Heterocycle Synthesis

Cycloisomerization Promoted by the Combination of a Ruthenium–Carbene Catalyst and Trimethylsilyl Vinyl Ether, and its Application in The Synthesis of Heterocyclic Compounds: 3-Methylene-2,3-dihydroindoles and 3-Methylene-2,3-dihydrobenzofurans**

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Transition-metal-catalyzed cyclization of α,ω-dienes is an efficient method for the construction of carbo- and heterocycles. One particularly interesting cyclization is olefin metathesis,[1] in which significant progress was made after the development of well-defined ruthenium–carbene catalysts, such as **A** and **B** (Scheme 1). In particular, the commercially available ruthenium–carbene catalyst **B** has shown enhanced activity in ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), and cross metathesis (CM).[1c,2] On the other hand, the nonmetathetic behaviors of ruthenium–carbene catalysts have been demonstrated in recent studies of olefin metatheses.[3] When a substrate cannot give a product by metathesis, nonmetathetic reactions, such as the Kharasch addition,[4] olefin isomerization,[5] and hydro-

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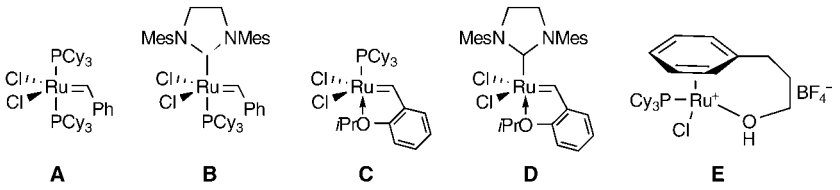


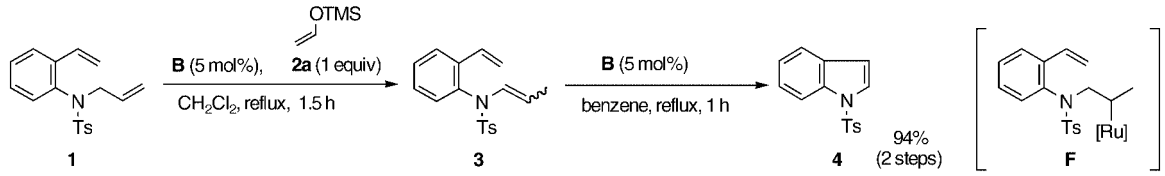
Scheme 1. Ruthenium catalysts. Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.

genation, either proceed efficiently or complete recovery of the starting materials is observed. These discoveries have expanded the synthetic utility of these catalysts beyond olefin metathesis. For example, olefin isomerization can be used in the deprotection of allyl ethers and amines,[5a–e] the synthesis of cyclic enol ethers,[5f,g] and the formation of dienamide from allenamide.[5h]

Another method that can be used to prepare cyclic compounds from α,ω-dienes is cycloisomerization.[6] In comparison to RCM, in which the carbon–carbon double bond is formed with the release of a stoichiometric amount of ethene, cycloisomerization proceeds without the loss of carbon units. Therefore, selective and catalytic cycloisomerization can be considered a highly atom-economic reaction. Recently, it has been shown that these reactions can be catalyzed by various transition metals, such as palladium,[7a–d,f] nickel,[7a] titanium,[7e] rhodium,[7f] and ruthenium.[8,9] Although ruthenium species that induce cycloisomerization, such as **E**[8a] and $[\{RuCl_2(p\text{-cymene})\}_2]$, (*p*-cymene = *p*-isopropyltoluene)[8b,c] have been identified, there are few successful reports. A highly selective cycloisomerization using a ruthenium catalyst was established by Itoh and co-workers, who used $[\{Ru(cod)Cl_2\}_n]$ (cod = 1,5-cyclooctadiene).[9]

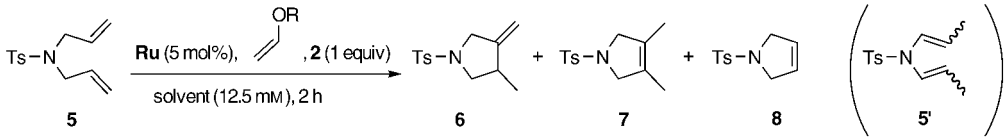
We have been studying the syntheses of nitrogen-containing heterocycles using ruthenium–carbene catalysts,[10] and have recently demonstrated the facile and selective isomerization of the terminal olefin by a combination of **B** and trimethylsilyl vinyl ether (**2a**). The aromatic enamides **3** that were obtained were subjected to standard RCM to give the corresponding indole **4** in excellent yield. The combination of these transformations established a novel synthesis for substituted indoles (Scheme 2).[11] Although the active ruthenium species for our isomerization was not characterized, we postulated that a low-valent ruthenium species, such as a ruthenium hydride, which might be generated by the reaction of **B** and **2a**, catalyzed the isomerization of an olefin via intermediate **F**. Based on our hypothesis, it is possible that **F**, which has another olefin at an appropriate position in the substrate, may undergo intramolecular olefin insertion into the Ru–C bond, followed by a *syn* β-H elimination to produce the cycloisomerized product. Herein, the cycloisomerization of α,ω-dienes using ruthenium–carbene catalyst **B** and **2a** is reported together with its application to the synthesis of heterocycles.

First, we examined the reaction of *N*,*N*-diallyl-*p*-toluenesulfonamide (**5**), which is widely used for RCM and cycloisomerization. When diene **5** was stirred with catalyst **B** (5 mol%) in dichloromethane at room temperature for two hours, the RCM product **8** was obtained quantitatively. In marked contrast, when **5** was stirred with **B** (5 mol%) and one equivalent of **2a** under the same conditions, the expected cycloisomerized product **6** was isolated in 65% yield, along with 21% of **8** (Table 1, entry 1). The same reaction at an elevated temperature (40 °C) led to higher yields of **6** and **7** (86 and 14%, respectively; entry 2). The amount of **7** formed increased at a higher temperature in toluene (entry 3). In fact, the isomerization of **6** to **7** proceeded under the same conditions. The use of **A** or **C** (entries 4 and 5) or ethyl



Scheme 2. Selective isomerization of a terminal olefin: the synthesis of an indole through RCM. Ts = *p*-toluenesulfonyl, TMS = trimethylsilyl.

Table 1: Reaction of *N*,*N*-diallyl-*p*-toluenesulfonamide (**5**). [a]



Entry	Ru		R	Solvent	*T* [°C]	Yield [%][b]			
						5	**6**	**7**	**8**
1	**B**	**2a**	TMS	CH_2Cl_2	RT	0	65	0	21
2	**B**	**2a**	TMS	CH_2Cl_2	40	0	86	(14)	0
3	**B**	**2a**	TMS	toluene	110	0	(22)	78	0
4	**A**	**2a**	TMS	CH_2Cl_2	40	28	10	0	59
5	**C**	**2a**	TMS	CH_2Cl_2	40	0	29	0	64
6	**D**	**2a**	TMS	CH_2Cl_2	40	0	71	24	0
7	**B**	**2b**	Et	CH_2Cl_2	40	58	37	0	5

[a] RT = Room temperature, TMS = trimethylsilyl. [b] Yields in parenthesis were estimated by ^1H NMR spectroscopy.

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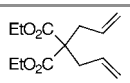
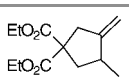
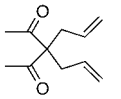
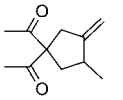
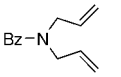
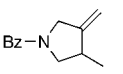
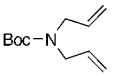
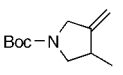
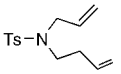
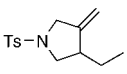
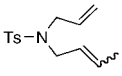
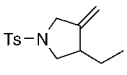
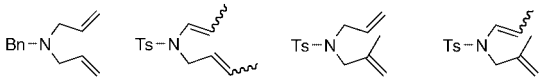
vinyl ether (**2b**) (entry 7) was less effective for the reaction, while **D** showed a high activity that was comparable to that of **B** (entry 6). Thus, the *N*-heterocyclic carbene (NHC) ligand of a ruthenium catalyst has been shown from these results to be important for highly efficient cycloisomerizations, in terms of regio- and chemoselectivity. The ruthenium complex $[RuCl(H)(CO)(PPh_3)_3]$,[12] which is known to catalyze cyclizations of enynes[12a] and isomerization of terminal olefins,[12b,c] did not promote the cycloisomerization of **5**, and isomerized compounds **5′** were obtained quantitatively instead of **6** or **7**. To the best of our knowledge, this is the first example of cycloisomerization with a α,ω-diene using a ruthenium–carbene catalyst as a precursor to the active species. By employing our conditions, a cycloisomerized compound can be selectively prepared even when the substrate can readily yield a RCM product.

The scope and limitations of this reaction are further shown in Table 2. Reactions of **9** and **10** gave the corresponding products **17** and **18** in respective yields of 83 and 87%. *N*-Benzoyldiallylamine (**11**) also gave **19** in good yield, although *N*-*tert*-butoxycarbonyldiallylamine (**12**) gave **20** in only 47% yield. The reaction of **12** heated in toluene to reflux did not increase the yield of **20**. In the case of **13**, neither cycloisomerization nor olefin migration occurred, perhaps because of an electron-donating effect. Both **14** and **15** gave **21** in low yields, along with **14′** (59 and 81%, respectively), while the reaction of **16**, which has a methallyl group, only gave isomerized products **16′**. Although the substituents at the nitrogen center and the terminal olefin functionality are very important, we thought that this reaction could have potential for the construction of nitrogen-containing heterocycles as well as carbocycles.

Table 2: Cycloisomerization of dienes.[a]

Entry	Substrate		Product		Yield [%][b]
1		**9**		**17**	83
2		**10**		**18**	87
3		**11**		**19**	75
4		**12**		**20**	47
5		**14**		**21**	18
6		**15**		**21**	13

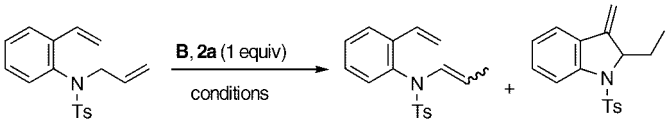
[a] Conditions: **B** (5 mol%), **2a** (1 equiv), CH_2Cl_2 (12.5 mM), heated to reflux, 2 h. [b] Yield of isolated product. Bn = benzyl.



13 **14′** **16** **16′**

Next, we investigated the application of this cycloisomerization to the synthesis of *N*- and *O*-benzo-fused heterocycles, which are important structures in many pharmacologically active compounds. Although the reaction of **1** with **2a** and **B** in dichloromethane heated to reflux gave enamides **3** in quantitative yields (Table 3, entry 1), the reaction of **1** to prepare the corresponding cycloisomerized product was investigated further. As a result, when the reaction of **1** was performed in toluene at 40 °C, the cycloisomerized indolidene **22** was obtained, albeit in low yield (entry 2). When the same reaction was carried out in either toluene or xylene heated to reflux, **22** was obtained in respective yields of 35 and 68% (entries 3 and 4). Finally, it was found that a higher temperature (in xylene at reflux) and greater amount of catalyst (10 mol%) were necessary to obtain **22** in excellent yield (entry 5). Initial isomerization of **1** converted it into **3**, which after cyclization led to the formation of **22**. This reaction pathway is indicated as the reaction of **3** under the optimized conditions (in xylene at reflux) yielded **22** in moderate yield with recovered **3** (62 and 38%, respectively). It is noteworthy that the reaction of **3** with $[\{Ru(cod)Cl_2\}_n]$ in isopropanol for 24 hours, which is the typical procedure reported by Itoh and co-workers,[9] did not produce **22** at all.

Table 3: Isomerization and cycloisomerization of α,ω-diene **1**.



1 **3** **22**

Entry	**B** [mol%]	Conditions	Yield [%][a]	
			3	**22**
1	5	CH_2Cl_2, reflux, 1.5 h	quant.	0
2	5	toluene, 40 °C, 2 h	97	3
3	5	toluene, reflux, 2 h	65	35
4	5	xylene, reflux, 2 h	30	68
5	10	xylene, reflux, 2 h	12	81

[a] Yields were estimated by ^{1}H NMR spectroscopy.

Several substituted *N*- and *O*-benzo-fused heterocycles were synthesized under our cycloisomerization conditions (Table 4). Compounds **23**–**25**, which have a chloro-substituted benzene ring, gave the corresponding indolidenes **31**–**33** in respective yields of 84, 78, and 78%. On the other hand, the reaction of **26**, which has a methoxy-substituted benzene ring, gave **34** in only 24% yield. The reaction of **27**, which has a butenyl group at the nitrogen center, also gave the cyclized product **35** in good yield. In contrast to the reactions of the nitrogen-containing substrates (**1**, **23**–**27**), the oxygen-containing substrates **28**–**30** readily cyclized to give the corresponding heterocycles **36**–**38** in good yields. The 3-methylene-2,3-dihydrobenzofurans **36**–**38** readily isomerized to the corresponding 3-methylbenzofurans **39**–**41** under acidic conditions, such as in HCl (1M) and trifluoroacetic acid.

To obtain more detailed information on the cycloisomerization the reaction of **5** with **B** and **2** in $[D_8]$toluene was monitored by spectroscopic analysis. The relative amounts of **5** and the cyclized products **6** and **7** were analyzed by ^{1}H NMR

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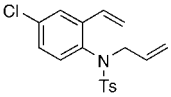
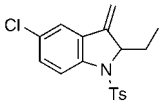
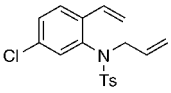
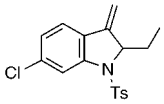
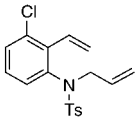
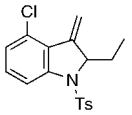
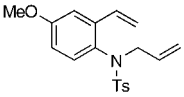
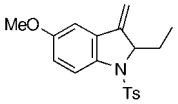
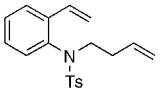
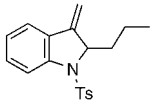
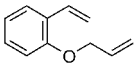
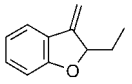
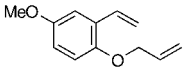
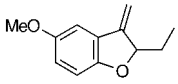
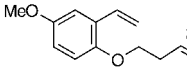
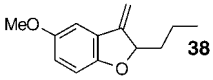
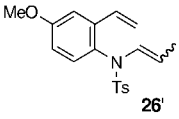
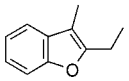
Table 4: Synthesis of 3-methylene-2,3-dihydroindoles and 3-methylene-2,3-dihydrobenzofurans.[a]

Entry	Substrate		Solvent	Product		Yield [%][b]
1		**23**	xylene		**31**	84
2		**24**	xylene		**32**	78
3		**25**	xylene		**33**	78
4		**26**	xylene		**34**	24[c]
5		**27**	xylene		**35**	58
6		**28**	toluene		**36**	78
7		**29**	toluene		**37**	76
8		**30**	toluene		**38**	73

[a] Conditions: **B** (10 mol% for entries 1–5; 5 mol% for entries 6–8), **2a** (1 equiv), solvent (12.5 mM), heated to reflux, 2 h. [b] Yield of isolated product unless otherwise noted. [c] Determined by ^{1}H NMR spectroscopy. Enamides **26′** were also obtained in 76% yield.



26′



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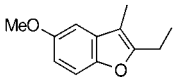

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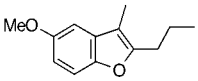

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spectroscopy, and the relative amounts of ruthenium complexes, including **B** and **G**,[13] were analyzed by ^{1}H and ^{31}P NMR spectroscopy. First, we periodically monitored the reaction of **5** with **B** in the presence of **2a** in [D_8]toluene (0.17 M) at 50 °C. The reaction was complete within 10 minutes and both **5** and **B** were consumed. Since the reaction rate under the above conditions was too fast to monitor, **2b** was used instead of **2a** to decrease the rate of the reaction, and the results are summarized in Figure 1. After 15 minutes of heating, ^{31}P NMR spectroscopy showed the disappearance of a signal at $\delta = 29.8$ ppm in the spectrum of **B**, accompanied by the emergence of a new signal at $\delta = 30.6$ ppm. Similarly, ^{1}H NMR spectroscopic analysis showed the disappearance of a signal at $\delta =$ 19.7 ppm from the spectrum of **B**, while a new signal appeared at $\delta = 14.2$ ppm. These observations show the rapid formation of Fischer-type carbene **G** from the reaction between **B** and **2b**. After 29 minutes, ^{31}P NMR spectroscopic analysis showed that **G** had partially decomposed to other unidentified ruthenium compounds ($\delta =$ 46.7, 32.5 ppm). In contrast to the reaction of **B**, the conversion of **5** to **6** proceeded gradually under these conditions and was complete after 45 minutes. The formation of **7** was not observed.

As demonstrated in the ^{1}H and ^{31}P NMR spectroscopic analyses, catalyst **G** appears to play an important role in the cycloisomerization process. According to Louie and Grubbs, **G** shows high reactivity for metathesis processes, such as ROMP and RCM.[13] Therefore, we synthesized **G** and confirmed that it efficiently catalyzes the RCM reaction of **5** in toluene at 50 °C to give **8** in 79% yield along with recovered **5** (21%). However, the reaction of **5** in the presence of both **G** (5 mol%) and one equivalent of **2b** gave **6** in 98% yield.

Although it is unclear which ruthenium species participate in this cycloisomerization, the ruthenium hydride species is a

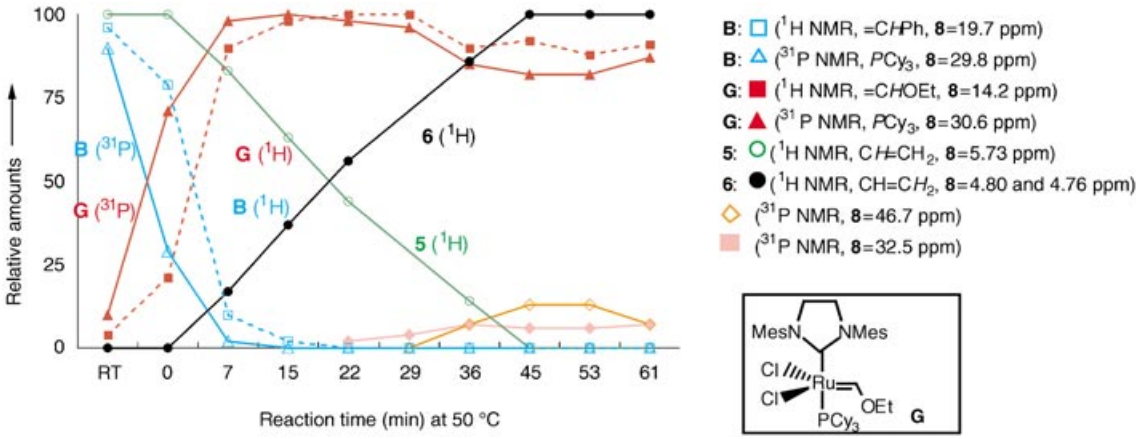

Figure 1. Cycloisomerization of *N*,*N*-diallyl-*p*-toluenesulfonamide (**5**) in [D_8]toluene (0.17 M) at 50 °C in the presence of **B** (5 mol%) and **2b** (1 equiv). The relative amounts of **B**, **G**, and decomposition products were estimated by ^{31}P NMR spectroscopic analysis using H_3PO_4 (85%) as the external standard and ^{1}H NMR spectroscopic analysis using 1,2;5,6-dibenzanthracene (5 mol%) as the internal standard. The relative amounts of **5** and **6** were estimated by ^{1}H NMR spectroscopy.

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possibility according to the mechanism proposed by Itoh and co-workers.[9a] Moreover, it has been reported that the ruthenium–hydride species[14] are generated from the Grubbs carbene complex through the formation of the ruthenium Fischer carbene.[15] However, the following findings allow an increased insight into ruthenium catalysis: 1) The experimental results show that $[RuCl(H)(CO)(PPh_3)_3]$[12] or reaction conditions using ruthenium–carbene catalysts without NHC ligands **A** and **C** were less effective for cycloisomerization. Also ruthenium catalysts **B** and **D** gave cycloisomerized products in good to excellent yields, which indicate that the presence of NHC ligands in the ruthenium–carbene catalyst is a key component for cycloisomerization. 2) Our cycloisomerization conditions can be used to prepare indolidenes, *N*-benzo-fused heterocycles. The preparation of which have not been reported using the most successful ruthenium catalyst $[\{Ru(cod)Cl_2\}_n]$. Further studies on the ruthenium species involved in the cycloisomerization process and an investigation of the reaction mechanism are currently in progress.

In conclusion, a new methodology for the cycloisomerization of dienes using a Grubbs carbene complex and trimethylsilyl vinyl ether has been established. The utility of this reaction was demonstrated in the synthesis of *exo*-methylene heterocyclic compounds, which could act as key intermediates for pharmacologically active compounds. We believe that these results offer a further insight into the chemistry of ruthenium–carbene complexes.

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