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[Rh^{III}(Cp*)]-Catalyzed *ortho*-Selective Direct C(sp^2)–H Bond Amidation/Amination of Benzoic Acids by *N*-Chlorocarbamates and *N*-Chloromorpholines. A Versatile Synthesis of Functionalized Anthranilic Acids**

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Abstract: A Rh^{III}-catalyzed direct *ortho*-C–H amidation/amination of benzoic acids with *N*-chlorocarbamates/*N*-chloromorpholines was achieved, giving anthranilic acids in up to 85% yields with excellent *ortho*-selectivity and functional-group tolerance. Successful benzoic acid aminations were achieved with carbamates bearing various amide groups including $NHCO_2Me$, NHCbz, and NHTroc (Cbz = carbobenzyloxy; Troc = trichloroethylchloroformate), as well as secondary amines, such as morpholines, piperizines, and piperidines, furnishing highly functionalized anthranilic acids. A stoichiometric reaction of a cyclometallated rhodium(III) complex of benzo[*h*]quinoline with a silver salt of *N*-chlorocarbamate afforded an amido–rhodium(III) complex, which was isolated and structurally characterized by X-ray crystallography. This finding confirmed that the C–N bond formation results from the cross-coupling of *N*-chlorocarbamate with the aryl–rhodium(III) complex. Yet, the mechanistic details regarding the C–N bond formation remain unclear; pathways involving 1,2-aryl migration and rhodium(V)–nitrene are plausible.

Introduction

Transition-metal-catalyzed C–N bond formation by C(sp^2)–H bond activation is currently receiving attention for the development of atom-economical syntheses of arylamines.[1,2] While significant advances have been accomplished in Pd-catalyzed intra- and intermolecular arene C–H amidations, these examples are mainly limited to amides as coupling partners.[3,4] Recently, extensive investigations have been directed to [Rh^{III}(Cp*)]-catalyzed (Cp* = pentamethylcyclopentadienyl) direct arene C–H aminations.[5,6] With $[RhCl_2(Cp^*)]_2$ and derivatives as catalysts, the aminations should initially involve *ortho*-selective arene C–H bond cleavage to form reactive aryl–rhodium(III) complexes.[7] The Glorius group and ours have already independently reported the coupling of the aryl–rhodium(III) complexes with *N*-chloroamines to afford *N*-arylamines.[5a–c] Other aminating reagents, such as arylsulfonylazides, arylazides, alkyl azides,[5d–i] aroyloxycarbamates,[5j] *N*-arenesulfonated imides,[5k] and *N*-fluorobenzenesulfonimide (NFSI)[5l] are shown to be effective coupling partners. Despite these apparent successes, direct aminations are limited to substrates bearing N-donor directing groups (DG = pyridines, amides, oximes; Scheme 1); related examples involving oxygen donors are sparse.[8]

Anthranilic acids (AAs) are important precursors to many medicinally active heterocycles, such as indoles, acridines, and quinolines.[9] Prompted by our earlier work on the direct C–H amidation of anilides,[3g] we pursued a rapid synthesis of AAs by Pd-catalyzed *ortho*-C–H amidation of benzoic acids with sulfonyloxycarbamates.[3f] However, the Pd-catalyzed reactions suffered from moderate yields and were limited to the mesitylsulfonyloxycarbamate reagents for effective reactions. Since prior derivatization of the benzoic acids to their lithium salts was required for effective transformations, the moderate product yields were attributed to the incompatibility of the mesitylsulfonyloxycarbamate with the alkaline medium.

Previously,[10] we achieved the [Rh^{III}(Cp*)]-catalyzed carbenoid C(sp^2)–H bond insertion to benzoic acids under alkaline-free conditions.[8n] In our study, when reacting 2,4-dimethylbenzoic acid (0.1 mmol) with $[Rh(Cp^*)(OAc)_2]$ (5 mol%) in $[D_4]$methanol at 60 °C for 20 min, 44% *ortho*-deuteriated benzoic acid was observed. This result suggests that $[Rh(Cp^*)(OAc)_2]$ can effect *ortho*-C–H bond activation of benzoic acids without prior derivatization. Motivated by this finding, we herein disclosed a Rh-catalyzed direct *ortho*-C–H amination of benzoic acids for the synthesis of functionalized anthranilic acids.

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[**] Cp* = pentamethylcyclopentadienyl.

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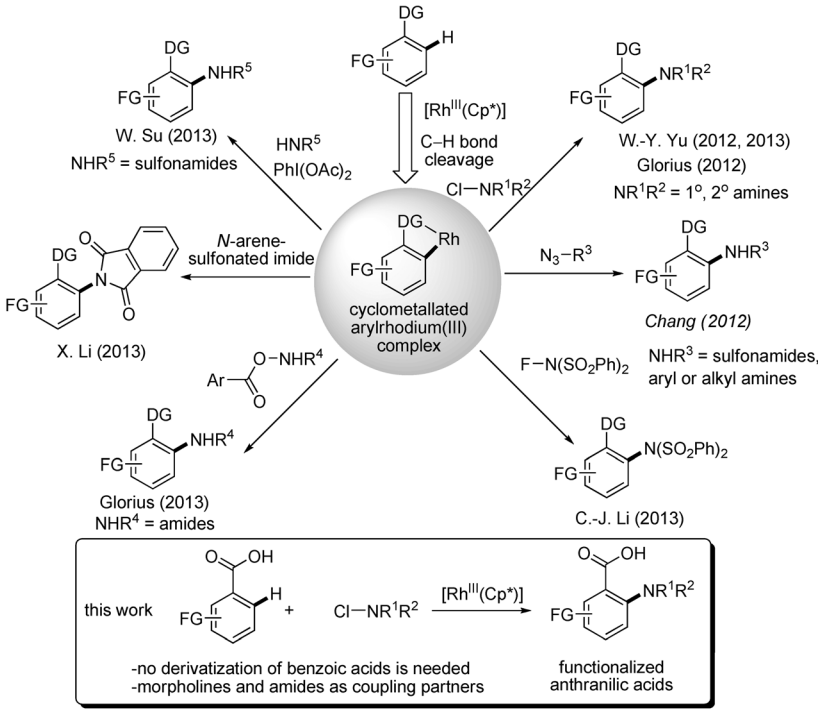


Scheme 1. Recent examples in Rh^{III}-catalyzed direct C–H aminations/amidations.

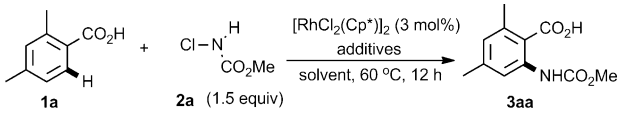
Results and Discussion

To begin, 2,4-dimethylbenzoic acid **1a** (0.2 mmol) was treated with $[RhCl_2(Cp^*)]_2$ (3 mol%), AgOAc (1.5 equiv), and methyl *N*-chlorocarbamate (**2a**) (1.5 equiv) in MeOH (2 mL) at 60 °C for 12 h, and **3aa** was obtained in 68% yield (Table 1, entry 1). In this work, employing phenylazide and sulfonyloxycarbamates as reagents failed to effect significant transformations, and the desired AAs were obtained in <5% yield (entries 2–4). No product formation was observed with AgOAc alone in the absence of the Rh catalyst (entry 5). When CsOAc (1.5 equiv) was used, **3aa** was formed in 5% yield (entry 6). According to our previous report, a substoichiometric amount of CsOAc (30 mol%) was needed for the Rh-catalyzed amination of acetophenone oximes.[5c] In this work, a combination of $AgSbF_6$ (1.5 equiv) and CsOAc (0–2 equiv) was examined. Unlike our previous finding, employing 0–0.3 equivalents of CsOAc resulted in negligible **3aa** formation (entries 7 and 8). When 1–2 equivalents of CsOAc was utilized, **3aa** was furnished in approximately 40% yield (entries 9 and 10). This finding suggested that a stoichiometric amount of acetate is required for effective catalytic turnovers. Low product yields were obtained with silver trifluoroacetate (AgTFA) (entry 11) and Ag_2CO_3 (entry 12) as additives. Up to 85% of **3aa** formation was accomplished when AgOAc was used along with *t*BuOH as solvent (entry 13). With MeOH as the solvent, the methyl ester of **1a** (~10%) was obtained as a side product. Employing nonalcoholic solvents, such as 1,2-dichloroethane (DCE), DMF, dioxane, and toluene, resulted in 25–42% product yields (entries 14–17).

Table 2 depicts the results of a substrate-scope study. Under the optimized conditions, all benzoic acids employed in this study were transformed to their corresponding anthranilic acids **3ba**–**3ea** in 40–85% yields with excellent *ortho*-selectivities. The amidation reactions exhibit good tolerance to the OAc, Br, I, and F substituents, which are useful functional groups for late-stage cross-coupling reactions. Notably, when the amidation of 2-bromobenzoic acid (**1c**) was performed by the Pd-catalyzed conditions (Li salt of **1c** (0.2 mmol), ethyl mesitylsulfonyloxycarbamate (1.5 equiv), $Pd(OAc)_2$ (10 mol%), and KOAc (1 equiv) in dioxane (1 mL) at 90 °C for 4 h), 2-[(ethoxycarbonyl)amino]benzoic acid (debrominated product) was formed exclusively in 20% yield (i.e., no **3ca** was obtained).

The *meta*-substituted trifluoromethyl- and phenoxy-benzoic acids were amidated at the less-

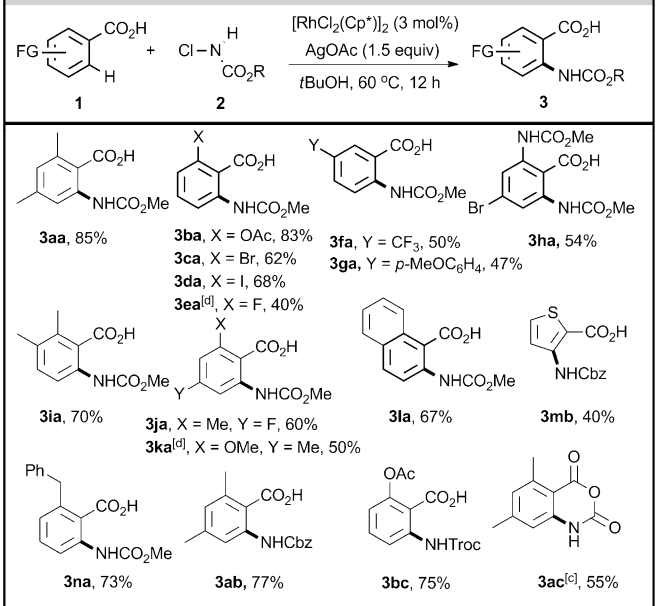
Table 1. Reaction optimization.[a]



Entry	Reagent [equiv]	Additives [equiv]	Solvent	Yield [%][b,c]
1	**2a**	AgOAc (1.5)	MeOH	(68)
2	phenylazide (2)	–	DCE	0
3	*N*-nosyloxy carbamate (1.2)	CsOAc (0.3)	MeOH	0
4	*N*-mesitylsulfonyl oxycarbamate (1.2)	CsOAc (0.3)	MeOH	5
5[d]	**2a**	AgOAc (1.5)	MeOH	0
6	**2a**	CsOAc (1.5)	MeOH	5
7	**2a**	$AgSbF_6$ (1.5)	MeOH	0
8	**2a**	$AgSbF_6$ (1.5) CsOAc (0.3)	MeOH	0
9	**2a**	$AgSbF_6$ (1.5) CsOAc (1)	MeOH	50
10	**2a**	$AgSbF_6$ (1.5) CsOAc (2)	MeOH	40
11	**2a**	AgTFA (1.5)	MeOH	30
12	**2a**	Ag_2CO_3 (1.5)	MeOH	36
13[e]	**2a**	AgOAc (1.5)	*t*BuOH	(85)
14	**2a**	AgOAc (1.5)	DCE	26
15	**2a**	AgOAc (1.5)	DMF	42
16	**2a**	AgOAc (1.5)	dioxane	28
17	**2a**	AgOAc (1.5)	toluene	25

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), $[RhCl_2(Cp^*)]_2$ (3 mol%), additives (0.3–2 equiv), solvent (2 mL), 60 °C for 12 h under a N_2 atmosphere. [b] NMR spectroscopic yields. [c] Isolated yields in parentheses. [d] The reaction ran without $[RhCl_2(Cp^*)]_2$. [e] Same result was obtained when **2a** (1.2 equiv) was used. DCE = 1,2-dichloroethane.

Table 2. Substrate scope studies.[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv), $[RhCl_2(Cp^*)]_2$ (3 mol%), AgOAc (1.5 equiv), *t*BuOH (2 mL), 60 °C under a N_2 atmosphere. [b] Isolated yields. [c] 0.5 equiv PivOH was added. [d] Isolated as the corresponding methylester.

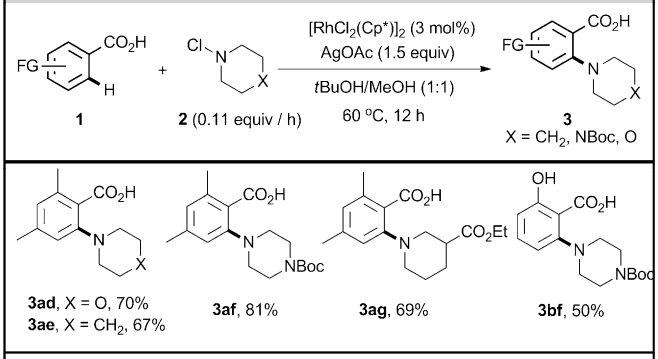
hindered *ortho*-C–H bond to give **3fa** (50%) and **3ga** (47%) with a mass balance of >90%. The analogous reaction of 4-bromobenzoic acid afforded 2,6-diamidated benzoic acid **3ha** exclusively in 54% yield with a >90% mass balance. Yet, doubling the quantity of **2a** failed to improve the yield of **3ha** even with an extended reaction time of 24 h. A similar diamidation was also reported by Glorius and co-workers in the study of the Rh-catalyzed amination of *O*-methylbenzohyroxamic acids.[5j] Facile reactions were also achieved for disubstituted benzoic acids bearing alkyl, halogen, and ethereal substituents to furnish **3ia**–**3ka** in 50–70% yields (mass balance of **3ka** = 85%).

According to our previous report, the Pd-catalyzed amidation of 1-naphthoic acid (**1l**) suffered low product yield (~30%). In this work, when 1-naphthoic acid was reacted with **2a** under the Rh-catalyzed conditions, **3la** was formed in 67% yield. Similarly, the analogous reaction of 3-thiophencarboxylic acid (**1m**) furnished **3mb** in 40% yield (mass balance = 80%). However, we found that treating the lithium salt of **1m** (0.2 mmol) with ethyl mesitylsulfonyloxycarbamate (1.5 equiv), $Pd(OAc)_2$ (10 mol%), and KOAc (1 equiv) in dioxane (1 mL) at 90 °C for 4 h did not produce any amide products. Thus, the Rh-catalyzed amidation appeared to be more general than the Pd-catalyzed reactions. Notwithstanding, carboxylic acids bearing some heteroaryl motifs, such as benzofuran, indole, and pyridine, were found to be poor substrates, which were fully recovered at the end of the reactions. The amidation of 2-benzylbenzoic acid occurred exclusively at the arene-C–H bond to furnish **3na** in 73% yield; products due to amidation at the benzyl-C–H bond were not obtained.[11] This result suggests that the outer-sphere nitrene-mediated C–H insertion is kinetically incompatible to the Rh-catalyzed arene amidation reactions.

The diversity of the N-coupling partners has been examined. For instance, reactions of benzyl *N*-chlorocarbamate (**2b**) and 2,2,2-trichloroethyl *N*-chlorocarbamate (**2c**) with **1a** under the Rh-catalyzed conditions afforded **3ab** and **3bc** in 77 and 75% yields. Notably, the OAc and NHTroc (Troc = trichloroethylchloroformate) groups can be selectively deprotected under orthogonal conditions for further transformations.[12] For the coupling of **1a** with **2c**, we obtained a mixture of *N*-Troc AA and a cyclized product **3ac** (combined yield = 50%). When the reaction was repeated with the presence of PivOH (0.5 equiv), **3ac** was obtained exclusively in 55% yield (mass balance = 70%). A similar cyclization reaction was also reported by Glorius and coworkers in the Rh^{III}-catalyzed C–H amidation of *O*-methylbenzohydroxamic acids with aroyloxycarbamates.[5j]

Direct C–H bond couplings of benzoic acids with *N*-chloromorpholines were also achieved (Table 3). Treatment of 2,4-dimethylbenzoic acid (0.2 mmol), *N*-chloromorpholine (1.2 equiv;

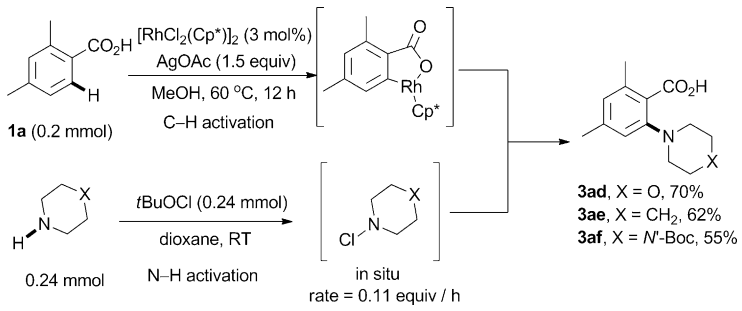
Table 3. Amine scope.[a–c]



[a] Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv), $[RhCl_2(Cp^*)]_2$ (3 mol%), AgOAc (1.5 equiv), *t*BuOH/MeOH (1:1), 60 °C under a N_2 atmosphere. [b] Isolated yields. [c] Chloroamines were added dropwise by using MeOH as a solvent; rate = 0.11 equiv/h.

0.11 equiv/h), $[RhCl_2(Cp^*)]_2$ (3 mol%), and AgOAc (1.5 equiv) in *t*BuOH/MeOH (1:1) at 60 °C for 12 h afforded **3ad** in 70% yield. No prior derivatization of the carboxylic acid group to an amide group is needed. Likewise, other *N*-chloroamines were successfully coupled to 2,4-dimethylbenzoic acid to give **3ae** (67%), **3af** (81%), and **3ag** (69%) under Rh catalysis. When 2-(acetyloxy)benzoic acid (**1b**) was reacted with *N*-chloro-*N*′-Boc-piperizine (**2f**) (Boc = *tert*-butoxycarbonyl), a deacetylated product **3bf** was obtained exclusively in 50% yield after workup. In this work, *N*-chloroamines derived from *N*-chlorocyclopentylamine were found to be ineffective coupling partners, and no desirable amination product was obtained with >90% recovery of the starting benzoic acid.

A cross-dehydrogenative coupling (CDC) between benzoic acids and amines involving twofold N–H and C–H activations has been developed (Scheme 2). In this work, the N–H activation was achieved by treating morpholines (0.24 mmol) with *tert*-butyl hypochlorite (0.24 mmol) in dioxane at room temper-



Scheme 2. Cross-dehydrogenative amination of benzoic acids involving in situ twofold N–H and C–H activations.

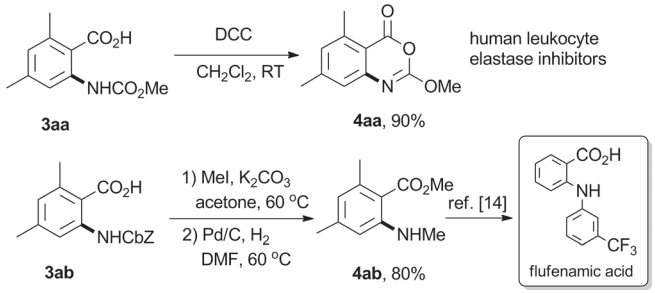
ature for 5 min to generate *N*-chloromorpholine in situ.[15] And it was directly employed without isolation for the Rh^{III}-catalyzed direct-C–H amination of benzoic acids. For instance, treating 2,4-dimethylbenzoic acid (**1a**), *N*-chloromorpholine (in situ; 0.11 equiv/h), $[RhCl_2(Cp^*)]_2$ (3 mol%), AgOAc (1.5 equiv) in MeOH at 60 °C for 12 h furnished **3ad** in 70% yield. Similarly, other amines, such as piperidine and *N*′-Boc-piperizine, were coupled to 2,4-dimethylbenzoic acid to give **3ae** (62%) and **3af** (55%).

In this study, anthranilic acid **3aa** was readily converted to the corresponding 4*H*-3,1-benzoxain-4-one (**4aa**) in 90% yield by *N*,*N*-dicyclohexylcarbodiimide (DCC) treatment (Scheme 3). Compound **4aa** was known to exhibit human leukocyte elastase inhibitory activities.[13] With the choice of the NHCbz group, **3ab** can be selectively derivatized to **4ab** bearing a free NH group by a sequence of esterification and hydrogenolysis. It is conceivable that the free NH group is open for the Buchwald–Hartwig arylation to afford the flufenamic acid derivatives.[14]

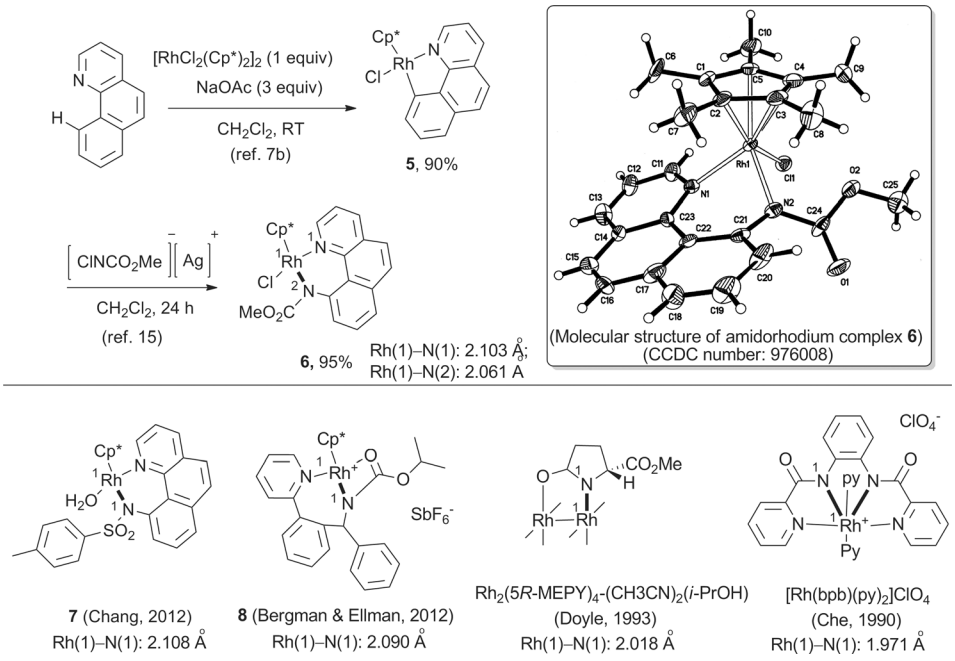
To ascertain the role of the aryl–rhodium(III) complex in the amination reaction, we prepared well-characterized aryl–rhodium(III) complex **5** by reacting $[RhCl_2(Cp^*)]_2$ (0.2 mmol) with benzo[*h*]quinoline (0.2 mmol) and NaOAc (0.44 mmol) in CH_2Cl_2 under room temperature for 24 h.[7b] When **5** (0.1 mmol) was subjected to the amidation conditions (i.e., methyl *N*-chlorocarbamate (**2a**; 0.12 mmol) and $AgSbF_6$ (0.1 mmol) in CH_2Cl_2), a complicated mixture was obtained. Attempts to purify the mixture were unsuccessful. Yet, when **5** was reacted with a silver salt of **2a** in CH_2Cl_2,[15] an amido–rhodium(III) complex **6** was obtained in 95% yield (Scheme 4).

Based on the single-crystal X-ray diffraction study, complex **6** was confirmed to be a metallacyclic amido–rhodium(III) complex that features a Rh(1)–N(2) bond length of 2.061 Å. This bond length value is comparable to corresponding values observed in some defined amido–rhodium(III) complexes (Scheme 4): sulfonamido–rhodium(III) complex **7**: 2.108 Å; cationic isopropylcarbamato–rhodium(III) complex **8**: 2.090 Å; tetrakis(carboxamidates)dirhodium(II) complex: 2.018 Å; and a 1,2-bis(2-pyridinecarboxamido)benzene rhodium(III) complex: 1.971 Å.[16,5i]

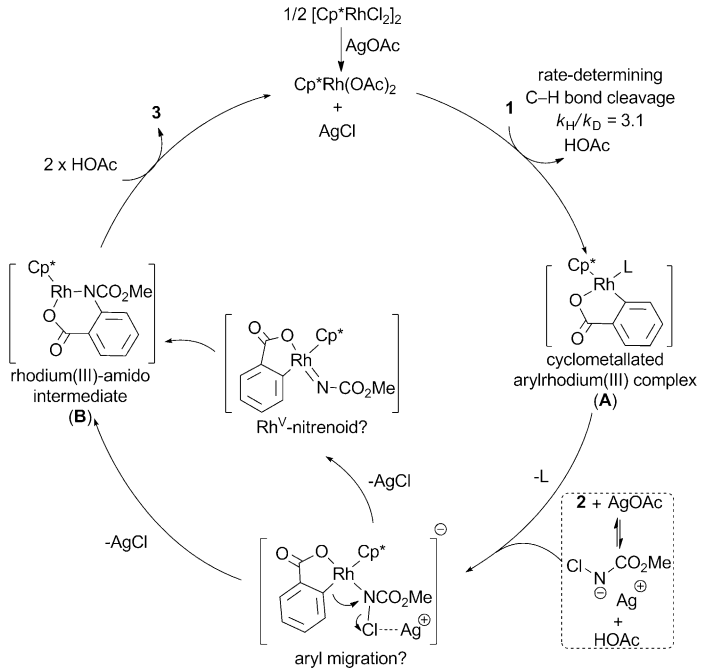
Scheme 5 depicts a plausible reaction mechanism. $[Rh(Cp^*)(OAc)_2]$[17] should be the active catalyst and undergoes an irreversible rate-limiting C–H bond cleavage to form a cyclometallated benzoate complex (**A**).[7c] This is supported by the observed notable primary kinetic isotope effect (KIE) $k_H/k_D = 3.1$.[18] Furthermore, upon treating **1a** (0.2 mmol),



Scheme 3. Synthetic applications.



Scheme 4. Characterization of the amido–rhodium(III) complex **6** (representative bond lengths: Rh(1)–N(1): 2.103 Å; Rh(1)–N(2): 2.061 Å) and selected examples of well-defined amido–rhodium(III) complexes. $[Rh_2(5R\text{-MEPY})_4]$ = dirhodium(II) tetrakis(methyl 2-oxopyrrolidine-5-carboxylates); H_2bpb = 1,2-bis(2-pyridinecarboxamido)benzene; py = pyridine.



Scheme 5. Proposed mechanism.

$[RhCl_2(Cp^*)]_2$ (3 mol%), AgOAc (1.5 equiv), and **2a** in $[D_4]$methanol at 60 °C for 20 min, no *ortho*-deuteriated benzoic acid was detected with **3aa** formed in 14% yield. On the contrary, when the analogous experiment was performed in the absence of **2a**, *ortho*-deuteriated benzoic acid was obtained in 54% based on ^{1}H NMR spectroscopic analysis. This result shows C–H bond cleavage in the Rh-catalyzed amidation reaction is irreversible.[19] Based on our stoichiometric studies, the C–N bond formation should be mediated by the coupling of the aryl–rhodium(III) complex and the *N*-chloroamidate anion, which is likely to be formed by reacting **2** with AgOAc. We hypothesized that the C–N bond formation may occur by 1,2-aryl migration with the cleavage of the N–Cl bond. However, an alternative pathway involving the formation of Rh^V nitrenoid species is also possible. In a computation study by Xia and coworkers on the $[Rh^{III}(Cp^*)]$-catalyzed cycloaddition of benzohydroxamic acids with alkenes, formation of Rh^V nitrene intermediate from a seven-membered rhodacycle containing a *N*-OPiv moiety by an acyloxy migration process was proposed.[20] Yet, both pathways should afford the same amido–rhodium(III) intermediate (**B**). Protodemetalation should regenerate the $[Rh(Cp^*)(OAc)_2]$ catalyst with release of the anthranilic acid products.

Conclusion

To conclude, a Rh^{III}-catalyzed direct C–H amidation/amination of benzoic acids is developed. The amidation offers a direct route for the synthesis of functionalized anthranilic acids, which are important building blocks to many medicinally active heterocycles. The amidation/amination reactions exhibit excellent regioselectivities and functional-group tolerance.

Experimental Section

General procedures for the Rh^{III}-catalyzed *ortho*-C–H amidation of benzoic acids

For *N*-chloroamides as a coupling partner: One-batch addition of reagent 2 (method A): Benzoic acids **1** (0.2 mmol), $[RhCl_2(Cp^*)]_2$ (3 mol%), and AgOAc (1.5 equiv) were added to a vial (8 mL) that was sealed with a Teflon liner cap. The vial was evacuated and backfilled with N_2 three times. Freshly distilled *t*BuOH (2 mL) was added to the reaction vial, followed by the addition of **2** (1.2 equiv) with a 50 μL-syringe in one portion (reagents **2b** and **2c**, which are solids at room temperature, were added to the reaction vial along with the benzoic acids). The reaction was stirred at 60 °C for 12 h. After cooling to room temperature, EtOAc (4 mL) and 2 M HCl (2 mL) were added. The organic layer was collected and the aqueous layer was washed with EtOAc (4 mL×2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a plug of glasswool. Solvents were removed by rotary evaporation and the residue was redissolved in a small amount of dichloromethane. The dissolved mixture was then purified by flash column chromatography on silica gel by gradient elution with 10% EtOAc in hexanes with 5% increment until 50% EtOAc in hexanes was reached, at which point the anthranilic acid products were eluted.

For *N*-chloroamines as a coupling partner: Slow addition of reagent 2 (method B): A mixture of benzoic acids (0.2 mmol), $[RhCl_2(Cp^*)]_2$ (3 mol%), and AgOAc (1.5 equiv) were dissolved in freshly distilled *t*BuOH (1 mL) in a 10 mL-Schlenk tube under a N_2 atmosphere. Chloroamine **2** was dissolved in MeOH (1 mL) and was added dropwise to the reaction tube by a syringe pump (rate = 0.11 equiv/h). The reaction was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction was diluted with EtOAc (4 mL). Saturated $NaHCO_3$ and 1 M HCl were added to adjust the pH of the crude mixture to 5. The organic layer was collected, and the aqueous layer was washed with EtOAc (4 mL×2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a plug of glasswool. Solvents were removed by rotary evaporation, and the residue was re-dissolved in a small amount of dichloromethane. The dissolved mixture was then purified by flash column chromatography on silica gel by gradient elution with 10% EtOAc in hexanes with 5% increment until 50% EtOAc in hexanes was reached, at which point the anthranilic acid products were eluted.

Cross-dehydrogenative coupling reaction between benzoic acids and amines

A mixture of 2,4-dimethylbenzoic acid (0.2 mmol), $[RhCl_2(Cp^*)]_2$ (3 mol%), and AgOAc (1.5 equiv) were dissolved in freshly distilled MeOH (1 mL) in a 10 mL-Schlenk tube under a N_2 atmosphere. In a separate 4 mL-vial, secondary amines (0.24 mmol) were mixed with *tert*-butyl hypochlorite (0.24 mmol) in dioxane (1 mL) for 5 min. To the Schlenk tube containing Rh^{III} and the benzoic acids, the secondary amine solution mixture in the vial was added dropwise by a syringe pump (rate = 0.11 equiv/h). The reaction mixture was stirred at 60 °C for 12 h, and then was treated by the same workup procedures as in method B.

Kinetic isotope effect (KIE) experiment

In a parallel experiment, benzoic acids **1a** (0.1 mmol) and [D_2]2,4-dimethyl-6-benzoic acid ([D_2]**1a**) (0.1 mmol) were added separately into two 8 mL-vials sealed with a Teflon liner cap. [$RhCl_2(Cp^*)]_2$ (3 mol%) and AgOAc (1.5 equiv) were added into the two separate reaction vials, and the vials were evacuated and back-filled with N_2 three times. Freshly distilled MeOH (2 mL) was added to the two reaction vials, followed by the addition of **2** (1.2 equiv) with a 50 μL-syringe in one portion. The two reactions were stirred at 60 °C for 20 min. After cooling to room temperature, EtOAc (4 mL) and 2 M HCl (2 mL) were added. The organic layer was collected and the aqueous layer was washed with EtOAc (4 mL×2). The combined organic fractions were dried over Na_2SO_4 and then filtered through a plug of glasswool. Solvents were removed by rotary evaporation to dryness. The residue was redissolved in [D]chloroform followed by the addition of internal standard (dibromomethane, 0.1 mmol). The conversions of **1a** and ([D_2]**1a**) were determined by ^{1}H NMR spectroscopy. The same set of experiments was repeated three times to obtain an average KIE value.

Synthesis of amido–rhodium(III) complex 6

Cyclometallated complex **5** (0.1 mmol) and the silver salt of **2a** (0.1 mmol) were added to a 10 mL-Schlenk tube. The tube was evacuated and back-filled with N_2 three times. Distilled dichloromethane (5 mL) was added to the reaction tube. The reaction mixture was stirred at room temperature overnight. The reaction crude was filtered through a plug of Celite and rinsed with dichloromethane. The filtrate was then evaporated to dryness under reduced pressure. The residue was washed with hexanes (5 mL×3), diethyl ether (5 mL×3), and a small amount of EtOAc (~1 mL). The resulted residue was dried in vacuo to afford complex **6**. To obtain a single-crystal for X-ray crystallographic study, complex **6** was dissolved in a minimum amount of dichloromethane and then layered with hexanes for 1 day.

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