

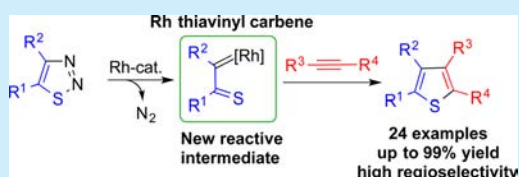
Rhodium Thiavinyl Carbenes from 1,2,3-Thiadiazoles Enable Modular Synthesis of Multisubstituted Thiophenes

Daria Kurandina and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7061, United States

S Supporting Information

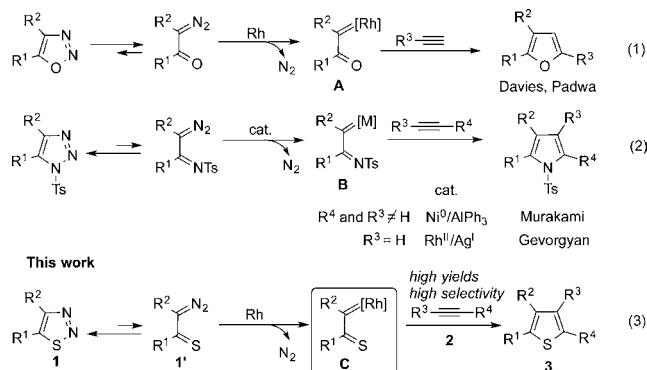
ABSTRACT: The rhodium-catalyzed transannulation reaction between 1,2,3-thiadiazoles and alkynes, proceeding via intermediacy of the previously unknown Rh thiavinyl carbene, toward a highly efficient and regioselective synthesis of up to fully substituted thiophenes is described.



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

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



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

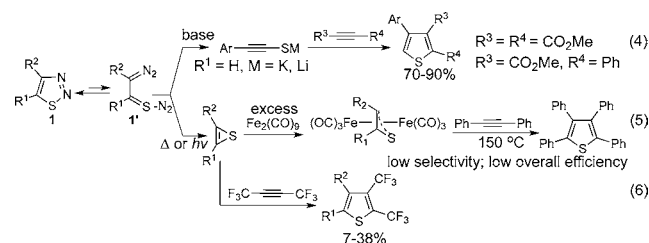


Table 1. Optimization of Transannulation Reaction of 1,2,3-Thiadiazoles with Alkynes^a

no.	cat. (2 mol %)	ligand (5 mol %)	<i>t</i> (°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	[Rh(COD)Cl] ₂	DPPF	60	7	100 (43.6:1)
6	Rh(PPh ₃) ₃ Cl ^d	DPPF	130	12	81 (7.4:1)
7	RhCl ₃ ·H ₂ O ^d	DPPF	130	3	100 (16.7:1)
8	Rh ₂ (Oct) ₄	DPPF	130	15	1 (0.4:1)

^aThe reactions were run on 0.1 mmol in PhCl (1 M) under inert atmosphere. ^bThe yield and ratio were determined by GC–MS with pentadecane as internal standard. ^cIsolated yield (ratio was determined by NMR). ^d4 mol % of catalyst has been used.

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

Received: February 25, 2016

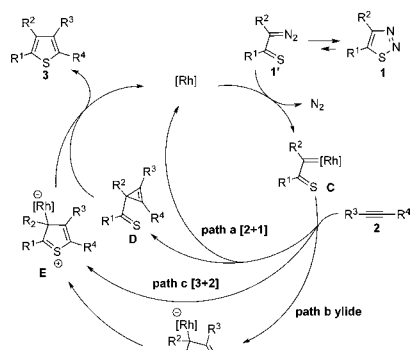
Published: March 25, 2016

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

no.	1	2	3 (or 4)	<i>t</i> (°C)/ time (h)	yield ^b (%)	no.	1	2	3 (or 4)	<i>t</i> (°C)/ time (h)	yield ^b (%)
1	1a	≡Ph 2a	HO ₂ C-4-phenylthiophene 4aa	60/7	98 ^c	13	1a	≡SiEt ₃ 2m	EtO ₂ C-4-(SiEt ₃)thiophene 3am	60/7	73
2	1a	≡C ₆ H ₄ p-OMe 2b	EtO ₂ C-4-(4-methoxyphenyl)thiophene 3ab	60/7	82	14	1b	2a	EtO ₂ C-4-phenylthiophene 3ba	60/0.5	96
3	1a	≡C ₆ H ₄ o-OMe 2c	HO ₂ C-4-(4-methoxyphenyl)thiophene 4ac	60/12	62 ^c	15	1b	≡Ph 2n	EtO ₂ C-4-phenylthiophene 3bn	80/1	82
4	1a	≡C ₆ H ₄ p-F 2d	EtO ₂ C-4-(4-fluorophenyl)thiophene 4ad	80/5	92 ^c	16	1b	≡OPiv 2o	EtO ₂ C-4-(4-isopropoxyphenyl)thiophene 3bo	80/1	96
5	1a	≡C ₆ H ₄ p-CF ₃ 2e	HO ₂ C-4-(4-(trifluoromethyl)phenyl)thiophene 4ae	80/12	57 ^c	17	1b	≡C ₈ H ₁₇ 2p	EtO ₂ C-4-(4-octylphenyl)thiophene 3bp	60/7	90
6	1a	≡2-furyl 2f	HO ₂ C-4-(2-furyl)thiophene 4af	80/12	67 ^{c,d}	18	1b	C ₃ H ₇ -≡-C ₃ H ₇ 2q	EtO ₂ C-4-(4-ethylphenyl)thiophene 3bq	130/24	58
7	1a	≡2-methyl-2-butynyl 2g	EtO ₂ C-4-(4-methylphenyl)thiophene 3ag	80/12	95	19	1c	2a	HO ₂ C-4-phenylthiophene 4ca	60/0.5	81 ^c
8	1a	≡C ₈ H ₁₁ 2h	EtO ₂ C-4-(4-octylphenyl)thiophene 3ah	80/7	94 ^d	20	1c	2h	Ph-4-octylthiophene 3ch	60/7	99
9	1a	≡cyclopentyl 2i	EtO ₂ C-4-(4-cyclopentylphenyl)thiophene 3ai	80/4	92 ^d	21	1d	2a	Ph-4-phenylthiophene 3da	60/7	84
10	1a	≡t-Bu 2j	EtO ₂ C-4-(4-tert-butylphenyl)thiophene 3aj	80/5	88	22	1d	2j	Ph-4-tert-butylthiophene 3dj	80/5	75
11	1a	≡C ₃ H ₆ CN 2k	EtO ₂ C-4-(4-cyanophenyl)thiophene 3ak	80/7	75	23	1d	≡C ₄ H ₉ 2r	Ph-4-nonylthiophene 3dr	60/7	97 ^e
12	1a	≡C ₃ H ₆ Cl 2l	EtO ₂ C-4-(4-chlorophenyl)thiophene 3al	80/7	98 ^d	24	1e	2j	Ph-4-tert-butylthiophene 3ej	80/2	80

^aReactions 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. ^bIsolated yield. ^cReactions were performed on 0.5 mmol scale. ^dRatio of regioisomers ≥20:1. ^eRatio 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 Fe₂(CO)₉, 1,2,3-thiadiazoles are believed to release dinitrogen to produce thiirene species, which are captured by Fe₂(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 **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*-CF₃ (**2e**) groups underwent a smooth transannulation reaction with **1a** to produce thiophenes **3** in a good yield with complete regiocontrol. Notably, electron-deficient aryl alkynes **2d,e** were less reactive compared to their more electron-rich analogs **2a–c** (entries 1–5). Heteroalkyne **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 cycloisomerizes²¹ 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)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vlad@uic.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank National Science Foundation (CHE-1362541) for financial support of this work. We also thank Dr. Olga Zatolochnaya for initial experiments and fruitful discussions.

■ DEDICATION

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

■ REFERENCES

- (1) For selected reviews on reactivity of transition metal carbenes, see: (a) Timmons, D. J.; Doyle, M. P. *J. Organomet. Chem.* **2001**, 617–618, 98. (b) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, 451, 417. (c) *Modern Rhodium Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005.

- (2) For a review on different transformations of diazocarbonyl compounds, see: Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. *Chem. Rev.* **2015**, *115*, 9981.
- (3) Nguyen, M. T.; Hegarty, A. F.; Elguero, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 713.
- (4) (a) Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343. (b) Davies, H. M. L.; Cantrell, W. R., Jr.; Romines, K. R.; Baum, J. S. *Org. Synth.* **1992**, *70*, 93. (c) Kinder, F. R.; Padwa, A. *Tetrahedron Lett.* **1990**, *31*, 6835. (d) Padwa, A.; Kassir, J. M.; Xu, S. L. *J. Org. Chem.* **1991**, *56*, 6971. (e) Padwa, A.; Kinder, F. R. *J. Org. Chem.* **1993**, *58*, 21.
- (5) For previous reports on the ring-opening of *N*-sulfonyl-1,2,3-triazoles, see: (a) Harmon, R. E.; Stanley, F.; Gupta, S. K.; Johnson, J. J. *Org. Chem.* **1970**, *35*, 3444. (b) Himbert, G.; Regitz, M. *Chem. Ber.* **1972**, *105*, 2963.
- (6) For reviews on reactivity of *N*-sulfonyl-1,2,3-triazoles, see: (a) Gulevich, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2013**, *52*, 1371. (b) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151.
- (7) For transannulation reactions of iminocarbenes derived from *N*-sulfonyl-1,2,3-triazoles, see: (a) Horneff, T.; Chuprakov, S.; Chernyak, N.; Gevorgyan, V.; Fokin, V. V. *J. Am. Chem. Soc.* **2008**, *130*, 14972. (b) Miura, T.; Yamauchi, M.; Murakami, M. *Chem. Commun.* **2009**, 1470. (c) Chattopadhyay, B.; Gevorgyan, V. *Org. Lett.* **2011**, *13*, 3746. (d) Parr, B. T.; Green, S. A.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 4716. (e) Alford, J. S.; Spangler, J. E.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 11712. (f) Zibinsky, M.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2013**, *52*, 1507. (g) Chuprakov, S.; Kwok, S. W.; Fokin, V. V. *J. Am. Chem. Soc.* **2013**, *135*, 4652. (h) Miura, T.; Tanaka, T.; Hiraga, K.; Stewart, S. G.; Murakami, M. *J. Am. Chem. Soc.* **2013**, *135*, 13652. (i) Miura, T.; Hiraga, K.; Biyajima, T.; Nakamuro, T.; Murakami, M. *Org. Lett.* **2013**, *15*, 3298. (j) Schultz, E. E.; Sarpong, R. *J. Am. Chem. Soc.* **2013**, *135*, 4696. (k) Shi, Y.; Gevorgyan, V. *Org. Lett.* **2013**, *15*, 5394. (l) Miura, T.; Funakoshi, Y.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 2272. (m) Kim, C.; Park, S.; Eom, D.; Seo, B.; Lee, P. H. *Org. Lett.* **2014**, *16*, 1900. (n) Yang, J.; Zhu, C.; Tang, X.; Shi, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 5142. (o) Shang, H.; Wang, Y.; Tian, Y.; Feng, J.; Tang, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 5662. (p) Chen, K.; Zhu, Z.-Z.; Zhang, Y.-S.; Tang, X.-Y.; Shi, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 6645. (q) Rajagopal, B.; Chou, C.-H.; Chung, C.-C.; Lin, P.-C. *Org. Lett.* **2014**, *16*, 3752. (r) Ran, R.-Q.; He, J.; Xiu, S.-D.; Wang, K.-B.; Li, C.-Y. *Org. Lett.* **2014**, *16*, 3704. (s) Medina, F.; Besnard, C.; Lacour, J. *Org. Lett.* **2014**, *16*, 3232. (t) Lindsay, V. N. G.; Viart, H. M.-F.; Sarpong, R. *J. Am. Chem. Soc.* **2015**, *137*, 8368. (u) Lei, X.; Li, L.; He, Y.-P.; Tang, Y. *Org. Lett.* **2015**, *17*, 5224.
- (8) For other reactions of iminocarbenes derived from *N*-1,2,3-sulfonyl-triazoles, see: (a) Grimster, N.; Zhang, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2010**, *132*, 2510. (b) Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2009**, *131*, 18034. (c) Selander, N.; Worrell, B. T.; Chuprakov, S.; Velaparthi, S.; Fokin, V. V. *J. Am. Chem. Soc.* **2012**, *134*, 14670. (d) Chuprakov, S.; Worrell, B. T.; Selander, N.; Sit, R. K.; Fokin, V. V. *J. Am. Chem. Soc.* **2014**, *136*, 195. (e) Chuprakov, S.; Malik, J. A.; Zibinsky, M.; Fokin, V. V. *J. Am. Chem. Soc.* **2011**, *133*, 10352. (f) Miura, T.; Biyajima, T.; Fujii, T.; Murakami, M. *J. Am. Chem. Soc.* **2012**, *134*, 194. (g) Miura, T.; Funakoshi, Y.; Morimoto, M.; Biyajima, T.; Murakami, M. *J. Am. Chem. Soc.* **2012**, *134*, 17440. (h) Selander, N.; Worrell, B. T.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2012**, *51*, 13054. (i) Boyer, A. *Org. Lett.* **2014**, *16*, 1660. (j) Jung, D. J.; Jeon, H. J.; Kim, J. H.; Kim, Y.; Lee, S. *Org. Lett.* **2010**, *16*, 2208. (k) Yadagiri, D.; Anbarasan, P. *Org. Lett.* **2014**, *16*, 2510. (l) Miura, T.; Funakoshi, Y.; Tanaka, T.; Murakami, M. *Org. Lett.* **2014**, *16*, 2760. (m) Miura, T.; Nakamuro, T.; Liang, C.-J.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 15905. (n) Miura, T.; Fujimoto, Y.; Funakoshi, Y.; Murakami, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 9967.
- (9) For different transformations of 1,2,3-thiadiazoles and methods of their synthesis, see: (a) Morzherin, Yu. Yu.; Glukhareva, T. V.; Bakulev, V. A. *Chem. Heterocycl. Compd.* **2003**, *39*, 679. (b) Bakulev, V. A.; Dehaen, W. *The Chemistry of 1,2,3-Thiadiazoles*; Taylor, E. C., Wipf, P., Weissberger, A., Eds.; John Wiley & Sons: Hoboken, NJ, 2004. For a recently developed new method for synthesis of 1,2,3-thiadiazoles, see: (c) Chen, J.; Jiang, Y.; Yu, J.-T.; Cheng, J. *Org. Chem.* **2016**, *81*, 271.
- (10) (a) Pannell, K. H.; Mayr, A. J.; Van Derveer, D. *J. Am. Chem. Soc.* **1983**, *105*, 6186. (b) Mayr, J.; Pannell, K. H.; Carrasco-Flores, B.; Cervantes-Lee, F. *Organometallics* **1989**, *8*, 2961.
- (11) For original report on [3 + 2] cycloaddition of alkynethiolates with activated alkynes, see: Rodionova, L. S.; Petrov, M. L.; Petrov, A. A. *Zh. Org. Khim.* **1978**, *14*, 2050.
- (12) For the report on the reaction of benzo[*b*]-1,2,3-triazoles with alkynes, see: Albertazzi, A.; Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Org. Chem.* **1984**, *49*, 4482.
- (13) (a) Mente, P. G.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1972**, 418. (b) Gilchrist, T. L.; Mente, P. G.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2165. (c) Schrauzer, G. N.; Kisch, H. *J. Am. Chem. Soc.* **1973**, *95*, 2501.
- (14) (a) Font, J.; Torres, M.; Gunning, H. E.; Strausz, O. P. *J. Org. Chem.* **1978**, *43*, 2487. (b) Krebs, A. W.; Franken, E.; Müller, M.; Colberg, H.; Cholcha, W.; Wilken, J.; Ohrenberg, J.; Albrecht, R.; Weiss, E. *Tetrahedron Lett.* **1992**, *33*, 5947.
- (15) For formation of Rh carbenes possessing the thioketone moiety, see, for example: Padwa, A.; Kinder, F. R.; Nadler, W. R.; Zhi, L. *Heterocycles* **1993**, *35*, 367.
- (16) For reviews on thiophenes, see, for example: (a) *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics*; Perepichka, I. F., Perepichka, D. F., Eds.; John Wiley & Sons: West Sussex, UK, 2009. (b) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868.
- (17) For chemistry of Rh(I) carbenes, see: (a) Rosenberg, M. L.; Krivokapic, A.; Tilset, M. *Org. Lett.* **2009**, *11*, 547. (b) Nishimura, T.; Maeda, Y.; Hayashi, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7324. (c) Rosenberg, M. L.; Vlasana, K.; Gupta, N. S.; Wragg, D.; Tilset, M. *J. Org. Chem.* **2011**, *76*, 2465. (d) Tsoi, Y.-T.; Zhou, Z.; Yu, W.-Y. *Org. Lett.* **2011**, *13*, 5370. (e) Ma, X.; Jiang, J.; Lv, S.; Yao, W.; Yang, Y.; Liu, S.; Xia, F.; Hu, W. *Angew. Chem., Int. Ed.* **2014**, *53*, 13136. (f) Xia, Y.; Liu, Z.; Liu, Z.; Ge, R.; Ye, F.; Hossain, M.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2014**, *136*, 3013. (g) Yada, A.; Fujita, S.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 7217. (h) Chen, D.; Zhang, X.; Qi, W.-Y.; Xu, B.; Xu, M.-H. *J. Am. Chem. Soc.* **2015**, *137*, 5268. (i) Torres, O.; Parella, T.; Sola, M.; Roglans, A.; Pla-Quintana, A. *Chem. - Eur. J.* **2015**, *21*, 16240.
- (18) See the [Supporting Information](#) for details.
- (19) For chemistry of Rh(III) carbenes, see: (a) Callot, H. J.; Metz, F. *Tetrahedron Lett.* **1982**, *23*, 4321. (b) Yu, X.; Yu, S.; Xiao, J.; Wan, B.; Li, X. *J. Org. Chem.* **2013**, *78*, 5444. (c) Chan, W.-W.; Lo, S.-F.; Zhou, Z.; Yu, W.-Y. *J. Am. Chem. Soc.* **2012**, *134*, 13565. (d) Lam, H.-W.; Man, K.-Y.; Chan, W.-W.; Zhou, Z.; Yu, W.-Y. *Org. Biomol. Chem.* **2014**, *12*, 4112. (e) Ng, F.-N.; Lau, Y.-F.; Zhou, Z.; Yu, W.-Y. *Org. Lett.* **2015**, *17*, 1676.
- (20) For reviews on the synthesis of thiophenes from alkynes, see: (a) Mancuso, R.; Gabriele, B. *Molecules* **2014**, *19*, 15687. See also: (b) Sasaki, S.; Adachi, K.; Yoshifuji, M. *Org. Lett.* **2007**, *9*, 1729. (c) Zhang, Y.; Bian, M.; Yao, W.; Gu, J.; Ma, C. *Chem. Commun.* **2009**, 4729. (d) Nandi, G. C.; Samai, S.; Singh, M. S. *J. Org. Chem.* **2011**, *76*, 8009. (e) Jiang, H.; Zeng, W.; Li, Y.; Wu, W.; Huang, L.; Fu, W. *J. Org. Chem.* **2012**, *77*, 5179. (f) Teiber, M.; Muller, T. J. *J. Chem. Commun.* **2012**, *48*, 2080. (g) Ge, L.-S.; Wang, Z.-L.; An, X.-L.; Luo, X.; Deng, W.-P. *Org. Biomol. Chem.* **2014**, *12*, 8473. (h) Zhang, G.; Yi, H.; Chen, H.; Bian, C.; Liu, C.; Lei, A. *Org. Lett.* **2014**, *16*, 6156. (i) Liu, W.; Chen, C.; Liu, H. *Adv. Synth. Catal.* **2015**, *357*, 4050. (j) Luo, X.; Ge, L.-S.; An, X.-L.; Jin, J.-H.; Wang, Y.; Sun, P.-P.; Deng, W.-P. *J. Org. Chem.* **2015**, *80*, 4611. For other selected reports on modular synthesis of thiophenes, see: (k) McKibben, B. P.; Cartwright, C. H.; Castelano, A. L. *Tetrahedron Lett.* **1999**, *40*, 5471. (l) Ransborg, L. K.; Albrecht, L.; Weise, C. F.; Bak, J. R.; Jorgensen, K. A. *Org. Lett.* **2012**, *14*, 724.
- (21) For cycloisomerization of 3-carbonylcyclopropenes into furans, see ref 4a,d; for reaction of 3-pyridylcyclopropenes into indolizines, see: Chuprakov, S.; Gevorgyan, V. *Org. Lett.* **2007**, *9*, 4463.
- (22) For an ylide mechanism involving rhodium carbenes, see: Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263.
- (23) For [3 + 2] cycloaddition of Rh carbenes with alkynes, see: Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669.