Cycloaddition

DOI: 10.1002/anie.201400426

The Divergent Synthesis of Nitrogen Heterocycles by Rhodium(II)-Catalyzed Cycloadditions of 1-Sulfonyl 1,2,3-Triazoles with 1,3-Dienes**

*Hai Shang, Yuanhao Wang, Yu Tian, Juan Feng, and Yefeng Tang**

Abstract: *The first rhodium(II)-catalyzed aza-[4+3] cycloadditions of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes have been developed, and enable the efficient synthesis of highly functionalized 2,5-dihydroazepines from readily available precursors. In some cases, the reaction pathway could divert to formal aza-[3+2] cycloadditions, thus leading to 2,3-dihydropyrroles. In this context, the titled reaction represents a capable tool for the divergent synthesis of two types of synthetically valuable aza-heterocycles from common rhodium(II) iminocarbene intermediates.*

Invention of new reactions that enable the divergent synthesis of different aza-heterocycles from common intermediates has been a subject of intensive research in organic synthesis. As a paradigm, rhodium(II) iminocarbenes,[1] which readily generated from 1-sulfonyl 1,2,3-triazoles upon treatment with rhodium(II) catalysts, have recently emerged as capable intermediates in the synthesis of various aza-heterocycles, including pyrrole,[2] imidazole,[3] oxazoline,[3b] pyrroloindoline[4] and others[5] (Figure 1 a), as described in the seminal contributions from the groups of Fokin, Gevorgyan, Murakami, and Davies. Formally, rhodium(II) iminocarbenes could serve either as a [1C] synthon to promote [2+1] cycloaddition,[6] C–H[7] insertion, and others,[8] or as an aza-[3C] synthon in various formal [3+2] cycloadditions.[2–5] So far, a wide range of unsaturated chemical bonds, including alkyne,[2a–c,5a,b] alkene,[6] allene,[2d,e] aldehyde,[3b] imine,[3b] nitrile,[3a] isocyanate, and isothiocyanate,[5c] have been employed as [2C] components in formal [3+2] cycloadditions. Comparably, cycloadditions of 1-sulfonyl 1,2,3-triazoles with conjugate dienes have been rarely explored.[9] In 2013, Parr and Davies reported the first rhodium(II)-catalyzed formal [4+3] cycloadditions of 4-alkenyl-1-sulfonyl-1,2,3-triazoles with 1,3-dienes (Figure 1 b).[10] However, the putative alkenyl rhodium(II) iminocarbene intermediates served as [3C] synthon instead of aza-[3C] synthon. More recently, the rhodium(II)-catalyzed cycloadditions of 1-sulfonyl 1,2,3-triazoles with α,β-unsaturated aldehydes were disclosed by Murakami and co-workers, however, only one case of an aza-[4+3] cycloaddition was documented as side-reaction.[5d] In this context, the aza-[4+3] cycloadditions of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes remain to be explored.

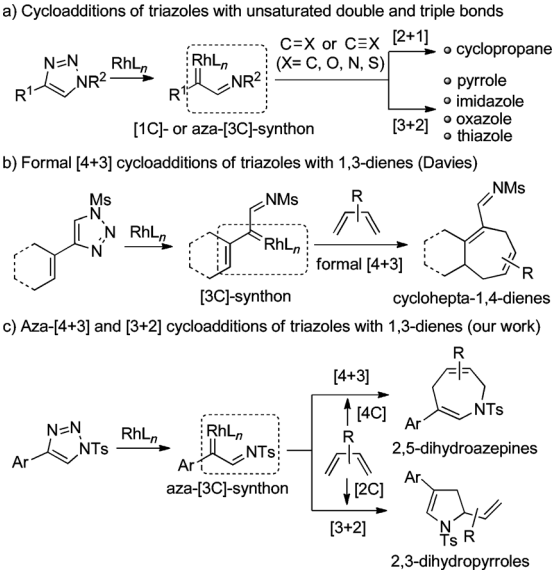


Figure 1. Cycloadditions of 1-sulfonyl 1,2,3-triazoles with unsaturated chemical bonds. Ms = methanesulfonyl, Ts = 4-toluenesulfonyl.

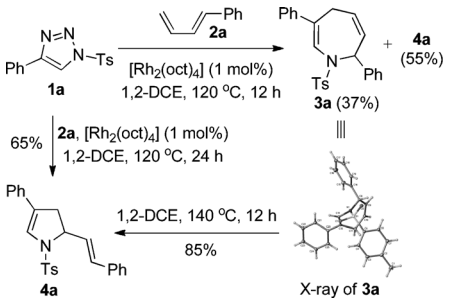
Azepines are fundamental structural elements widely distributed in natural products and pharmaceuticals.[11] Among the many strategic bond disconnections of azepine frameworks,[12] [4+3] cycloadditions are particularly attractive for their remarkable efficiency and convergency. Despite some advances on this subject,[13] the development of a new variant of [4+3] cycloadditions to assemble azepines remains highly desirable. Given that rhodium(II) iminocarbenes have demonstrated their versatile reactivities in the [2+1] and [3+2] cycloadditions, we anticipated that they could also be applied to aza-[4+3] cycloadditions. As a result, we report herein the first rhodium(II)-catalyzed aza-[4+3] cycloadditions of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes, a reaction enabling the efficient synthesis of highly functionalized 2,5-dihydroazepines from readily available precursors (Figure 1 c). Notably, in some cases the reaction pathway could

[*] Dr. H. Shang,[+] Y. Wang,[+] J. Feng, Prof. Dr. Y. Tang
The Comprehensive AIDS Research Center, Department of Pharmacology & Pharmaceutical Sciences, School of Medicine
Tsinghua University, Beijing 100084 (China)
E-mail: yefengtang@tsinghua.edu.cn
Dr. Y. Tian
Institute of Medicinal Plant Development, Chinese Academy of Medical Sciences, Peking Union Medical College
Beijing 100193 (China)
[+] These authors contributed equally to this work.

[**] We acknowledge the financial support from the National Science Foundation of China (21102081, 21272133), New Teachers' Fund for Doctor Stations, Ministry of Education (20110002120011), and Beijing Natural Science Foundation (2132037).We also thank J. K. Fu of Peking University for the initiation of this work.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201400426.

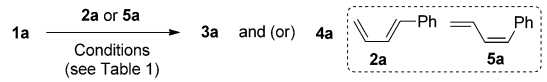
divert to formal [3+2] cycloadditions, thus mainly leading to 2,3-dihydropyrroles, another important class of aza-heterocycles which are widely employed as key intermediates in organic synthesis.[14]

We initiated our study by treatment of the readily accessible triazole **1a**[15] and (*E*)-1-phenyl-1,3-butadiene (**2a**)[16] with 1 mol% $[Rh_2(oct)_4]$ in 1,2-DCE at 120°C for 12 hours. Fortunately, two major products formed, and one of them, isolated in 37% yield, was unambiguously confirmed as the aza-[4+3] cycloadduct **3a** by X-ray crystallography (Scheme 1).[17] The other one, isolated in 55% yield, turned



Scheme 1. Initial results of cycloaddition of 1-sulfonyl 1,2,3-triazole with (*E*)-1-phenyl-1,3-diene.

Table 1: Screening for rhodium(II)-catalyzed cycloadditions of 1,2,3-triazoles with 1,3-dienes.[a]



Entry	Cat.	Solvent	Other conditions	Yield [%][b]	
				3a	**4a**
1	$[Rh_2(oct)_4]$	1,2-DCE	**2a**, 140°C, 12 h	–	85
2	$[Rh_2(oct)_4]$	1,2-DCE	**2a**, 100°C, 2 h	47	25
3	$[Rh_2(oct)_4]$	1,2-DCE	**2a**, 80°C, 12 h	15	trace
4	$[Rh_2(OAc)_4]$	1,2-DCE	**2a**, 140°C, 12 h	–	51
5	$[Rh_2(TFA)_4]$	1,2-DCE	**2a**, 140°C, 12 h	–	trace
6	$[Rh_2(S\text{-ptad})_4]$	1,2-DCE	**2a**, 140°C, 12 h	–	80
7	$[Rh_2(S\text{-dosp})_4]$	1,2-DCE	**2a**, 140°C, 12 h	–	79
8	$[Rh_2(oct)_4]$	$CHCl_3$	**2a**, 140°C, 12 h	–	67
9	$[Rh_2(oct)_4]$	toluene	**2a**, 140°C, 12 h	–	61
10	$[Rh_2(oct)_4]$	xylene	**2a**, 140°C, 12 h	–	55
11	$[Rh_2(oct)_4]$	PhCl	**2a**, 140°C, 12 h	–	64
12	$[Rh_2(oct)_4]$	1,2-DCE	**5a**, 140°C, 0.5 h	61	5
13	$[Rh_2(oct)_4]$	1,2-DCE	**5a**, 4 Å M.S., MW 120°C, 5 min	81	–

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.3 mmol) or **5a** (0.4 mmol), and rhodium(II) catalyst (0.002 mmol) in DCE (1.0 mL). [b] Yield of isolated product. DCE = dichloroethane, (*S*)-dosp = 4-(dodecyl-phenyl)sulfonyl-(2*S*)-prolinate, M.S. = molecular sieves, MW = microwave, oct = octanoate, (*S*)-ptad = *N*-phthaloyl-(*S*)-adamantylglycine, TFA = trifluoroacetate.

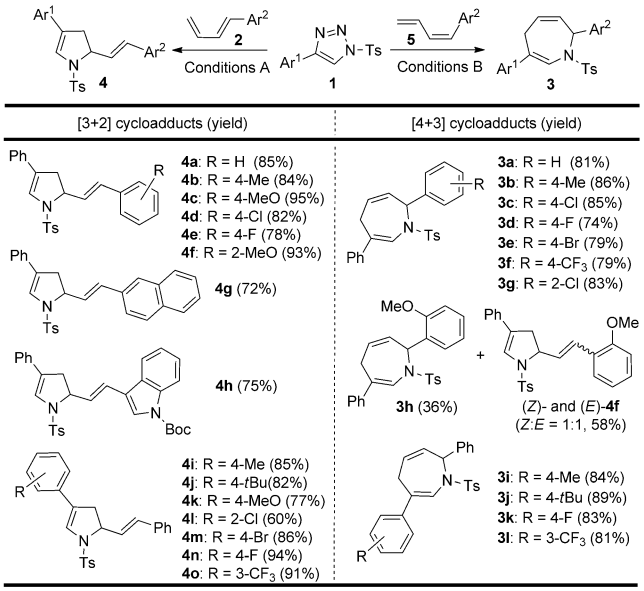
out to be **4a**, a formal [3+2] cycloadduct. Interestingly, we found that extending the reaction time resulted in the formation of **4a** as the sole product in 65% yield, and thus indicated that **3a** could gradually be converted into **4a** under the reaction conditions. This speculation was subsequently proved by the conversion of the isolated **3a** into **4a** under thermal conditions (1,2-DCE, 140°C, 12 h), presumably by a metal-free, thermo-promoted allylic amine 1,3-migration.[18]

Encouraged by the preliminary results, we conducted a systematic condition screening to improve both the efficiency and selectivity of the reaction. A simple evaluation of the effect of reaction temperature showed that high temperature (140°C) and long reaction times gave **4a** as sole product in 85% yield (entry 1, Table 1), whereas low temperature (100°C) and short reaction times favored the formation of **3a** as major product (entry 2). A further decrease in the temperature to 80°C only resulted in poor conversion (entry 3). Next, various rhodium(II) catalysts and solvents were evaluated in the reaction, however, none of them led to satisfying results (entries 4–11). Most of the cases afforded a mixture of **3a** and **4a** in the early stage of the reaction, and then **4a** as dominant product in the end. Serendipitously, we found the geometry of 1,3-diene partner had a profound influence on the outcome: when (*Z*)-1-phenyl-1,3-diene (**5a**) was employed, **3a** was isolated in 61% yield, along with only small amount of **4a** (entry 12). Moreover, no *Z* isomer of **4a** (structure not shown) was observed in this reaction. Following this route, we finally identified the optimal reaction conditions (**5a**, 4 Å M.S., MW, 120°C, 5 min) which afforded **3a** in excellent yield (entry 13). Notably, it was crucial to control the reaction temperature and time for obtaining good results.

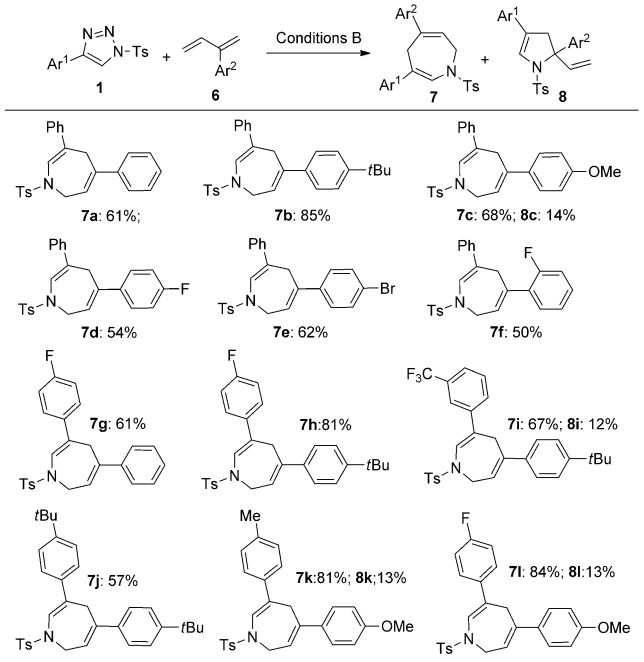
With the optimal reaction conditions secured, we turned to evaluate their generality. First of all, the scope of the [3+2] cycloadditions was examined. It was found that various (*E*)-1-aryl-1,3-dienes underwent the desired reactions with **1a** to afford the 2,3-dihydropyrroles **4a–h** in good to excellent yields (Scheme 2). Generally, the electron-rich dienes showed better reactivity than the electron-deficient ones. An array of 4-aryl-1-sulfonyl-1,2,3-triazoles were also examined with **2a** as the diene partner. It turned out that all of them gave satisfying outcomes, although the electron-deficient triazoles usually performed better than the electron-rich ones. In alignment with the previous observations, the reactions with *E*-1,3-dienes generally afforded a mixture of [4+3] and [3+2] cycloadducts at the early stage of the reaction, and then the latter as dominant product in the end.

In parallel, the scope of [4+3] cycloadditions was also evaluated by employing various (*Z*)-1-aryl-1,3-dienes and 4-aryl-1-sulfonyl-1,2,3-triazoles. It was found that most of the reactions worked well to give the corresponding 2,5-dihydroazepines **3a–g** and **3i–l** in good to excellent yields (Scheme 2). The only exception was the reaction with 2-methoxyphenyl-1,3-diene, which gave a mixture of **3h** and **4f** in excellent combined yields but poor selectivity.

In addition to 1-aryl-1,3-dienes, we also employed 2-aryl-1,3-dienes **6** in the reactions (Scheme 3). Interestingly, it was shown that the 2-aryl-1,3-dienes displayed properties distinct from the 1-aryl-1,3-dienes. Firstly, all of the reactions with 2-aryl-1,3-dienes afforded the corresponding [4+3] cycloadducts **7a–f** in good to excellent yields, thus showing little substituent effects with respect to both the diene and triazole partners. Notably, although we did isolate a small amount of the [3+2] adducts (e.g. **8c**, **8i**, **8k** and **8l**) in some cases, the

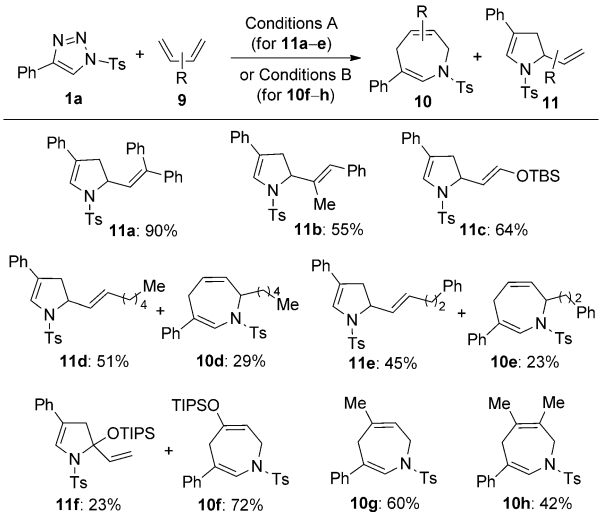


Scheme 2. Scope of [3+2] and [4+3] cycloadditions. Conditions A: **1** (0.20 mmol), **2** (0.30 mmol), and $[Rh_2(oct)_4]$ (0.002 mmol) in DCE (1.0 mL) at 140 °C for 12 h. Conditions B: **1** (0.20 mmol), **5** (0.40 mmol), 4 Å M.S., and $[Rh_2(oct)_4]$ (0.002 mmol) in DCE (1.0 mL) at 120 °C with microwave irridation for 5-10 min. Yields are those of the isolated products.



Scheme 3. Scope of [4+3] cycloadditions with 2-aryl-1,3-dienes. Conditions B are the same as those described in Scheme 2. Yields are those of the isolated products.

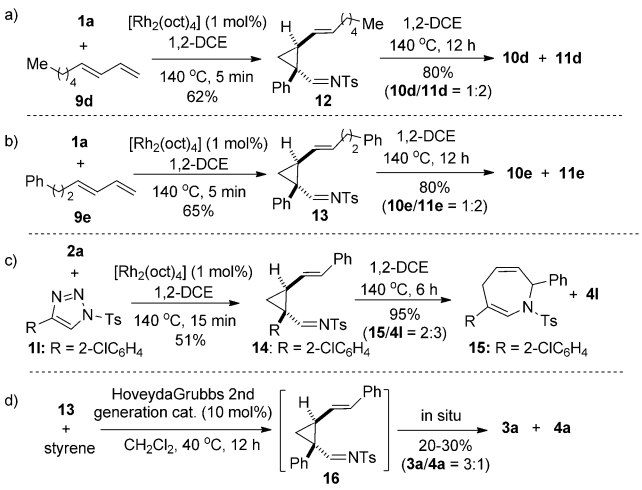
selectivities of the cycloadditions were generally good. Secondly, in contrast of the previous observations, all of the 2,5-dihydroazepines resulting from 2-aryl-dienes were rather stable and did not evolve into the corresponding 2,3-dihydropyrroles, even with long reaction times.



Scheme 4. Cycloadditions of **1a** with other 1,3-dienes. Conditions A and B are the same as those described in Scheme 2. Yields are those of the isolated products. TBS = *tert*-butyldimethylsilyl, TIPS = triisopropylsilyl.

To further extend the substrate scope, we next examined several other types of 1,3-dienes. As depicted in Scheme 4, the 1,1-diphenyl-, 1-phenyl-2-methyl-, and 1-TBSO-substituted 1,3-dienes displayed similar propensity to that of 1-aryl-1,3-dienes, mainly leading to 2,3-dihydropyrroles (**11a–c**) under the reaction conditions A (Scheme 4). Comparably, for the 1-alkyl-substituted 1,3-dienes **9d** and **9e**, although the reactions worked well, the selectivities (**10d**/**11d** and **10e**/**11e**) were only modest (ca. 1:2). Not surprisingly, in alignment with the previous observations for 2-aryl-1,3-dienes, the 2-methyl-, 2,3-dimethyl- and 2-TIPSO-1,3-dienes predominantly gave the [4+3] cycloadducts (**10f–h**) under the reaction conditions B (Scheme 4).

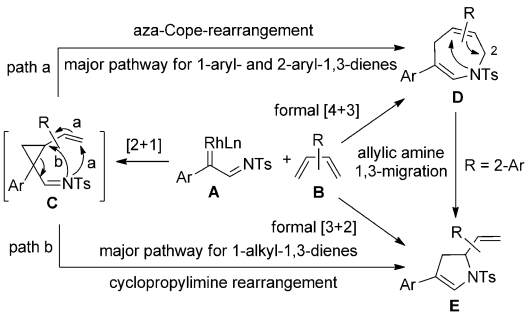
Notably, in the cycloadditions with **9d** and **9e**, some intermediates could be monitored at the early stage of the reaction. To gain insight into the mechanism, the intermediates derived from **9d** and **9e** were isolated, and were respectively proven to be the cyclopropylaldimines **12** and **13** (Scheme 5a,b).[19] We also found that **12** and **13** could be converted into the corresponding [3+2]- and [4+3]-cycloadducts under thermal conditions (1,2-DCE, 140 °C, 12 h), while the resulting **10d** or **10e** failed to advance to **11d** or **11e**, respectively, under the same reaction conditions. A similar phenomenon was also observed in the cycloaddition of **2a** with **1l** (Scheme 5c). However, we failed to identify such intermediates in most of the other cycloadditions with aryl-substituted 1,3-dienes. We speculated that it could be attributed to the fleeting nature of the cyclopropylaldimine intermediates involved in these cases. This assumption was supported by the following experiments: upon treatment of **13** with styrene in the presence of catalytic amount of the Hoveyda–Grubbs second-generation catalyst in CH_2Cl_2 at 40 °C for 12 hours, a mixture of **3a** and **4a** (**3a**/**4a** = 3:1) were obtained, apparently via the putative intermediate **16** (Scheme 5d). While the yield of the transformation was modest without further optimization, we did not identify **10e**



Scheme 5. Identification of the cyclopropane intermediate.

and **11e** in this reaction. It indicated that **16** was more reactive than **13**, which, once formed, immediately underwent the following ring-expansion to give the observed products.

The above outcomes provide information on the plausible mechanism of the described cycloadditions, as rationalized in Scheme 6. Thus, the rhodium(II) iminocarbene **A** first reacts with the 1,3-diene **B** to yield cyclopropylaldimine intermediate **C**, which then advances to **D** by a aza-Cope rearrangement[20] (path a) and/or **E** by a cyclopropylimine rearrangement[21] (path b). While a full account of the effect of substitution pattern and geometry of 1,3-diene partners on the reactions remains to be achieved, it seems that the reactions with 1-aryl- and 2-aryl-1,3-dienes mainly follow path a to afford **D**. Notably, for 1-aryl-1,3-dienes, the resulting **D** (R = 2-Ar, Scheme 6) could readily undergo allylic amine 1,3-migration to evolve into **E** (e.g. **4a–o**). In contrast, for 1-alkyl-1,3-dienes (e.g. **9d** and **9e**), both the paths a and b occur concurrently to yield a mixture of **D** and **E**, generally favoring **E** as major product.



Scheme 6. Proposed mechanism of cycloadditions of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes.

In summary, the novel rhodium(II)-catalyzed cycloadditions of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes has been developed, and enable the efficient and divergent synthesis of two types of aza-heterocycles, 2,5-dihydroazepines and 2,3-dihydropyrroles, respectively through formal aza-[4+3] and [3+2] cycloadditions. The easy availability of the starting materials, high synthetic value of the resulting products, and intriguing mechanism of the titled reactions render it not only conceptually novel, but also synthetically useful. Further mechanistic studies and applications of the method to the syntheses of bioactive molecules are in progress.

Received: January 15, 2014
Revised: March 10, 2014
Published online: ■■ ■■, ■■■■

Keywords: carbenes · cycloaddition · nitrogen heterocycles · rhodium · synthetic methods

[1] For leading reviews, see: a) B. Chattopadhyay, V. Gevorgyan, *Angew. Chem.* **2012**, *124*, 886 – 896; *Angew. Chem. Int. Ed.* **2012**, *51*, 862 – 872; b) A. V. Gulevich, V. Gevorgyan, *Angew. Chem.* **2013**, *125*, 1411 – 1413; *Angew. Chem. Int. Ed.* **2013**, *52*, 1371 – 1373.

[2] a) B. Chattopadhyay, V. Gevorgyan, *Org. Lett.* **2011**, *13*, 3746 – 3749; b) Y. Shi, V. Gevorgyan, *Org. Lett.* **2013**, *15*, 5394 – 5396; c) T. Miura, M. Yamauchi, M. Murakami, *Chem. Commun.* **2009**, 1470 – 1471; d) T. Miura, K. Hiraga, T. Biyajima, T. Nakamuro, M. Murakami, *Org. Lett.* **2013**, *15*, 3298 – 3301; e) E. E. Schultz, R. Sarpong, *J. Am. Chem. Soc.* **2013**, *135*, 4696 – 4699; f) J. S. Alford, J. E. Spangler, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 11712 – 11715; g) B. T. Parr, S. A. Green, H. M. J. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 4716 – 4718.

[3] a) T. Horneff, S. Chuprakov, N. Chernyak, V. Gevorgyan, V. V. Fokin, *J. Am. Chem. Soc.* **2008**, *130*, 14972 – 14974; b) M. Zibinsky, V. V. Fokin, *Angew. Chem.* **2013**, *125*, 1547 – 1550; *Angew. Chem. Int. Ed.* **2013**, *52*, 1507 – 1510.

[4] J. E. Spangler, H. M. L. Davies, *J. Am. Chem. Soc.* **2013**, *135*, 6802 – 6805.

[5] a) S. Chuprakov, F. W. Hwang, V. Gevorgyan, *Angew. Chem.* **2007**, *119*, 4841 – 4843; *Angew. Chem. Int. Ed.* **2007**, *46*, 4757 – 4759; b) S. Chuprakov, V. Gevorgyan, *Org. Lett.* **2007**, *9*, 4463 – 4466; c) S. Chuprakov, S. W. Kwok, V. V. Fokin, *J. Am. Chem. Soc.* **2013**, *135*, 4652 – 4655; d) T. Miura, T. Tanaka, K. Hiraga, S. G. Stewart, M. Murakami, *J. Am. Chem. Soc.* **2013**, *135*, 13652 – 13655; e) T. Miura, Y. Funakoshi, M. Murakami, *J. Am. Chem. Soc.* **2014**, *136*, 2272 – 2275.

[6] a) S. Chuprakov, S. W. Kwok, L. Zhang, L. Lercher, V. V. Fokin, *J. Am. Chem. Soc.* **2009**, *131*, 18034 – 18035; b) N. Grimster, L. Zhang, V. V. Fokin, *J. Am. Chem. Soc.* **2010**, *132*, 2510 – 2511; c) J. S. Alford, H. M. L. Davies, *Org. Lett.* **2012**, *14*, 6020 – 6023.

[7] S. Chuprakov, J. A. Malik, M. Zibinsky, V. V. Fokin, *J. Am. Chem. Soc.* **2011**, *133*, 10352 – 10355.

[8] a) T. Miura, T. Biyajima, T. Fujii, M. Murakami, *J. Am. Chem. Soc.* **2012**, *134*, 194 – 196; b) Y. Funakoshi, M. Morimoto, T. Biyajima, M. Murakami, *J. Am. Chem. Soc.* **2012**, *134*, 17440 – 17443; c) N. Selander, B. T. Worrell, S. Chuprakov, S. Velaparthi, V. V. Fokin, *J. Am. Chem. Soc.* **2012**, *134*, 14670 – 14673; d) N. Selander, B. T. Worrell, V. V. Fokin, *Angew. Chem.* **2012**, *124*, 13231 – 13234; *Angew. Chem. Int. Ed.* **2012**, *51*, 13054 – 13057; e) N. Selander, V. V. Fokin, *J. Am. Chem. Soc.* **2012**, *134*, 2477 – 2480; f) T. Miura, T. Tanaka, T. Biyajima, A. Yada, M. Murakami, *Angew. Chem.* **2013**, *125*, 3975 – 3978; *Angew. Chem. Int. Ed.* **2013**, *52*, 3883 – 3886; g) R. H. Liu, M. Zhang, G. Winston-McPherson, W. P. Tang, *Chem. Commun.* **2013**, *49*, 4376 – 4378; h) S. Chuprakov, B. T. Worrell, N. Selander, R. K. Sit, V. V. Fokin, *J. Am. Chem. Soc.* **2014**, *136*, 195 – 202.

[9] In Ref. [6c], two cases of cyclopropanations of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes were documented, however, the 1,3-

dienes functioned as the [2C]-component instead of the [4C]-component.

[10] B. T. Parr, H. M. L. Davies, *Angew. Chem.* **2013**, *125*, 10228 – 10231; *Angew. Chem. Int. Ed.* **2013**, *52*, 10044 – 10047.

[11] For reviews, see: a) T. Kametani, K. Fukumoto, *Heterocycles* **1975**, *3*, 931 – 1004; b) B. Renfroe, C. Harrington, G. R. Proctor, *Heterocyclic Compounds: Azepines*, Wiley & Interscience, New York, **1984**; c) C. R. Ganellin, D. J. Triggle, *Dictionary of Pharmacological Agents*, Chapman & Hall/CRC, London, **1996**.

[12] For radical methods, see: a) L. Yet, *Tetrahedron* **1999**, *55*, 9349 – 9403; b) C. E. Masse, A. J. Morgan, J. S. Panek, *Org. Lett.* **2000**, *2*, 2571 – 2573; for ring-expansion methods, see: c) T. J. V. Bergen, R. M. Kellogg, *J. Org. Chem.* **1971**, *36*, 978 – 983; d) E. J. Kantorowski, M. J. Kurth, *Tetrahedron* **2000**, *56*, 4317 – 4353; for ring-closing metathesis methods, see: e) M. E. Maier, *Angew. Chem.* **2000**, *112*, 2153 – 2157; *Angew. Chem. Int. Ed.* **2000**, *39*, 2073 – 2077; f) P. Jakubec, A. Hawkins, W. Felzmann, D. J. Dixon, *J. Am. Chem. Soc.* **2012**, *134*, 17482 – 17485; for metal-catalyzed cyclizations: g) H. Ohno, H. Hamaguchi, M. Ohata, S. Kosaka, T. Tanaka, *J. Am. Chem. Soc.* **2004**, *126*, 8744 – 8754; h) I. Nakamura, M. Okamoto, Y. Sato, M. Terada, *Angew. Chem.* **2012**, *124*, 10974 – 10977; *Angew. Chem. Int. Ed.* **2012**, *51*, 10816 – 10819; i) Z. Shi, C. Grohmann, F. Glorius, *Angew. Chem.* **2013**, *125*, 5503 – 5507; *Angew. Chem. Int. Ed.* **2013**, *52*, 5393 – 5397.

[13] a) D. J. Anderson, A. Fiassner, *J. Am. Chem. Soc.* **1971**, *93*, 4339 – 4340; b) N. D. Shapiro, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 9244 – 9245; c) H. Liu, X. Li, Z. Chen, W.-X. Hu, *J. Org. Chem.* **2012**, *77*, 5184 – 5190; d) L. Wang, J. Huang, S. Peng, H. Liu, X. Jiang, J. Wang, *Angew. Chem.* **2013**, *125*, 1812 – 1816; *Angew. Chem. Int. Ed.* **2013**, *52*, 1768 – 1772.

[14] For selected examples, see: a) J. M. Humphrey, Y. Liao, A. Ali, T. Rein, Y.-L. Wong, H.-J. Chen, A. K. Courtney, S. F. Martin, *J. Am. Chem. Soc.* **2002**, *124*, 8584 – 8592; b) S. B. Herzon, A. G. Myers, *J. Am. Chem. Soc.* **2005**, *127*, 5342 – 5344; c) R. Martin, A. Jäger, M. Böhl, S. Richter, R. Fedorov, D. J. Manstein, H. O. Gutzeit, H.-J. Knölker, *Angew. Chem.* **2009**, *121*, 8186 – 8190; *Angew. Chem. Int. Ed.* **2009**, *48*, 8042 – 8046; d) J. Wegner, S. V. Ley, A. Kirschning, A.-L. Hansen, J. M. Garcia, I. R. Baxendale, *Org. Lett.* **2012**, *14*, 696 – 699; e) Y. G. Zhu, C. W. Zhai, Y. L. Yue, L. P. Yang, W. H. Hu, *Chem. Commun.* **2009**, 1362 – 1364; f) H. M. Zhang, E. B. Hay, S. J. Geib, D. P. Curran, *J. Am. Chem. Soc.* **2013**, *135*, 16610 – 16617.

[15] J. Raushel, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4952 – 4955.

[16] A. Lishchynskyi, K. Muñiz, *Chem. Eur. J.* **2012**, *18*, 2212 – 2216.

[17] CCDC 979317 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] For cases of ring-contraction by palladium-catalyzed allylic amine 1,3-migration, see: a) I. Dubovyk, D. Pichugin, A. K. Yudin, *Angew. Chem.* **2011**, *123*, 6046 – 6048; *Angew. Chem. Int. Ed.* **2011**, *50*, 5924 – 5926; b) I. Dubovyk, D. G. Watson, A. K. Yudin, *J. Org. Chem.* **2013**, *78*, 1559 – 1575.

[19] **12** and **13** are not very stable and partially hydrolyzed into the corresponding aldehydes when chromatographed. Thus, their structures were assigned based on the aldehyde derivatives (for details, see the Supporting Information). A similar strategy was also applied to **14**.

[20] For a similar case, see: R. K. Boeckman, Jr., M. D. Shair, J. R. Vargas, L. A. Stolz, *J. Org. Chem.* **1993**, *58*, 1295 – 1297.

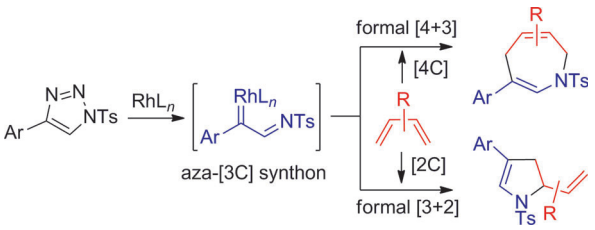
[21] When this manuscript was under review, a very similar case of cyclopropylimine rearrangements leading to 2,3-dihydropyrroles was disclosed by Fokin and co-workers. See: a) S. W. Kwok, L. Zhang, N. P. Grimster, V. V. Fokin, *Angew. Chem.* **2014**, *126*, 3520 – 3524; *Angew. Chem. Int. Ed.* **2014**, *53*, 3452 – 3456. For other relevant references, see: b) H. N. C. Wong, M.-Y. Hon, C.-W. Tse, Y.-C. Yip, J. Tanko, T. Hudlicky, *Chem. Rev.* **1989**, *89*, 165 – 198; c) R. C. Stevens, *Acc. Chem. Res.* **1984**, *17*, 289 – 296; d) S. Kagabu, I. Kawai, *J. Chem. Soc. Chem. Commun.* **1990**, 1393 – 1394; e) Y. V. Tomilov, D. N. Platonov, A. E. Frumkin, D. L. Lipilin, R. F. Salikov, *Tetrahedron Lett.* **2010**, *51*, 5120 – 5123; f) S. Saha, Ch. V. R. Reddy, B. Patro, *Tetrahedron Lett.* **2011**, *52*, 4014 – 4016; g) D. C. Lathbury, P. J. Parsons, I. Pinto, *J. Chem. Soc. Chem. Commun.* **1988**, 81 – 82.

Communications

Cycloaddition

H. Shang, Y. Wang, Y. Tian, J. Feng, Y. Tang* ——— ■■■■–■■■■

The Divergent Synthesis of Nitrogen Heterocycles by Rhodium(II)-Catalyzed Cycloadditions of 1-Sulfonyl 1,2,3-Triazoles with 1,3-Dienes



On the (di)verge: Rhodium(II)-catalyzed cycloadditions of 1-sulfonyl 1,2,3-triazoles with 1,3-dienes have been developed and enable the efficient and divergent synthesis of two types of synthetically valuable nitrogen heterocycles, 2,5-dihydroazepines and 2,3-dihydropyrroles, by formal [4+3] and [3+2] cycloadditions, respectively. Ts = 4-toluenesulfonyl.

