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Synthesis and Reactivities of Cationic Diruthenium Complexes with Terminal Vinylidene Ligands. Hydration and Novel Cyclization of Acetylenes on the Diruthenium Center

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The cationic diruthenium complexes with a terminal vinylidene ligand [Cp*RuCl(μ_2-SPr^i)$_2$-Ru(=C=CHR)Cp*][OTf] (**3a**, R = COOMe; **3b**, R = COMe; **3c**, R = H; Cp* = η^5-C$_5$Me$_5$, OTf = OSO$_2$CF$_3$) were obtained in high yields by the reaction of [Cp*RuCl(μ_2-SPr^i)$_2$Ru(OH$_2$)-Cp*][OTf] with HC≡CR. Hydration of **3a** and **3b** gave the carbonyl complex [Cp*RuCl(μ_2-SPr^i)$_2$Ru(CO)Cp*][OTf] and CH$_3$R in almost quantitative yields, while the reaction of **3c** with water gave the μ_2-acetyl complex [Cp*RuCl(μ_2-SPr^i)$_2${μ_2-C(=O)Me}RuCp*][OTf] (**5**). A reaction mechanism for the former reactions is proposed, which includes hydration of the vinylidene ligands to form the μ_2-β-ketoacetyl complexes with a six-membered dimetallacyclic structure [Cp*Ru(μ_2-SPr^i)$_2$(η^1:η^1-μ_2-COCH$_2$COR′)RuCp*]$^+$ (R′ = OMe, Me) and the following decarbonylation reaction of the μ_2-COCH$_2$COR′ ligand on the bimetallic center to produce the carbonyl complex and CH$_3$COR′ via the enolato−carbonyl complexes [Cp*Ru(CO)(μ_2-SPr^i)$_2$Ru(OCR′=CH$_2$)Cp*]$^+$. In accordance with this mechanism, the reaction of **3a** with MeOH afforded [Cp*Ru(μ_2-SPr^i)$_2${η^1:η^1-μ_2-C(OMe)=CHCOOMe}RuCp*][OTf] (**7**). Complexes **3a** and **3b** reacted with *p*-tolylacetylene to form the dinuclear metallacyclic complexes **9a** and **9b** [Cp*Ru(μ_2-SPr^i)$_2${η^1:η^1-μ_2-C(Tol)=CCCH=C(R′)O}RuCp*][OTf] (**9a**, R′ = OMe; **9b**, R′ = Me), respectively. The structures of **3b**, **5**, **7**, and **9a** have been determined by X-ray crystallography.

Introduction

Intensive efforts have recently been devoted to investigations into the syntheses and reactivities of multinuclear transition metal complexes, because novel chemical transformations are expected to occur at the multimetallic centers.[1] In our precedent studies on thiolato- or sulfido-bridged multinuclear complexes, we have synthesized a series of dinuclear Cp*Ru−thiolato complexes, such as [Cp*Ru(μ_2-SPr^i)$_2$RuCp*],[2] [Cp*Ru-(μ_2-SPr^i)$_3$RuCp*],[3] and [Cp*RuCl(μ_2-SPr^i)$_2$Ru(OH$_2$)Cp*]-[OTf][4,5] (**1**), and revealed that these complexes provide unique bimetallic reaction sites for various stoichiometric and catalytic transformations of substrates such as alkynes, organic halides, and hydrazines.[6] Of special interest are the facile couplings of HCCR (R = Ph, Tol, cyclohexenyl) at the bimetallic center of the cationic diruthenium complex **1** to form complexes with an indan-type framework[4a] (**2**) (eq 1), and the linear di- and trimerization of ferrocenylacetylene catalyzed by **1**.[4b] In these reactions, dinuclear species with a terminal vinylidene ligand are considered to play a critical role. However, such species have not yet been prepared from complex **1**, although a diruthenium complex with a terminal allenylidene ligand was obtained from **1** and 1,1-diaryl-2-propyn-1-ol.[4a]

On the other hand, it has been well-documented that the hydration of terminal alkynes promoted by certain transition metal complexes affords acyl or alkyl−carbonyl complexes.[7] Such reactions have been considered

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(5) In a previous paper[4a] we reported that complex **1** had a formula of [Cp*Ru(μ_2-Cl)(μ_2-SPr^i)$_2$RuCp*][OTf]. However, on the basis of more detailed studies by variable temperature ^{1}H NMR spectroscopy, preliminary X-ray crystallography, and carefully repeated elemental analyses, we have finally concluded that complex **1** is formulated as [Cp*RuCl(μ_2-SPr^i)$_2$Ru(OH$_2$)Cp*][OTf] in the solid state, and in solution, a rapid exchange between Cl and H$_2$O ligands on the two ruthenium atoms takes place to make the Cp* protons virtually equivalent in ^{1}H NMR at room temperature. ^{1}H NMR (CDCl$_3$): δ 4.05 (sep, 2 H, J = 6.8 Hz, SC*H*Me$_2$), 2.97 (br, 2 H, Ru(OH$_2$)), 1.64 (s, 30 H, Cp*), 1.52 (d, 12 H, J = 6.8 Hz, SCH*Me$_2$*). At −50 °C, the Me signals at δ 1.64 and 1.52 split into two singlets (δ 1.63, 1.59 (15 H each)) and two doublets (δ 1.52, 1.44 (6 H each)), respectively, and the signal at δ 2.97 due to the H$_2$O ligand shifted to δ 3.13. Anal. Calcd for C$_{27}$H$_{46}$ClF$_3$O$_4$Ru$_2$S$_3$: C, 39.29; H, 5.62; Cl, 4.29; S, 11.66. Found: C, 38.83; H, 5.59; Cl, 4.67; S, 11.81.

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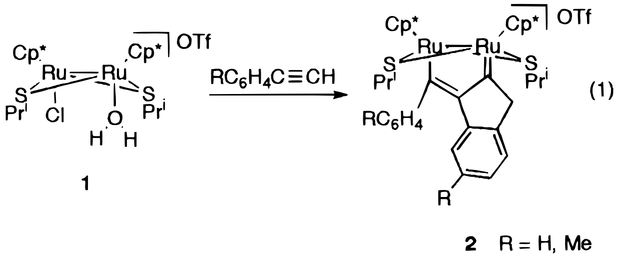
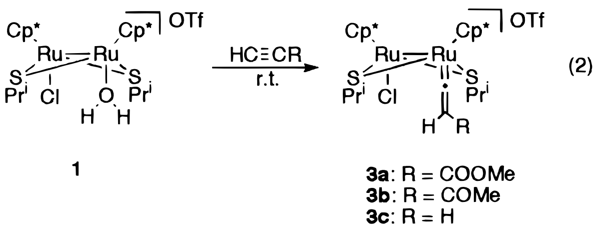


to include the hydrolysis of vinylidene ligands derived from terminal alkynes, although only a limited number of studies have provided direct information about the details of this reaction mechanism.[7a] This background prompted us to investigate the reactivities of the isolable diruthenium vinylidene complexes derived from terminal alkynes and complex **1**.

In this article, we describe the synthesis and reactivities of the cationic diruthenium complexes with a terminal vinylidene ligand [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CHR)Cp*][OTf] (**3a** R = COOMe; **3b**, R = COMe; **3c**, R = H). Interestingly, the hydration of **3a** and **3b** results in the very facile decarbonylation of the initially formed acyl ligand on the dinuclear center through a diruthenacyclic intermediate. The reactions of complexes **3a** and **3b** with *p*-tolylacetylene produce novel diruthenacycles fused with a furan ring.

Results and Discussion

Preparation and Characterization of the Cationic Diruthenium Vinylidene Complexes. Treatment of complex **1** with methyl propiolate, in dry CH$_2$Cl$_2$ at room temperature for 10 min, resulted in the almost quantitative formation of the dinuclear vinylidene complex [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CHCOOMe)Cp*][OTf] (**3a**) (eq 2). Similar reactions of **1** with 3-butyn-2-one and acetylene gas also afforded the corresponding vinylidene complexes [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CH-COMe)Cp*][OTf] (**3b**) and [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CH$_2$)Cp*][OTf] (**3c**), respectively.



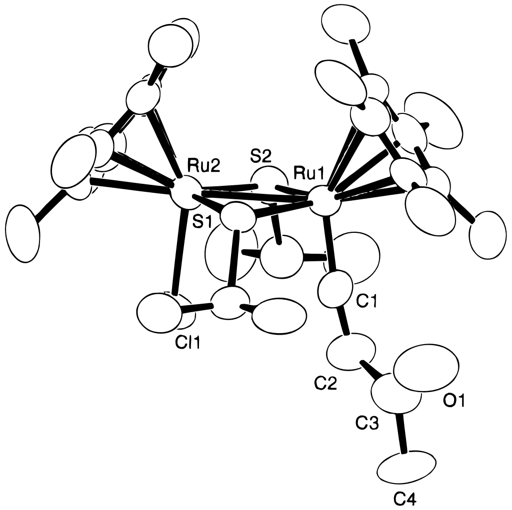


Figure 1. ORTEP drawing for the cationic part of **3b**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for 3b

Distances (Å)			
Ru(1)−Ru(2)	2.806(1)	Ru(2)−S(2)	2.288(3)
Ru(1)−S(1)	2.321(2)	O(1)−C(3)	1.25(1)
Ru(1)−S(2)	2.338(3)	C(1)−C(2)	1.30(1)
Ru(1)−C(1)	1.785(9)	C(2)−C(3)	1.52(1)
Ru(2)−Cl(1)	2.413(3)	C(3)−C(4)	1.50(1)
Ru(2)−S(1)	2.295(2)		
Angles (deg)			
Ru(2)−Ru(1)−C(1)	99.3(3)	Ru(1)−C(1)−C(2)	173.3(9)
S(1)−Ru(1)−S(2)	103.79(9)	C(1)−C(2)−C(3)	126(1)
Ru(1)−Ru(2)−Cl(1)	95.58(7)	O(1)−C(3)−C(2)	122(1)
S(1)−Ru(2)−S(2)	106.27(9)	O(1)−C(3)−C(4)	117(1)
Ru(1)−S(1)−Ru(2)	74.87(7)	C(2)−C(3)−C(4)	119(1)
Ru(1)−S(2)−Ru(2)	74.68(8)		

The ^{1}H NMR spectra of **3a**−**c** exhibited two singlets attributable to nonequivalent Cp* ligands and two doublets due to the diastereotopic methyl protons of the SPr^i ligands, suggesting that complex **3** has an unsymmetrically substituted diruthenium core bridged by two SPr^i ligands. The ^{13}C{^{1}H} NMR spectra of **3a**−**c** showed typical low-field resonances at δ 361.6−365.8, as well as signals at δ 93.3−113.8, which are diagnostic of the α- and β-carbon atoms of the vinylidene ligands, respectively.[8] The vinyl proton signals observed in the ^{1}H NMR (**3a**, δ 4.77; **3b**, δ 5.22; **3c**, δ 3.87) also confirmed the formation of the vinylidene ligands from the starting alkynes. The IR spectra of **3** showed strong ν(C=C) absorptions (**3a**, 1601 cm^{-1}; **3b**, 1549 cm^{-1}; **3c**, 1601 cm^{-1}) which are characteristic of the vinylidene ligands. These spectroscopic features clearly indicate that one molecule of each alkyne is incorporated onto the diruthenium center to form the terminal vinylidene complexes **3a**−**c**, as formulated in eq 2.

The molecular structure of **3b** was unambiguously determined by X-ray crystallography. An ORTEP drawing of **3b** is shown in Figure 1, with selected bond lengths and angles summarized in Table 1. The ORTEP view displays an unsymmetrically substituted dinuclear structure, in which the terminal vinylidene and chloro ligands are coordinated to the respective ruthenium centers in mutual cis configuration, and is in full accordance with the NMR and IR observations. The Ru(1)=C(1)=C(2) moiety is almost linear (173.3(9)°), and the Ru(1)=C(1) and C(1)=C(2) bond distances (1.785(9) and 1.30(1) Å, respectively) fall within the range of the reported values for vinylidene complexes.[8] The intramolecular distance between the two ruthenium atoms (2.806(1) Å) corresponds to a Ru−Ru single bond (2.6−2.9 Å).[2−4]

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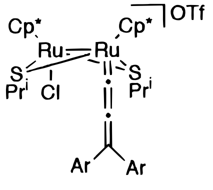
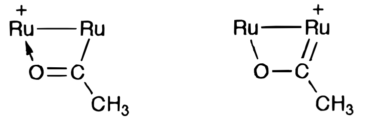
Chart 1



4: Ar = Ph, Tol

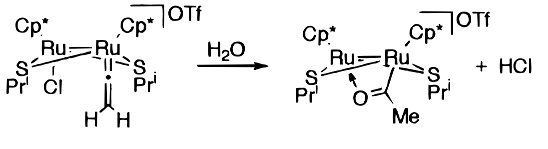
Chart 2



5A: acetyl form **5B**: oxycarbene form

We have previously reported that the reaction of complex **1** with HCCC(OH)Ar$_2$ (Ar = Ph, Tol) affords the terminal allenylidene complexes [Cp*RuCl(μ_2-SPr^i)$_2$-Ru(=C=C=CAr$_2$)Cp*][OTf][4a] (Chart 1, **4**), while the reaction with arylacetylene or cyclohexenylacetylene does not lead to isolation of vinylidene complexes but results in the coupling of the initially formed vinylidene ligand with a second alkyne molecule (eq 1). The lower reactivity of methyl propiolate, 3-butyn-2-one, and acetylene gas, compared with either arylacetylene or cyclohexenylacetylene, enabled the high-yield synthesis of the vinylidene complexes **3**. The isolation of complexes **3** also suggests that the first step of the alkyne coupling reaction depicted in eq 1 is the formation of the corresponding terminal vinylidene complexes.

Reactions of the Vinylidene Complexes 3 with H$_2$O and Methanol. Although the previously reported diruthenium allenylidene complex **4** failed to react with nucleophiles such as H$_2$O and alcohol, the vinylidene complexes **3** reacted with H$_2$O smoothly. Thus, hydration of **3c**, performed on an alumina column, gave the stable μ_2-acetyl complex [Cp*Ru(μ_2-SPr^i)$_2${μ_2-C(=O)Me}-RuCp*][OTf] (**5**) in high yield (eq 3). The IR spectrum of **5** shows a significantly low ν(C=O) absorption (1395 cm^{-1}), indicating that the acetyl ligand derived from the vinylidene ligand is coordinated to the two metals in a μ_2-fashion with a considerable contribution of the oxycarbene structure (Chart 2, **5B**).



(3)

3c **5** (81 %)

The molecular structure of **5** was further determined by X-ray crystallography. Selected bond distances and angles are summarized in Table 2. The ORTEP view of **5** given in Figure 2 clearly shows that the acetyl ligand is bound to the diruthenium core in a η^1:η^1-μ_2-fashion, forming a diruthenacyclic structure. The Ru(1)−C(1) bond (2.005(6) Å) is considerably longer than the Ru=C(vinylidene) bond (1.785(9) Å) found in **3b**, but significantly shorter than the Ru−C single bond lengths found in [Cp*RuBr(μ_2-SPr^i)$_2$Ru(CH$_2$CH$_2$Ph)Cp*] (2.152(8) Å),[2a] [Cp*Ru{μ_2-C(=CHFc)CCFc}(μ_2-SPr^i)$_2$RuCp*][OTf] (Fc = ferrocenyl) (2.091(10) Å),[4b] and [Cp*(Bu^{t}NC)Ru(μ_2-SPr^i)[μ_2-C(Tol)=CHC{C(Tol)=CH-SPr^i}=CH(Tol)]RuCp*] (2.166(7) Å).[2d] The Ru(1)−C(1) bond is considerably inclined toward the Ru(2) atom (Ru(2)−Ru(1)−C(1), 71.1(2)°), suggesting a strong interaction between the Ru(2) and O(1) atoms. The C(1)−O(1) bond distance (1.264(7) Å) falls between the values expected for acyl and oxycarbene ligands.[9] These metrical features also support the large contribution of the oxycarbene structure in complex **5**.

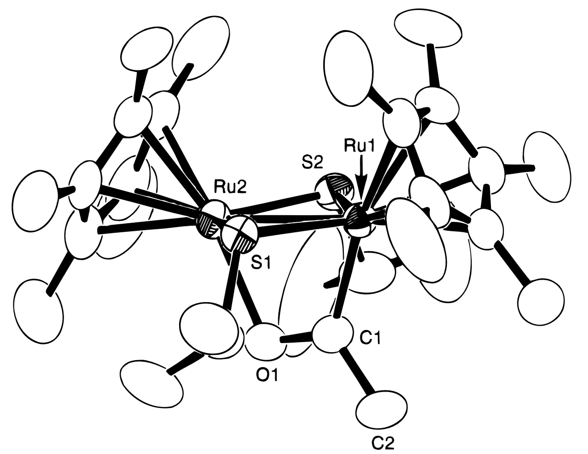


Figure 2. ORTEP drawing for the cationic part of **5**. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances and Angles for 5

Distances (Å)			
Ru(1)−Ru(2)	2.6950(8)	Ru(2)−S(2)	2.319(2)
Ru(1)−S(1)	2.295(2)	Ru(2)−O(1)	2.189(4)
Ru(1)−S(2)	2.303(2)	O(1)−C(1)	1.264(7)
Ru(1)−C(1)	2.005(6)	C(1)−C(2)	1.490(8)
Ru(2)−S(1)	2.317(2)		

Angles (deg)			
Ru(2)−Ru(1)−C(1)	71.1(2)	Ru(1)−S(2)−Ru(2)	71.33(5)
S(1)−Ru(1)−S(2)	108.96(6)	Ru(2)−O(1)−C(1)	104.7(4)
Ru(1)−Ru(2)−O(1)	68.8(1)	Ru(1)−C(1)−O(1)	115.4(4)
S(1)−Ru(2)−S(2)	107.66(6)	Ru(1)−C(1)−C(2)	127.7(5)
Ru(1)−S(1)−Ru(2)	71.52(5)	O(1)−C(1)−C(2)	116.9(6)

In contrast, the reaction of **3a** with H$_2$O in CH$_2$ClCH$_2$Cl at room temperature resulted in the quantitative formation of methyl acetate and the cationic carbonyl complex [Cp*RuCl(μ_2-SPr^i)$_2$Ru(CO)Cp*][OTf] (**6**), the latter of which was characterized spectroscopically. Gas chromatographic analysis of the reaction solution over a period of 64 h confirmed the clean formation of methyl acetate as the only volatile organic product (eq 4). Similarly, **3b** reacted with H$_2$O to give acetone and complex **6** in high yields. Interestingly, this type of decarbonylation was not observed in the hydration of **3c**, although the initial step of the hydration−decarbonylation of **3a** and **3b** is also considered to proceed via the acyl complexes formed by the nucleophilic addition of H$_2$O to the vinylidene ligands. We presume that the two adjacent ruthenium centers cooperatively promote the decarbonylation (deinsertion of CO) of the acyl ligands formed from complexes **3a** and **3b**. A plausible mechanism for this hydration-decarbonylation

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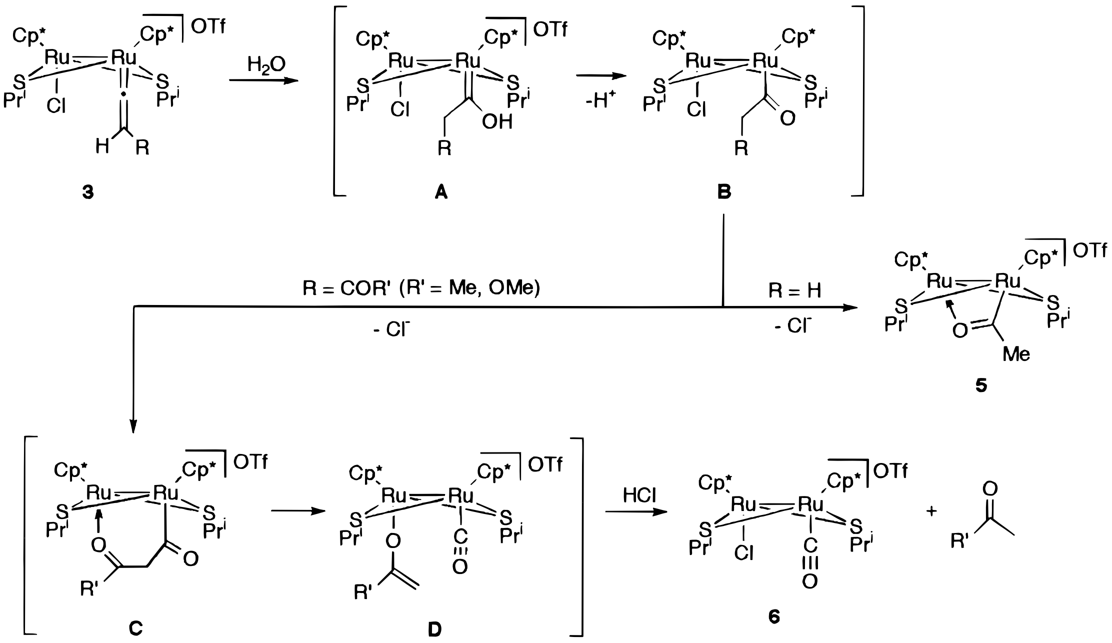
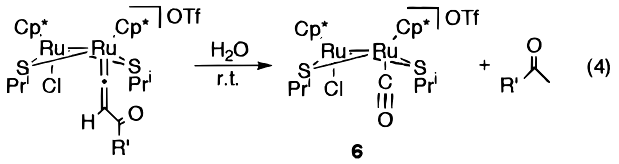
Scheme 1



reaction is shown in Scheme 1.

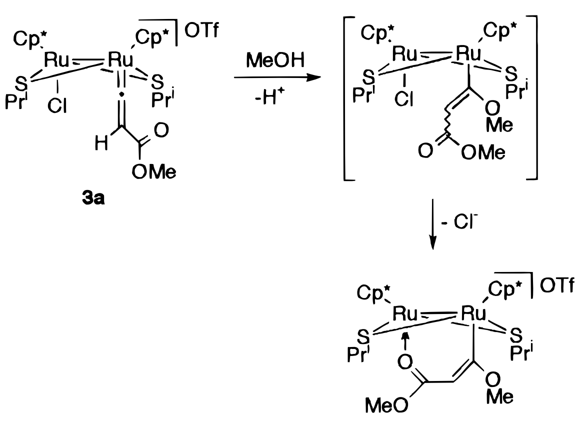


	6	
3a (R' = OMe)	96 %	95 %
3b (R' = Me)	99 %	78 %

At first, the α-carbon of the vinylidene ligand in **3** is attacked by H_2O to give the hydroxycarbene complex **A**, whose deprotonation generates the acyl intermediate **B**. In the reaction of **3c**, substitution of the chloro ligand by the acetyl oxygen results in the formation of the μ_2-acetyl complex **5**, which was isolated as a stable product. However, in the case of **3a** and **3b**, coordination of the other remote carbonyl group in the acyl moiety to the adjacent ruthenium center gives rise to the μ_2-acyl intermediate **C**, and the succeeding C−C bond cleavage in the bridging acyl ligand leads to the enolato−carbonyl complex **D**. Finally, acidolysis of complex **D** affords the final product **6** with either methyl acetate or acetone. In principle, the decarbonylation of an acyl ligand demands an additional vacant site on the metal center to accommodate both the generated CO and alkyl ligands. However, the conversion of **C** to **D** demands no further vacant site to realize the decarbonylation of the acyl ligand, and the reaction is considered to be a facile process compared with the decarbonylation of **5**. We are inclined to believe that the two adjacent ruthenium atoms participate cooperatively in the decarbonylation process and the six-membered dimetallacyclic structure of **C** is responsible for the facile decarbonylation observed during the hydration of **3a** and **3b**, although none of the intermediates **A**−**D** were observed by ^{1}H NMR.

In order to obtain further information about the mechanism, we have examined the reaction of **3a** with methanol. Treatment of **3a** with excess methanol in CH_2ClCH_2Cl at 90 °C led to the isolation of the cationic vinyl complex [Cp*Ru(μ_2-SPr^i)$_2${η^1:η^1-μ_2-C(OMe)=CHCOOMe}RuCp*][OTf] (**7**) in good yield (Scheme 2), and its molecular structure was determined by X-ray analysis. An ORTEP drawing for **7** is shown in Figure 3, and selected bond lengths and angles are summarized in Table 3. The ORTEP view clearly shows the μ_2-coordination of the −C(OMe)=CHCOOMe ligand by way of both the σ-bond at the vinylic carbon C(1) and the σ-donation of the lone pair on the carbonyl oxygen O(3). The ^{1}H NMR signal at δ 4.97, assignable to the vinyl proton, and the IR absorption at 1495 cm^{-1}, attributable to the coordinated ester group, are both compatible with the crystal structure. The Ru(2)−O(3) distance (2.120(7) Å) is somewhat shorter than that of the bridging acetyl ligand of **5** (2.189(4) Å), but falls within the range of Ru−O distances found for metallacyclic complexes containing a coordinated ester functionality such as [Cp*Ru(CHMeCH$_2$COOMe)(NO)][B{3,5-C$_6$H$_3$-(CF$_3$)$_2$}$_4$] (2.146(8) Å)[10] and [Ru{C(COOMe)=CH-COOMe}(CO)$_2$(PMe$_2$Ph)$_2$][HgCl$_3$] (2.13(1) Å).[11] The six-

Scheme 2



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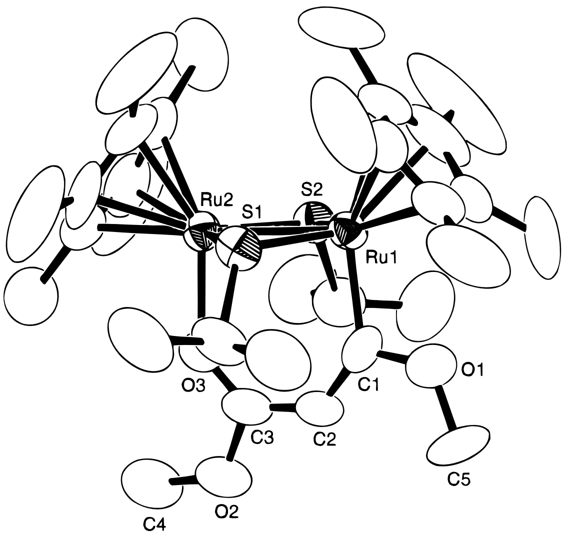


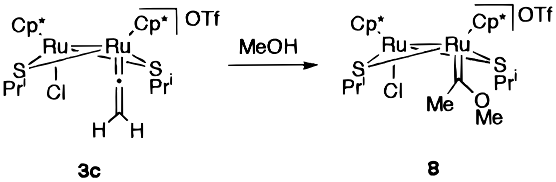
Figure 3. ORTEP drawing for the cationic part of **7**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances and Angles for 7

Distances (Å)			
Ru(1)−Ru(2)	2.774(1)	Ru(2)−O(3)	2.120(7)
Ru(1)−S(1)	2.286(3)	O(1)−C(1)	1.35(1)
Ru(1)−S(2)	2.293(3)	O(2)−C(3)	1.34(1)
Ru(1)−C(1)	2.08(1)	O(3)−C(3)	1.26(1)
Ru(2)−S(1)	2.322(3)	C(1)−C(2)	1.35(1)
Ru(2)−S(2)	2.316(3)	C(2)−C(3)	1.39(1)
Angles (deg)			
Ru(2)−Ru(1)−C(1)	94.7(3)	Ru(1)−C(1)−O(1)	107.1(8)
S(1)−Ru(1)−S(2)	106.8(1)	Ru(1)−C(1)−C(2)	135.8(9)
Ru(1)−Ru(2)−O(3)	93.2(2)	O(1)−C(1)−C(2)	117(1)
S(1)−Ru(2)−S(2)	104.9(1)	C(1)−C(2)−C(3)	128(1)
Ru(1)−S(1)−Ru(2)	74.01(9)	O(2)−C(3)−O(3)	116(1)
Ru(1)−S(2)−Ru(2)	73.99(9)	O(2)−C(3)−C(2)	113(1)
Ru(2)−O(3)−C(3)	136.8(8)	O(3)−C(3)−C(2)	131(1)

membered diruthenacycle is essentially planar and perpendicular to the Ru_2S_2 core.

Complex **7** is obviously formed through the nucleophilic attack of a methanol molecule at the α-carbon of the vinylidene ligand in **3a**, followed by the substitution of the chloride ligand by the carbonyl oxygen (Scheme 2). The 1-methoxyvinyl ligand in **7** thus formed corresponds to the enol ether form of the μ-acyl ligand in the intermediate **C** depicted in Scheme 1. Therefore, the ready formation of **7** strongly supports that the dimetallacyclic μ-acyl complex **C** is involved in the hydration−decarbonylation reaction of **3a** as a key intermediate. On the other hand, the reaction of **3c** with methanol resulted in the formation of the methoxycarbene complex $[Cp^*RuCl(\mu_2\text{-}SPr^i)_2Ru\{=CMe(OMe)\}Cp^*][OTf]$ (**8**) (eq 5), which corresponds to the ether form of the hydroxycarbene intermediate **A** in Scheme 1.

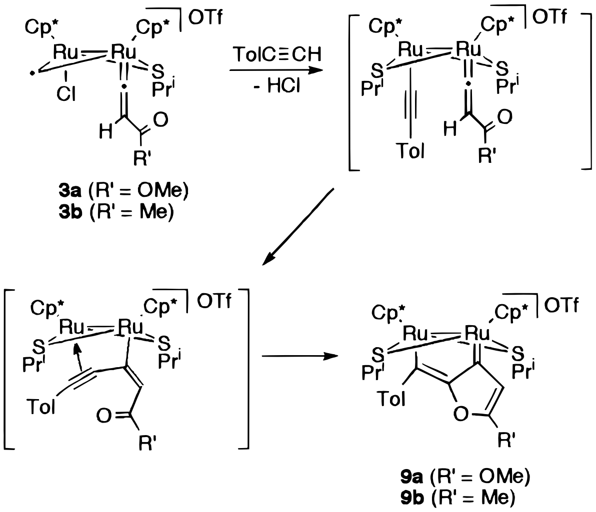


(5)

3c **8**

Reactions of the Vinylidene Complexes 3 with *p*-Tolylacetylene. As depicted in eq 1, the diruthenium core of complex **1** provides an effective reaction site for the intriguing coupling of arylacetylenes. This reaction is considered to proceed via the vinylidene−acetylide coupling on the cationic diruthenium center forming an intermediary butenynyl complex followed by its intramolecular cyclization to give the fused metallacycle.[4a] Although several vinylidene−acetylide coupling reactions on monometallic centers have been reported to afford butenynyl complexes,[12] the subsequent cyclization of the butenynyl ligands occurring on the diruthenium site is very unique and seems to be characteristic of the cationic dinuclear core. In order to gain further insight into the reactivity of diruthenium vinylidene complexes, we have examined the reaction of complex **3** with tolylacetylene.

Scheme 3



Treatment of complex **3a** with *p*-tolylacetylene in CH_2ClCH_2Cl at reflux for 3 h afforded a new metallacyclic complex **9a** in 48% yield, along with complex **2** (R = Me) (Scheme 3). Formation of **2** indicates that the vinylidene ligand in **3a** is partly dissociated to form methyl propiolate and a coordinatively unsaturated diruthenium complex under heating. Under similar conditions, complex **3b** reacted with *p*-tolylacetylene to produce an analogous metallacycle **9b** in 62% yield, but complex **3c** afforded complex **2** (R = Me) as the only identified product.

The molecular structure of **9a** was fully determined by X-ray analysis. An ORTEP drawing for **9a** is shown in Figure 4, and selected bond lengths and angles are summarized in Table 4. The ORTEP view shows that a diruthenacyclopentadiene unit fused with a furan ring is formed on the cationic diruthenium core by the coupling of the vinylidene ligand and tolylacetylene. Therefore this reaction accomplishes the stepwise incorporation of two different acetylenes, i.e., methyl propiolate and tolylacetylene, on the bimetallic center of **1**. The fused ring system (Ru(1), Ru(2), C(1), C(2),

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(12) (a) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (b) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565. (c) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604. (d) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444. (e) Field, L. D.; George, A. V.; Malouf, E. Y.; Slip, I. H. M.; Hambley, T. W. *Organometallics* **1991**, *10*, 3842. (f) Field, L. D.; George, A. V.; Purches, G. R.; Slip, I. H. M. *Organometallics* **1992**, *11*, 3019. (g) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837. (h) Schäfer, V. M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem.* **1993**, *105*, 1377. (i) Bianchini, C.; Innocenti, P.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Organometallics* **1996**, *15*, 272.

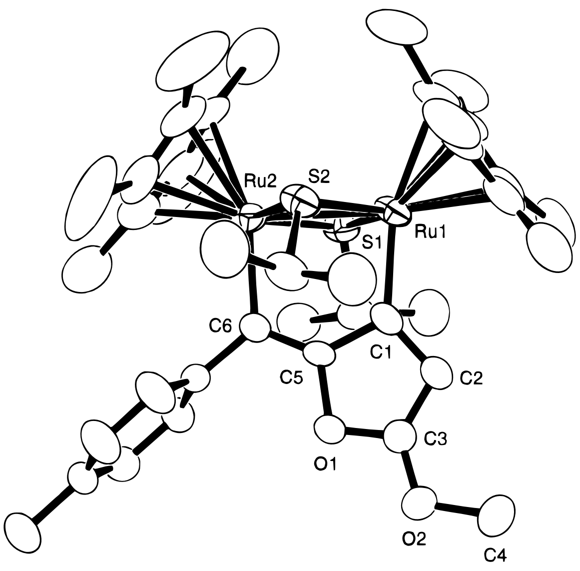


Figure 4. ORTEP drawing for the cationic part of **9a**. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances and Angles for 9a

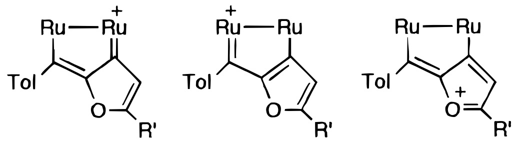
Distances (Å)

Ru(1)−Ru(2)	2.7942(6)	O(1)−C(3)	1.329(4)
Ru(1)−S(1)	2.297(1)	O(1)−C(5)	1.443(4)
Ru(1)−S(2)	2.303(1)	C(1)−C(2)	1.392(5)
Ru(1)−C(1)	2.009(4)	C(1)−C(5)	1.435(5)
Ru(2)−S(1)	2.308(1)	C(2)−C(3)	1.374(5)
Ru(2)−S(2)	2.304(1)	C(5)−C(6)	1.344(5)
Ru(2)−C(6)	2.063(4)		

Angles (deg)

Ru(2)−Ru(1)−C(1)	85.1(1)	C(1)−C(2)−C(3)	107.5(4)
S(1)−Ru(1)−S(2)	105.50(4)	O(1)−C(3)−O(2)	113.0(4)
Ru(1)−Ru(2)−C(6)	87.2(1)	O(1)−C(3)−C(2)	113.7(4)
S(1)−Ru(2)−S(2)	105.09(4)	O(2)−C(3)−C(2)	133.3(4)
Ru(1)−S(1)−Ru(2)	74.72(3)	O(1)−C(5)−C(1)	108.1(3)
Ru(1)−S(2)−Ru(2)	74.69(4)	O(1)−C(5)−C(6)	121.0(3)
C(3)−O(1)−C(5)	104.8(3)	C(1)−C(5)−C(6)	130.8(4)
Ru(1)−C(1)−C(2)	134.3(3)	Ru(2)−C(6)−C(5)	116.8(3)
Ru(1)−C(1)−C(5)	119.8(3)	Ru(2)−C(6)−C(7)	125.6(3)
C(2)−C(1)−C(5)	105.8(3)	C(5)−C(6)−C(7)	117.6(4)

Chart 3



9A **9B** **9C**

C(3), C(5), C(6), and O(1)) is almost planar. The Ru(1)−C(1) (2.009(4) Å) and C(5)−C(6) (1.344(5) Å) distances are clearly shorter than the Ru(2)−C(6) (2.063(4) Å) and C(1)−C(5) (1.435(5) Å) distances, respectively. These data indicate that contribution of the resonance structure **9B** is small in **9a**, which is in contrast to the delocalized diruthenacyclopentadiene structure found in **2**.[3a] On the other hand, the O(1)−C(3) bond (1.329(4) Å) is significantly shorter than the O(1)−C(5) bond (1.443(4) Å), suggesting the important contribution of the resonance structure **9C** (Chart 3).

The above metallacycle formation is considered to proceed via a mechanism similar to that proposed for the formation of complex **2**.[3a] Thus, *p*-tolylacetylene is at first incorporated onto the diruthenium center of **3** as an acetylide ligand, and the following vinylidene−acetylide coupling affords a butenynyl complex. Further intramolecular nucleophilic attack of the carbonyl oxygen atom on the acetylenic carbon coordinated to the cationic ruthenium center results in the formation of complex **9** (Scheme 3). This type of transformation of a butenynyl ligand to a dimetallacycle-furan fused cyclic system is unprecedented and is probably realized only on the adjacent bimetallic centers. Studies aimed at developing further reactivities of sulfur-bridged multinuclear complexes are actively in progress in our group.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were dried by standard methods and distilled before use. NMR spectra were recorded on a JEOL EX-270 spectrometer, and IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400II CHN analyzer. A Shimadzu GC-14A instrument equipped with a flame ionization detector was employed for quantitative analyses of organic products. Alumina for column chromatography was purchased from Nakarai Tesque, Inc. (Alumina Activated 200). The starting material [Cp*RuCl(μ_2-SPr^i)$_2$Ru(OH$_2$)Cp*] (**1**) was prepared by a published method.[4a] Other reagents were obtained from commercial sources and used without further purification.

Preparation of [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CHCOOMe)Cp*][OTf] (3a). To a CH_2Cl_2 (10 mL) solution of **1** (397 mg, 0.481 mmol) was added methyl propiolate (41 μL, 0.49 mmol), and the mixture was stirred at room temperature for 10 min. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from CH_2Cl_2−ether to give **3a** as brown crystals (401 mg, 94%). IR (KBr): ν(C=O) 1703 cm^{-1}; ν(C=C) 1601 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.77 (s, 1 H, vinyl), 4.72 (sep, 2 H, J = 6.6 Hz, SC*H*Me$_2$), 3.63 (s, 3 H, OMe), 1.97, 1.68 (s, 15 H each, Cp*), 1.63, 1.43 (d, 6 H each, J = 6.6 Hz, SCH*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 361.6 (C$_\alpha$), 163.1 (C=O), 105.3 (C$_\beta$), 110.0, 101.0 (Cp*), 51.3 (OMe), 42.8 (S*C*HMe$_2$), 23.4, 23.2 (SCH*Me*$_2$), 10.6, 10.1 (Cp*). Anal. Calcd for $C_{31}H_{48}ClF_3O_5Ru_2S_3$: C, 41.77; H, 5.43, Found: C, 41.58; H, 5.41.

Preparation of [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CHCOMe)Cp*][OTf] (3b). To a CH_2Cl_2 (5 mL) solution of **1** (457 mg, 0.554 mmol) was added 3-butyn-2-one (44 μL, 0.56 mmol), and the mixture was stirred at 0 °C for 1 min. After removal of the solvent under reduced pressure, the resulting solid was recrystallized from CH_2Cl_2−ether to give **3b** as brown crystals (370 mg, 76%). IR (KBr): ν(C=O) 1686 cm^{-1}; ν(C=C) 1549 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.22 (s, 1 H, vinyl), 4.70 (sep, 2 H, J = 6.6 Hz, SC*H*Me$_2$), 1.94 (s, 3 H, COMe), 1.98, 1.69 (s, 15 H each, Cp*), 1.64, 1.44 (d, 6 H each, J = 6.6 Hz, SCH*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 362.0 (C$_\alpha$), 193.5 (C=O), 113.8 (C$_\beta$), 110.6, 101.4 (Cp*), 43.5 (S*C*HMe$_2$), 31.3 (CO*Me*), 24.0, 23.9 (SCH*Me*$_2$), 11.2, 10.7 (Cp*). Anal. Calcd for $C_{31}H_{48}ClF_3O_4Ru_2S_3$: C, 42.53; H, 5.53. Found: C, 42.15; H, 5.51.

Preparation of [Cp*RuCl(μ_2-SPr^i)$_2$Ru(=C=CH$_2$)Cp*][OTf] (3c). Acetylene gas was bubbled through a CH_2Cl_2 (10 mL) solution of **1** (251 mg, 0.311 mmol) at room temperature for 5 min. After removal of the solvent under reduced pressure, the residual solid was recrystallized from CH_2Cl_2−ether to give **3c** as brown crystals (248 mg, 96%). IR (KBr): ν(C=C) 1622 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.68 (sep, 2 H, J = 6.7 Hz, SC*H*Me$_2$), 3.87 (s, 2 H, vinyl), 1.90, 1.67 (s, 15 H each, Cp*), 1.56, 1.42 (d, 6 H each, J = 6.7 Hz, SCH*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 365.8 (C$_\alpha$), 107.3, 100.1 (Cp*), 93.3 (C$_\beta$), 41.6 (S*C*HMe$_2$), 23.5 (SCH*Me*$_2$), 10.7, 10.3 (Cp*). Anal. Calcd for $C_{29}H_{46}ClF_3O_3Ru_2S_3$: C, 41.79; H, 5.56. Found: C, 41.66; H, 5.56.

Reaction of 3a with Water. To a CH_2ClCH_2Cl (4 mL) solution of **3a** (117 mg, 0.131 mmol) was added a drop of water,

Table 5. X-ray Crystallographic Data for 3b, 5, 7, and 9a

	3b	5	7	9a
formula	$C_{31}H_{48}ClF_3O_4S_3Ru_2$	$C_{29}H_{47}F_3O_4S_3Ru_2$	$C_{32}H_{51}F_3O_6S_3Ru_2$	$C_{40}H_{55}F_3O_5S_3Ru_2$
fw	875.49	815.00	887.07	971.19
space group	*Pbca*	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
cryst syst	orthorhombic	monoclinic	triclinic	triclinic
cryst color	dark brown	dark brown	dark brown	dark brown
cryst dimens, mm	0.50 × 0.40 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.40 × 0.70	0.20 × 0.40 × 0.70
a, Å	31.373(4)	15.807(3)	12.424(1)	13.441(2)
b, Å	16.337(2)	14.236(3)	15.187(1)	15.205(2)
c, Å	14.167(3)	16.590(2)	10.3468(9)	11.288(1)
α, deg			94.98(1)	96.210(9)
β, deg		114.949(9)	92.270(10)	101.133(9)
γ, deg			100.396(7)	69.987(9)
V, Å^3	7260(1)	3384.9(7)	1909.8(3)	2124.5(5)
Z	8	4	2	2
D_{calcd}, g cm^{-1}	1.602	1.599	1.542	1.518
$F(000)$, e	3568	1664	908	996
μ(Mo Kα), cm^{-1}	11.27	11.26	10.08	9.12
2θ range, deg	$5 < 2\theta < 55$	$4 < 2\theta < 55$	$6 < 2\theta < 55$	$5 < 2\theta < 50$
scan rate, deg min^{-1}	16	16	16	16
rflns measd	$+h,+k,+l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,\pm k,\pm l$
no. of unique rflns	9129	8103	8787	7462
trans factors	0.93−1.00	0.85−1.00	0.79−1.00	0.81−1.00
no. of rflns used	3251 [$I > 3\sigma(I)$]	4374 [$I > 3\sigma(I)$]	4810 [$I > 3\sigma(I)$]	5276 [$I > 3\sigma(I)$]
no. of variables	398	371	381	479
R^a	0.054	0.045	0.059	0.034
$R_w{}^b$	0.030	0.039	0.051	0.024
GOF^c	1.92	1.66	4.13	2.21
max resd dens, e Å^{-3}	1.16	0.76	1.38	0.60

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. [c] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parms})]^{1/2}$.

and the mixture was stirred for 64 h at room temperature. GC analysis of the resulting solution indicated the formation of methyl acetate in 95% yield. Removal of the solvent in vacuo gave **6** as a brown powder (107 mg, 96%). IR (KBr): ν(CO) 2000 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.46 (sep, 2 H, J = 6.6 Hz, SC*H*Me$_2$), 1.94, 1.68 (s, 15 H each, Cp*), 1.57, 1.42 (d, 6 H each, J = 6.6 Hz, SCH*Me*$_2$). Anal. Calcd for $C_{28}H_{44}ClF_3O_4Ru_2S_3$: C, 40.26; H, 5.31. Found: C, 39.87; H, 5.40.

Reaction of 3b with Water. To a CH_2ClCH_2Cl (5 mL) solution of **3b** (141 mg, 0.161 mmol) was added a drop of water, and the mixture was stirred for 78 h at room temperature. GC analysis of the resulting solution indicated the formation of acetone in 78% yield. Removal of the solvent in vacuo gave **6** as a brown powder (136 mg, 99%).

Reaction of 3c with Water. A CH_2Cl_2 (3 mL) solution of **3c** (66 mg, 0.079 mmol) was passed through a column packed with activated alumina. Slow elution with CH_2Cl_2 gave a brown band, which was collected and evaporated to give **5** (52 mg, 81%). IR (KBr): ν(C=O) 1395 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.82 (sep, 2 H, J = 6.6 Hz, SC*H*Me$_2$), 1.87 (s, 3 H, CO*Me*), 1.86, 1.80 (s, 15 H each, Cp*), 1.57, 1.49 (d, 6 H each, J = 6.6 Hz, SCH*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 291.0 (Ru*C*OMe), 93.7 (Cp*), 43.7 (S*C*HMe$_2$), 39.5 (RuCO*Me*), 27.6, 26.0 (SCH*Me*$_2$), 11.7, 11.1 (Cp*). Anal. Calcd for $C_{29}H_{47}F_3O_4Ru_2S_3$: C, 42.74; H, 5.81. Found: C, 42.61; H, 5.74.

Reaction of 3a with Methanol. To a CH_2ClCH_2Cl (5 mL) solution of **3a** (87 mg, 0.098 mmol) was added excess methanol (1 mL), and the mixture was stirred at 90 °C for 3 h. After removal of the solvent under reduced pressure, the resulting solid was dissolved in CH_2Cl_2 and loaded on an activated alumina column. Elution with CH_2Cl_2 gave a brown band, which was collected and evaporated to give **7** (58 mg, 66%). IR (KBr): ν(C=O) 1495 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.97 (s, 1 H, vinyl), 3.56 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.20 (sep, 2 H, J = 6.8 Hz, SC*H*Me$_2$), 1.66, 1.65 (s, 15 H each, Cp*), 1.44, 1.21 (d, 6 H each, J = 6.8 Hz, SCH*Me*$_2$). Anal. Calcd for $C_{32}H_{51}F_3O_6Ru_2S_3$: C, 43.33; H, 5.79. Found: C, 43.51; H, 5.75.

Reaction of 3c with Methanol. A methanol solution (10 mL) of **3c** (48 mg, 0.058 mmol) was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the resulting solid was recrystallized form CH_2Cl_2−hexane to give **8** as brown crystals (36 mg, 72%). ^{1}H NMR (CDCl$_3$): δ 4.13 (s, 3 H, OMe), 4.00 (sep, 2 H, J = 6.7 Hz, SC*H*Me$_2$), 2.69 (s, 3 H, Me), 1.70, 1.59 (s, 15 H each, Cp*), 1.70, 1.43 (d, 6 H each, J = 6.7 Hz, SCH*Me*$_2$). Anal. Calcd for $C_{30}H_{50}ClF_3O_4Ru_2S_3$: C, 41.63; H, 5.82. Found: C, 41.59; H, 5.89.

Reaction of 3a with Tolylacetylene. A CH_2ClCH_2Cl (5 mL) solution of **3a** (120 mg, 0.135 mmol) and tolylacetylene (20 μL, 0.16 mmol) was heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residual solid was dissolved in CH_2Cl_2 and loaded on an activated alumina column. Elution with CH_2Cl_2 gave two bands. The first, green fraction, which contained complex **2** (R = Me), was discarded. The second, brown fraction was collected and evaporated to give **9a** (63 mg, 48%). ^{1}H NMR (CDCl$_3$): δ 7.10, 6.40 (d, 2 H each, J = 7.9 Hz, C$_6$*H*$_4$Me), 6.23 (s, 1 H, vinyl), 3.94 (s, 3 H, OMe), 3.06 (sep, 2 H, J = 6.6 Hz, SC*H*Me$_2$), 2.33 (s, 3 H, C$_6$H$_4$*Me*), 1.86, 1.47 (s, 15 H each, Cp*), 1.46, 1.09 (d, 6 H each, J = 6.6 Hz, SCH*Me*$_2$). Anal. Calcd for $C_{40}H_{55}F_3O_5Ru_2S_3$: C, 49.47; H, 5.71. Found: C, 49.58; H, 5.66.

Reaction of 3b with Tolylacetylene. A CH_2ClCH_2Cl (5 mL) solution of **3b** (158 mg, 0.180 mmol) and tolylacetylene (25 μL, 0.20 mmol) was heated at reflux for 4 h. After removal of the solvent, the resulting solid was dissolved in CH_2Cl_2 and loaded on an activated alumina column. Elution with CH_2Cl_2 gave two green bands. The first fraction, which contained complex **2** (R = Me), was discarded, and the second fraction was collected and evaporated to give **9b** (107 mg, 62%). ^{1}H NMR (CDCl$_3$): δ 7.12, 6.38 (d, 2 H each, J = 7.9 Hz, C$_6$*H*$_4$Me), 6.59 (s, 1 H, vinyl), 2.88 (sep, 2 H, J = 6.9 Hz, SC*H*Me$_2$), 2.33 (s, 3 H, C$_6$H$_4$*Me*), 2.05 (s, 3 H, Me), 1.83, 1.46 (s, 15 H each, Cp*), 1.42, 1.00 (d, 6 H each, J = 6.9 Hz, SCH*Me*$_2$). Anal. Calcd for $C_{40}H_{55}F_3O_4Ru_2S_3$: C, 50.30; H, 5.80. Found: C, 50.42; H, 6.02.

X-ray Diffraction Studies. Single crystals of **3b**, **5**, **7**, and **9a** were sealed in glass capillaries under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC7R four-circle automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å) at 20 °C using the ω scan technique for **3b** and the $\omega-2\theta$ scan technique for **5**, **7**, and **9a**. The orientation matrices and unit cell parameters were determined by least-squares refinement of 25 machine-centered reflections with 29° < 2θ < 39° for **3b**,

$28° < 2\theta < 34°$ for **5**, $35° < 2\theta < 40°$ for **7**, and $39° < 2\theta < 40°$ for **9a**. Intensity data were corrected for Lorentz and polarization effects and for absorption (empirical, Ψ scans). For all crystals, no significant decay was observed for three standard reflections monitored every 150 reflections during the data collection. Details of the X-ray diffraction study are summarized in Table 5.

The structure solution and refinement were carried out by using the teXsan program package.[13] The positions of the non-hydrogen atoms were determined by Patterson methods (DIRDIF PATTY) and subsequent Fourier syntheses. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic thermal parameters except for the carbon, oxygen, and fluorine atoms of the OTf anion in **7**. The OTf anion in **7** was found to be disordered to a minor extent, and the atoms of this anion except for the sulfur atom were refined isotropically. Hydrogen atoms were placed at the calculated positions and were included in the final stage of refinement with fixed isotropic parameters.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, and full bond lengths and angles for **3b**, **5**, **7**, and **9a** (47 pages). Ordering information is given on any current masthead page.

OM970307F

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(13) teXsan: Crystal Structure Analysis Package, Molecular Structure Corp. (1985 and 1992).