μ-OH)}$_2$] (0.025 equiv), (*R*,*R*)-diop (0.05 equiv), and **3a** (3.0 equiv). [d] The reaction was carried out in dry toluene. [e] $RhCl_3$ (0.03 equiv) was used instead of [{(cod)Rh(μ-OH)}$_2$]. [f] [{(coe)$_2$Rh(μ-Cl)}$_2$] (0.015 equiv) was used instead of [{(cod)Rh(μ-OH)}$_2$] (coe = *cis*-cyclooctene). Binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, dpppentane = 1,5-bis(diphenylphosphanyl)pentane, dppb = 1,4-bis(diphenylphosphanyl)butane, dppp = 1,3-bis(diphenylphosphanyl)propane, dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, xantphos = 4,5-bis(diphenylphosphanyl)-9,9-dimethylxanthene.

(19:1) in 96% combined yield (Table 1, entry 3). In this case, a larger excess of the olefin **3a** (3.0 equiv) was required: this substrate presumably also serves as a sacrificial hydrogen acceptor. Thus, the chemoselectivity of the reaction could be reversed with a different phosphine ligand, and our catalyst system could potentially serve as an alternative for the palladium-catalyzed decarboxylative Heck–Mizoroki reaction described by Myers and co-workers, who required a stoichiometric amount of a silver salt.[5]

Having established the standard reaction conditions, we tested **2a** with other electron-poor olefin substrates in conjugate addition reactions. Ethyl- and *tert*-butyl acrylate, as well as *N*,*N*-dimethylacrylamide, reacted with **2a** to give the corresponding conjugate-addition products **4j–l** in good yields (Table 2, entries 10–12). Methyl vinyl ketone showed poor reactivity (Table 2, entry 13), and more-hindered substrates, such as 2-cyclohexen-1-one and ethyl (*E*)-2-crotonate, were unreactive.

Table 2: Scope of the decarboxylative conjugate addition.[a]

Entry	ArCOOH	Olefin	Product	Yield [%][b]
1	 **2a**	 **3a**	 **4a**	87 (99)
2	 **2b**	**3a**	 **4b**	70 (75)
3	 **2c**	**3a**	 **4c**	80 (90)
4	 **2d**	**3a**	 **4d**	56 (72)
5	 **2e**	**3a**	 **4e**	75 (89)
6	 **2f**	**3a**	 **4f**	48 (61)
7[c]	 **2g**	**3a**	 **4g**	55
8[d]	 **2h**	**3a**	 **4h**	(18)
9[e]	 **2i**	**3a**	 **4i**	0
10	**2a**	 **3b**	 **4j**	65 (74)
11	**2a**	 **3c**	 **4k**	63 (82)
12	**2a**	 **3d**	 **4l**	56 (68)
13	**2a**	 **3e**	 **4m**	(20)

[a] Reaction conditions: **2** (0.23 mmol), **3** (1.5 equiv), [{(cod)Rh(OH)}$_2$] (0.015 equiv), *rac*-binap (0.030 equiv), NaOH (1.0 equiv), toluene/H_2O (1.0 mL/100 μL), 120°C, 24 h. [b] Average yield of the isolated product from two reactions. The yield determined by GC is given in parentheses. [c] The reaction was carried out with H_2O (150 μL) in toluene (1.0 mL) and with *n*-butyl acrylate in greater excess (5.0 equiv). The Mizoroki–Heck product (11%) and 1,3,5-trimethoxybenzene (25%) were also formed. [d] The reaction was carried out at 150°C for 24 h. [e] Substrate **2i** was recovered unchanged.

In terms of the benzoic acid substrate, high reactivity was limited to derivatives with fluoro substituents at both *ortho* positions. These compounds underwent the conjugate addition to form the corresponding products **4a–f** in good yields

and without detectable amounts of Mizoroki–Heck by-products (Table 2, entries 1–6). 2,4,6-Trimethoxybenzoic acid was less reactive: the conjugate-addition product **4g** was formed in 55% yield together with by-products from the Mizoroki–Heck reaction and reductive decarboxylation when a larger excess of *n*-butyl acrylate (5 equiv) was used (Table 2, entry 7). 2-Fluorobenzoic acid displayed significantly reduced reactivity (Table 2, entry 8), and the parent compound benzoic acid was inert under the reaction conditions (Table 2, entry 9). Other less substituted benzoic acids showed little or no decarboxylation reactivity.[23] Reduced reactivity towards decarboxylation has been a common observation for benzoic acids that lack *ortho* substituents[4] and is proposed to result partly from competitive *ortho* C–H activation.[5a,7]

In conclusion, a new method for catalytic conjugate addition reactions has been developed on the basis of the decarboxylative generation of rhodium(I) aryl intermediates from fluorinated benzoic acids. Current efforts are focused on ligand modification and further mechanistic probing. We envision that an improved catalytic system would enable us to overcome the current limitation in terms of substrate scope and to develop applications in asymmetric catalysis.

Experimental Section

General procedure: Compound **2** (0.225 mmol), **3** (0.34 mmol), and NaOH (0.225 mmol) were placed in a 4 mL screw-cap vial equipped with a magnetic stirrer bar in a nitrogen-filled glovebox. Degassed H_2O (100 μL) and a stock solution of $[\{(cod)Rh(OH)\}_2]$ (0.034 mmol) and binap (0.068 mmol) in toluene (1.0 mL) were added with a syringe. The reaction vessel was sealed with a silicone-lined screw cap and removed from the glove box, and the reaction mixture was stirred at 120 °C for 24 h. The mixture was then cooled to room temperature, and all volatile materials were removed under reduced pressure. The residue was extracted into EtOAc (30 mL), washed with brine (3 × 20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. Purification by flash column chromatography (SiO_2, 2–15% EtOAc/hexane) yielded the corresponding product **4**.

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[20] Such π–π stacking was not observed in the related structure of [(diphos)Rh(*p*-tolyl)(pyridine)] (diphos = 1,2-bis(diphenylphosphanyl)ethane),[19b] which suggests the existence of an additional, ligand-dependent thermodynamic driving force for decarboxylation.
[21] We suspect that reversible decarboxylation/carboxylation may occur for certain substrates and that NaOH may act as a CO_2 scavenger to promote decarboxylation. Additionally, the formation of sodium benzoate may promote the decarboxylation process as suggested in Ref. [6e].
[22] (*R*,*R*)-Diop = (4*R*,5*R*)-(−)-4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane.
[23] Since the rhodium(I)-catalyzed conjugate addition of aryl boronic acids displays much broader substrate scope,[2] this limitation in terms of the type of benzoic acids that can be used appears to originate from limited decarboxylation reactivity. In particular, the observation of the highest reactivity with 2,6-difluoro or 2,6-dimethoxy substituents is consistent with calculations by Gooßen et al., the results of which indicated highest decarboxylation reactivities for copper(I) benzoates with two strongly σ withdrawing substituents.[7a]

