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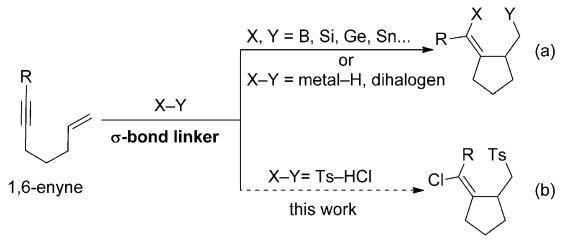
Rhodium-Catalyzed Carbocyclization and Chlorosulfonylation of 1,6-Enynes with Sulfonyl Chlorides

Chen Chen, Jianhua Su, and Xiaofeng Tong*[a]

The transition-metal catalyzed cyclization of enyne has been one of the most efficient methods for the synthesis of various types of cyclic compounds.[1] The metal-catalyzed addition–carbocyclization reactions[2] of 1,6-enyne with reagents containing interheteroatom X–Y bonds [X–Y = metal–metal reagent (B, Si, Ge, Sn, etc.),[3] metal–H reagent,[4] dihalogen[5]] constitute synthetically highly versatile processes, which furnish the formation of a new C–C bond along with C–X and C–Y bonds in a one-step fashion and represent a facile route to carbocyclic and heterocyclic ring systems (Scheme 1 a). Although related reactions have been



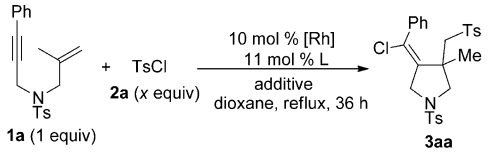
Scheme 1. Metal-catalyzed addition–cyclization of 1,6-enyne.

extensively investigated recently, their power and scope is ultimately impeded by the limitation of the above-mentioned linkers; no other type of σ-bond linkers, to the best of our knowledge, have been reported. Therefore, the development of novel linkers for the addition–carbocyclization reactions, especially under the guidance of novel reaction mechanism(s), is still highly desirable.

Recent discoveries have heralded a renaissance for sulfonyl chlorides as readily available, inexpensive, and versatile reagents for metal-catalyzed transformations.[6] It occurred to us that sulfonyl chlorides might serve as a novel linkers for catalytic addition–carbocyclization reactions. In fact, the addition of sulfonyl chlorides across terminal alkynes has been successfully achieved with the assistance of Cu or Fe complexes,[7] demonstrating their similar potential[2] as for the above mentioned element–element linkers. As part of our continuous research on the catalytic cyclization of 1,6-enynes,[8] we herein report the first example of the Rh^I-catalyzed carbocyclization and chlorosulfonylation of 1,6-enynes with sulfonyl chlorides as a linker, in which three different bonds, C–Cl, C–C, and C–S, are efficiently formed with high regioselectivity and stereoselectivity (Scheme 1 b).

We started our investigation by screening different metal catalysts for the carbocyclization and chlorosulfonylation reaction of 1,6-enyne **1a** (1 equiv) with TsCl **2a** (1.5 equiv).[9] Whereas most of the tested catalysts, including CuCl, [Fe(acac)$_2$], and [Ru(PPh$_3$)$_2$Cl$_2$], showed no activity for the attempted transformation and substrate **1a** was recovered, Wilkinson's catalyst [Ru(PPh$_3$)$_3$Cl] (10 mol %) was found to enable the complete consumption of **1a**, although a complicated reaction resulted (Table 1, entry 1). Fortunately, compound **3aa** was indeed obtained, albeit only in 6% yield after very careful chromatography. The structure of **3aa** was unambiguously determined by X-ray diffraction analysis (Figure 1, left).[10] The (*E*)-configuration of *exo*-double bond in **3aa** implied that the chloride might attack the triple bond of **1a** from the opposite direction of alkyne–rhodium complex (see below). Indeed, the addition of LiCl–H$_2$O (1 equiv) significantly improved the reaction performance, leading to the isolation of **3aa** in 43% yield (Table 1, entry 2). These promising results promted us to test the

Table 1. Optimization of reaction conditions.[a]



Entry	*x*	[Rh]	L	Additive	Yield[b] [%]
1	1.5	[Rh(PPh$_3$)$_3$Cl]	–[c]	–[c]	6
2	1.5	[Rh(PPh$_3$)$_3$Cl]	–[c]	LiCl–H$_2$O[d]	43
3	1.5	[Rh(cod)Cl]	DPPF	LiCl–H$_2$O	77
4	1.5	[Rh(cod)Cl]	DPPE	LiCl–H$_2$O	42
5	1.5	[Rh(cod)Cl]	DPPP	LiCl–H$_2$O	26
6	1.5	[Rh(cod)Cl]	DPPB	LiCl–H$_2$O	30
7	2.0	[Rh(cod)Cl]	DPPF	LiCl–H$_2$O	83
8	2.5	[Rh(cod)Cl]	DPPF	LiCl–H$_2$O	92

[a] Reaction conditions: enyne **1** (0.2 mmol), catalyst precursor (0.02 mmol), ligand (0.022 mmol), 3 mL dioxane. [b] Yield of isolated product. [c] Without ligand or additive. [d] 1.0 equiv LiCl–H$_2$O was used.

[a] C. Chen, Prof. J. Su, Dr. X. Tong
Shanghai Key Laboratory of Functional Materials Chemistry
East China University of Science and Technology
Meilong Road, 130, Shanghai 200237 (P.R. China)
Fax: (+86) 21-64253881
E-mail: tongxf@ecust.edu.cn

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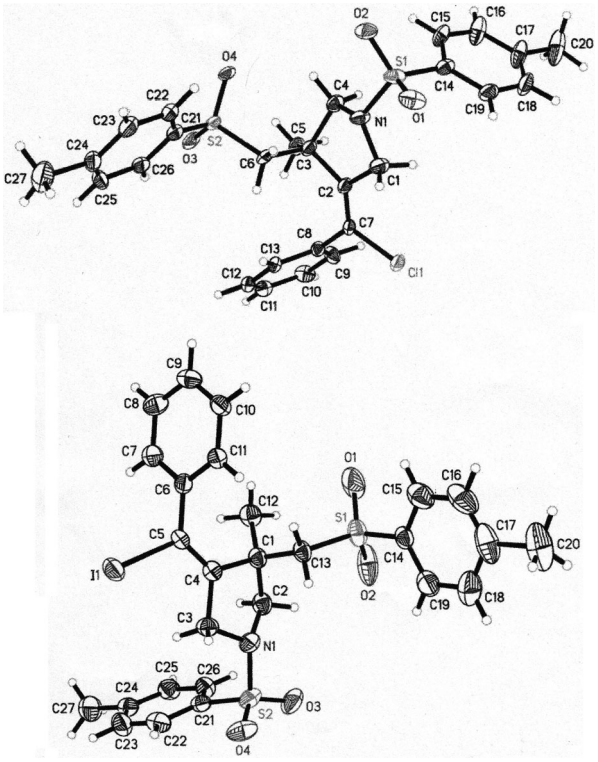
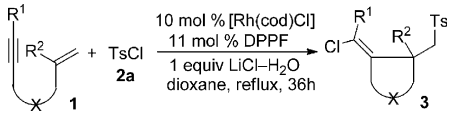


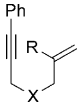
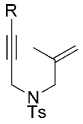
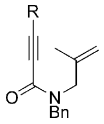
Figure 1. X-ray crystal structures of **3aa** (top) and **3aa-I** (bottom).

effect of ligand on the reaction performance with the use of [Rh(cod)Cl] (cod = cyclooctadiene) as a catalyst precursor and LiCl–H_2O as an additive. When 1,1′-bis(diphenylphosphino)ferrocene (DPPF) ligand was used, the yield of **3aa** was further increased to 77% (Table 1, entry 3). We further examined a variety of ligands, such as 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), and 1,4-bis(diphenylphosphino)butane (DPPB), which did not exhibit any superior performance over DPPF (Table 1, entries 4–6). To our delight, when 2 equivalents of TsCl was used the reaction performance was significantly improved, providing **3aa** in 83% yield (Table 1, entry 7). The use of 2.5 equivalents of TsCl could further increase the yield to 92% (Table 1, entry 8).

After establishing the optimized reaction conditions, we surveyed the synthetic scope of the reaction with various 1,6-enynes (Table 2). In general, a wide range of 1,6-enynes reacted well with TsCl **2a** to afford the corresponding products in moderate to excellent yields. The reaction of **1b** with ethyl substitution on the alkene moiety gave **3ba** in 62% yield, whereas in the case of **1c** with phenyl substitution, the corresponding yield of **3ca** dropped to 41%. The dependence of the yield upon substitution partners likely relied on the corresponding steric hindrance. However, the reaction of enyne **1d** with single-substituted alkene was somewhat complicated, affording the desired product **3da** in 45% yield along with some unidentified byproducts. Similarly, substitution on the alkyne moiety also strongly affected the reaction performance. Indeed, enynes **1f** and **1g** with electron-poor aromatic substitution gave the corresponding

Table 2. The scope of the reactions of enynes with **2a**.[a]



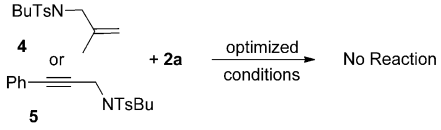
1,6-Enyne **1**		**3**, Yield [%][b]
	**1a**: R = Me, X = NTs	**3aa**, 92
	1b: R = Et, X = NTs	**3ba**, 62
	1c: R = Ph, X = NTs	**3ca**, 41
	1d: R = H, X = NTs	**3da**, 45[c]
	1e: R = Me, X = O	**3ea**, 75
	**1f**: R = 4-CN-C_6H_4	**3fa**, 61
	1g: R = 4-Ac-C_6H_4	**3ga**, 58
	1h: R = 4-Me-C_6H_4	**3ha**, 98
	**1i**: R = Ph	**3ia**, 47
	1j: R = Bu	**3ja**, 40

[a] Reaction conditions: enyne **1** (0.2 mmol), TsCl (0.5 mmol), LiCl–H_2O (0.2 mmol), [Rh(cod)Cl] (0.02 mmol), DPPF (0.022 mmol), 3 mL dioxane. [b] Yield of isolated product. [c] With some unidentified byproducts.

products in lower yields, whereas the reaction of substrate **1h** with a 4-Me-C_6H_4 group on the alkyne moiety gave a near-quantitative amount of **3ha**. When the substrates with electron-poor alkyne moieties, such as **1i** and **1j**, were employed, the yield was also decreased to around 40%. We were pleased to find that the transformation was also applicable to the oxygen-tethered enyne. Indeed, the reaction of substrate **1e** gave product **3ea** in the yield of 75%.

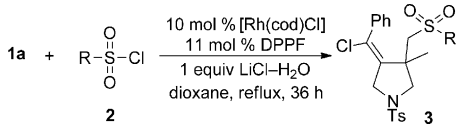
The catalytic carbocyclization and chlorotosylation reaction was then extended to other sulfonyl chlorides. As shown in Table 3, a wide range of sulfonyl chlorides reacted well with 1,6-enyne **1a**, and generally good yields were achieved. No reaction was observed in the case of mesitylsulfonyl chloride **2g**, likely due to its large steric hindrance. Notably, the reaction could also be realized for methanesulfonyl chloride **2h**, resulting in the isolation of **3ah** in 78% yield.

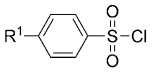
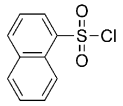
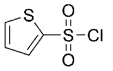
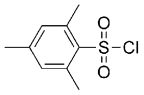
To gain a better understanding of the reaction mechanism, a series of control experiments were conducted. In a first set of experiments, compounds **4** and **5** were instead employed as substrates and subjected to the optimized conditions, respectively [Eq. (1)]. No corresponding chlorotosylation products were observed and the starting materials were recovered nearly quantitatively. These results clearly indicated that the combination of alkene and alkyne moieties into one molecule might be essential for this Rh^I-catalyzed transformation.



(1)

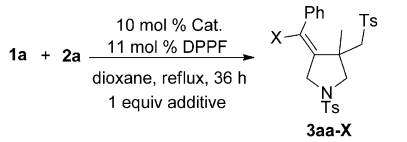
Table 3. The scope of the reactions of **1a** with sulfonyl chlorides.[a]



	2	3, Yield [%][b]
	**2a**: R^1 = Me	**3aa**, 92
	2b: R^1 = OMe	**3ab**, 90
	2c: R^1 = H	**3ac**, 90
	2d: R^1 = Cl	**3ad**, 72
	**2e**	**3ae**, 62
	**2f**	**3af**, 47
	**2g**	**3ag**, 0
	**2h**	**3ah**, 78

[a] Reaction conditions: **1a** (0.2 mmol), sulfonyl chloride (0.5 mmol), LiCl–H_2O (0.2 mmol), [Rh(cod)Cl] (0.02 mmol), DPPF (0.022 mmol), 3 mL dioxane. [b] Yield of isolated product.

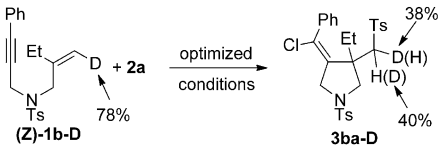
In another set of experiments, the possibility of the corresponding carbocyclization and bromotosylation or iodotosylation was investigated (Scheme 2). To our delight, the bromotosylation product **3aa-Br** was readily obtained in 88% yield with the use of LiBr–H_2O as additive under otherwise identical conditions. For iodotosylation, the catalyst precursor [$RhCl(CO)(PPh_3)_2$] and additive KI were found to be optimal, giving **3aa-I** in 57% yield (isolated product; Scheme 2). The structure of **3aa-I** was also determined by X-ray diffraction analysis.[10] These results further pointed out that the formation of the C–X bond might arise from an *anti*-halo-rhodation process, furnishing the *exo*-double bond with (*E*)-configuration.



Cat.	Additive	X	**3aa-X** / Yield [%]
[Rh(cod)Cl]	LiBr–H_2O	Br	**3aa-Br** / 88
[$RhCl(CO)(PPh_3)_2$]	KI	I	**3aa-I** / 57

Scheme 2. Carbocyclizative bromotosylation and iodotosylation.

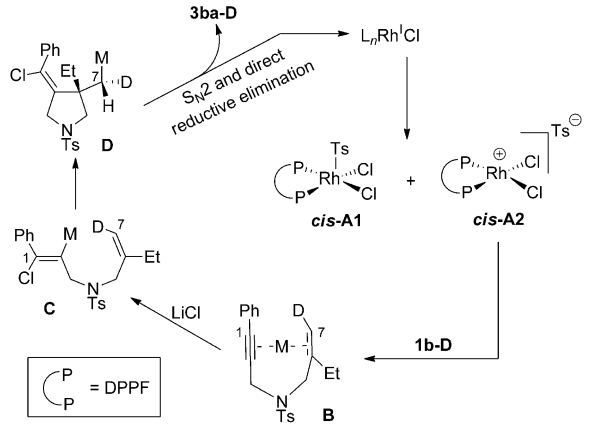
In a final set of experiments, we employed the deuterium-labelled enyne to investigate the chemistry of the C–S bond formation. Indeed, enyne **1b-D**, with a (*Z*)-configured terminal olefin, reacted well with **2a** to give product **3ba-D** in 70% yield without deuterium erosion but with deuterium scrambling [Eq. (2)].



(2)

Apparently, the observation of deuterium scrambling seems to support the radical-involved reaction mechanism. However, a control experiment showed that the presence of the radical inhibitor, butylhydroxytoluene (BHT) or 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), did not affect the carbocyclization and chlorotosylation reaction of **1b** with TsCl and **3ba** was still isolated in around 60% yield. These results are particularly interesting because a free-radical, redox-transfer chain mechanism has been generally accepted for the metal-catalyzed addition of sulfonyl chloride to terminal alkynes[7] or alkenes[11].

Although highly speculative, the above results led us to propose the mechanism depicted in Scheme 3 for the present transformation (with **1b-D** and **2a** as substrates). This



Scheme 3. Mechanistic proposal [(M = Rh^{III})].

could initially involve oxidative addition of TsCl to the Rh^I center.[12] Indeed, ESI-MS analysis of the reaction between [Rh(cod)Cl], DPPF, and TsCl (1:1:1) in dioxane solvent allowed us to identify the intermediate [Rh(DPPF)-(dioxane)$TsCl_2$] according to the high resolution mass data ($[C_{45}H_{43}Cl_2FeO_4P_2SRh+Na]^+$ calcd 993.0031, found 993.0021). Furthermore, a ^{31}P NMR spectroscopic study on this reaction indicates the formation of two species. Both species show doublet signals: 22.98 ppm (J_{P-Rh} = 152 Hz) and 22.58 ppm (J_{P-Rh} = 151 Hz).[13] These species might correspond to two Rh^{III} complexes ***cis*-A1** and ***cis*-A2**[14] that are

formed by the oxidative addition of TsCl to a Rh^{I}-center (Scheme 3). Therefore, they are likely to be present in solution and thus potential intermediates in the catalytic cycle. We speculated that alkyne and alkene of **1b-D** preferentially coordinate to the Rh^{III} center of ***cis*-A2** due to its cationic character, generating complex **B**. Subsequently, the activated alkyne is attacked by external chloride to form the vinyl-Rh^{III} intermediate **C**.[15] Afterwards, alkene stereospecifically inserts into the vinyl–Rh^{III} bond of intermediate **C** to form the alkyl-Rh^{III} intermediate **D** with well-defined stereochemistry,[16] which is followed by reductive elimination of the alkyl-Rh–S bond to form product **3ba-D** and regenerate the Rh^{I} catalyst. The observation of deuterium scrambling led us to hypothesize that the reductive elimination might proceed via two different pathways, S_N2-type or direct reductive elimination.[17] Although the proposed mechanism lacks solid evidence, it does account for the observed chemical outcome, especially the stereochemistry of the exocyclic alkene and the formation of the C–S bond. Nevertheless, the exact catalytic mechanism still needs more investigation.

In summary, we have developed a novel Rh^{I}-catalyzed carbocyclization and chlorosulfonylation of 1,6-enyne with sulfonyl chloride, which results in the formation of C–Cl, C–C, and C–S bonds in a one-pot fashion. Sulfonyl chloride is proved to be an efficient linker in addition–carbocyclization reactions, which complements the known element–element examples. Further work will focus on the mechanistic investigation and synthetic applications of this reaction.[18]

Acknowledgements

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Keywords: 1,6-enynes · cyclization · chlorosulfonylation · linkers · rhodium · sulfonyl chlorides

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[9] During our preparation of this manuscript, Nakamura and co-workers reported the Fe-catalyzed carbocyclization and chlorotosylation of 1,6-enyne (Ref. [7 f]). In their paper, only one 1,6-enyne substrate was reported. More importantly, the regioselectivity is very different from our examples. It should be noted that our conditions are not applicable to the 1,6-enyne with a terminal alkyne group.

[10] CCDC-902637 (**3aa**) and CCDC-902466 (**3aa-I**) contain 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.

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[18] Two primary synthetic applications related to the vinyl–I bond of **3aa-I** have been realized. For details, see the Supporting Information.

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