Cross-coupling

DOI: 10.1002/ange.201309198

Rhodium-Catalyzed C–H Alkynylation of Arenes at Room Temperature**

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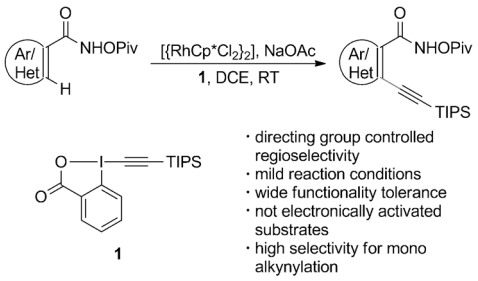
Abstract: *The rhodium(III)-catalyzed ortho C–H alkynylation of non-electronically activated arenes is disclosed. This process features a straightforward and highly effective protocol for the synthesis of functionalized alkynes and represents the first example of merging a hypervalent iodine reagent with rhodium(III) catalysis. Notably, this reaction proceeds at room temperature, tolerates a variety of functional groups, and more importantly, exhibits high selectivity for monoalkynylation.*

Alkynes rank among the most important functional groups in synthetic chemistry because of their versatility to be transformed into various useful molecules and also their ubiquity in naturally occurring compounds, advanced materials, and pharmaceutics.[1] The most popular and reliable method for the introduction of alkynyl functionality is the Sonogashira coupling reaction by virtue of its operational simplicity and wide spectrum of functionality tolerance.[2] With the surge in C–H functionalization, much effort has been focused on the discovery of new synthetic methods which could obviate the use of halogenated starting materials and, more importantly, allow the ease of transformation for cases where specific aryl halides are not easily accessible.[3] Compared with the substantial advancement attained in the area of C–H alkenylation,[4] the analogous C–H alkynylation is largely underexplored, mainly because of the susceptibility of terminal alkynes to homocoupling under the commonly employed oxidative reaction conditions.[5] In this context, the electronically reversed Sonogashira coupling reaction between non-prefunctionalized arenes and an electrophilic alkyne species is an attractive approach, and several elegant works, using different transition metals and electrophilic alkynes, have already been reported in the past few years.[6] Elegant examples using hypervalent alkynyl iodine as the electrophilic alkyne reagent for C–H alkynylation of electron-rich aromatic substrates (indole, pyrrole, furan, thiophene and anilines), catalyzed by gold or palladium, have been reported by Waser and co-workers.[7]

While considerable progress has been achieved in the arena of C–H alkynylation, the reported methods commonly rely on the use of electronically activated arenes, with electron-neutral or the more-challenging electron-deficient arenes being largely underdeveloped. However, Chatani and co-workers described the alkynylation of an aromatic acid and 2-phenylpyridine derivatives by using palladium or ruthenium as a catalyst and alkynyl bromide as an alkynylation reagent.[8,9] However, the need for the reactions to be carried out at high temperature, the use of impractical directing groups, and more importantly, the lack of selectivity for mono and bis-alkynylation encouraged us to search for a highly selective alkynylation of arenes. Specifically, we were interested in discovering a method for alkynylation of unactivated substrates under much milder reaction conditions, which would be applicable in the late-stage functionalization of complex molecules. With our continuing interest in the rhodium catalysis,[10] we report herein the first example of rhodium-catalyzed electronically reversed Sonogashira coupling of electron-poor arenes by taking advantage of the hypervalent iodine reagent **1** as the alkyne source without the need for undesirable metallic oxidants (Scheme 1).[11] Our



Scheme 1. Rhodium-catalyzed C–H alkynylation of electronically unbiased arenes. Cp* = C_5Me_5, DCE = 1,2-dichloroethane, Piv = pivaloyl, TIPS = triisopropylsilyl.

protocol also allows selective access to monoalkynylation, which represents a major issue in directed C–H functionalizations, with no bis-alkynylation products observed in all cases examined.

With 4-methyl-*N*-(pivaloyloxy)benzamide (**2a**) and **1** as model substrates, the reaction conditions were investigated (Table 1). We were rather pleased to find that with [{$RhCp^*Cl_2$}$_2$] as the catalyst, NaOAc as an additive, and methanol as the solvent, the reaction worked smoothly at room temperature to produce the desired alkynylation

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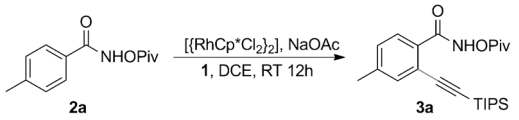
[**] We gratefully acknowledge the USTC Research Fund, the Nanyang Technological University, and the Singapore Ministry of Education Academic Research Fund (ETRP 1002 111, MOE2010-T2-2-067, MOE 2011-T2-1-013) for the funding of this research.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309198.

Table 1: Optimization of reaction conditions.[a]



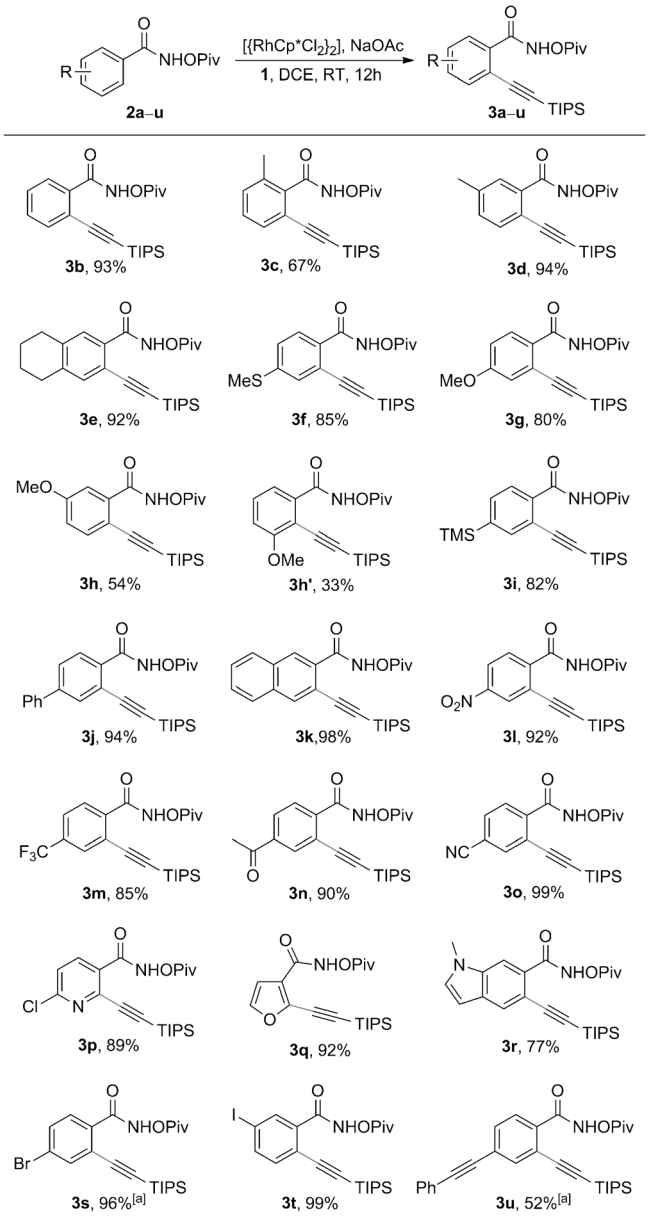
2a 3a

Entry	Additive	Yield [%][b]
1	NaOAc	89
2	CsOAc	89
3	CsOPiv	88
4	NaOAc	92[c]
5	PivOH	–[d]
6	–	–[d]
7	NaOAc	9[e,g]
8	NaOAc	8[f,g]
9	NaOAc	n.r.[h]

[a] Unless otherwise noted, the reactions were carried out at room temperature using **2a** (0.1 mmol), **1** (0.11 mmol), additive (0.025 mmol), catalyst (0.002 mmol) in solvent (0.5 mL) for 12 h. [b] Yields of isolated products. [c] NaOAc (0.1 mmol). [d] No desired product. [e] Bromotriisopropylsilylethyne was used instead of **1**. [f] Iodotriisopropylsilylethyne was used instead of **1**. [g] Yield was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [h] No rhodium catalyst added. n.r. = no reaction.

product **3a** in 62% yield (see the Supporting Information). Screening of the solvent proved DCE to be the optimal choice, as it delivered **3a** in 89% yield (Table 1, entry 1). When CsOAc and CsOPiv were employed in place of NaOAc, comparable chemical yields were obtained (Table 1, entries 2 and 3). On the contrary, PivOH, which is known to be involved in the key step of C–H bond cleavage in many documented C–H functionalization reactions, did not show any positive effect on this reaction (Table 1, entry 5).[12] This result indicated that although the acetate or pivalate anion may promote the envisioned C–H bond cleavage, the base-promoted association of amide substrates with a rhodium catalyst proved to be the prerequisite. By increasing the stoichiometry of NaOAc, the yield of **3a** was further improved to 92% (Table 1, entry 4). Furthermore, NaOAc was found to be essential for the success of this reaction and no desired product could be detected with its absence (Table 1, entry 6). It should be noted that the use of other commonly employed alkynylation reagents such as bromo- or iodotriisopropylethylene gave rise to the desired product in less than 10% yield (Table 1, entries 7 and 8). Finally, the control experiment clearly demonstrated the indispensability of the rhodium catalyst, without which, no reaction occurred (Table 1, entry 9).

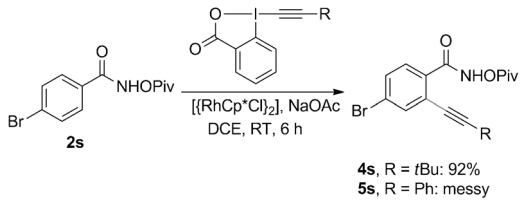
Having obtained the optimal reaction conditions, the generality of the amide coupling partner was investigated, and the results are summarized in Scheme 2. In general, this reaction showed extremely high reaction efficiency with diversified functionalities ranging from electron-withdrawing to electron-releasing ones, thus affording the desired alkynylation products in high to excellent yield. Specifically, electron-donating groups such as alkyl, methoxy, trimethylsilyl, and even oxidative labile methylsulfanyl were all well tolerated. When the *ortho*-methyl-containing substrate **2c** was employed, the desired product **3c** was isolated in 67% yield, and is attributed to the distorted coplanar geometry arising from the steric repulsion which weakens the interaction between the rhodium catalyst and proximate aromatic C–H bond. When substrates holding *meta* substituents were employed, the reaction tended to occur at a sterically more accessible site to avoid the steric congestion (**3d**, **3e**, **3k**, **3t**). Interestingly, when the *meta*-methoxy-substituted amide **2h** was submitted to the optimal reaction conditions, the two regioisomeric products **3h** and **3h′** were produced in 54 and 33% yield, respectively, thus highlighting the coordination effect of the methoxy substituent (**3d** versus **3h**/**3h′**) in stabilizing the aryl rhodium intermediate. Furthermore,



Scheme 2. Reaction scope of amide derivatives. Unless otherwise noted, the reactions were carried out at room temperature using **2** (0.1 mmol), **1** (0.11 mmol), NaOAc (0.1 mmol), and [{RhCp*Cl$_2$}$_2$] (0.002 mmol) in DCE (0.5 mL) for 12 h. Yield of isolated products are given. [a] Reaction time 6 h.

biphenyl and naphthalyl substrates (**2j**,**k**) also worked nicely to afford the desired product in excellent yield. Substrates containing electron-withdrawing substituents such as NO_2, CF_3, Ac, and CN all participated in this reaction. Notably, heterocycles such as pyridine, furan, and indole were also effective substrates and compatible with these reaction conditions. The compound **2p** is much more intriguing considering that the pyridine moiety exhibits a strong chelation effect to the rhodium catalyst. What also needs to be mentioned is that when **2p** and **2q** were subjected to the optimized reaction conditions, the corresponding alkynylation reactions tended to occur at the site of the more acidic proton. This phenomenon suggested that such C–H alkynylation may proceed through a concerted metallation–deprotonation pathway. As was expected, the halogens Cl, Br, and even I, were all nicely tolerated under these reaction conditions, thus providing the opportunity for further manipulation through traditional cross-coupling reactions.[13] In addition, the alkyne-containing substrate **2u** successfully engaged in such transformations for the synthesis of dialkynyl benzene derivatives, but the product **3u** was isolated in moderate yield by using a shorter the reaction time.[14] It is worth mentioning that this C–H alkynylation reaction was scalable and a comparable yield was obtained when the reaction was conducted on a gram scale.[15]

To evaluate the generality and limitations of the hypervalent alkynyl iodine reagents, *tert*-butyl- and phenyl-based alkynylation reagents were tested using **2s** as the model substrate (Scheme 3). It was pleasing to observe that when

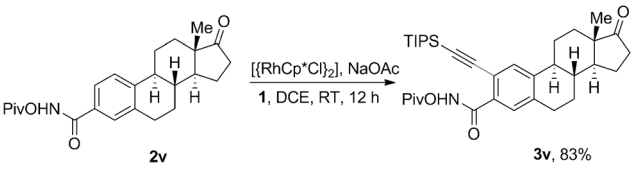


Scheme 3. C–H alkynylation using *tert*-butyl and phenyl ethynyl benziodoxolones.

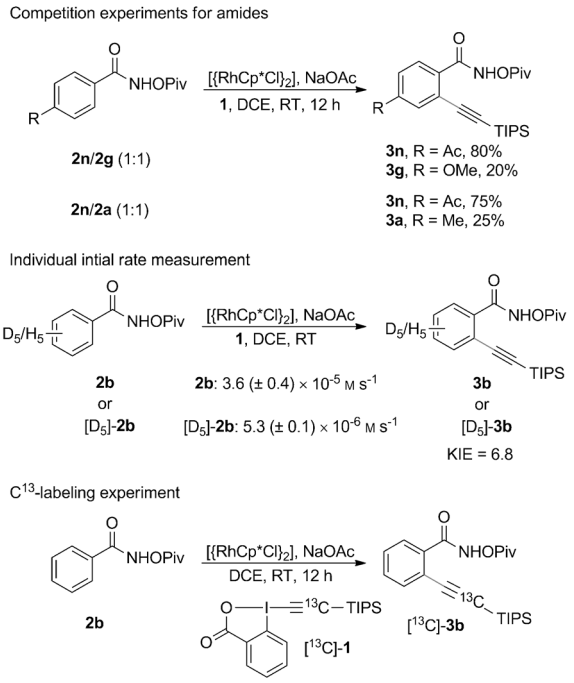
tert-butyl-substituted ethynyl benziodoxone was employed, the reaction proceeded smoothly to afford the desired product **4s** in 92% yield. However, when phenyl-substituted reagent was used, the reaction turned out to be rather messy and none of the desired **5s** could be obtained.

To further showcase the applicability of this protocol to the synthesis of natural products or related complex molecules, the estrone-derived substrate **2v** was synthesized and subjected to the optimized reaction conditions (Scheme 4). The reaction proceeded smoothly to afford the desired alkynylation product **3v** in 83% yield.

To further determine the electronic bias of the C–H activation step, competition experiments using **2n**/**2g** and **2n**/**2a** were examined (Scheme 5). When an equimolar mixture of **2n**, **2g**, and **1** were subjected to the optimized reaction conditions, the desired products **3n** and **3g** were formed in 80 and 20% yield, respectively.[16] Similarly, the competition



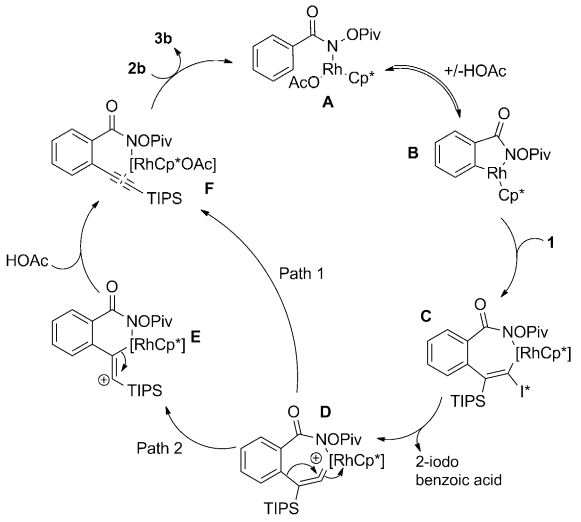
Scheme 4. C–H alkynylation of an estrone derivative.



Scheme 5. Mechanistic studies.

reaction between **2n** and **2a** afforded the desired products **3n** and **3a** in 75 and 25% yield, respectively. These experiments clearly demonstrate that electronically-deficient arenes are more favored in the C–H activation step of this reaction, thus ruling out the electrophilic aromatic substitution pathway. To determine whether the C–H activation is involved as the rate-determining step in the catalytic cycle, an intermolecular KIE experiment was conducted with **2b** and [D_5]-**2b**, and it produced a KIE value of 9.0 (refer to the Supporting Information). Furthermore, the individual initial reaction rate of **2b** or [D_5]-**2b** with **1** was measured and the KIE value was obtained as 6.8.[17] When the ^{13}C-labeled reagent **1** was employed, the reaction of **2b** afforded product [^{13}C]-**3b**, and thud precluded the involvement of a silyl migration step in the catalytic cycle.

Based on the precedent of rhodium-catalyzed C–H activation involving regioselective insertion of unsymmetrical alkynes, the reaction mechanism was tentatively proposed as shown in Scheme 6.[18] The reaction starts with base-assisted ligand exchange of the rhodium catalyst and **2b** to generate the intermediate **A**, which undergoes reversible C–H bond activation through a concerted metalation-deprotonation (CMD) pathway to afford the rhodacycle **B**.[19] The following regioselective carborhodation of **1** occurs to produce **C**, which



Scheme 6. Proposed reaction mechanism.

further undergoes α-elimination to generate the rhodium vinylidene **D**, accompanied by the extrusion of 2-iodobenzoic acid.[7a,d,20,22] Subsequently, intramolecular concerted 1,2-aryl migration[21] and heterolytic cleavage of the C–Rh bond allows generation of the intermediate **F** (Fritsch–Buttenberg–Wiechell-type rearrangement, Path 1).[22] Alternatively, **D** could follow stepwise migration and elimination via **E** to arrive at the same intermediate **F** (Path 2). Finally, protonation of **F** with another molecule of **2b** delivered the desired alkynylation product with concomitant regeneration of **A**. It needs to be noted that carborhodation with reversed alkyne selectivity followed by β-elimination could also account for the generation of the product **3b** and cannot be firmly excluded at this stage.

In conclusion, we have reported the first example of hypervalent-rhodium-catalyzed C–H alkynylation as an electronically reversed Sonogashira coupling by taking advantage of the recyclable reagent **1** as the alkynyl source. This reaction shows extremely high efficiency in furnishing only the monoalkynylated products in excellent yields under very mild reaction conditions. The tolerance of this method to a variety of synthetically useful functional groups also makes this protocol a powerful tool for the late-stage functionalization of complex molecules.

Experimental Section

An oven-dried 5 mL round-bottomed flask was charged with the hypervalent alkynyl iodine regent **1** (47 mg, 0.11 mmol), **2a** (23.5 mg, 0.1 mmol), [{RhCp*Cl_2}$_2$] (1.2 mg, 0.002 mmol), and NaOAc (8.2 mg, 0.1 mmol) in sequence, with subsequent addition of anhydrous DCE (0.5 mL) by syringe. After stirring at room temperature for 12 h, saturated sodium bicabonate was added and the resulting mixture was extracted with dichloromethane (2 × 20 mL). Removal of the solvent in vacuo and purification of the residue by silica gel column chromatography afforded the desired product **3a** (38.3 mg, yield: 92%).

Received: October 22, 2013
Revised: December 19, 2013
Published online: February 7, 2014

Keywords: alkynes · C–H activation · cross-coupling · iodine · rhodium

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[13] The reaction yield of **3s** slightly decreased when **2s** was conducted with prolonged reaction time, the exact reason was not clear at present.

[14] When **2u** was employed for 12 h the reaction turned out to be rather messy, probably because of the side reaction pathway arising from the *para*-phenylethynyl substituent with a prolonged reaction time.

[15] See the Supporting Information for details.

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