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Rhodium-Catalyzed Dealkenylative Arylation of Alkenes with **Arylboronic Compounds**

Guangying Tan, Mowpriya Das, Iván Maisuls, Cristian A. Strassert, and Frank Glorius*

Dedicated to Prof. Christian Bruneau

Abstract: The C-C bond formation reaction represents a fundamental and important transformation in synthetic chemistry, and exploring new types of C-C bond formation reactions is recognized as appealing, yet challenging. Herein, we disclose the first example of rhodium-catalyzed dealkenylative arylation of alkenes with arylboronic compounds, thereby providing an unconventional access to bi(hetero)aryls with excellent chemoselectivity. In this method, C(aryl)-C(alkenyl) and C(alkenyl)-C(alkenyl) bonds in various alkenes and 1,3-dienes can be cleaved via a hydrometalation and followed by beta-carbon elimination pathway for Suzuki-Miyaura reaction. Furthermore, a series of novel organic fluorescent molecules with excellent photophysical properties has been efficiently constructed with this protocol.

Introduction

Transition-metal catalyzed cross-coupling reactions of alkenes with arylboronic compounds have emerged as a rapid and efficient C-C bond forming transformation that utilize of abundant and/or commercially available feedstocks to produce various value-added alkenylarenes as well as alkylarenes,^[1] thereby has received increasing attention from the synthetic community. According to the difference of the products, these reactions could be categorized into two main types. The first type is Heck-type arylation of alkenes via transition-metal catalysis,^[2,3] the pathway involves the formation of an alkylmetallic intermediate via an intermolecular carbometalation of alkenes and a subsequent beta-H elimination to give alkenylarenes (Scheme 1a). Another type refers to the hydroarylation of alkenes.^[4,5] In this type, transition-metal catalyst reacts firstly with hydride reagents to generate an active catalyst species [TM]-H. Then, [TM]-H interacts with alkenes and arylboronic compounds through a hydrometalation and transmetalation process in sequence to form an arylalkylmetallic intermediate, which further undergoes a reductive elimination to deliver a hydroarylated product (Scheme 1b). Beyond the above two types, herein we disclose a new type of coupling reaction between alkene and arylboronic compound via rhodiumcatalyzed dealkenylative arylation, which is much more

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challenging than the direct Heck arylation and hydroarylation because of the thermodynamic and kinetic stability of most C-C bonds (Scheme 1c).^[6,7] In this work, C(aryl)-C(alkenyl) and C(alkenyl)-C(alkenyl) bonds in various alkenes and 1,3-dienes could be cleaved for Suzuki-Miyaura reaction with arylboronic compounds under the help of chelation group, thereby providing a rapid and unconventional access to bi(hetero)aryls. To the best of our knowledge, there are only three reported examples on transition-metal catalyzed C(aryl)-C(alkenyl) bond cleavage, namely: 1) Youn's Pd-catalyzed cascade reactions between 2alkenylphenyl beta-ketoesters and alkenes via aromatizationdriven beta-carbon elimination;^[8] 2) Lautens' Pd-catalyzed remote C-H alkylation and C-C bond cleavage;[9] and 3) Kakiuchi's Rh-catalyzed olefin extrusion-reinsertion of styrenes.^[10] Notably, the cleavage of C(alkenyl)–C(alkenyl) bond in 1,3-dienes remains unknown to date.

a) Transition-metal catalyzed Heck arylation of alkenes with arylboronic compounds



b) Transition-metal catalyzed hydroarylation of alkenes arylboronic compounds



c) This work: rhodium catalyzed dealkenylative arylation of alkenes with arylboronic compounds



- more challenging than direct arylation or hydroarylation
- alkenyl as leaving group · unconventional access to bi(hetero)aryls · excellent chemo-selectivety
- activation of unstrained C(aryl)-C(alkenyl) and C(alkenyl)-C(alkenyl) bonds



new organic fluorescent molecules

Scheme 1. Transition-metal catalyzed coupling reactions between alkenes and arylboronic compounds. [TM] = transition-metal. DG = directing group.

Results and Discussion

Optimization of the Reaction Conditions. Inspired by Kakiuchi's work,^[10] we began our study with the reaction between 1-(2-methyl-6-(prop-1-en-2-yl)phenyl)-1H-pyrazole (1a) tyrosine, reacted smoothly with 1e under the standard reaction and (4-methoxyphenyl)boronic acid (2a) in the presence of a conditions, producing the desired products 4m and 4n in 65% and 57% yields respectively. -B(OH)₂ Ar

Cp*Rh(III) catalyst (see Supporting Information for the details, Table S1). To our delight, the best yield for the desired product 3a reached 69% under the optimal catalytic system composed of [RhCp*(MeCN)₃][SbF₆]₂ (10 mol%) and Ag₂O (2.0 equiv) in EtOH (0.2 M) at 100 °C for 20 h, and only a trace amount of by-product 3aa resulting from the direct oxidative Heck arylation of 1a with 2a was observed (Table S1, entry 1). The control experiments showed that both [RhCp*(MeCN)₃][SbF₆]₂ and Ag₂O were indispensable for this reaction (Table S1, entries 2 and 3). Catalysts played a crucial role in the chemoselectivity of dealkenylative arylation over Heck arylation. Replacing [RhCp*(MeCN)₃][SbF₆]₂ with [RhCp*Cl₂]₂/AgSbF₆, the chemoselectivity of this reaction switched completely and 3aa was obtained as main product in 36% vield (Table S1, entry 4). In addition, [IrCp*Cl₂]₂ and [CoCp*(CO)l₂]₂, the congeners of [RhCp*Cl2]2, showcased negligible catalytic activity for this transformation (Table S1, entries 5 and 6). When Ag₂O was replaced with Ag₂CO₃ as oxidant, **3a** was delivered in a slightly decreased yield (Table S1, entry 7) and the reaction was shut down completely when employing AgOAc and Cu(OAc)₂ as oxidant (Table S1, entries 8 and 9). Moreover, solvents also significantly affect the chemoselectivity (Table S1, entries 10-15). For example, CF₃CH₂OH gave a moderate yield of **3a** along with a trace amount of the by-product 3aa. However, the undesired Heck arylation were more favored when employing other solvents such as MeOH, ^tBuOH, DCE, 1,4-dioxane, and toluene. Furthermore, sensitivity screening revealed that this reaction was relatively robust (Table S2),[11] only suffering from diminished yields with water addition or at larger scales.

Substrate Scope. With the optimized conditions in hand, the scope of (hetero)arylboronic acids was tested firstly in the reaction with 1a. As shown in Table 1, a series of (hetero)arylboronic acids smoothly underwent this transformation, producing a variety of bi(hetero)aryl skeletons in moderate to good yields (3a-3x). Phenylboronic acids with electron donating or electron withdrawing groups such as methoxyl, methyl, tert-butyl, iso-butyl, trimethylsilyl, phenyl, vinyl, fluoro, chloro, trifluromethyl, and ester at the para- or metaposition of the phenyl ring could react with 1a in good yields (3a-3s). Moreover, naphthalen-1-ylboronic acid, naphthalen-2ylboronic acid, and (5-bromobenzo[b]thiophen-2-yl)boronic acid were suitable for this transformation (3t-3v). Furthermore, the carbazolye and triphenylamine containing boronic acids could also undergo this dealkenylative arylation (3w and 3x).

Subsequently, the reactivity of different types of alkenes was inspected (Table 2). To our delight, 1-(5-methyl-2-(1phenylvinyl)phenyl)-1H-pyrazole (1b) and 1,2-disubstituted internal alkenes such as (E)-1-(5-methyl-2-styrylphenyl)-1Hpyrazole (1c) and (E)-1-(5-methyl-2-(pent-1-en-1-yl)phenyl)-1Hpyrazole (1d) could be cleaved for the dealkenylative arylation with (4-methoxyphenyl)boronic acid (2a) in moderate yields. Then, the scope with respect to directing group-containing alkene substrates (1) was investigated. As summarized in Table 2, various pyrazole or pyridine containing alkenes could undergo this dealkenylative arylation, delievering the corresponding biaryls in moderate to good yields (4a-4I). To highlight the synthetic usefulness, this method was examined in the late10.1002/anie.202105355

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[a] Reaction conditions: 1a (0.2 mmol), 2 (0.4 mmol), [RhCp*(MeCN)₃][SbF₆]₂ (10 mol%), and Ag₂O (2.0 equiv) in EtOH (1.0 mL) at 100 °C under Ar for 20 h. [b] Isolated vields.

To our delight, our protocol could also be extended to the dealkenylative arylation of 1,3-dienes with the aid of pyridine unit as directing group (Table 3). It needs to be noted that the cleavage of C(alkenyl)-C(alkenyl) bond in 1,3-dienes is unknown to date. First, arylboronic compounds with either electron-donating or electron-withdrawing groups engaged in this reaction with 2-((2Z,4E)-3-methyl-5-phenylpenta-2,4-dien-2yl)pyridine (5a) in moderate yields (6a-6i). Subsequently, the scope of 1,3-dienes was examined by using arylboronic compounds 2z as the coupling partner. As summarized in Table 3, various 2-pyridyl-containing 1,3-dienes underwent this method, delivering the corresponding products in moderate yields (6j-6r). In addition, 2-((1Z,3E)-4-phenylbuta-1,3-dien-1-yl)pyridine and 2-((2Z,4E)-5-phenylpenta-2,4-dien-2-yl)pyridine failed to give the desired products.

Considering the synthetic usefulness of this protocol, we further illustrated the transformation of the directing group. As shown in Scheme 2a, the pyrazolyl group could be easily transformed into an amino group. To gain some insight into the reaction mechanism, a set of control experiments were conducted. First, treating 1e under the standard reaction

conditions delivered the direct dealkenylatived product 8 in 76% yield. Moreover, the direct dealkenylation reaction of 1e was also observed in the absence of Ag₂O by using EtOH or ⁱPrOH as solvent. The above alcohol-mediated dealkenylation reactions of 1e suggested that the dealkenylative product 8 might be an intermediate of this dealkenylation reaction. To corroborate this possibility, two parallel competition experiments of 1e or 8 with 2a under the standard reaction conditions for 3 h were conducted, and the desired product 4a was obtained in 52% and 37% yields individually. Furthermore, an intermolecular competition experiment was also performed, treating of 1 equiv each of 1e, 9, and 2a in one pot under the standard reaction conditions for 3 h. As shown in Scheme 2c and 2d, the results evidenced that the arylation reaction from C-C cleavage was much faster than that from C-H activation. Therefore, the direct dealkenylative arylation reaction of 1e is more favored than the cascade dealkenylation and rhodium-catalyzed ortho C-H arylation.[12-13] However, at this stage, this possibility cannot be completely ruled out.



[a] Reaction conditions: 1 (0.2 mmol), 2 (0.4 mmol), $[RhCp^*(MeCN)_3][SbF_6]_2$ (10 mol%), and Ag₂O (2.0 equiv) in EtOH (1.0 mL) at 100 °C under Ar for 20 h. [b] Isolated yields. [c] The diarylated product 4b' was obtained in 12% yield. [c] The diarylated product 4e' was obtained in 13% yield.

Table 3: Scope of 2-pyridyl-containing 1,3-dienes.[a,b]



[a] Reaction conditions: ${\bf 5}~(0.2~mmol),~{\bf 2}~(0.4~mmol),~[RhCp*(MeCN)_3][SbF_6]_2~(10~mol%), and Ag_2O~(2.0~equiv) in EtOH (1.0~mL) at 100 °C under Ar for 36 h. [b] Isolated yields.$

Based on the above observations and relevant literature, [10,14, ^{15]} a plausible mechanistic pathway is proposed as illustrated in Scheme 3. Firstly, the reaction of [RhCp*(MeCN)₃][SbF₆]₂ with EtOH forms an active catalyst species $[Cp*Rh^{III}X]-H$ (X = SbF₆ or OEt) along with CH₃CHO (CH₃CHO was detected by GCMS after the reaction of 1e and 2a, see Supporting Information).^[14] The resulting rhodium hydride species interacts with substrate 1 to give the intermediate IM1, followed by a hydrometalation of alkene units to generate the intermediate IM2. Then. intermediate IM2 goes through a beta-carbon elimination to deliver an alkene coordinated intermediate IM3, which further providing the intermediate IM4 through the release of an alkene. Subsequently, intermediate IM4 reacts with arylboronic acids to give intermediate IM5 via a transmetalation process. Since the direct dealkenylative product was observed after the reaction (Scheme 2b and 2d), intermediate IM4 suffers from a reversible dealkenylation reaction in the presence of hydrogen ion at the same time. Finally, intermediate IM5 undergoes a reductive elimination to provide the desired products 3 along with the release of Cp*Rh^I species. The later one will be further reoxidized to Cp*Rh^{III} species by Ag₂O to close the catalytic cycle.







Scheme 2. a) Removal of directing group. b) Alcohol-mediated direct dealkenylation of 1e. c) Two parallel competition experiment. d) Intermolecular competition experiment.



Scheme 3. Plausible mechanistic pathway.



Scheme 4. Synthesis of organic fluorescent molecules **10**, **11**, and **12** through programmed arylations (for detailed reaction conditions, see supporting information). Conditions: **1**) [RhCp*(MeCN)₃][SbF₆]₂ and Ag₂O in EtOH at 100 °C. 2) [RhCp*Cl₂]₂/AgSbF₆ and Ag₂O in dioxane at 120 °C. 3) Pd(PPh₃)₄, Na₂CO₃ in a mixture of toluene, EtOH and H₂O at 100 °C. [a] Total yields. [b] Emission maximum and Φ_F (± 2%, toluene, RT). [c] Φ_F in a glassy matrix (± 4%, 2-Me-THF,77 K). [d] Emission maximum and Φ_F in solid state (± 2%, RT).

Following the above studies, we devoted our efforts on the strategic application of this protocol. As it is widely known, organic fluorescent molecules have broad applications in chemosensors, organic light-emitting diodes, field-effect transistors, memory devices, and bioprobes etc.^[16] In addition, triphenylamine (TPA) derivatives are considered versatile materials because they possess nonplanar characteristic, excellent electron-donating property, and hole-transporting capability.^[17] Therefore, we designed and synthesized three triphenylamine (TPA) derivatives containing organic fluorescent molecules (**10-12**) through a programmed rhodium-catalyzed dealkenylative arylation and C–H arylation, and palladium-catalyzed Suzuki-Miyama reaction of **1h** with different arylboronic acids (Scheme 4, see also Supporting Information for details).



Figure 1. (a) Normalized absorption spectra of compounds **10**, **11**, and **12** in fluid toluene at RT. (b) Photoluminescence spectra of compounds **10**, **11**, and **12** in fluid toluene (10^{-5} M) and in the solid state at RT. Inset: Photographs of compounds **10**, **11**, and **12** in toluene at RT (10^{-5} M), while photoexcited with a UV lamp. Further photophysical data and photoluminescence spectra at 77 K are found in the Supporting Information.

Finally, the photophysical properties of the newly synthesized organic fluorophores (**10-12**) were measured, including absorption and photoluminescence spectra, fluorescence quantum yields (Φ_F) and excited singlet state lifetimes (t) in fluid

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solution and in the solid state at room temperature (RT) as well as in glassy matrices at 77 K (see Supporting Information for details). As shown in Scheme 4 and in Figure 1, the absorption and emission maxima in toluene (10-5 M) are centered at around 345 nm and 400 nm, respectively. Surprisingly high $\phi_{\rm F}$ around 44% was observed in fluid toluene (Scheme 4). Notably, this value further increased to roughly 75% at low temperature (77 K), where also a slight blue-shift is observed. Contrastingly, a significant red-shift of the photoluminescence (around 30 nm) was observed in the solid state, if compared with fluid solutions, which is attributed to an enhanced dielectric constant favoring the charge-transfer character while dropping the $\Phi_{\rm F}$ to 20%, 13%, and 21%, respectively. Clearly, these compounds display a bright and intense blue fluorescence both in solution and in the solid state (Figure 1). Based on the obtained $\phi_{\rm F}$ and τ values (Tables S3-S4), we calculated the fluorescence (k_F) and nonradiative (k_{nr}) deactivation rate constants (Table S5). The comparably high value of $k_{\rm F}$ for the three species implies a predominant π - π * character of the fluorescent S1 states. In frozen matrices at 77 K and in apolar solvents at RT, the π - π * character is increased while boosting $k_{\rm r}$, whereas in the more polar solid state the charge-transfer character is enhanced with generally lower radiative and higher radiationless deactivation rates. At 77 K, radiationless processes are suppressed due to reduced rotovibrational degrees of freedom while providing the intrinsically high fluorescence rate constant due to a maximized π - π^* character in the absence of solvent stabilization of the photoexcited states.

Conclusion

In summary, we have demonstrated the first example of rhodium(III)-catalyzed dealkenylative arylation of alkenes with arylboronic compounds, thereby providing an unconventional access to bi(hetero)aryls with excellent chemo-selectivity. In addition, this transformation was also amenable to 1,3-dienes. In this method, C(aryl)–C(alkenyl) and C(alkenyl)–C(alkenyl) bonds in various alkenes and 1,3-dienes can be cleaved via a hydrometalation and followed by beta-carbon elimination pathway for Suzuki-Miyaura reaction. Furthermore, a new class of bright fluorophores was made accessible providing a blue luminescence with lifetimes in the ns range and up to 75% quantum yields.

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Keywords: rhodium catalysis • dealkenylation arylation • alkenes • C–C bond cleavage • organic fluorescent molecules

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A rhodium(III)-catalyzed dealkenylation arylation of alkenes and 1,3-dienes with arylboronic compounds has been developed for the first time to provide an unconventional access to bi(hetero)aryls with excellent chemo-selectivity.

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Rhodium-Catalyzed Dealkenylative Arylation of Alkenes with Arylboronic Compounds