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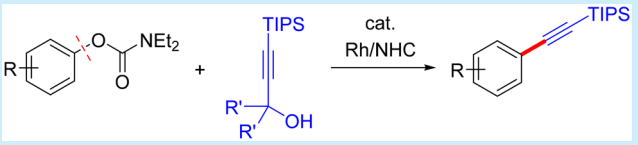
Rhodium-Catalyzed C−O Bond Alkynylation of Aryl Carbamates with Propargyl Alcohols

Kosuke Yasui, Naoto Chatani,* and Mamoru Tobisu*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

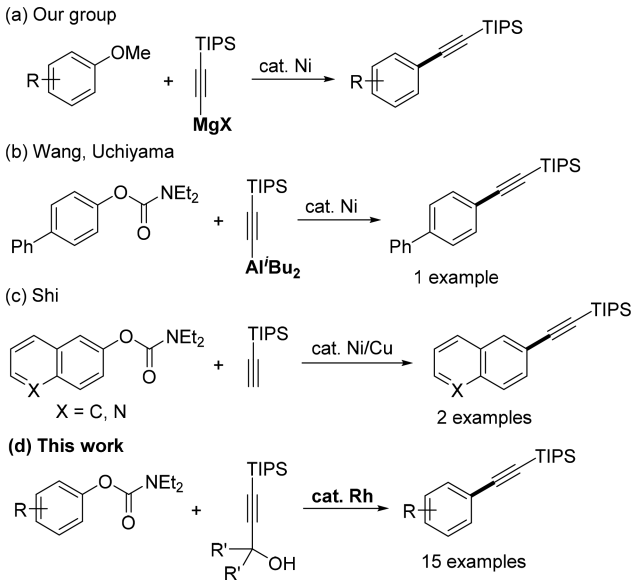
Supporting Information

ABSTRACT: The rhodium-catalyzed alkynylation of aryl carbamates with propargyl alcohols is described. This methodology can provide aryl acetylenes from aryl carbamates via C−O bond activation. The use of propargyl alcohols as alkynylating agents allows the use of a variety of functional groups that are incompatible with organometallic nucleophiles. This reaction also serves to broaden the utility of a carbamate moiety as a convertible *ortho* directing group.



Given the widespread use of aromatic alkynes in organic chemistry, developing methods to synthesize these compounds continues to be a subject of great interest.[1] The Sonogashira-type cross-coupling reaction is among the most powerful methods for the construction of a C(sp)−C(sp^2) bond using aryl halides and terminal alkynes.[2] Considering that phenols are abundant chemical feedstock,[3] it is of great synthetic value to develop catalytic systems that use phenol and its derivatives instead of aryl halides. A classical way to use phenols in cross-coupling reactions is to convert them to aryl triflates, thereby activating the C(aryl)−O bond toward oxidative addition. Despite the synthetic utility of aryl triflates, these reactions can be costly and generate harmful waste derived from the fluorine-based leaving group. Nonfluorinated phenol derivatives such as ethers, esters, and carbamates have recently emerged as a less expensive and more environmentally benign alternative to aryl halides and triflates.[4−7] Although significant progress has been made in the catalytic transformation of inert phenol derivatives, the use of Sonogashira type cross-coupling has had limited success.[5h,8,9] We have previously described a nickel-catalyzed cross-coupling of anisoles with alkynyl Grignard reagents (Scheme 1a),[5h] while Uchiyama developed a nickel-catalyzed alkynylation of aryl carbamates using alkynylaluminum reagents (Scheme 1b).[8] Although these two methods pioneered the Sonogashira-type reaction of inert phenol derivatives, the use of strong organometallic nucleophiles limits functional group compatibility. Shi reported a unique Ni/Cu cocatalytic system that allows the direct use of terminal alkynes in the alkynylation of aryl carbamates, although only two specific substrates were examined, and a detailed investigation was not carried out.[9] In the field of C(aryl)−O bond activation of inert phenol derivatives, the vast majority of the reported reactions use nickel as the catalyst.[4,6] In contrast, we have developed several rhodium catalysts that can activate inert C(aryl)−O bonds.[7] Importantly, the use of rhodium enabled transformations that were not possible with nickel catalysts. For example, the use of rhodium allows cross-coupling with nonorganometallic reagents, such as arenes bearing a directing group,[7d] and isopropanol as a hydride equivalent.[7e]

Scheme 1. Alkynylation of Inert Phenol Derivatives



Mechanistic investigation of the latter reaction revealed that the hydride incorporated at the ipso position of aryl carbamates is derived from the β-hydrogen of the isopropanol and is transferred through β-hydrogen elimination. We envisioned that aryl carbamates would undergo C−O bond alkynylation in the presence of our rhodium catalyst, as propargyl alcohols serve as alkynylating reagents under rhodium(I) catalysis via β-carbon elimination.[10,11] We also expected that a broad range of aryl carbamates could be used by avoiding the use of organometallic alkynylating reagents.

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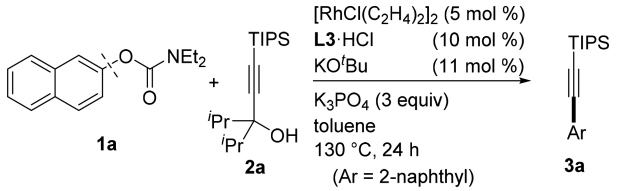
Our study began by optimizing the conditions for the reaction between 2-naphthyl carbamate **1a** and alkynylating reagents **2a**–**2g** in the presence of a rhodium/NHC catalyst. After systematic screening, the target alkynylation product **3a** was formed in 74% isolated yield when **2a** was used as an alkynylating reagent, with **L3** as the ligand and K_3PO_4 as the stoichiometric base (Table 1, entry 1).

The use of terminal alkyne **2b** significantly decreased the yield of **3a** due to the formation of enyne byproducts, which are generated through dimerization of **2b** (entry 2).[12] Propargyl alcohols **2c**, **2d**, and **2e** failed to give **3a** efficiently, again due to the formation of the enyne byproducts (entries 3–5). The use of **2a** completely suppressed the formation of the enyne byproduct, presumably as its bulkiness prevented **2a** from reacting with an alkynylrhodium intermediate. A TIPS protecting group is critical, as evidenced by the lack of a product formed with TMS- and phenyl-substituted derivative **2f** and **2g**, respectively, presumably due to oligomerization of **2f** and **2g** (entries 6 and 7). Despite the limited scope of the propargyl alcohols, the TIPS group can be easily removed from the alkynylated products to give corresponding terminal alkynes, which are amenable to further elaboration (vide infra). Several other bases, such as KOAc, K_2CO_3, and K_2HPO_4, gave inferior yields to that obtained with K_3PO_4 (entries 8–10). NHC ligands with an *N*-mesityl structure (such as **L1** and **L2**) promoted the reaction, with **L3** exhibiting the best activity (entries 11 and 12). Both methyl groups on the imidazole ring and the methoxy groups of **L3** are important for enhancing the catalytic activity. The use of **L4** or **L5**, however, led to a significant reduction in yield of **3a** (entries 13 and 14). Increasing the ratio of the NHC ligand to rhodium to 2:1 did not improve the yield of **3a** (entry 15), which indicated that the catalytically active species generated in situ is the rhodium complex bearing one NHC ligand. The $[RhCl(C_2H_4)(\mathbf{L3})]_2$ species could be observed in the catalyst solution by using ^{13}C NMR and HRMS (see Supporting Information (SI) for details).[13]

With the optimized reaction conditions in hand, the scope of the aryl carbamates was evaluated next (Scheme 2). Aryl carbamates **1b** and **1c** underwent alkynylation without affecting

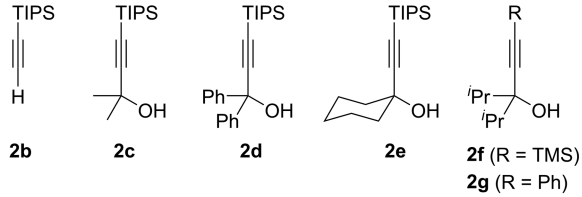
Table 1. Optimization of the Reaction Conditions[a]



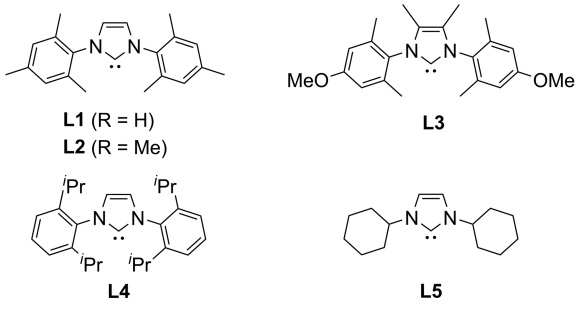
entry	variation from above	GC yields [%] 3a	1a	2
1	none	75 (74)	0	0
2	**2b** instead of **2a**	18	12	trace
3	**2c** instead of **2a**	35	15	0
4	**2d** instead of **2a**	25	9	trace
5	**2e** instead of **2a**	22	7	0
6	**2f** instead of **2a**	0	64	0
7	**2g** instead of **2a**	0	>95	0
8	KOAc instead of K_3PO_4	23	39	0
9	K_2CO_3 instead of K_3PO_4	47	trace	0
10	K_2HPO_4 instead of K_3PO_4	28	trace	0
11	**L1** instead of **L3**	20	3	0
12	**L2** instead of **L3**	53	2	0
13	**L4** instead of **L3**	trace	68	0
14	**L5** instead of **L3**	12	47	trace
15	2.0 equiv of **L3**	73	0	0
16	$[RhCl(cod)]_2$ instead of $[RhCl(C_2H_4)_2]_2$	trace	>95	>95

[a]Conditions: $[RhCl(C_2H_4)_2]_2$ (0.015 mmol), **L**·HCl (0.030 mmol), KO^{t}Bu (0.033 mmol), base (0.90 mmol), **1** (0.30 mmol) and **2** (0.45 mmol) in toluene (1.0 mL) at 130 °C for 24 h. Yield in parentheses is isolated yield.

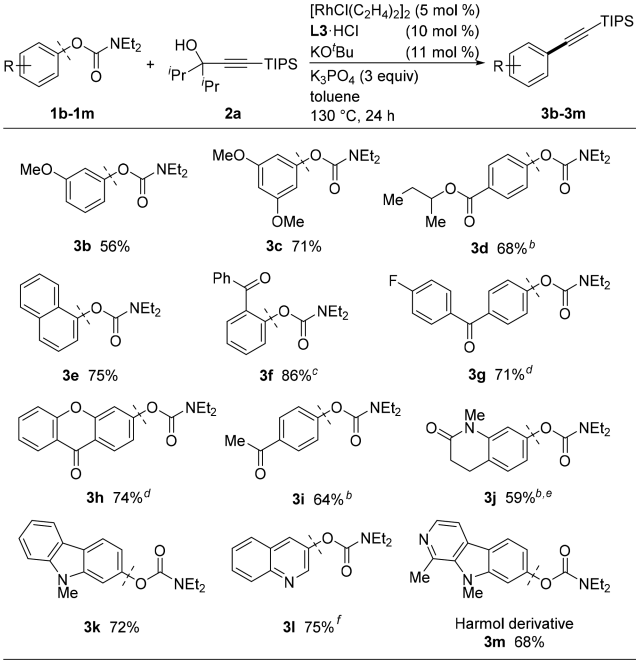
Variety of alkynes



Variety of NHC ligands



Scheme 2. Reaction Scope[a]



[a]Conditions: $[RhCl(C_2H_4)_2]_2$ (0.015 mmol), **L3**·HCl (0.030 mmol), KO^{t}Bu (0.033 mmol), K_3PO_4 (0.90 mmol), **1** (0.30 mmol), and **2c** (0.45 mmol) in toluene (1.0 mL) at 130 °C for 24 h. Isolated yields of alkynylated products are shown. [b]Reacted at 120 °C. [c]**L5**·HCl (0.030 mmol) was used instead of **L3**·HCl. [d]At 110 °C. [e]$[RhCl(C_2H_4)_2]_2$ (0.023 mmol), **L3**·HCl (0.045 mmol), and KO^{t}Bu (0.050 mmol) were used. [f]At 140 °C.

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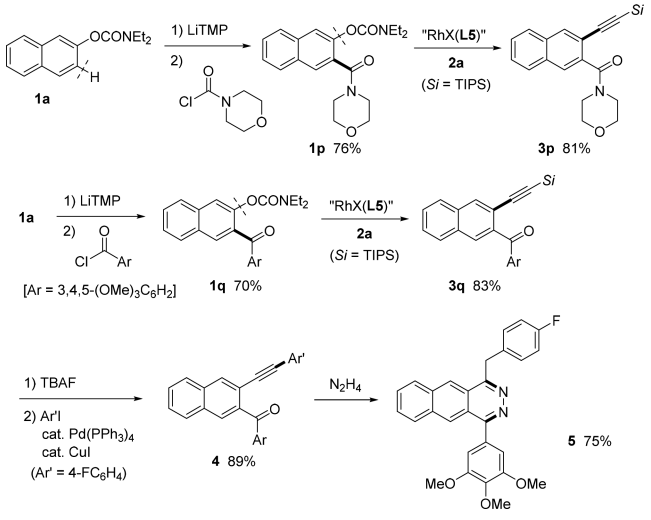
the methoxy group, which can be reactive with nickel catalysts.[5g] The use of **2a** as an alkynylating reagent allows the use of aryl carbamates bearing a carbonyl functional group, such as esters (**1d**), ketones (**1f**–**1i**), and amides (**1j**), which are incompatible with organometallic alkynylating reagents. Although nickel-catalyzed α-arylations of ketones and amides using aryl esters as an aryl donor have been reported,[14] this rhodium system did not produce such an α-arylation product, even when aryl carbamates bearing an enolizable ketone (**1i**) and amide (**1j**) were used. Sterically hindered 1-naphthyl carbamate **1e** provided the corresponding alkynylated product in 75% yield. In addition, the use of more sterically congested *ortho* benzoyl carbamate **1f** was also possible by using smaller ligand **L5**.[15] In this transformation, a carbamate bearing a fluorine (**1g**) is also compatible, whereas C–F bonds often react in nickel-catalyzed cross-couplings of inert phenol derivatives.[5h,16] Moreover, heteroaromatic carbamates, such as carbazole **1k** and quinoline **1l**, successfully afforded the corresponding alkynylated products. This catalytic system could be used for the derivatization of biologically active phenol compounds, as exemplified by the synthesis of alkynylated Harmol **3m**.[17,18]

Because a carbamoyl group is known to be a powerful *ortho* directing group in arene functionalization reactions,[19] *ortho*-substituted aryl alkynes can readily be accessed via an *ortho* C–H functionalization/*ipso* alkynylation sequence of simple aryl carbamates. For example, *ortho* lithiation of **1a** by LiTMP, followed by reaction with carbamoyl chloride, forms carbamate **1p**, which can be converted into alkyne **3p** (Scheme 3).

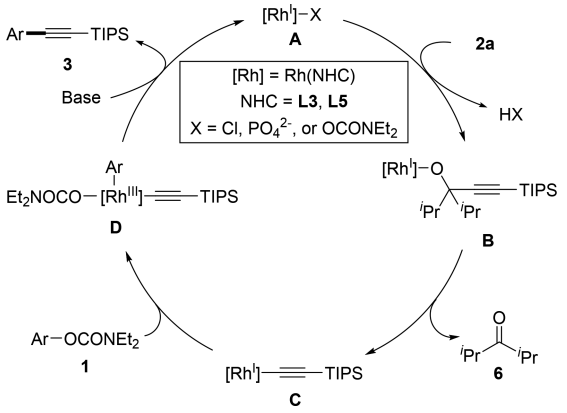
Scheme 3. Synthetic Applications



Similarly, *ortho*-acylated aromatic alkyne **3q** was successfully synthesized in a straightforward manner. Although our method requires the use of TIPS-protected propargyl alcohols, the TIPS group in the product can be easily removed and replaced with a different group via the established methods. For example, deprotection of **3q**, followed by arylation under Sonogashira conditions afforded diaryl alkyne **4**. It should also be noted that the resulting *ortho* acylated aromatic alkynes are valuable precursors of a range of heterocycles.[20] For example, the reaction of **4** with hydrazine led to the construction of a phthalazine skeleton,[21] which can further serve as a diene component in aza Diels–Alder reactions.[22]

A plausible mechanism for this transformation is shown in Scheme 4. Initially, rhodium complex **A** is generated *in situ* and

Scheme 4. Possible Mechanism



reacts with propargyl alcohol **2** to form rhodium alkoxide **B**. β-Carbon elimination of **B** then forms alkynylrhodium **C**, releasing ketone **6**. The formation of intermediate **C** is supported by the isolation and X-ray analysis of analogous alkynylrhodium complexes.[11g,23] Intermediate **C** mediates the oxidative addition of the C–O bond in aryl carbamate **1** to form rhodium(III) intermediate **D**, which provides the alkynylated product **3** via reductive elimination with regeneration of the catalyst.

In summary, we have developed a rhodium-catalyzed alkynylation of aryl carbamates using propargyl alcohols as the alkynylating agents. The use of propargyl alcohols allows this inert C–O bond alkynylation to be compatible with a range of functional groups, such as ketones, esters, and amides, which are incompatible with previously reported cross-couplings using organometallic nucleophiles. This alkynylation method enables the use of a carbamate directing group as a handle for the synthesis of functionalized aromatic alkynes, which serve as useful building blocks in organic synthesis. Further studies investigating the catalytic transformation of inert bonds using a rhodium/NHC system are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00674.

Detailed experimental procedures and characterization of products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: chatani@chem.eng.osaka-u.ac.jp.
*E-mail: tobisu@chem.eng.osaka-u.ac.jp.

ORCID

Naoto Chatani: 0000-0001-8330-7478
Mamoru Tobisu: 0000-0002-8415-2225

Notes

The authors declare no competing financial interest.

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(18) Notes: (a) 2-Napthyl pivalate also underwent this alkynylation to form **3a** in 68% yield under the typical conditions shown in Scheme 2. (b) Alkynylation of phenyl carbamate did not proceed efficiently (ca.10% yield). (c) Although we routinely generate **L3** by pretreatment of **L3·HCl** with KO^{t}Bu, a similar result can be obtained when the reaction was performed in the absence of KO^{t}Bu.

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