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Rhodium Thiavinyl Carbenes from 1,2,3-Thiadiazoles Enable Modular Synthesis of Multisubstituted Thiophenes

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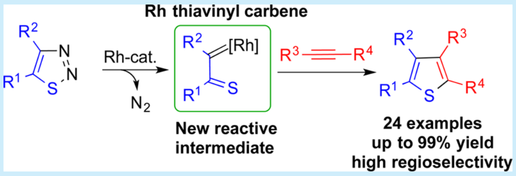
Ⓢ *Supporting Information*

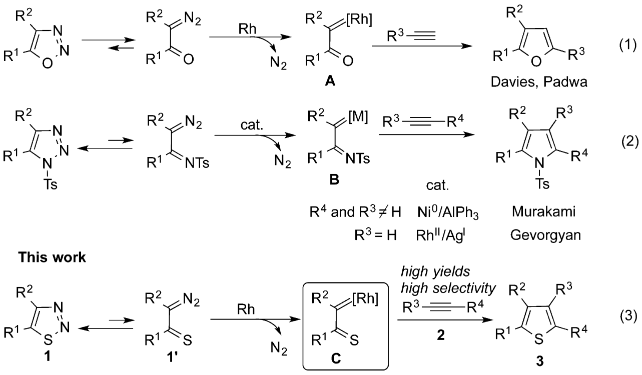
ABSTRACT: The rhodium-catalyzed transannulation reaction between 1,2,3-thiadiazoles and alkynes, proceeding via intermediacy of the previously unknown Rh thiavinyl carbene, toward a highly efficient and regioselective synthesis of up to fully substituted thiophenes is described.



α-Carbonyl-derived metal carbenes are versatile synthetic intermediates employed in a wide variety of organic transformations,[1] including heterocyclization reactions. Among these, Rh oxavinyl carbene **A**, originated from diazocarbonyl compound,[2] a stable open-chain tautomer of 1,2,3-oxadiazole,[3] was efficiently utilized by Davies[4a,b] and Padwa[4c−e] in annulation with alkynes toward furans (Scheme 1, eq 1). More recently, it has been reported that *N*-tosyldiazoimine, a minor open-chain tautomer of *N*-tosyl-1,2,3-triazole,[5] can be trapped by transition metals to form azavinyl carbene **B**. The latter has received increased attention as a highly useful precursor for a variety of organic transformations,[6−8] including cycloaddition with alkynes to form a pyrrole ring, as shown by Murakami[7b] (M = Ni) and our group[7c] (M = Rh) (eq 2). Herein, we report the first efficient generation of Rh thiavinyl carbene **C** from 1,2,3-thiadiazole **1** that can undergo regioselective annulation reaction with alkynes to produce thiophenes **3** in good to excellent yields (eq 3).

A 1,2,3-thiadiazole core is a great source of highly reactive intermediates used in the formation of a variety of acyclic and cyclic sulfur-containing compounds,[9] including thiophenes. However, the reported methods for synthesis of thiophenes from 1,2,3-thiadiazoles suffer a limited scope of reactive alkynes and 1,2,3-thiadiazoles, harsh reaction conditions, lack of regioselectivity, and low efficiency (Scheme 2). Hence, α-diazothione **1′**,[10] in the presence of stoichiometric amounts of strong base, decomposes into alkynethiolate (eq 4).[11] The latter, upon [3 + 2] cycloaddition with activated alkynes, leads to the

Scheme 1. Transition-Metal-Catalyzed Transannulation Reactions of Azoles



Scheme 2. Reported Syntheses of Thiophenes from 1,2,3-Thiadiazoles

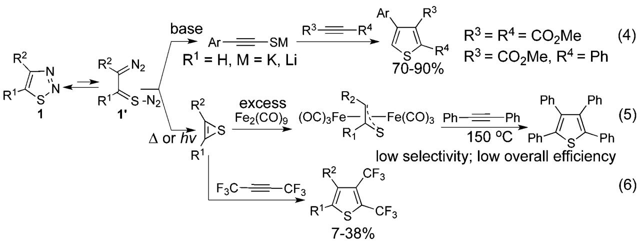
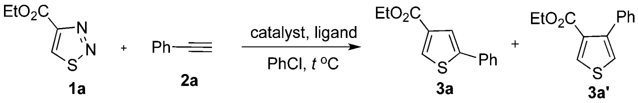


Table 1. Optimization of Transannulation Reaction of 1,2,3-Thiadiazoles with Alkynes[a]



no.	cat. (2 mol %)	ligand (5 mol %)	*t* (°C)	time (h)	yield[b] (%) (ratio 3a:3a′)
1	$Rh_2(Oct)_4$		130	15	1 (1:1)
2	$[Rh(COD)Cl]_2$		130	12	5 (only 3a)
3	$[Rh(COD)Cl]_2$	Josiphos	130	12	70[c] (10:1)
4	$[Rh(COD)Cl]_2$	DPPF	130	0.1	98 (19.0:1)
5	$\mathbf{[Rh(COD)Cl]_2}$	**DPPF**	**60**	**7**	**100 (43.6:1)**
6	$Rh(PPh_3)_3Cl$[d]	DPPF	130	12	81 (7.4:1)
7	$RhCl_3{\cdot}H_2O$[d]	DPPF	130	3	100 (16.7:1)
8	$Rh_2(Oct)_4$	DPPF	130	15	1 (0.4:1)

[a] The reactions were run on 0.1 mmol in PhCl (1 M) under inert atmosphere. [b] The yield and ratio were determined by GC−MS with pentadecane as internal standard. [c] Isolated yield (ratio was determined by NMR). [d] 4 mol % of catalyst has been used.

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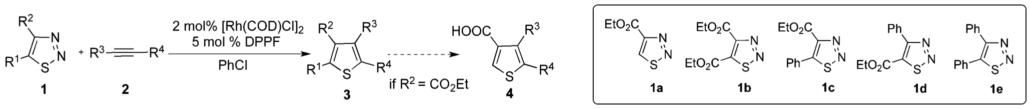
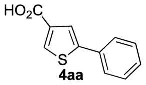
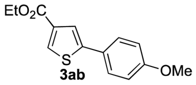
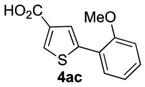
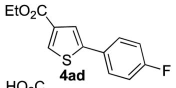
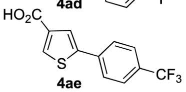
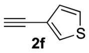
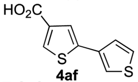
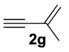
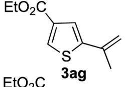
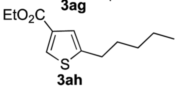
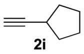
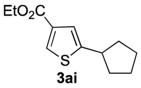
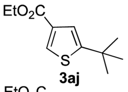
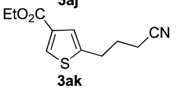
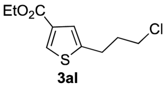
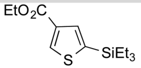
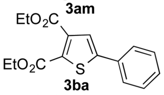
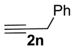
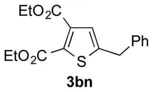
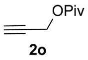
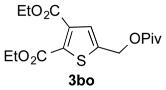
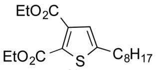
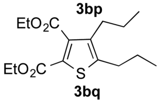
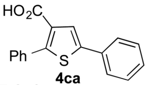
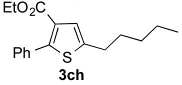
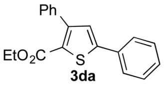
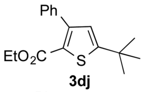
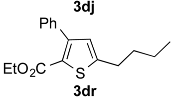
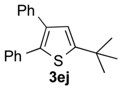
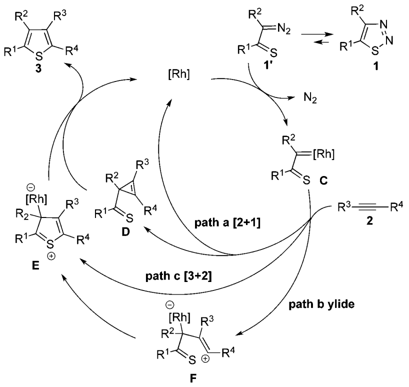
Table 2. Synthesis of Thiophenes via Rh-Catalyzed Transannulation of 1,2,3-Thiadiazoles with Alkynes[a]



no.	1	2	3(or 4)	t (°C)/ time (h)	yield[b] (%)
1	**1a**	≡—Ph **2a**	 **4aa**	60/7	98[c]
2	**1a**	≡—C_6H_4p-OMe **2b**	 **3ab**	60/7	82
3	**1a**	≡—C_6H_4o-OMe **2c**	 **4ac**	60/12	62[c]
4	**1a**	≡—C_6H_4p-F **2d**	 **4ad**	80/5	92[c]
5	**1a**	≡—C_6H_4p-CF_3 **2e**	 **4ae**	80/12	57[c]
6	**1a**	 **2f**	 **4af**	80/12	67[c,d]
7	**1a**	 **2g**	 **3ag**	80/12	95
8	**1a**	≡—C_5H_{11} **2h**	 **3ah**	80/7	94[d]
9	**1a**	 **2i**	 **3ai**	80/4	92[d]
10	**1a**	≡—^{t}Bu **2j**	 **3aj**	80/5	88
11	**1a**	≡—C_3H_6CN **2k**	 **3ak**	80/7	75
12	**1a**	≡—C_3H_6Cl **2l**	 **3al**	80/7	98[d]
13	**1a**	≡—$SiEt_3$ **2m**	 **3am**	60/7	73
14	**1b**	**2a**	 **3ba**	60/0.5	96
15	**1b**	 **2n**	 **3bn**	80/1	82
16	**1b**	 **2o**	 **3bo**	80/1	96
17	**1b**	≡—C_8H_{17} **2p**	 **3bp**	60/7	90
18	**1b**	C_3H_7—≡—C_3H_7 **2q**	 **3bq**	130/24	58
19	**1c**	**2a**	 **4ca**	60/0.5	81[c]
20	**1c**	**2h**	 **3ch**	60/7	99
21	**1d**	**2a**	 **3da**	60/7	84
22	**1d**	**2j**	 **3dj**	80/5	75
23	**1d**	≡—C_4H_9 **2r**	 **3dr**	60/7	97[e]
24	**1e**	**2j**	 **3ej**	80/2	80

[a]Reactions conditions: **1** (0.25 mmol), **2** (0.5 mmol, 2 equiv), $[Rh(COD)Cl]_2$ (0.005 mmol, 2 mol %), DPPF (0.0125 mmol, 5 mol %), chlorobenzene (1 M), inert atmosphere. [b]Isolated yield. [c]Reactions were performed on 0.5 mmol scale. [d]Ratio of regioisomers ≥20:1. [e]Ratio of regioisomers 11:1.

Scheme 3. Plausible Pathways for Rh-Catalyzed Transannulation of 1,2,3-Thiadiazoles with Alkynes



corresponding trisubstituted thiophenes.[12] Alternatively, upon heating with over stoichiometric amounts of $Fe_2(CO)_9$, 1,2,3-thiadiazoles are believed to release dinitrogen to produce thiirene species, which are captured by $Fe_2(CO)_9$ to give the thiavinyl carbene complex in low yields and regioselectivity.[13] It has been reported[13c] that one of these symmetric carbene complexes could undergo cycloaddition with diphenylacetylene toward tetraphenylthiophene (eq 5). The formation of thiirene has also been postulated upon photolytic decomposition of **1**, which in the presence of hexafluoro-2-butyne led to formation of notable amounts of the corresponding thiophene (eq 6).[14]

We hypothesized that if the generation of a putative Rh thiavinyl carbene[15] **C** from 1,2,3-thiadiazole **1** is possible, it could potentially become a useful intermediate for a number of transformations, including the annulation reaction with alkynes toward thiophenes **3**.[16] To this end, we examined a possible transannulation reaction of 1,2,3-thiadiazole-4-carboxylate **1a** with phenylacetylene (Table 1). Initially, Rh(II) complex, efficiently employed in the formation of Rh oxavinyl carbene **A**[4] and Rh azavinyl carbene **B**,[6] has been tested in this transformation. However, the starting thiadiazole decomposed under these conditions (entry 1). Employment of Rh(I) complex,[17] however, produced a 5% of thiophene **3a** (entry 2). Gratifyingly, addition of Josiphos ligand led to a dramatic improvement of the reaction outcome *producing thiophene **3a** in isolated 70% yield* in 10:1 ratio with its minor regioisomer **3a′** (entry 3). Other bulky bidentate ligands tested were efficient but less selective.[18] DPPF appeared to be a superior ligand for this reaction both in terms of reactivity and selectivity, quickly producing **3a** in a nearly quantitative yield and excellent regioselectivity (entry 4). Decreasing the reaction temperature to 60 °C allowed for further improvement of the selectivity, though the reaction required 7 h for completion (entry 5). Wilkinson's catalyst was less efficient in this reaction (entry 6). Interestingly, employment of Rh(III)[19] catalyst in a combination with DPPF was also efficient, though less selective (entry 7). Notably, Rh(II) complex while combined with DPPF ligand still did not show substantial improvement (entry 8).

With the best optimized conditions in hand, the scope of this novel transannulation reaction has been examined (Table 2). First, the reaction of ethyl-1,2,3-thiadiazole-4-carboxylate (**1a**) with different alkynes has been tested. It was found that arylalkynes possessing *p*-MeO (**2b**), *o*-MeO (**2c**), *p*-F (**2d**), and *p*-CF_3 (**2e**) groups underwent a smooth transannulation reaction with **1a** to produce thiophenes **3** in a good yield with complete regiocontrol. Notably, electron-defficient aryl alkynes **2d**,**e** were less reactive compared to their more electron-rich analogs **2a**−**c** (entries 1−5). Heterylalkyne **2f** and enyne **2g** reacted uneventfully (entries 6−7). It deserves mention that some of the produced carbethoxy thiophenes were not easily separable from the byproducts of alkyne trimerization; therefore, these thiophenes were isolated as the corresponding acids **4** after hydrolysis. Importantly, primary (**2h**), secondary (**2i**), and tertiary (**2j**) alkylacetylenes (entries 8−10) underwent transannulation with **1a** at 80 °C with high yields and regioselectivities. Alkylacetylenes possessing functional groups at the side chain, including cyano (**2k**) and chloro (**2l**) substituents, as well as (triethylsilyl)acetylene (**2m**), successfully reacted with **1a** to produce the corresponding 2,4-disubstituted thiophenes in good yields (entries 11−13).

Next, the scope of 1,2,3-thiadiazoles (Table 2, **1b**−**e**) was examined. All of these compounds appeared to be competent substrates in the transannulation reaction, revealing the following reactivity trend toward **2a**: **1c** > **1b** > **1d** > **1e** ≥ **1a**. Hence, reactions of **1b** and **1c** were completed in 30 min only, producing the corresponding thiophenes in high yields (entries 14 and 19). Likewise, the reactions of **1b** and **1c** with alkylacetylenes (**2n**-**p**,**h**) were completed in just 1 h at 80 °C (entries 15, 16) or in 7 h at 60 °C (entries 17, 20). Moreover, 1,2,3-thiadiazole **1b** was able to react with internal alkyne **2q** to produce the fully substituted thiophene **2bq** in a reasonable yield (entry 18). 1,2,3-Thiadiazoles **1d** and **1e** possessing a phenyl group at the C-4 position also underwent transannulation with aryl- (**2a**) and alkylacetylenes (**2j**,**r**) to give the corresponding thiophenes with good yields (entries 21−24).

Modular two-component cycloaddition of various thio-containing substrates with alkynes is one of the most efficient approaches toward construction of the thiophene ring.[20] The transannulation protocol developed herein can serve as a new complementary method toward thiophenes, and it also features several advantages over the existing methods, such as employment of easily available and stable thiadiazoles and a wider scope of alkynes. For instance, both terminal and internal alkynes possessing important functional groups could be efficiently employed in this transannulation reaction toward densely substituted and functionalizable thiophenes.

We propose the following plausible pathways for this new transannulation reaction (Scheme 3). First, the rhodium carbene species **C** is generated upon the denitrogenative reaction of Rh with the open form of 1,2,3-thiadiazole **1′**. A [2 + 1] cycloaddition of **C** with alkyne (path a) would lead to cyclopropene intermediate **D**, which then cycloisomerizes[21] into thiophene **3**. On the other hand, **C** may undergo a nucleophilic attack by alkyne (path b) to produce an ylide **F**, which then cyclizes into zwitterion **E**.[22] Alternatively, the latter can form via a direct [3 + 2] cycloaddition of **C** with **2** (path c).[23] A release of Rh catalyst from **E** produces reaction product, thiophene **3**. Apparently, the observed higher reactivity of electron-rich alkynes fits the ylide mechanism well (path b). On the other hand, based on the observed high regioselectivity of the process, we tentatively consider path a as less likely. Unmistakably, more detailed studies are required to establish the precise mechanism for this transformation.

In summary, we have demonstrated for the first time that reactive Rh thiavinyl carbene species can be effectively generated from 1,2,3-thiadiazoles. Useful analogues of the widely known Rh oxa- and -azavinyl carbenes, Rh thiavinyl carbenes enabled a new modular approach for the construction of a multisubstituted thiophene ring by transannulation of 1,2,3-thiadiazoles with alkynes. The developed method features a wide scope and high efficiency and selectivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00541.

Experimental details, characterization data for the products, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to the memory of Prof. Alexander Butin.

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