Ruthenium-Catalyzed Dienyne Formation from Propargylic Alcohols and 1,3-Conjugated Dienes

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Ruthenium-catalyzed carbon−carbon bond forming reactions between propargylic alcohols and acyclic and cyclic 1,3-conjugated dienes give the corresponding dienyne compounds in good to high yields. Only the use of thiolate-bridged diruthenium complexes promotes the catalytic reactions, where a ruthenium−alkynyl complex, a resonance structure of a ruthenium−allenylidene complex, works as a key intermediate. This carbon−carbon bond forming reaction is considered to proceed via a stepwise reaction pathway. The finding described in this article reveals another novel catalytic reactivity of chalcogenolate-bridged diruthenium complexes.

Introduction

Transition metal−allenylidene complexes, which belong to a series of unsaturated carbene derivatives, have attracted a great deal of interest as a new type of organometallic intermediates from synthetic and theoretical viewpoints and also as new materials.[1,2] Although only a few examples of catalytic reactions via such complexes as key intermediates have been reported before,[3] we have recently found that the efficient ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with various heteroatom- and carbon-centered nucleophiles proceeded via ruthenium−allenylidene complexes as intermediates to afford the corresponding propargylic-substituted products in high yields with complete selectivity.[4] Interestingly, these reactions were catalyzed only by chalcogenolate-bridged diruthenium complexes such as $[Cp^*RuCl(\mu_2\text{-}YR)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$, Y = S, Se, Te; **1**) and not by a variety of conventional mono- and diruthenium complexes.[5] As a related work, we reported more recently the carbon−carbon bond forming reactions between propargylic alcohols and alkenes (Scheme 1), which were explained reasonably by proposing a concerted ruthenium−allenylidene−ene reaction process.[6] Unfortunately, only α-methylstyrene derivatives could be employed as starting alkenes, where the corresponding 1,5-enynes were obtained in moderate yields.[6a] As an extension of our study on this type of reactions, we have now found that both acyclic and cyclic 1,3-conjugated dienes worked as effective reagents for ruthenium-catalyzed intermolecular carbon−carbon bond forming reactions to give the corresponding dienyne compounds in good to high yields, the results of which are described here.

Results and Discussion

Treatment of 1-phenyl-2-propyn-1-ol (**2a**) with 2,4-dimethyl-1,3-pentadiene (**3a**) (5 equiv to **2a**) in $ClCH_2CH_2Cl$ in the presence of a catalytic amount of $[Cp^*RuCl(\mu_2\text{-}S^iPr)]_2$ (**1a**) (5 mol % to **2a**) at 60 °C for 1 h afforded 2-methyl-4-methylene-6-phenyl-2-octen-7-yne (**4a**) in 78% isolated yield (Scheme 2). When $[Cp^*RuCl(\mu_2\text{-}SMe)]_2$ (**1b**) was used in place of **1a** as a

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(5) Preparation of various chalcogenolate-bridged diruthenium complexes including X-ray analysis and their catalytic activities toward the propargylic substitution reactions, see: (a) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26. (b) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 5100.

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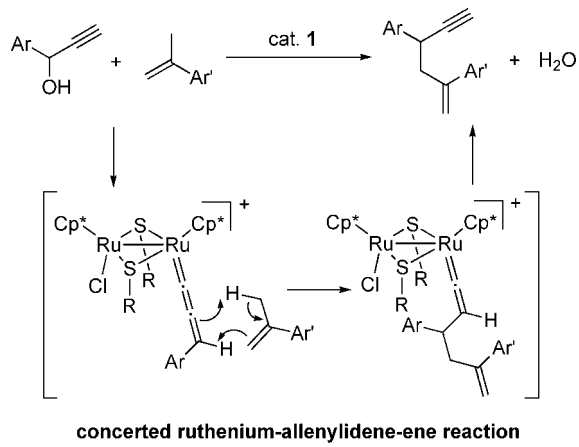
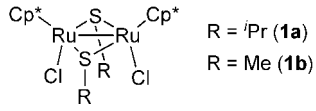
Scheme 1





Scheme 2

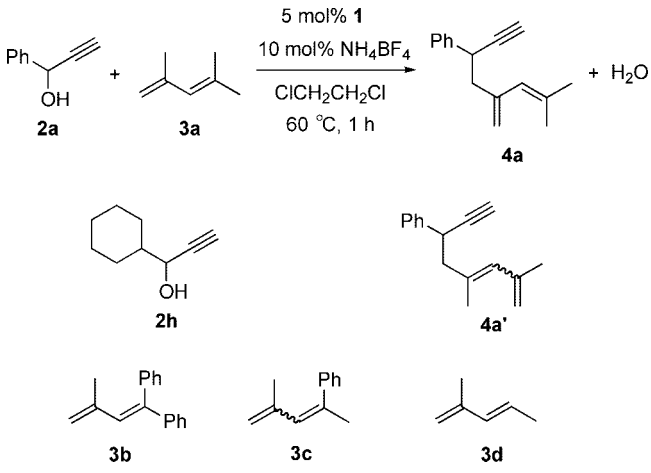


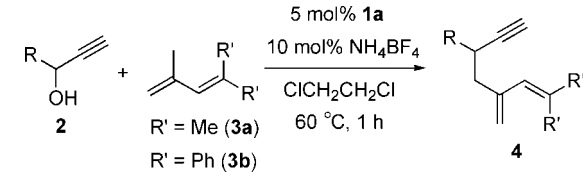
Table 1. Reactions of 1-Phenyl-2-propyn-1-ol (2a) with 2,4-Dimethyl-1,3-pentadiene (3a) Catalyzed by Ruthenium Complexes[a]

run	ruthenium complex	yield of **4a** (%)[b]
1	[Cp*RuCl(μ_2-S^{i}Pr)$_2$] (**1a**)	78
2	[Cp*RuCl(μ_2-SMe)$_2$] (**1b**)	49[c]
3	[$RuCl_2(PPh_3)_3$]	0
4	[$RuCl_2$(*p*-cymene)]$_2$	0
5	[$CpRuCl(PPh_3)_2$]	0
6	[(indenyl)$RuCl(PPh_3)_2$]	0
7	[Cp*$RuCl_2$]$_2$	0

[a] All reactions of **2a** (0.60 mmol) with **3a** (3.00 mmol) were carried out in the presence of ruthenium complex (0.03 mmol) and NH_4BF_4 (0.06 mmol) in $ClCH_2CH_2Cl$ (15 mL) at 60 °C for 1 h. [b] Isolated yield. [c] Two stereoisomeric 2,4-dimethyl-6-phenyl-1,3-octadien-7-ynes (**4a′**) were obtained in 39% yield.

catalyst, a lower yield (49%) of **4a** was obtained together with two stereoisomeric 2,4-dimethyl-6-phenyl-1,3-octadien-7-ynes (**4a′**) (39%). Typical results are shown in Table 1. It is noteworthy that only thiolate-bridged diruthenium complexes (**1a** and **1b**) worked effectively as catalysts (Table 1, runs 1 and 2). Other conventional mono- and diruthenium complexes such as [$RuCl_2(PPh_3)_3$], [$RuCl_2$(*p*-cymene)]$_2$, [$CpRuCl(PPh_3)_2$], [(indenyl)$RuCl(PPh_3)_2$], and [Cp*$RuCl_2$]$_2$ were not effective at all as catalysts (Table 1, runs 3–7).

Table 2. Reactions of Propargylic Alcohols (2) with Acyclic Dienes (3) Catalyzed by Diruthenium Complex 1a[a]

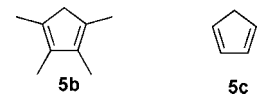


run	R = **2**	diene (**3**)	yield of **4** (%)[b]
1	Ph (**2a**)	**3a**	78 (**4a**)
2	*p*-MeC_6H_4 (**2b**)	**3a**	80 (**4b**)
3	*p*-ClC_6H_4 (**2c**)	**3a**	73 (**4c**)
4	*p*-BrC_6H_4 (**2d**)	**3a**	76 (**4d**)
5	*p*-$NO_2C_6H_4$ (**2e**)	**3a**	70 (**4e**)
6	*p*-$CF_3C_6H_4$ (**2f**)	**3a**	27 (**4f**)
7	$Ph_2C{=}CH$ (**2g**)	**3a**	77 (**4g**)
8	Ph (**2a**)	**3b**	67 (**4h**)

[a] All reactions of **2** (0.60 mmol) with **3** (3.00 mmol) were carried out in the presence of **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) in $ClCH_2CH_2Cl$ (15 mL) at 60 °C for 1 h. [b] Isolated yield.

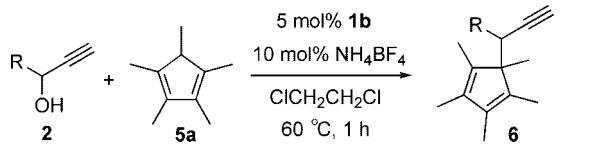
Reactions of a variety of propargylic alcohols with **3a** were carried out in the presence of a catalytic amount of **1a**. Typical results are shown in Table 2. The presence of a substituent such as methyl, chloro, bromo, and nitro groups at the *para*-position in the benzene ring of propargylic alcohols did not give much effect on the yield of the produced dienyne (**4**) (70–80%) (Table 2, runs 1–5), while the presence of a trifluoromethyl group dramatically decreased its yield (27%) (Table 2, run 6). Reaction of propargylic alcohol bearing an alkenyl moiety at the propargylic position (**2g**) with **3a** proceeded smoothly to give the corresponding trienyne (**4g**) in 77% isolated yield (Table 2, run 7). Unfortunately, no reaction took place at all by using 1-cyclohexyl-2-propyn-1-ol (**2h**) as a propargylic substrate. The alcohol **2a** reacted with 3-methyl-1,1-diphenyl-1,3-butadiene (**3b**) to give 3-methylene-1,1,5-triphenyl-1-hepten-6-yne (**4h**) in 67% isolated yield (Table 2, run 8), while no reaction occurred when other conjugated 1,3-dienes such as 2-methyl-4-phenyl-1,3-pentadiene (**3c**) and 2-methyl-1,3-pentadiene (**3d**) were employed in place of **3a** or **3b**.

Next, reactions of propargylic alcohols with a cyclic conjugated 1,3-diene such as 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (**5a**) were investigated. Treatment of **2a** with **5a** in $ClCH_2CH_2Cl$ in the presence of a catalytic amount of **1b** (5 mol% to **2a**) at 60 °C for 1 h afforded 1,2,3,4,5-pentamethyl-5-(1-phenyl-2-propynyl)-1,3-cyclopentadiene (**6a**) in 64% isolated yield (Table 3, run 1). Introduction of an electron-donating substituent such as a methoxy group at the *para*-position in the benzene ring of **2a** dramatically increased the yield of the corresponding propargylated cyclopentadiene (**6b**) (Table 3, run 2). Reactions of other propargylic alcohols such as 1-(2-naphthyl)-2-propyn-1-ol (**2k**) and **2g** with **5a** also proceeded smoothly (Table 3, runs 6 and 7). Here also, no reaction with the alcohol **2h** took place at all. On the other hand, only a complex mixture was obtained when 1,2,3,4-tetramethyl-1,3-cyclopentadiene (**5b**) and 1,3-cyclopentadiene (**5c**) were used as dienes in place of **5a**.



As in the case of the reaction with α-methylstyrenes (Scheme 1),[6a] reactions with acyclic dienes such as **3a** and **3b** might be considered to proceed via a concerted ruthenium−allenylidene−ene reaction pathway as shown in Scheme 3. However, the result

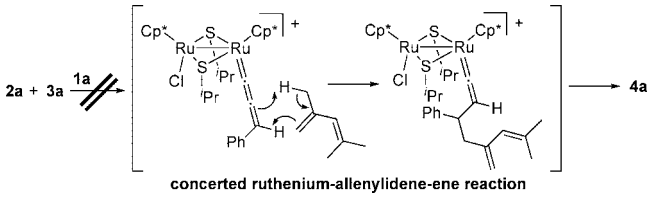
Table 3. Reaction of Propargylic Alcohols (2) with 1,2,3,4,5-Pentamethylcyclopentadiene (5a) Catalyzed by Diruthenium Complex 1b[a]



run	R of **2**	yield of **6** (%)[b]
1	Ph (**2a**)	64 (**6a**)
2	*p*-$MeOC_6H_4$ (**2i**)	92 (**6b**)
3	*p*-MeC_6H_4 (**2b**)	69 (**6c**)
4	*p*-ClC_6H_4 (**2c**)	50 (**6d**)
5	*p*-FC_6H_4 (**2j**)	79 (**6e**)
6	2-naphthyl (**2k**)	77 (**6f**)
7	$Ph_2C{=}CH$ (**2g**)	59 (**6g**)

[a] All reactions of **2** (0.60 mmol) with **5a** (3.00 mmol) were carried out in the presence of **1b** (0.03 mmol) and NH_4BF_4 (0.06 mmol) in $ClCH_2CH_2Cl$ (15 mL) at 60 °C for 1 h. [b] Isolated yield.

Scheme 3



of reactions with cyclic conjugated 1,3-dienes such as **5a** under the same reaction conditions allows us to reconsider the reaction pathway, because the formation of a compound like **6a** cannot be explained by a concerted ruthenium−allenylidene−ene reaction process. We now propose a stepwise reaction pathway as another possibility for this catalytic reaction (Scheme 4).[7] Namely, the alkene moiety in **5a** attacks the alkynyl complex bearing a cationic γ-carbon (**A**), which is a resonance structure of the allenylidene complex prepared from a propargylic alcohol and the diruthenium complex, to give an alkynyl complex **B**. The final product **6a** can be formed from a vinylidene complex (**C**) via the complex **B**. To examine the possibility of this proposed stepwise reaction process, we carried out the reaction of **2a** with an acyclic diene such as 4-methyl-2-phenyl-1,3-pentadiene (**3e**), where no reaction is expected to occur if the reaction proceeds via the concerted ruthenium−allenylidene−ene reaction pathway. Unexpectedly, however, the reaction of **2a** with **3e** in the presence of a catalytic amount of **1a** at 60 °C for 1 h led to the formation of two stereoisomeric 2-methyl-4,6-diphenyl-1,3-octadien-7-ynes (**4i**) in 56% isolated yield (Scheme 5). A slightly higher yield of **4i** was observed when **1b** was used as a catalyst in place of **1a**. The formation of this type of compounds can be explained by a newly proposed stepwise reaction process (Scheme 6). The driving force for this process seems to be the stability of the intermediate carbocationic species **E**. The isomerization of both double bonds in **3e** might take place during the catalytic reaction.

In order to know whether the reaction pathway shown in Scheme 6 is energetically favorable or not, we investigated the density functional theory calculation at the B3LYP/LANL2DZ level of theory for the model reaction of $[CpRuCl(\mu_2\text{-}SMe)_2RuCp(=C=C=CH_2)]^+$ (**I**; Cp = η^5-C_5H_5) with 4-methyl-1,3-pentadiene (**3f**) (Scheme 7).[8] A relative energy diagram and optimized structures are shown in Figure 1. As shown in Figure 1, the expected nucleophilic attack of **3f** on the cationic γ-carbon in **I** was revealed to occur easily to give the corresponding alkynyl complex (**III**) through a complex **II**. Then, it is followed by the smooth transfer of one of the terminal protons into the alkynyl moiety to give the corresponding vinylidene complex (**V**) via a transition state **TS3**. This result indicates that such a stepwise reaction pathway for the formation of **4i** is energetically favorable and reasonable. However, we do not yet have any reasonable explanation for the formation of **4a′** by use of the catalyst **1b**. Here, the use of the complex bearing a sterically more demanding S^{i}Pr moiety (**1a**) inhibited the formation of **4a′** (Table 1, run 2).

In summary, we have found the ruthenium-catalyzed carbon−carbon bond forming reactions between propargylic alcohols and acyclic and cyclic 1,3-conjugated dienes to give the corresponding dienyne compounds in good to high yields. Only the use of thiolate-bridged diruthenium complexes promoted these catalytic reactions, where ruthenium−alkynyl complexes, resonance structures of ruthenium−allenylidene complexes, worked as key intermediates. It was proposed that the catalytic reaction proceeds via a stepwise reaction pathway. The finding described in this article revealed another novel catalytic reactivity of chalcogenolate-bridged diruthenium complexes.

Experimental Section

General Method. ^{1}H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using $CDCl_3$ as solvent. GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. IR spectra were recorded on a JASCO FT/IR 4100 Fourier transform infrared spectrophotometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. GC-MS analyses were carried out on a Shimazu GC-MS QP-5000 spectrometer. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by usual methods and distilled before use. Preparation of propargylic alcohols (**2**) was carried out according to the literature methods.[4c]

Ruthenium-Catalyzed Carbon−Carbon Bond Forming Reaction between Propargylic Alcohol and 1,3-Conjugated Diene. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with 2,4-dimethyl-1,3-pentadiene (**3a**) in the presence of $[Cp^*Ru(\mu_2\text{-}S^iPr)Cl]_2$ (**1a**) as a catalyst is described below. In a 20 mL round-bottomed flask were placed **1a** (20.8 mg, 0.03 mmol) and NH_4BF_4 (6.3 mg, 0.06 mmol) under N_2. Anhydrous $ClCH_2CH_2Cl$ (15 mL) was added, and then the mixture was magnetically stirred at room temperature for 5 min. After the addition of **2a** (79.3 mg, 0.60 mmol) and **3a** (288.5 mg, 3.0 mmol), the reaction flask was kept at 60 °C for 1 h. The reaction mixture was concentrated under reduced pressure by an aspirator, and then the residue was purified by column chromatography (SiO_2) with hexane to give 2-methyl-4-methylene-6-phenyl-2-octen-7-yne (**4a**) as a colorless oil (98.4 mg, 0.47 mmol; 78% yield).

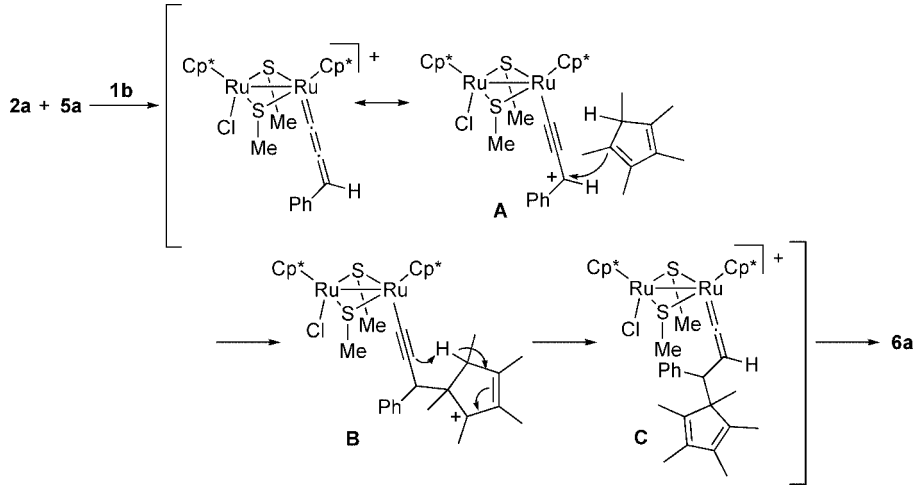
4a: colorless oil; ^{1}H NMR δ 1.76 (s, 3H), 1.79 (s, 3H), 2.24 (d, 1H, J = 2.6 Hz), 2.46 (dd, 1H, J = 6.6 and 13.5 Hz), 2.56 (dd, 1H, J = 8.6 and 13.5 Hz). 3.72 (ddd, 1H, J = 2.6, 6.6 and 8.6 Hz), 4.80 (s, 1H), 4.96 (s, 1H), 5.57 (s, 1H), 7.18–7.36 (m, 5H); ^{13}C NMR δ 20.1, 25.7, 29.9, 41.5, 67.1, 86.1, 108.4, 123.1, 126.3, 127.9, 128.4, 136.3, 140.2, 151.1. Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.67. Found: C, 91.36; H, 8.54.

Spectroscopic data and isolated yield of other products are as follows.

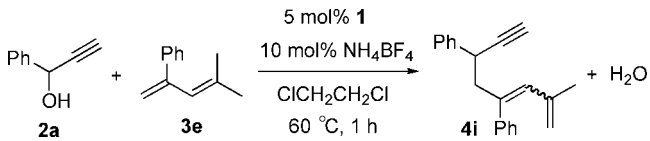
(7) Gotoh, H.; Masui, R.; Ogino, H.; Shoji, M.; Hayashi, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 6853.

(8) See Supporting Information for details.

Scheme 4



Scheme 5



1a; 56% (3.4:1)
1b; 63% (6.4:1)

4b: yield 80%; colorless oil; ^{1}H NMR δ 1.76 (s, 3H), 1.79 (s, 3H), 2.23 (d, 1H, J = 2.4 Hz), 2.31 (s, 3H), 2.44 (dd, 1H, J = 6.8 and 13.4 Hz), 2.53 (dd, 1H, J = 8.6 and 13.4 Hz), 3.68 (ddd, 1H, J = 2.4, 6.8 and 8.6 Hz), 4.80 (s, 1H), 4.96 (s, 1H), 5.57 (s, 1H), 7.09–7.22 (m, 4H); ^{13}C NMR δ 19.6, 21.0, 26.5, 36.4, 46.8, 70.8, 86.1, 115.4, 125.2, 127.3, 129.1, 136.2, 136.3, 138.2, 142.8. Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.79; H, 8.98.

4c: yield 73%; colorless oil; ^{1}H NMR δ 1.75 (s, 3H), 1.79 (s, 3H), 2.26 (d, 1H, J = 2.4 Hz), 2.42 (dd, 1H, J = 7.1 and 21 Hz), 2.55 (dd, 1H, J = 8.3 and 21 Hz), 3.69 (ddd, 1H, J = 2.4, 7.1 and 8.3 Hz), 4.80 (s, 1H), 4.93 (s, 1H), 5.54 (s, 1H), 7.25–7.27 (m, 4H); ^{13}C NMR δ 19.6, 26.5, 36.2, 46.7, 71.3, 85.3, 115.8, 125.0, 128.5, 128.9, 132.5, 136.5, 139.6, 142.2; HRMS calcd for $C_{16}H_{17}Cl$ [M], 244.1019; found, 244.1022.

4d: yield 76%; colorless oil; ^{1}H NMR δ 1.75 (s, 3H), 1.78 (s, 3H), 2.26 (d, 1H, J = 2.6 Hz), 2.42 (dd, 1H, J = 7.2 and 13.5 Hz), 2.55 (dd, 1H, J = 8.2 and 13.5 Hz), 3.68 (ddd, 1H, J = 2.6, 7.2 and 8.2 Hz), 4.80 (s, 1H), 4.93 (s, 1H), 5.54 (s, 1H), 7.17–7.45 (m, 4H); ^{13}C NMR δ 19.7, 26.3, 30.1, 43.7, 67.1, 85.8, 108.1, 120.1, 122.4, 129.9, 132.2, 135.1, 140.5, 150.9. Anal. Calcd for $C_{16}H_{17}Br$: C, 66.45; H, 5.92. Found: C, 66.51; H, 6.00.

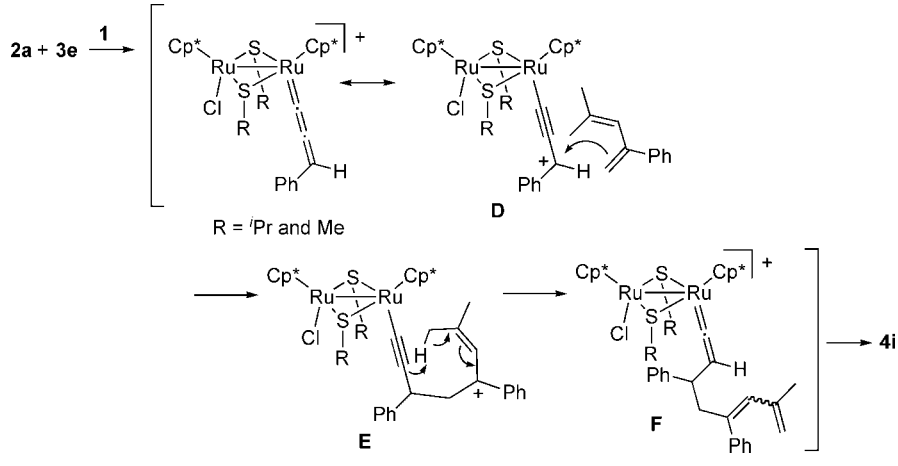
4e: yield 70%; yellow oil; ^{1}H NMR δ 1.76 (s, 3H), 1.79 (s, 3H), 2.33 (d, 1H, J = 2.5 Hz), 2.46 (dd, 1H, J = 7.2 and 13.5 Hz), 2.62 (dd, 1H, J = 8.0 and 13.5 Hz), 3.84 (ddd, 1H, J = 2.5, 7.2 and 8.0 Hz), 4.72 (s, 1H), 4.81 (s, 1H), 5.54 (s, 1H), 7.26–8.18 (m,4H); ^{13}C NMR δ 19.6, 26.3, 30.4, 43.8, 67.1, 87.2, 108.1, 122.1, 123.6, 129.3, 135.2, 146.1, 147.5, 151.3. Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71. Found: C, 75.51; H, 6.83.

4f: yield 27%; colorless oil; ^{1}H NMR δ 1.75 (s, 3H), 1.79 (s, 3H), 2.29 (d, 1H, J = 2.6 Hz), 2.46 (dd, 1H, J = 6.9 and 20.7 Hz), 2.59 (dd, 1H, J = 8.6 and 20.7 Hz), 3.78 (ddd, 1H, J = 2.6, 6.9, and 8.6 Hz), 4.81 (s, 1H), 4.94 (s, 1H), 5.54 (s, 1H), 7.42–7.59 (m, 4H); ^{13}C NMR δ 19.6, 26.5, 36.7, 46.6, 71.7, 84.9, 115.9, 124.1 (q, J = 271.6 Hz), 124.9, 125.3 (q, J = 6.5 Hz), 127.9, 129.1 (q, J = 30.2 Hz), 130.6, 136.7, 142.1. Anal. Calcd for $C_{17}H_{17}F_3$: C, 73.36; H, 6.16. Found: C, 73.58; H, 6.28.

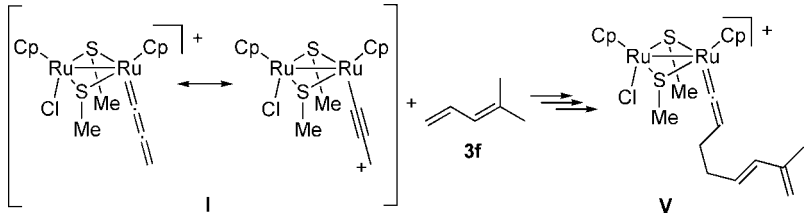
4g: yield 77%; yellow oil; ^{1}H NMR δ 1.54 (s, 3H), 1.67 (s, 3H), 2.16 (d, 1H, J = 2.4 Hz), 2.33 (dd, 1H, J = 8.0 and 13.4 Hz), 2.44 (dd, 1H, J = 7.1 and 13.4 Hz), 3.23–3.31 (m, 1H), 4.81 (s, 1H), 5.03 (s, 1H), 5.31 (s, 1H), 5.92 (d, 1H, J = 10.1 Hz), 7.21–7.38 (m, 10H); ^{13}C NMR δ 19.7, 22.5, 25.7, 41.9, 67.1, 85.5, 108.1, 115.3, 122.1, 126.2, 127.7, 128.4, 134.9, 135.1, 140.1, 150.9. Anal. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 92.03; H, 7.76.

4h: yield 67%; yellow oil; ^{1}H NMR δ 2.24 (d, 1H, J = 2.4 Hz), 2.31 (dd, 1H, J = 8.9 and 13.4 Hz), 2.40 (dd, 1H, J = 6.0 and 13.4 Hz), 3.68 (ddd, 1H, J = 2.4, 6.0 and 8.9 Hz), 4.98 (s, 1H), 5.01 (s, 1H), 6.50 (s, 1H), 7.13–7.33 (m, 15H); ^{13}C NMR δ 36.9,

Scheme 6



Scheme 7



44.7, 71.5, 85.4, 119.9, 126.7, 127.3, 127.4, 127.8, 128.1, 128.2, 128.3, 128.5, 128.6, 130.3, 140.4, 140.9, 142.5, 142.6, 143.3; HRMS calcd for $C_{26}H_{22}$ [M], 334.1721; found, 334.1715.

4i: yield 56% (major isomer:minor isomer = 3.4:1); colorless oil; ^{1}H NMR δ major isomer, 1.39 (s, 3H), 2.27 (d, 1H, J = 2.5 Hz), 2.76 (d, 2H, J = 7.7 Hz), 3.51 (dt, 1H, J = 2.5 and 7.7 Hz), 4.77 (s, 1H), 4.80 (s, 1H), 6.07 (s, 1H), 7.18–7.42 (m, 10 H); minor isomer, 2.31 (d, 1H, J = 2.5 Hz), 3.62 (dt, 1H, J = 2.5 and 7.7 Hz), 6.11 (s, 1H); ^{13}C NMR δ major isomer, 22.2, 36.2, 49.9, 71.6, 85.3, 117.2, 126.7, 126.8, 126.9, 127.3, 127.9, 128.4, 128.7, 131.9, 138.1, 140.5, 141.8; HRMS calcd for $C_{21}H_{20}$ [M], 271.1565; found, 272.1552.

6a: yield 64%; yellow oil; ^{1}H NMR δ 1.22 (s, 3H), 1.45 (s, 3H), 1.48 (s, 3H), 1.76 (s, 3H), 2.01 (s, 3H), 2.28 (d, 1H, J = 2.6 Hz), 3.75 (d, 1H, J = 2.6 Hz), 7.02–7.09 (m, 5H); ^{13}C NMR δ 10.5, 10.6, 10.8, 12.1, 19.6, 43.2, 58.4, 72.4, 84.7, 126.3, 126.5, 127.5, 135.5, 135.6, 137.5, 137.6, 138.0. Anal. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.06; H, 8.89.

6b: yield 92%; orange solid; 47.3–48.2 °C; ^{1}H NMR δ 1.21 (s, 3H), 1.48 (s, 3H), 1.51 (s, 3H), 1.75 (s, 3H), 2.01 (s, 3H), 2.27 (d, 1H, J = 2.7 Hz), 3.71 (s, 3H), 3.77 (d, 1H, J = 2.7 Hz), 6.63 (d, 2H, J = 8.8 Hz), 6.97 (d, 2H, J = 8.8 Hz); ^{13}C NMR δ 10.4, 10.6, 10.7, 11.9, 19.5, 42.3, 55.0, 58.3, 72.2, 85.0, 112.0, 128.6, 130.0, 135.6, 135.7, 137.8, 138.8, 158.1. Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.31; H, 8.44.

6c: yield 69%; yellow solid; 59.5–60.0 °C; ^{1}H NMR δ 1.22 (s, 3H), 1.50 (s, 3H), 1.53 (s, 3H), 1.75 (s, 3H), 2.02 (s, 3H), 2.24 (s, 3H), 2.26 (d, 1H, J = 2.7 Hz), 3.74 (d, 1H, J = 2.7 Hz), 6.89–6.97 (m, 4H); ^{13}C NMR δ 10.5, 10.6, 10.7, 11.9, 19.7, 21.0, 42.7, 58.2, 72.2, 85.0, 127.4, 127.5, 134.7, 135.5, 135.6, 135.8, 137.9, 138.9. Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.53; H, 9.14.

6d: yield 50%; white solid; 54.1–54.8 °C; ^{1}H NMR δ 1.22 (s, 3H), 1.48 (s, 3H), 1.49 (s, 3H), 1.75 (s, 3H), 2.00 (s, 3H), 2.31 (d, 1H, J = 2.7 Hz), 3.73 (d, 1H, J = 2.7 Hz), 6.97 (d, 2H, J = 8.5 Hz), 7.06 (d, 2H, J = 8.5 Hz); ^{13}C NMR δ 10.4, 10.5, 10.7, 12.0, 19.4, 42.4, 58.2, 72.8, 84.2, 126.7, 128.9, 132.1, 136.0, 136.1, 136.2, 137.5, 138.5. Anal. Calcd for $C_{19}H_{21}Cl$: C, 80.12; H, 7.43. Found: C, 80.11; H, 7.62.

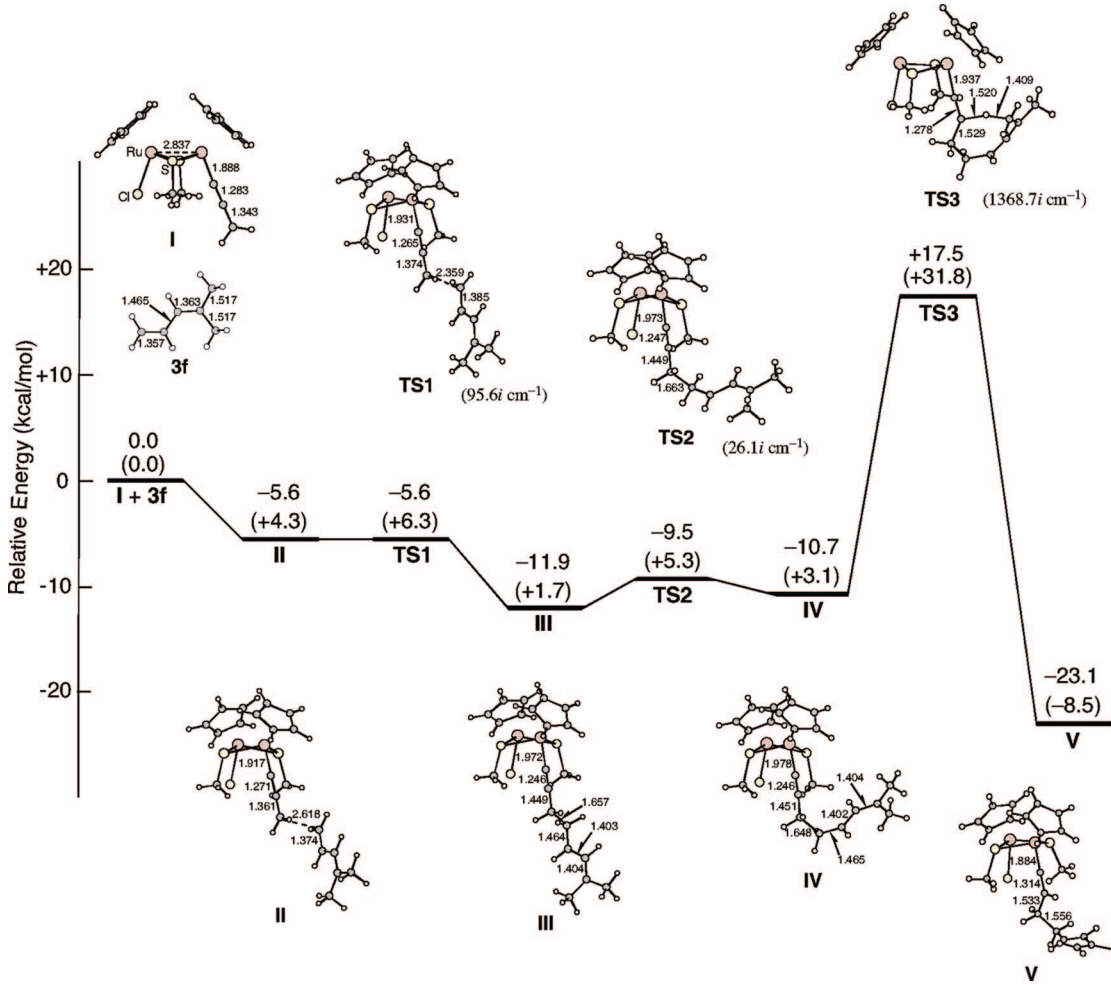


Figure 1. Relative energy diagram (kcal/mol) for the model reaction of $[CpRuCl(SMe)_2RuCp(=C=C=CH_2)]^+$ (**I**; Cp = η^5-C_5H_5) with 4-methyl-1,3-pentadiene (**3f**) at the B3LYP/LANL2DZ level of theory. Values in parentheses are relative free energies at 298.15 K.

6e: yield 79%; white solid, 49.5–50.2 °C; ^{1}H NMR δ 1.21 (s, 3H), 1.47 (s, 3H), 1.48 (s, 3H), 1.75 (s, 3H), 2.00 (s, 3H), 2.30 (d, 1H, J = 3.0 Hz), 3.73 (d, 1H, J = 3.0 Hz), 6.73–6.79 (m, 2H), 6.97–7.02 (m, 2H). ^{13}C NMR δ 10.4, 10.5, 10.7, 12.0, 19.4, 42.2, 58.2, 72.6, 84.4, 113.1 (d, J = 21.2 Hz), 128.8 (d, J = 7.8 Hz), 133.1 (d, J = 3.4 Hz), 135.7, 135.8, 137.3, 138.3, 161.3 (d, J = 243.1 Hz). Anal. Calcd for $C_{19}H_{21}F$: C, 85.03; H, 7.89. Found: C, 84.74; H, 7.91.

6f: yield 77%; white solid; 85.2–85.6 °C; ^{1}H NMR δ 1.27 (s, 3H), 1.39 (s, 3H), 1.43 (s, 3H), 1.79 (s, 3H), 2.07 (s, 3H), 2.32 (d, 1H, J = 2.5 Hz), 3.92 (d, 1H, J = 2.5 Hz), 7.20 (d, 1H, J = 8.2 Hz), 7.33–7.36 (m, 2H), 7.51–7.56 (m, 2H), 7.67–7.71 (m, 2H); ^{13}C NMR δ 10.7, 10.8, 12.2, 14.2, 19.9, 43.2, 58.5, 72.7, 84.7, 125.1, 125.2, 125.9, 126.2, 126.3, 127.2, 127.6, 132.3, 132.6, 135.3, 135.7, 135.8, 137.7, 138.7. Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.73; H, 8.16.

6g: yield 59%; red oil; ^{1}H NMR δ 1.03 (s, 3H), 1.21 (s, 3H), 1.77 (s, 3H), 1.87 (s, 3H), 2.00 (s, 3H), 2.24 (d, 1H, J = 2.6 Hz), 3.27 (dd, 1H, J = 2.6, 10.1 Hz), 5.26 (d, 1H, J = 10.1 Hz), 6.93–6.97 (m, 2H), 7.17–7.37 (m, 8H); ^{13}C NMR δ 9.5, 11.1, 11.2, 11.9, 19.2, 36.2, 57.8, 71.7, 85.0, 126.2, 126.9, 127.1, 127.7, 127.8, 127.9, 130.0, 134.4, 135.6, 138.9, 139.6, 139.7, 142.2, 143.1. Anal. Calcd for $C_{27}H_{28}$: C, 91.99; H, 8.01. Found: C, 91.81; H, 7.84.

Computational Details. All the density functional theory (DFT) calculations were carried out with the Gaussian 03 program package.[9] Geometry optimization and analytical vibrational frequency analysis were performed by the Kohn–Sham DFT method using the B3LYP hybrid functional.[10] The double-ζ valence basis set with the Hay−Wadt effective core potential (ECP) for Ru, Cl, and S and the Dunning−Hay valence double-ζ basis set for C and H were used for the Gaussian basis functions (LANL2DZ).[11,12]

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Supporting Information Available: Computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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