J|A|C|S
COMMUNICATIONS

Published on Web 02/15/2008

Ruthenium-Catalyzed Vinylic Substitution Reactions with Nucleophiles via Butatrienylidene Intermediates

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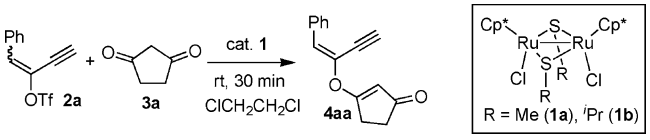
Transition metal complexes of cumulated alkylidenes such as metal−carbene, −vinylidene, and −allenylidene complexes have been widely used as versatile organometallic species having a double bond between a metal and a carbon.[1] The metal−carbon double bond is reactive enough to be employed for many organic 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−vinylidenes[3] and −allenylidenes[4] 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, vinylidene, and allenylidene complexes,[1] the chemistry of higher cumulenylidene complexes is so far limited only to the isolation and stoichiometric reactions of metal−cumulenylidene complexes.[5,6] We have now found the first example of the ruthenium-catalyzed novel reactions via metal−butatrienylidene complexes[5] as key intermediates.

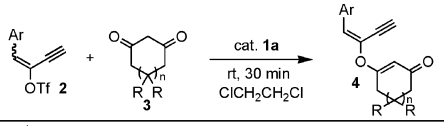
Treatment of 2-(1-phenyl-1-buten-3-ynyl) trifluoromethanesulfonate (**2a**), as a mixture of two stereoisomers (isomer ratio 58/42), with 1,3-cyclopentanedione (**3a**) (3 equiv to **2a**) in the presence of 3 mol % of $[Cp^*RuCl(\mu_2\text{-}SMe)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; **1a**)[4] in $ClCH_2CH_2Cl$ 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 S^iPr moiety $[Cp^*RuCl(\mu_2\text{-}S^iPr)]_2$ (**1b**) did not affect the yield of **4aa**, while that of the corresponding cationic diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*(OH_2)]OTf$ (OTf = OSO_2CF_3; **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]

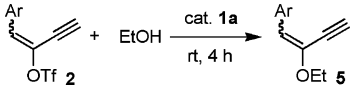


run	2[b]	3	4	yield of 4,(%)[c]	isomer ratio (*E*/*Z*)[d]
1	Ar = Ph (**2a**)	**3a**		91 (**4aa**)	>99/<1
2	Ar = *p*-MeC_6H_4 (**2b**)	**3a**		87 (**4ba**)	>99/<1
3	Ar = *p*-ClC_6H_4 (**2c**)	**3a**		86 (**4ca**)	>99/<1
4	Ar = Ph (**2a**)	**3b**		82[e] (**4ab**)	>99/<1
5	Ar = *p*-MeC_6H_4 (**2b**)	**3b**		55[e] (**4bb**)	>99/<1
6	Ar = *p*-ClC_6H_4 (**2c**)	**3b**		42[e] (**4cb**)	>99/<1
7	Ar = Ph (**2a**)	**3c**		88 (**4ac**)	>99/<1
8	Ar = *p*-MeC_6H_4 (**2b**)	**3c**		84 (**4bc**)	>99/<1
9	Ar = *p*-ClC_6H_4 (**2c**)	**3c**		77 (**4cc**)	>99/<1
10	Ph, Ph, OTf **2d**	**3a**		84 (**4da**)	>99/<1
11	OTf **2e**	**3a**		89 (**4ea**)	>99/<1
12	Ar = Ph (**2a**)	Et, **3d**		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 $ClCH_2CH_2Cl$ (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 $^iPr_2NEt$ in $ClCH_2CH_2Cl$ at room temperature for 20 min

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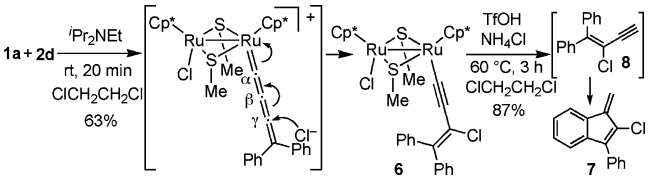
10.1021/ja710013y CCC: $40.75

gave the corresponding butenynyl 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 butenynyl 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]

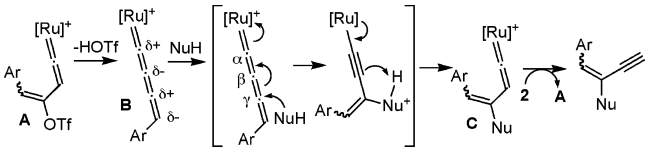
Treatment of **6** with 1 equiv of TfOH in the presence of 5 equiv of NH_4Cl gave **7**[10] in 87% yield (Scheme 3). The indene **7** seems to be produced in situ via Brønsted acid catalyzed intramolecular Friedel−Crafts-type cyclization of **8** released in situ from **6**. These results indicate that 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]

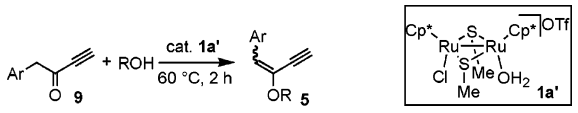
Scheme 4



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 alcohol[12] 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

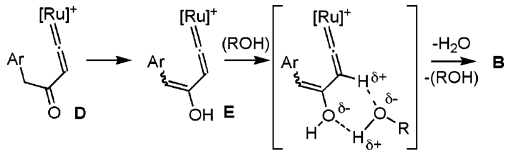
Table 2. Ruthenium-Catalyzed Reactions of **9** with Alcohols in the Presence of **1a′**[a]



run	Ar of **9**	ROH	yield of **5** (%)[b]	isomer ratio[c]
1	Ph (**9a**)	EtOH	60 (**5aa**)	74/26
2	*p*-MeC_6H_4 (**9b**)	EtOH	62 (**5ba**)	77/23
3	*p*-ClC_6H_4 (**9c**)	EtOH	59 (**5ca**)	79/21
4	*p*-$MeOC_6H_4$ (**9d**)	EtOH	55 (**5da**)	77/23
5	*p*-FC_6H_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 ^{1}H 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.

References

(1) For a recent review, see: Bruneau, C.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 2176.
(2) For a recent review, see: Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760.
(3) For a recent review, see: Varela, J. A.; Saá, C. *Chem.−Eur. J.* **2006**, *12*, 6450.
(4) For recent examples, see: (a) Yamauchi, Y.; Onodera, G.; Sakata, K.; Yuki, M.; Miyake, Y.; Uemura, S.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 5175. (b) Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 6488. For a review, see: (c) Nishibayashi, Y.; Uemura, S. *Curr. Org. Chem.* **2006**, *10*, 135.
(5) For reviews, see: (a) Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **1998**, *178−180*, 409. (b) Selegue, J. P. *Coord. Chem. Rev.* **2004**, *248*, 1543. (c) Bruce, M. I. *Coord. Chem. Rev.* **2004**, *248*, 1603. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627.
(6) Ilg, K.; Werner, H. *Chem.−Eur. J.* **2002**, *8*, 2812.
(7) See Supporting Information for experimental procedures.
(8) The molecular structure of **4bc** was also determined by X-ray analysis.
(9) Lomprey, J. R.; Selegue, J. P. *Organometallics* **1993**, *12*, 616.
(10) Cappelli, A.; Galeazzi, S.; Giuliani, G.; Anzini, M.; Donati, A.; Zetta, L.; Mendichi, R.; Aggravi, M.; Giorgi, G.; Paccagnini, E.; Vomero, S. *Macromolecules* **2007**, *40*, 3005.
(11) The result of the reaction of **2a** with EtOD in the presence of **1a** also supports our proposed reaction pathway. See Supporting Information for details.
(12) Ammal, S. C.; Yoshikai, N.; Inada, Y.; Nishibayashi, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, *127*, 9428.
(13) For reviews, see: (a) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474. (b) Okuyama, T. *Acc. Chem. Res.* **2002**, *35*, 12.
(14) For a recent example, see: Miyauchi, H.; Chiba, S.; Fukamizu, K.; Ando, K.; Narasaka, K. *Tetrahedron* **2007**, *63*, 5940 and references therein.
(15) Okimoto, Y.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1590.
(16) Separately, we confirmed that no reaction occurred when **2** and **9** bearing an internal alkyne moiety were used as substrates.

JA710013Y