Organic LETTERS

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[Rh^{III}(Cp*)]-Catalyzed Cascade Arylation and Chlorination of α-Diazocarbonyl Compounds with Arylboronic Acids and *N*-Chlorosuccinimide for Facile Synthesis of α-Aryl-α-chloro Carbonyl Compounds

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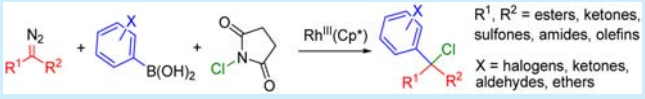
Supporting Information

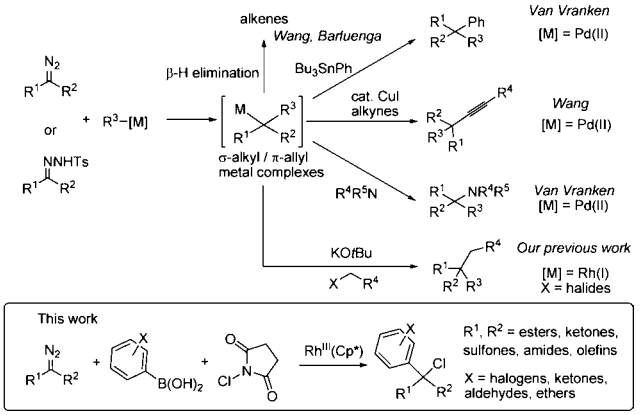
ABSTRACT: A Rh(III)-catalyzed cascade arylation and chlorination of α-diazocarbonyl compounds with arylboronic acids and *N*-chlorosuccinimide was achieved. The reaction exhibits excellent functional group tolerance on the organoboron and the diazo reagents; the functionalized α-aryl-α-chlorocarbonyl compounds were obtained in up to 86% yields. The cascade reaction should involve migratory carbene insertion of arylrhodium(III) to form some reactive rhodium(III)−diketonate complexes. Its subsequent reaction with *N*-chlorosuccinmide afforded the α-chlorocarbonyl products.



Analogous to carbon monoxide, migratory insertion of metal−carbene complexes derived from diazo compounds is attracting growing attention for transition-metal-catalyzed C−C bond coupling reactions.[1−4] Pioneered by van Vranken,[2a−c] extensive investigation by Barluenga,[2d,e] Wang,[2f,g] Liang,[2h,i] and our group[7a,b] showed that arylpalladium(II) would react with diazo compounds to furnish palladium−carbene complexes, which subsequently undergo migratory carbene insertion to afford reactive σ-alkylpalladium(II) complexes. Owing to the facile β-hydride elimination reactivity, attempts to bring about further transformation(s) of the alkylpalladium(II) complexes for formation of a second C−C/C−X bond have met with limited success. Notably, Wang et al. successfully intercepted σ-organopalladium after the migratory carbene insertion by copper-acetylides, and cascade formation of two C−C bonds was accomplished.[5] Van Vranken et al. showed that π-allylpalladium(II) complex formation after migratory carbene insertion constitutes a fruitful strategy to effect three-component coupling reactions (Scheme 1).[6]

Alternative to Pd catalysis, we[7] accomplished the Rh(I)-catalyzed three-component coupling reactions of arylboronates, α-aryldiazoacetate, and alkyl halides.[7e] With [Rh^{I}(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene) as the catalyst and KO^{t}Bu as the base, the coupling reaction afforded quaternary α,α-heterodiaryl carboxylic acids in good yields. Mechanistically, the reaction is likely mediated by diazo coupling with arylrhodium(I) complexes to furnish oxa-π-allylrhodium(I) complexes. The second C−C bond formation was achieved by S$_N$2 displacement with the alkyl halides after metathesis with KO^{t}Bu. Recently, we achieved Rh^{III}(Cp*)-catalyzed direct arene C−H insertion with diazomalonates (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl).[7d] This reaction involves diazo-malonate coupling with arylrhodium(III) complexes as the principal step, and the product σ-alkylrhodium(III) complex has been structurally characterized. This alkylrhodium(III) would undergo protonolysis for catalyst turnover with concomitant C−H bond formation. Yet, it became clear that the alkylrhodium(III) would undergo intramolecular N−O bond cleavage with benzohydroxamic acids as substrates, and C−N bond formation resulted.[3e,g,7c] Thus, by exploiting the reactivity of the alkylrhodium(III) complexes, we envisioned developing a catalytic synthesis of quaternary stereocenters by cascade difunctionalization on the carbene center with the formation of C−C and C−X (X = halogen) bonds. Herein we report a [Rh^{III}(Cp*)]-catalyzed cascade arylation/chlorination of α-diazocarbonyl compounds with arylboronic acids and *N*-

Scheme 1. Selected Examples for Intercepting σ-Alkyl/π-Allyl Metal Complexes after Carbene Migratory Insertion



Received: February 11, 2015
Published: March 16, 2015

DOI: 10.1021/acs.orglett.5b00440
Org. Lett. 2015, 17, 1676−1679

chlorosuccimide (NCS) for the synthesis of α-aryl-α-chloro carbonyl compounds.

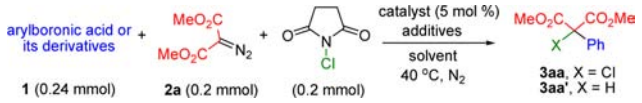
We began by examining the hydroarylation reaction of diazomalonate with arylboronic acids. Treating phenylboronic acid (**1a**, 0.2 mmol) with methyl diazomalonate (**2a**, 0.2 mmol) and $[Rh(Cp^*)(OAc)_2]$ (5 mol %) in a dioxane−water mixture (10:1, v/v) at rt for 6 h, α-phenyldimethylmalonate (**3aa′**) was obtained in 90% yield. The hydroarylation reaction presumably occurred via diazomalonate coupling with arylrhodiun(III) complexes to furnish the rhodium(III)-enolates, which undergo protonolysis to give the α-phenyldimethylmalonate. Encouraged by this finding, we turned to examine the analogous chloroarylation of diazomalonate with electrophilic chlorinating reagents.

When **1a** (0.24 mmol) reacted with **2a** (0.2 mmol), *N*-chlorosuccinimide (NCS; 0.2 mmol) and $[Rh(Cp^*)(OAc)_2]$ (5 mol %) in dry DMF (1 mL) at 40 °C for 6 h, the desired dimethyl α-phenyl-α-chloromalonate (**3aa**) was produced in 70% yield (Table 1, entry 1). No hydroarylation products **3aa′** were obtained. Other arylboronic acid derivatives were found to give less satisfactory results. For instance, by employing PhBpin (pin = pinacol ester) (0.24 mmol) and KO^{t}Bu (0.24 mmol) as the arylation reagent, **3aa** was produced in <5% yield (entry 2). With potassium phenyltrifluoroborate ($PhBF_3K$) as the reagent, no **3aa** formation was detected (entry 3). Interestingly, when boric acid (0.2 mmol) was employed as an additive, the reaction with $PhBF_3K$ (0.24 mmol) afforded **3aa** in 63% yield (entry 4). Notably, no **3aa** was formed in the absence of $[Rh(Cp^*)(OAc)_2]$ (entry 5). Other Rh catalysts such as $[Rh(Cp^*)Cl_2]$ and $[Rh(COD)OH]_2$ were found to be ineffective catalysts for the chloroarylation (entries 6 and 7). Furthermore, $[Ir(Cp^*)Cl_2]_2$, $[Cu(OAc)_2]$, [CuCl], and $[Pd(OAc)_2]$ also did not effect any catalytic chloroarylations (entries 8−11).

In this work, several common solvents such as toluene, DCE, ^{t}BuOH, and DMA gave inferior results compared to DMF (entries 12−15). Employing batchwise addition of either **1a** (0.08 mmol/h) or NCS (0.06 mmol/h) resulted in lower yields (5% and 46%) of **3aa** (entries 16 and 17). During our optimization study, we observed a significant amount of dimethyl mesoxalate formation in many cases. The mesoxalate was likely derived from the reaction of diazomalonate, NCS, and residual water.[8] Gratifyingly, the mesoxalate formation can be suppressed by employing more **1a** (0.4 mmol) (entry 18). Under the optimized conditions [**1a** (0.4 mmol), **2a** (0.2 mmol), NCS (0.2 mmol), and $[Rh(Cp^*)(OAc)_2]$ (5 mol %) in DMF at 40 °C for 6 h], **3aa** can be obtained in 85% yield. Yet, other electrophilic halogenation agents such as $CuCl_2$, $PhICl_2$, *N*-bromosuccinimde, *N*-iodosuccinimide, and *N*-fluorobenzenesulfonimide were less effective halogenation reagents, and the undesired hydroarylation products were formed dominantly (see Supporting Informations).

Scheme 2 depicts the substrate scope of the chloroarylation reaction. With diazomalonate (**2a**) as the substrate, arylboronic acids bearing ethereal, halogen, aldehyde, ketone, and ester substituents were all tolerated with **3ba**−**3ha** being obtained in 58−74% yields. Apparently, the analogous transformation with

Table 1. Reaction Optimization[a]

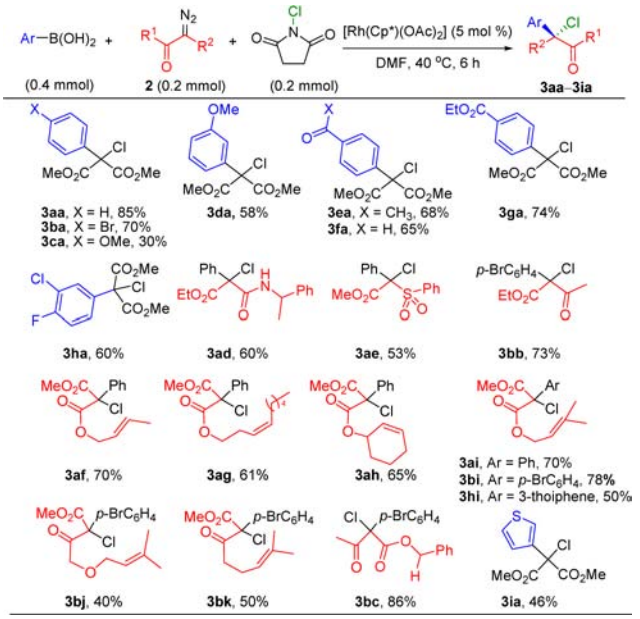


1 (0.24 mmol) 2a (0.2 mmol) (0.2 mmol)

entry	1	catalyst	additives (mmol)	solvent	3aa[b] (%)
1	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	DMF	70
2	PhBpin	$[Rh(Cp^*)(OAc)_2]$	KOtBu (0.24)	DMF	<5
3	$PhBF_3K$	$[Rh(Cp^*)(OAc)_2]$	–	DMF	0
4	$PhBF_3K$	$[Rh(Cp^*)(OAc)_2]$	$B(OH)_3$ (0.2)	DMF	63
5	$PhB(OH)_2$	–	–	DMF	0
6	$PhB(OH)_2$	$[Rh(Cp^*)Cl_2]_2$	–	DMF	0
7	$PhB(OH)_2$	$[Rh(COD)OH]_2$	–	DMF	0
8	$PhB(OH)_2$	$[Ir(Cp^*)Cl_2]_2$	$AgSbF_6$ (0.02)	DMF	0
9	$PhB(OH)_2$	$[Cu(OAc)_2]$	–	DMF	0
10	$PhB(OH)_2$	[CuCl]	Phen (0.04)	DMF	0
11	$PhB(OH)_2$	$[Pd(OAc)_2]$	–	DMF	0
12	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	toluene	0
13	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	DCE	0
14	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	^{t}BuOH	25
15	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	DMA	5
16[c]	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	DMF	5
17[d]	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	DMF	46
18[e]	$PhB(OH)_2$	$[Rh(Cp^*)(OAc)_2]$	–	DMF	(85)

[a]Reaction conditions: phenylboronic acid or its derivatives (0.24 mmol), **2a** (0.2 mmol), NCS (0.2 mmol), catalyst (5 mol %), additives (0.02 mmol−0.24 mmol), dry DMF (1 mL) at 40 °C for 6 h under a N_2 atmosphere. [b]NMR yields, isolated yield in parentheses. [c]Batchwise addition of **1a** (0.08 mmol/h). [d]Batchwise addition of NCS (0.06 mmol/h). [e]$PhB(OH)_2$ (0.4 mmol) was employed.

Scheme 2. Substrate Scope Studies[a]



[a]Reaction conditions: arylboronic acids (0.4 mmol), **2** (0.2 mmol), NCS (0.2 mmol), $[Rh(Cp^*)(OAc)_2]$ (5 mol %), dry DMF (1 mL) at 40 °C for 6 h under a N_2 atmosphere.

DOI: 10.1021/acs.orglett.5b00440
Org. Lett. 2015, 17, 1676−1679

4-methoxyphenylboronic acid produced **3ca** in a modest 30% yield. It could be attributed by the competitive protodeboration of the electron-rich arylboronic acids in the reaction mixture.

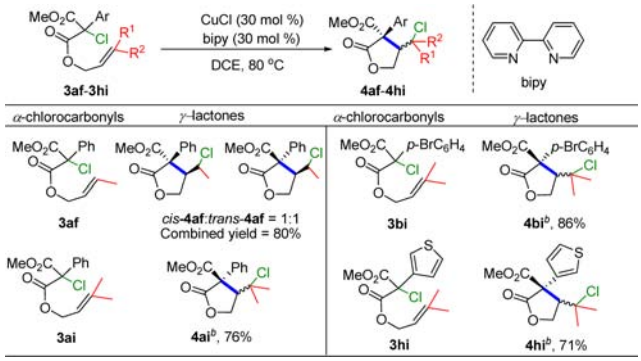
Other acceptor−acceptor diazo substrates were tested. For instance, by subjecting diazoacetates bearing an amide group (**2d**) and a phenylsulfonyl group (**2e**) to the chloroarylation reaction [phenylboronic acid (0.4 mmol), NCS (0.2 mmol), and $[Rh(Cp^*)(OAc)_2]$ (5 mol %) in DMF at 40 °C for 6 h], the desired **3ad** and **3ae** were produced in 60% and 53% yields. Similarly, the analogous α-ketodiazoacetate (**2b**) was transformed to **3bb** in 73% yield with 4-bromophenylboronic acid (**1b**) as a reagent. However, the reactions of cyclic diazo compounds derived from Meldrum's acid were unsuccessful, and 80% of the diazo starting material was recovered. When α-phenyldiazoacetate was employed as the substrate, no chloroarylation products were formed with methyl phenyloxoacetate being isolated in 41% yield. The phenyloxoacetate was probably produced by the competitive diazo oxidation with the NCS and the residual moisture.[8]

According to the literature, rhodium−carbene complexes would react with alkenes to afford cyclopropanes.[9] In this work, when diazoesters bearing a disubstituted C=C bond were employed for the Rh^{III}-catalyzed chloroarylation, the desired **3af** (70%), **3ag** (61%), and **3ah** (65%) were obtained exclusively without any cyclopropanes being formed. Similarly, diazoesters bearing a more reactive trisubstituted C=C bond were transformed selectively to the corresponding α-chlorocarbonyl compounds (**3ai**, **3bi**, **3hi**, **3bj**, and **3bk**) in 40−78% yields. Assuming an arylrhodium(III) intermediate, these findings suggested that migratory carbene insertion is kinetically more competitive than intramolecular cyclopropanation.

Apparently, the migratory carbene insertion is more competitive than carbenoid C−H insertion.[10] For example, when benzyl diazoacetylacetate (**2c**) reacted with 4-bromophenylboronic acid (**1b**) for the chloroarylation reaction, the desired α-chloroketone **3bc** was isolated in 86% yield exclusively (i.e., no benzylic/aryl C−H carbene insertion products were obtained). Yet, thiophene groups are known to react with the Rh−carbene complex to form reactive ylides,[10] which would undergo further transformations such as dipolar cycloaddition. In this work, when 3-thienylboronic acid (**1i**) was treated with **2a** and NCS, the desired coupling product **3ia** was furnished in 46% yield selectively and no ylide-derived product was detected.

In this work, the functionalized α-chlorocarbonyl compounds were further transformed into γ-lactones by the Cu-catalyzed atom transfer radical cyclization.[11] By treating α-chlorocarbonyl compounds **3af** with CuCl (30 mol %), 2,2′-bipyridine (30 mol %) in DCE at 80 °C for 12 h, two 5-*exo* γ-lactones *cis*-**4af** and *trans*-**4af** were obtained in 80% combined yields (*cis*-**4af**/*trans*-**4af** = 1:1) (Scheme 3). The molecular structure of *cis*-**4af** was established by X-ray crystallographic study, and the *cis*-stereochemistry of the phenyl and 3-chloro alkyl group in *cis*-**4af** was also confirmed. Similarly, α-chlorocarbonyl compounds **3ai**, **3bi**, and **3hi** were converted to γ-lactones **4ai** (76% yields), **4bi** (86% yield), and **4hi** (71% yield) by the Cu-catalyzed radical cyclizations. However, radical cyclization for **3ag**, **3ah**, and **3bk** were unsuccessful; only the corresponding protodechlorination side products were isolated. Interestingly, the reaction of α-chlorocarbonyl compound **3bj** did not give the expected 6-*exo* cyclization product. Instead, the tandem radical cyclization/radical aromatic C−H substitution occurred to afford a tricyclic product **4bj** in 22% yield (see Supporting Information).

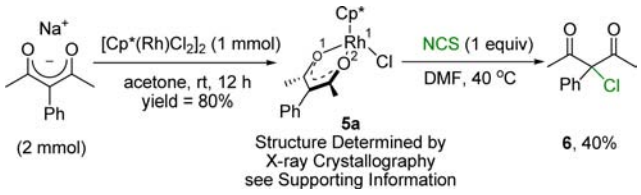
Scheme 3. Synthesis of γ-Lactones by Cu-Catalyzed Radical Cyclization[a]



[a]Reaction conditions: α-chlorocarbonyl compounds (0.1 mmol), CuCl (30 mol %), 2,2′-bipyridine (30 mol %), DCE (5 mL) at 80 °C for 12 h under a N_2 atmosphere. [b]Combined yield of diastereomers, and the absolute configuration of the individual diastereomers were not determined.

To understand the mechanistic underpinning of the chlorination step, we synthesized a well-defined rhodium(III)−diketonate complex (**5a**). By reacting $[Rh(Cp^*)Cl_2]_2$ (1 mmol) and Na(α-phenylacetylacetone) (2 mmol) in acetone at rt for 12 h, **5a** was isolated in 80% yield (Scheme 4). X-ray crystallographic study established that the diketonate ligand binds nearly symmetrically to the rhodium center through an O−O′-κ^2 fashion: [Rh(1)−O(1): 2.0907 (14) Å vs Rh(1)−O(2): 2.0847 (15) Å]. Complex **5a** features a Rh(1)−O(1) bond distance of 2.0907 (14) Å, which is comparable to the corresponding distance of the $[Rh_2^{III}(Cp^*)_2(acac)_2][BF_4]_2$ complex Rh−O(acac): [2.103 (4) Å].[12] When **5a** was treated with NCS in DMF at 40 °C for 1 h, α-phenyl-α-chloroacetylacetone (**6**) was formed in 40% yield (Scheme 4). This result suggested that the rhodium(III)−diketonate complex is a likely intermediate for the chlorination step.

Scheme 4. Synthesis of Rhodium(III)−Diketonate Complex 5a and Its Reaction with NCS

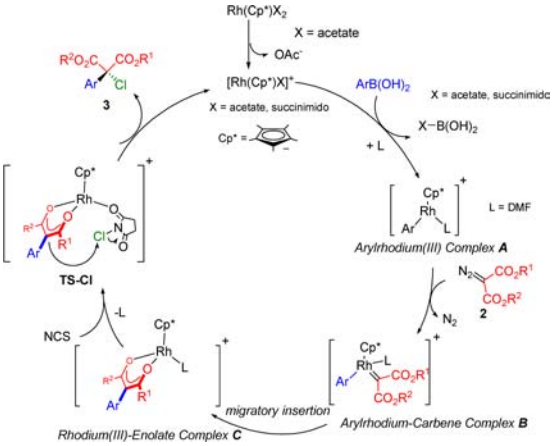


A plausible reaction mechanism (Scheme 5) should involve initial transmetalation of arylboronic acids to $[Rh(Cp^*)(OAc)_2]$ to afford the arylrhodium(III) complex **A**.[13] A putative arylrhodium−carbene complex **B** would undergo migratory carbene insertion to the aryl group to furnish the rhodium(III)−diketonate complex **C**. The chlorination step may be mediated by prior coordination of the *N*-chlorosuccinimide to complex **C**, followed by nucleophilic displacement of the N−Cl group by the diketonate ligand.

To conclude, a Rh(III)-catalyzed cascade arylation and chlorination of α-diazocarbonyl compounds with arylboronic acids and *N*-chlorosuccinimide is developed. The reaction offers a direct route to α-aryl-α-chlorocarbonyl compounds, which can be converted to γ-lactones by Cu-catalyzed chlorine atom transfer radical cyclizations. Preliminary mechanistic studies of

DOI: 10.1021/acs.orglett.5b00440
Org. Lett. 2015, 17, 1676−1679

Scheme 5. Plausible Reaction Mechanism



the reaction showed that a rhodium-diketonate intermediate is likely involved in the chlorination step.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, analytical data, and copies of NMR spectra of the products. This material is available free from charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank The Hong Kong Research Grants Council (PolyU503811P) for financial support.

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DOI: 10.1021/acs.orglett.5b00440
Org. Lett. 2015, 17, 1676−1679