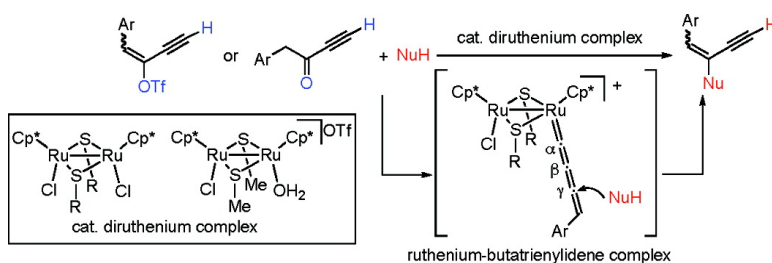


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Ruthenium-Catalyzed Vinylic Substitution Reactions with Nucleophiles via Butatrienylidene Intermediates

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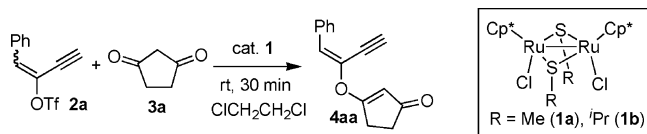
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Transition metal complexes of cumulated alkylenes such as metal–carbene, –vinyliene, and –allenylidene complexes have been widely used as versatile organometallic species having a double bond between a metal and a carbon.¹ The metal–carbon double bond is reactive enough to be employed for many organic transformations catalytically as well as stoichiometrically.¹ In fact, metathesis of alkenes via metal–carbenes may be one of the most powerful tools in recent organic synthesis,² while metal–vinylienes³ and –allenylidenes⁴ are also revealed to be the important organometallic species in various organic transformations of terminal alkynes. In sharp contrast to the rich chemistry of these carbene, vinyliene, and allenylidene complexes,¹ the chemistry of higher cumulenyliene complexes is so far limited only to the isolation and stoichiometric reactions of metal–cumulenyliene complexes.^{5,6} We have now found the first example of the ruthenium-catalyzed novel reactions via metal–butatrienylidene complexes⁵ as key intermediates.

Treatment of 2-(1-phenyl-1-buten-3-ynyl) trifluoromethanesulfonate (**2a**), as a mixture of two stereoisomers (isomer ratio 58/42), with 1,3-cyclopentanedione (**3a**) (3 equiv to **2a**) in the presence of 3 mol % of [Cp*₂RuCl(μ₂-SMe)]₂ (Cp* = η⁵-C₅Me₅; **1a**)⁴ in ClCH₂CH₂Cl at room temperature for 30 min gave 3-((E)-1-phenyl-1-buten-3-yn-2-yloxy)-2-cyclopentenone (**4aa**) in 91% isolated yield with a complete selectivity (Scheme 1 and Table 1).⁷ Interestingly, **3a** worked as O-nucleophiles, in sharp contrast to the propargylic substitution reactions.^{4c} No stereoisomers were detected by ¹H NMR. The molecular structure of **4aa** was determined by X-ray analysis.^{7,8} The use of the complex bearing a sterically more demanding SⁱPr moiety [Cp*₂RuCl(μ₂-SⁱPr)]₂ (**1b**) did not affect the yield of **4aa**, while that of the corresponding cationic diruthenium complex [Cp*₂RuCl(μ₂-SMe)₂RuCp*(OH₂)]OTf (OTf = OSO₂CF₃; **1a'**) in place of **1a** gave **4aa** in 69% yield.

Scheme 1



Catalytic reactions of other 2-(1-aryl-1-buten-3-ynyl) trifluoromethanesulfonates (**2**) with cyclic 1,3-diketones (**3**) were investigated by using **1a** as a catalyst. When **3b** was used in place of **3a**, lower yields of vinylic ethers (**4**) were obtained even from the reactions using a larger amount (5 mol %) of **1a** and for a longer reaction time (1 h) (Table 1, runs 4–6). In contrast, reactions with **3c** proceeded smoothly to give **4** in high yields with a complete selectivity (Table 1, runs 7–9). Reactions of **2d** and **2e** with **3a**

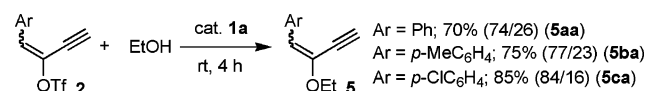
Table 1. Ruthenium-Catalyzed Reactions of **2** with **3** in the Presence of **1a**^a

run	2 ^b	3	4	yield of 4 , (%) ^c	isomer ratio (<i>E/Z</i>) ^d
1	Ar = Ph (2a)	3a	4a	91 (4aa)	>99/<1
2	Ar = <i>p</i> -MeC ₆ H ₄ (2b)	3a	4b	87 (4ba)	>99/<1
3	Ar = <i>p</i> -ClC ₆ H ₄ (2c)	3a	4c	86 (4ca)	>99/<1
4	Ar = Ph (2a)	3b	4b'	82 ^e (4ab)	>99/<1
5	Ar = <i>p</i> -MeC ₆ H ₄ (2b)	3b	4bb	55 ^e (4bb)	>99/<1
6	Ar = <i>p</i> -ClC ₆ H ₄ (2c)	3b	4cb	42 ^e (4cb)	>99/<1
7	Ar = Ph (2a)	3c	4c	88 (4ac)	>99/<1
8	Ar = <i>p</i> -MeC ₆ H ₄ (2b)	3c	4bc	84 (4bc)	>99/<1
9	Ar = <i>p</i> -ClC ₆ H ₄ (2c)	3c	4cc	77 (4cc)	>99/<1
10	Ph OTf 2d	3a	4da	84 (4da)	>99/<1
11	2e	3a	4ea	89 (4ea)	>99/<1
12	Ar = Ph (2a)	3d	4ad	93 (4ad)	98/2

^a All reactions of **2** (0.30 mmol) with **3** (0.90 mmol) were carried out in the presence of **1a** (0.009 mmol) in ClCH₂CH₂Cl (8 mL) at room temperature for 30 min. ^b The isomer ratio is shown in Supporting Information. ^c Isolated yield. ^d Determined by ¹H NMR. ^e The reaction was carried out in the presence of **1a** (0.015 mmol) for 1 h.

gave the corresponding vinylic ethers (**4da** and **4ea**) in 84 and 89% isolated yields, respectively (Table 1, runs 10 and 11). Unfortunately, no reaction occurred at all when acyclic 1,3-diketones such as 2,4-pentanedione and cyclic β-ketoesters such as β-lactones were used in place of **3**. Interestingly, the reaction of **2a** with **3d** proceeded smoothly to give the corresponding vinylic ether (**4ad**) in 93% isolated yield with an excellent stereoselectivity (*E/Z* = 98/2) (Table 1, run 12). In addition to cyclic 1,3-diketones, alcohols can also be employed as nucleophiles for this substitution reaction. Thus, when the sulfonates **2** were treated with ethanol in the presence of 5 mol % of **1a** at room temperature for 4 h, the corresponding vinylic ethers (**5**) were obtained in good yields as a mixture of stereoisomers (Scheme 2).

Scheme 2



In order to obtain some information on the reaction pathway, the following stoichiometric and catalytic reactions were investigated. Treatment of **1a** with 1 equiv of **2d** in the presence of 2 equiv of ⁱPr₂NEt in ClCH₂CH₂Cl at room temperature for 20 min

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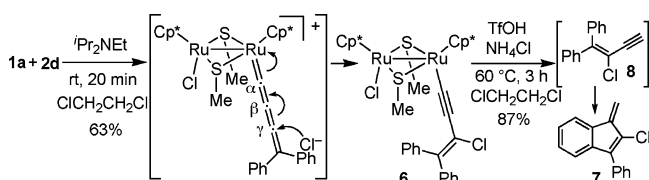
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gave the corresponding butatrienyl complex (**6**) in 63% isolated yield (Scheme 3). The structure of **6** was unambiguously characterized by X-ray crystallography (Figure S1).⁷ The complex **6** is considered to be obtained by nucleophilic attack of a chloride ion to the γ -carbon of the butatrienylidene complex, which may be generated in situ from **1a** and **2d**. A similar mononuclear ruthenium butatrienyl complex has already been obtained and characterized by Selegue and his co-worker, where the complex was obtained from the reaction of the corresponding butatrienylidene complex with trifluoroacetic anhydride.⁹

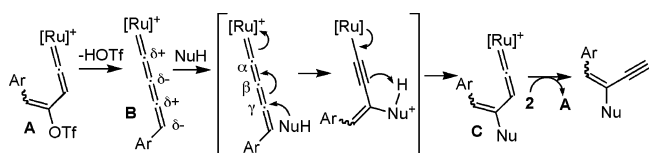
Treatment of **6** with 1 equiv of TfOH in the presence of 5 equiv of NH_4Cl gave **7**¹⁰ in 87% yield (Scheme 3). The indene **7** seems to be produced in situ via Brønsted acid catalyzed intramolecular Friedel–Crafts-type cyclization of **8** released in situ from **6**. These results indicate that the catalytic reaction might proceed via a butatrienylidene complex as a key intermediate.¹¹ Furthermore, the reaction of **2d** with **3a** in the presence of 3 mol % of **6** at room temperature for 30 min afforded **4da** in 84% yield.

Scheme 3



A proposed reaction pathway is shown in Scheme 4. The initial step is the formation of a vinylidene complex (**A**) by the reaction of **1a** with **2**, followed by its conversion into a butatrienylidene complex (**B**).⁶ Subsequent attack of a nucleophile on the C_γ atom of **B** results in the formation of another vinylidene complex (**C**). In the reactions with **3**, the steric repulsion between substituents in both **B** and **3** might lead to predominant formation of (*E*)-**C**. Finally, the complex **C** liberates a vinylic-substituted product by reaction with another **2**, regenerating **A**. We believe that the synergistic effect in the diruthenium complexes is quite important for the promotion of this catalytic reaction.⁴

Scheme 4



Next, we investigated the reactions of α -ketoacetylenes (**9**) with nucleophiles because α -ketoacetylenes are considered to be suitable substrates to generate butatrienylidene complexes.⁹ Treatment of **9a** in ethanol in the presence of 10 mol % of **1a'** at 60 °C for 2 h gave the vinylic ether (**5aa**) in 60% isolated yield as a mixture of two stereoisomers (Table 2, run 1). Almost the same yield of **5aa** was obtained when **1a** was used as a catalyst. The presence of a substituent at the *para*-position in the benzene ring of **9a** did not practically influence the yield of **5** (Table 2, runs 2–6). A variety of alcohols are available as nucleophiles (Table 2, runs 7–9), but no formation of **4** was observed when reactions of **9** with **3** were carried out under the same reaction conditions.

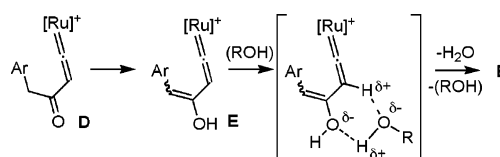
These reactions are also considered to proceed via butatrienylidene complexes as key intermediates.⁹ Dehydration from a vinylidene complex (**E**) assisted with an alcohol¹² may give **B** (Scheme 5), which is the same reactive intermediate as that in the reactions of **2** with alcohols (Schemes 2 and 4). In fact, the ratio of stereoisomers of **5** from the reaction of **9** with alcohols is almost the same

Table 2. Ruthenium-Catalyzed Reactions of **9** with Alcohols in the Presence of **1a'**^a

run	Ar of 9	ROH	yield of 5 (%) ^b	isomer ratio ^c
1	Ph (9a)	EtOH	60 (5aa)	74/26
2	<i>p</i> -MeC ₆ H ₄ (9b)	EtOH	62 (5ba)	77/23
3	<i>p</i> -ClC ₆ H ₄ (9c)	EtOH	59 (5ca)	79/21
4	<i>p</i> -MeOC ₆ H ₄ (9d)	EtOH	55 (5da)	77/23
5	<i>p</i> -FC ₆ H ₄ (9e)	EtOH	49 (5ea)	80/20
6	2-naphthyl (9f)	EtOH	63 (5fa)	71/29
7	Ph (9a)	ⁿ PrOH	63 (5ab)	78/22
8	Ph (9a)	ⁱ PrOH	53 (5ac)	83/17
9	Ph (9a)	ⁿ BuOH	68 (5ad)	77/23

^a All reactions of **9** (0.30 mmol) with alcohol (15 mL) were carried out in the presence of **1a'** (0.03 mmol) at 60 °C for 2 h. ^b Isolated yield. ^c Determined by ¹H NMR.

Scheme 5



as that from **2**. In the attempted reactions of **9** with **3**, we consider that no dehydration from **E** occurs due to a low basicity of **3**.

In summary, we have disclosed novel ruthenium-catalyzed vinylic substitution reactions of vinylic trifluoromethanesulfonates with nucleophiles which are considered to be a new type of vinylic substitution reaction,^{13–15} proceeding via ruthenium–butatrienylidene complexes as key intermediates.¹⁶ We believe that this finding will open up a further aspect of the chemistry of metal–cumulenylidene complexes.

Supporting Information Available: Experimental procedures, spectroscopic data, and X-ray data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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