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Novel Reactivities of Terminal Diacetylides on the Thiolate-Bridged Diruthenium Center. Their Chemical Transformations into Diruthenacyclopentadienoindane Structure and 1,4-Disubstituted 1,3-Diynes

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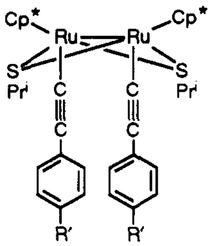
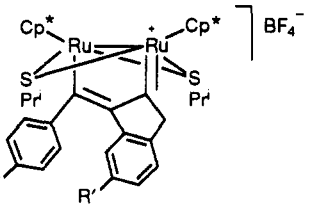
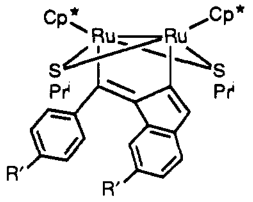
Paramagnetic complex $Cp^*Ru(\mu_2\text{-}SPr^i)_3RuCp^*$ (1) ($Cp^* = \eta^5\text{-}C_5Me_5$) reacts with terminal alkynes at room temperature to give the diamagnetic dinuclear terminal diacetylide complexes $Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (2) (**2a**, R = Tol; **2b**, R = Ph; **2c**, R = $\overline{C{=}CH(CH_2)_3CH_2}$). Similar treatment of 1 with $HC{\equiv}CBu^t$ affords the dinuclear monoacetylide complex $Cp^*Ru(C{\equiv}CBu^t)(\mu_2\text{-}SPr^i)_2Ru(SPr^i)Cp^*$ (**3**), which further reacts with terminal alkynes at 90 °C to form the (mixed) diacetylide complexes $Cp^*Ru(C{\equiv}CBu^t)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (**4a**, R = Tol; **4b**, R = Ph; **4c**, R = $\overline{C{=}CH(CH_2)_3CH_2}$; **2d**; R = Bu^t). Complexes **2a** and **2b** readily react with HBF_4 to give the diruthenacyclopentadienoindane complexes **5a** and **5b** in excellent yield, respectively, which have been formed by the coupling of two terminal acetylide ligands on the thiolate-bridged diruthenium center accompanied by aromatic C–H bond activation. Quantitative deprotonation reactions of **5a** and **5b** smoothly proceed to give the diruthenacyclopentenoindene complexes **6a** and **6b**, respectively. Complexes **6a** and **6b** can be readily protonated with HBF_4 to reproduce **5a** and **5b**. The mechanisms is proposed for these transformations. On the other hand, reactions of complexes **2a** and **2b** with I_2 yield 1,4-disubstituted 1,3-butadiynes $RC{\equiv}CC{\equiv}CR$ (**9a**, R = Tol; **9b**, R = Ph) and $Cp^*Ru(I)(\mu_2\text{-}SPr^i)_2Ru(I)Cp^*$ (**10**). Complexes **2a**, **5a**, and **6a** have been crystallographically characterized: **2a**, $P2_1/n$ (monoclinic), $a = 19.484$ (7) Å, $b = 19.291$ (13) Å, $c = 10.953$ (4) Å, $\beta = 91.35$ (3)°, $Z = 4$, $R = 0.099$, $R_w = 0.11$; **5a**; $P2_12_12_1$ (orthorhombic), $a = 16.391$ (9) Å, $b = 19.476$ (7) Å, $c = 13.055$ (5) Å, $Z = 4$, $R = 0.078$, $R_w = 0.092$; **6a**; $P2_1/n$ (monoclinic), $a = 10.754$ (2) Å, $b = 19.536$ (3) Å, $c = 19.013$ (5) Å, $\beta = 97.27$ (2)°, $Z = 4$, $R = 0.047$, $R_w = 0.034$.



2a: R' = Me
b: R' = H



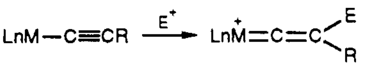
5a: R' = Me
b: R' = H



6a: R' = Me
b: R' = H

Introduction

The transition metal–acetylide is an important functionality in common organic and organometallic chemistry due to its involvement in many catalytic and stoichiometric transformations such as vinylidene formation, cycloaddition reactions, and oligomerization and polymerization of alkynes.[1] Mononuclear η^1-acetylides have been well-known to react with electrophiles at the β-carbon to form stable vinylidenes (eq 1), which can be further converted



$$LnM{-}C{\equiv}CR \xrightarrow{E^+} Ln\overset{+}{M}{=}C{=}C\begin{matrix}E\\R\end{matrix} \qquad (1)$$

to a variety of η^1-carbon-bonded ligands such as vinyl

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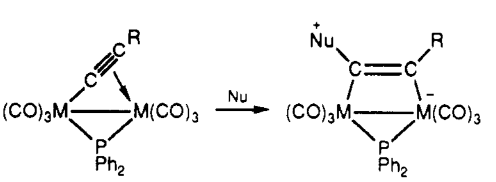
ethers, carbenes, acyls, and alkyls.[1,2] Recently considerable attention has been focused on σ,π-bonded monoacetylide ligands bound to metal clusters.[3] The interest in this chemistry is mainly due to the wish of gaining better knowledge of the interactions of small molecules with metal clusters, because this type of complexes can be considered as useful models for both chemisorption of small molecules on metal surfaces and the carbon–carbon triple bond activation and reduction. In contrast, the overall chemistry of *polyacetylides on multinuclear centers* has been relatively less developed, although compounds of this class have been expected to show a wide variety of structures, and thus, reactivity patterns significantly different from those of not only mononuclear systems but also polynuclear monoacetylide complexes. The well-documented polynuclear monoacetylides whose chemistry has been investigated in detail involve the σ,π-bonded acetylides originally reported by Carty and co-workers. They found that phosphido-bridged compounds with the σ,π-bonded monoacetylide can be obtained by reactions between tertiary alkynylphosphines and di- and trinuclear carbonyls of the iron group metals.[4] These bridging acetylides, especially $Fe_2(CO)_6(\eta^1{:}\eta^2\text{-}\mu_2\text{-}C{\equiv}CR)(\mu_2\text{-}PPh_2)$, are extremely reactive toward various nucleophiles such as amines, phosphines, and isocyanides. The nucleophiles predominantly attack C_α (eq 2), although the reaction at C_β has been observed.[5,6] Recently analogous σ,π-bonded monoacetylides with bridging thiolates have been prepared by using bromoalkynes as the acetylide ligand source, and employed for mixed-metal cluster construction.[7]



(2)

In our continuing studies on dinuclear Cp*Ru complexes ($Cp^* = \eta^5\text{-}C_5Me_5$) with bridging thiolate ligands,[8] we have recently found that reaction of a paramagnetic complex, $Cp^*Ru(\mu_2\text{-}SPr^i)_3RuCp^*$ (1), with $HC{\equiv}CSiMe_3$ results in unusual oxidative coupling of the alkyne to form a novel bridging alkyne complex $Cp^*Ru(\mu_2\text{-}H)(\mu_2\text{-}SPr^i)[\eta^2\text{-}\mu_2\text{-}Me_3SiC{\equiv}CC({=}CHSiMe_3)C{\equiv}CSiMe_3]RuCp^*$, which easily releases an alkyne $(Me_3SiC{\equiv}C)_2C{=}CHSiMe_3$ upon air oxidation.[9] These findings have led us to investigate reactivities of alkynes and alkyne-derived ligands *on the thiolate-bridged diruthenium center* in 1. As reported in detail herein and earlier communicated,[9] complex 1 has been revealed to be a useful precursor for a new series of dinuclear diacetylide complexes, $Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (2, R = Tol, Ph, $\overline{C{=}CH(CH_2)_3C}H_2$), containing the terminal acetylide ligand on each Ru atom. To our knowledge, these are the first polynuclear complexes containing two terminal acetylide ligands. Thus, complexes 2 have been spectroscopically and crystallographicaly characterized, and aspects of their reactivities have been examined. In an attempt to examine the reactivities of the terminal acetylides on the thiolate-bridged diruthenium center in 2, we have investigated reactivities of 2 toward HBF_4 or I_2. Unexpectedly these reactions did not yield the corresponding dinuclear vinylidene complexes but instead gave an unprecedented series of transformations. Particularly interesting is the facile coupling of the terminal acetylide ligands accompanied by aromatic C–H bond activation to give a

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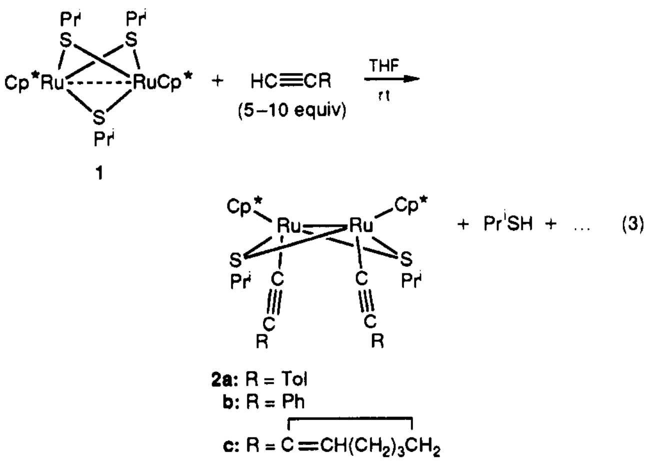
diruthenacyclopentadienoindane structure, when reacted with HBF_4. Also intriguing is another type of the coupling reaction between two acetylide ligands on the diruthenium center upon treatment with I_2 to afford 1,4-disubstituted1,3-butadiynes. Here we wish to describe in detail these novel reactivities of terminal diacetylides on the thiolate bridged diruthenium center.[10]

Results

Reaction of $Cp^*Ru(\mu_2\text{-}SPr^i)_3RuCp^*$ (1) with Terminal Alkynes To Form Dinuclear Terminal Diacetylide Complexes. Complex 1 readily reacted with terminal alkynes $HC{\equiv}CR$ (R = Tol, Ph, $\overline{C{=}CH(CH_2)_3C}H_2$) to give dinuclear terminal diacetylide complexes of the form $Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (**2a**, R = Tol; **2b**, R = Ph; **2c**, R = $\overline{C{=}CH(CH_2)_3C}H_2$) (eq 3).



They were obtained as brown microcrystalline solids and have been spectroscopically characterized. Furthermore, the structure of **2a** has been determined by an X-ray diffraction study (Figure 1). Direct GLC analysis of the reaction mixture revealed that stoichiometric amount of Pr^iSH was formed during the transformation of **1** to **2a** or **2b**. However, only a small amount of H_2 gas (<5%) was detected by GLC, and the formation of $H_2C{=}CHR$ (R = Tol, Ph) was not observed. Thus the fate of about a half of the acetylenic hydrogen atom of the consumed $HC{\equiv}CR$ is not yet clear. The IR spectrum of **2a** shows a $\nu_{C\equiv C}$ band at 2100 cm^{-1}. The ^1H NMR spectrum of **2a** exhibits characteristic resonances due to Cp* (δ 1.69) and μ_2-SPr^i (δ 5.03 (sep, 2 H), 1.66 (d, 12 H)) as well as those attributed to tolyl protons. The spectroscopic data for **2b** and **2c** (see the Experimental Section) are fully consistent with the crystal structure of **2a**.

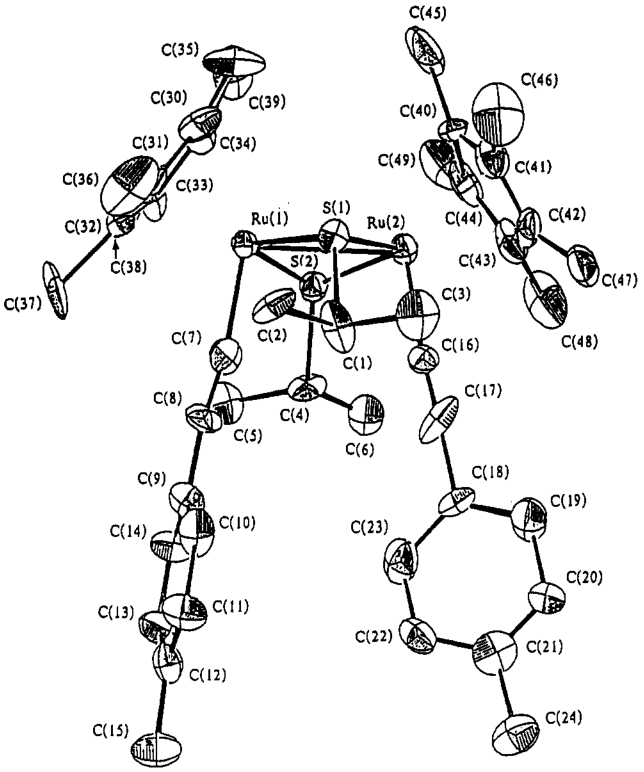
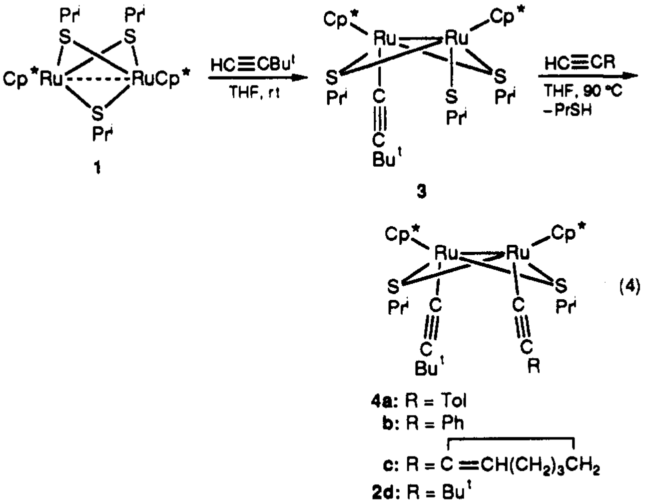


Figure 1. Molecular structure and labeling scheme for complex **2a**.

In contrast to the above reactions to form diacetylide complexes **2**, analogous treatment of **1** with $HC{\equiv}CBu^t$ gave the dinuclear terminal monoacetylide complex $Cp^*Ru(C{\equiv}CBu^t)(\mu_2\text{-}SPr^i)_2Ru(SPr^i)Cp^*$ (**3**), which further reacted with several terminal alkynes at elevated temperatures to afford the dinuclear (mixed) diacetylide complexes $Cp^*Ru(C{\equiv}CBu^t)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (**4a**, R = Tol; **4b**, R = Ph; **4c**, R = $\overline{C{=}CH(CH_2)_3C}H_2$); **2d**, R = Bu^t) (eq 4). These observations clearly demonstrate



that diacetylide complexes **2** were formed through the monoacetylides like **3** as common intermediates. Again, a substantial amount of neither H_2 gas nor $H_2C{=}CHBu^t$ was detected during the transformation of **1** to **3**, whereas the formation of a stoichiometric amount of free Pr^iSH was observed during that of **3** to **4** or **2d**.

Complexes **3**, **4**, and **2d** were isolated as brown microcrystalline solid and spectroscopically characterized. The ^1H NMR spectrum of **3** shows characteristic resonances attributed to bridging SPr^i (δ 4.25 (sep, 2 H), 1.75, 1.63 (d,

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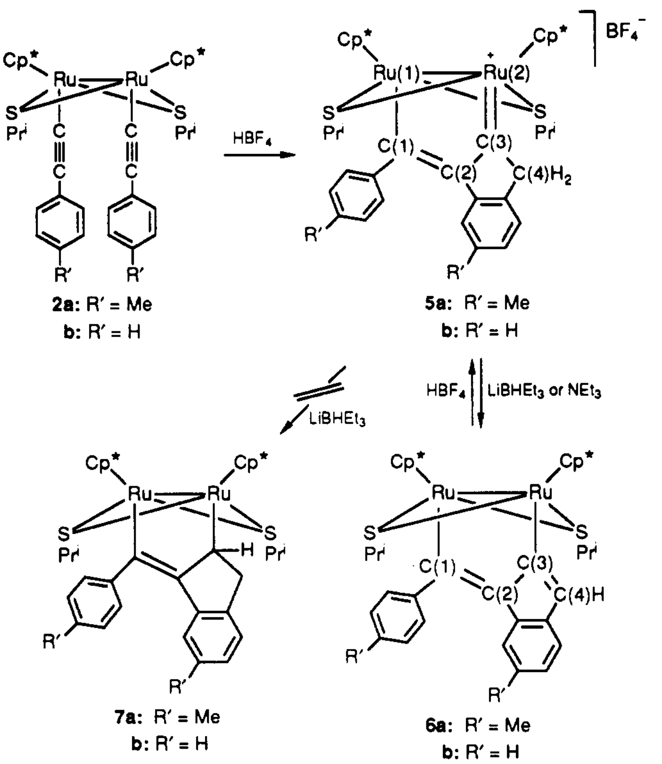
Scheme I



2a: R′ = Me
b: R′ = H

5a: R′ = Me
b: R′ = H

7a: R′ = Me
b: R′ = H

6a: R′ = Me
b: R′ = H

6 H each)) and terminal SPr^i (δ 2.74 (sep, 1 H), 1.57 (d, 6 H)) groups, as well as Cp* (δ 1.68, 1.44) and Bu^t (δ 1.35) resonances. In contrast, the ^{1}H NMR spectrum of **4a** exhibits signals only due to the bridging SPr^i ligands (δ 4.94 (sep, 2 H), 1.76, 1.64 (d, 6 H each)), together with those attributed to Cp* (δ 1.68, 1.67), Bu^t (δ 1.25), and tolyl (δ 7.39, 7.05, 2.17) protons.

Reaction of 2a or 2b with HBF$_4$ To Form Diruthenacyclopentadienoindane Complexes 5. As illustrated in Scheme I, addition of HBF$_4$ (2 equiv) to a THF solution of **2a** or **2b** was found to give rapid and almost quantitative formation of the novel diruthenacyclopentadienoindane complexes (**5a**, R′ = Me; **5b**, R′ = H). They were isolated as green columnar crystals and have been spectroscopically characterized, with the complex **5a** further defined by X-ray crystallography (Figure 2).[11]

The most surprising feature of this structure is the indane unit formed by coupling of two terminal acetylide ligands on each Ru atom accompanied by aromatic C–H bond activation. To the best of our knowledge, this is the first example of any kind of transformations in which acetylides are converted to form the metallacycle having this specific structure. The ^{1}H NMR spectrum of complex **5a** shows a resonance at δ 3.63 (s, 2 H) attributed to the methylene protons (vide infra) and characteristic resonances of aryl protons (δ 7.29 (d, 2 H), 7.05 (d, 1 H), 6.71 (d, 1 H), 6.28 (d, 2 H), 4.91 (s, 1 H)), as well as those assigned to two Cp* and two μ_2-SPr^i groups. The spectroscopic data for **5b** (see Experimental Section) are essentially similar to those for **5a**. On the other hand, complex mixtures were formed when mixed diacetylides **4a–c** were protonated under the similar reaction conditions.

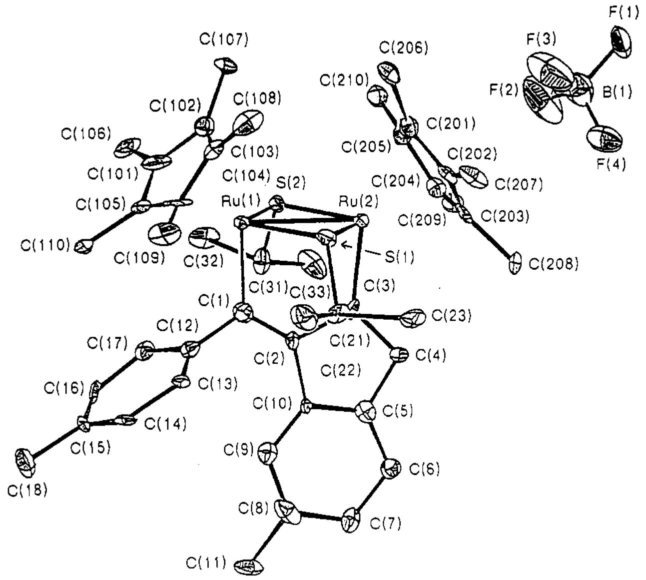


Figure 2. Molecular structure and labeling scheme for complex **5a**.

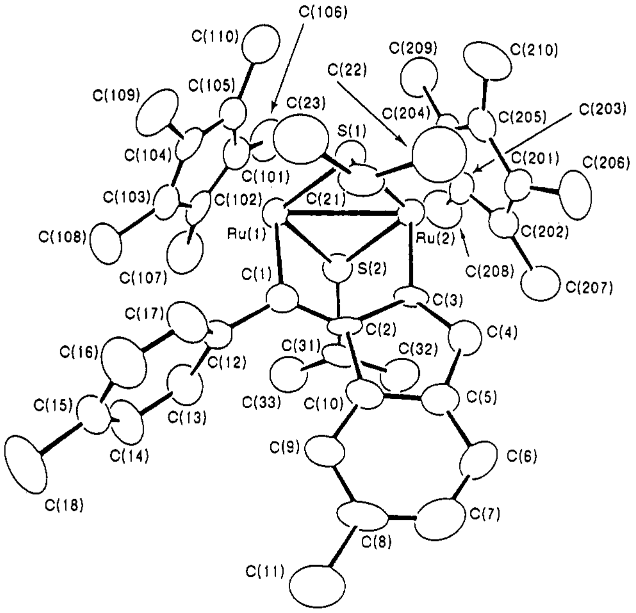


Figure 3. Molecular structure and labeling scheme for complex **6a**.

Conversion of 5 to Diruthenacyclopentenoindene Complexes 6 by Deprotonation. The crystal structure of **5a** (Figure 2) shows that the C(3) in **5a** may possess carbene character for the carbon attached to the cationic metal center and thus is expected to be highly susceptible to nucleophilic attack. However, as illustrated in Scheme I, hydride did not add to the C(3) to give **7** when **5a** and **5b** were allowed to react with LiBHEt$_3$, but instead deprotonation from C(4) rapidly proceeds to afford the diruthenacyclopentenoindene complexes **6a** and **6b** in almost quantitative yield (98–99%), respectively.[11] They were obtained as dark brown prisms and spectroscopically characterized, with **6a** further defined by X-ray structural analysis (Figure 3). The ^{1}H NMR spectrum of **6a** shows a resonance at δ 5.79 (1 H) attributed to the vinyl proton, whereas a resonance at δ 3.63 (2 H) due to the methylene

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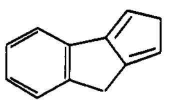
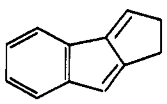
[11] The diruthenacyclopentadienoindane and diruthenacyclopentenoindene nomenclature is derived from the organic rings:



cyclopentadienoindane



cyclopentenoindene

Table I. Crystal and Data Collection Parameters for Complexes 2a, 5a, and 6a

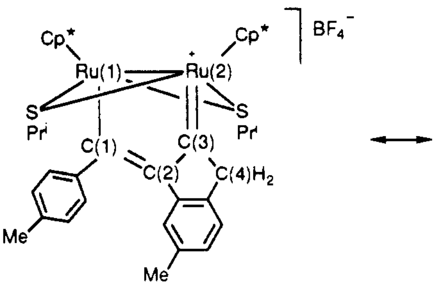
	2a	**5a**	**6a**
	A. Crystal Data		
formula	$C_{44}H_{58}S_2Ru_2$	$C_{44}H_{59}BF_4S_2Ru_2$	$C_{44}H_{58}S_2Ru_2$
mol wt	853.2	941.04	853.20
space group (cryst system)	$P2_1/n$ (monoclinic)	$P2_12_12_1$ (orthorhombic)	$P2_1/n$ (monoclinic)
cryst color	dark brown	green	deep wine red
a, Å	19.484 (7)	16.391 (9)	10.754 (2)
b, Å	19.291 (13)	19.476 (7)	19.536 (3)
c, Å	10.953 (4)	13.055 (5)	19.013 (5)
β, deg	91.35 (3)		97.27 (2)
cell vol, Å^3	4116	4168	3963 (2)
Z	4	4	4
D_{measd} (flotation), g cm^{-3}	1.36 (5)	1.61	1.45
D_{calcd}, g cm^{-3}	1.377	1.64	1.43
$F(000)$, electrons	1768	1936	1768
μ(Mo Kα)$_{calcd}$, cm^{-1}	8.45	8.74	8.77
cryst dimens, mm	0.24 × 0.32 × 0.40	0.39 × 0.15 × 0.13	0.37 × 0.35 × 0.11
	B. Data Collection		
diffractometer	Rigaku AFC-6A	MAC MXC-18	Rigaku AFC-5S
monochrometer		graphite	
radiation (λ, Å)		Mo Kα (0.7107)	
temp		room temp	
2θ range, deg	$3 < 2Z\theta < 45$	$3 < 2\theta < 45$	$3 < 2\theta < 50$
scan method	ω ($2\theta < 30°$), ω–2θ ($2\theta > 30°$)	$\omega - 2\theta$	$\omega - 2\theta$
scan speed, deg min^{-1}	4	16	16
reflectns measd	$\pm h,+k,+l$	$+h,+k,+l$	$+h,+k,\pm l$
used data	3251 ($F_o > 5\sigma(F_o)$)	2627 ($F_o > 3\sigma(F_o)$)	2917 ($I > 3\sigma(I)$)
	C. Solution and Refinement		
no. of parameters refined	666	479	433
R	0.099	0.078	0.047
R_w	0.11	0.092	0.034

protons observed in **5a** (vide supra) disappears. The spectroscopic data for **6b** (see Experimental Section) are similar to those for **6a**, which strongly support the analogous structure as **6a**.

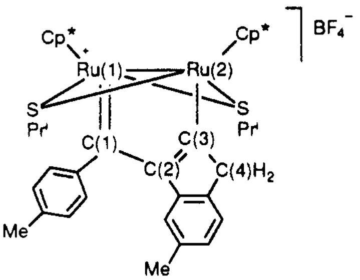
Crystal and Molecular Structures of 2a, 5a, and 6a. ORTEP drawings of these three complexes are given in Figures 1–3 and pertinent crystallographic details are set out in Tables I–VII. Each of these complexes possesses two Cp* Ru units joined by a Ru–Ru bond and bridged by two SPr^i ligands. The Ru–Ru bond distances of the three complexes are similar (**2a**, 2.809 (3); **5a**, 2.776 (3); **6a**, 2.761 (1) Å) and are in the range of typical Ru–Ru single bonds.[8c,d,9] Each complex has the structure with cis configuration of two Cp* rings and the syn (axial–axial) configuration of two Pr^i groups.

Complex **2a** crystallizes in the space group $P2_1/n$ and has the doubly bridged dinuclear structure with a terminal acetylide ligand on each Ru atom (Figure 1). Two acetylide ligands are in mutually cis configuration. The Ru_2S_2 core is not planar but has a butterfly structure, and the dihedral angle between the plane including Ru(1), Ru(2), and S(1) atoms and that defined by the Ru(1), Ru(2), and S(2) atoms is 163.7°. The coordination geometry of Cp* and SPr^i groups around the Ru atoms in **2a** is similar to that observed in Cp*Ru(H)(μ_2-SPr^i)$_2$Ru(H)Cp* (**8**)[8d] so that the previously proposed terminal dihydride structure of **8** has now been indirectly confirmed. The distances of carbon–carbon triple bonds (1.16 (4) and 1.14 (4) Å) are apparently shorter than that reported for $Ru_2(CO)_6(\mu_2$-η^2-C≡CBu^t)(μ_2-PPh$_2$) (1.218 (4) Å)[4b] or $Ru_3(CO)_9(\mu_3$-η^2-C≡CPr^i)(μ_2-PPh$_2$) (1.284 (8) Å)[4e] and are in the range for typical terminal acetylides.[1c]

Complex **5a** (Figure 2) crystallizes in the space group $P2_12_12_1$. The diruthenacyclopentadiene metallacycle formed by Ru(1), Ru(2), C(1), C(2), and C(3) atoms is nearly planar (maximum deviation: Ru(1), −0.001; Ru(2), 0.005; C(1), −0.006; C(2), 0.013; C(3), −0.012 Å). The C(1)–C(2) distance of 1.38 (3) Å is apparently shorter than that of 1.49 (3) Å for C(2)–C(3), and nearly corresponds to a carbon–carbon double bond. Thus the molecule appears best described as a diruthenacyclopentadienoindane, having the important resonance structure **5a-I**, and the contribution of the resonance structure **5a-II** is small. This is in good accord with the slightly shorter Ru(2)–C(3) distance of 1.98 (2) Å compared to that of 2.04 (3) Å for Ru(1)–C(1). The Ru_2S_2 core is almost planar and the dihedral angle between the Ru(1)–Ru(2)–S(1) plane and the Ru(1)–Ru(2)–S(2) plane is 178.4°. The increase of the dihedral angle compared to that observed in **2a** (163.7°, vide supra) is apparently due to the formation of the large bridging ligand by coupling of two terminal acetylides.



5a-I



5a-II

Table II. Atomic Coordinates (×10⁴) for Complex 2a with Estimated Standard Deviations in Parentheses

	x	y	z	B_{eq},[a] Å^2
Ru(1)	6498.6 (8)	2400.4 (9)	2718.6 (15)	3.0
Ru(2)	7877.5 (9)	2709.5 (10)	3293.9 (16)	3.6
S(1)	7465 (3)	1919 (3)	1900 (5)	3.8
S(2)	6919 (3)	3353 (3)	3740 (5)	3.7
C(1)	7607 (13)	2198 (18)	230 (19)	6.9
C(2)	7165 (16)	1632 (15)	–487 (23)	6.2
C(3)	8380 (16)	1985 (18)	67 (29)	7.7
C(4)	6817 (14)	4172 (11)	2962 (24)	4.7
C(5)	6039 (13)	4368 (14)	2992 (24)	5.2
C(6)	7237 (16)	4724 (16)	3512 (31)	7.1
C(7)	6376 (13)	2993 (15)	1190 (23)	5.4
C(8)	6204 (13)	3320 (13)	345 (24)	4.8
C(9)	6085 (13)	3776 (13)	–699 (22)	4.7
C(10)	6300 (14)	3602 (18)	–1862 (21)	6.5
C(11)	6210 (17)	4069 (15)	–2790 (24)	6.2
C(12)	5946 (13)	4744 (14)	–2601 (22)	4.8
C(13)	5729 (16)	4897 (17)	–1387 (26)	6.4
C(14)	5836 (16)	4410 (15)	–456 (25)	6.1
C(15)	5860 (18)	5249 (15)	–3626 (24)	6.8
C(16)	8086 (12)	3346 (11)	1907 (21)	3.8
C(17)	8262 (15)	3666 (16)	1092 (27)	6.6
C(18)	8467 (13)	4101 (12)	6 (21)	4.3
C(19)	7986 (15)	4389 (17)	–812 (26)	6.5
C(20)	8186 (15)	4768 (15)	–1830 (26)	5.9
C(21)	8895 (16)	4892 (15)	–1984 (26)	6.3
C(22)	9349 (15)	4484 (15)	–1266 (25)	5.8
C(23)	9150 (15)	4166 (17)	–262 (26)	6.6
C(24)	9125 (19)	5333 (17)	–3042 (29)	7.7
C(30)	6165 (16)	1346 (17)	3482 (27)	7.0
C(31)	5789 (13)	1544 (15)	2359 (24)	5.8
C(32)	5394 (13)	2121 (16)	2659 (28)	6.7
C(33)	5556 (10)	2386 (14)	3782 (21)	4.5
C(34)	6008 (13)	1883 (14)	4361 (22)	4.8
C(35)	6548 (22)	702 (13)	3612 (33)	9.3
C(36)	5739 (24)	1065 (25)	1310 (33)	12.3
C(37)	4809 (16)	2485 (30)	1757 (30)	13.6
C(38)	5199 (15)	2885 (17)	4605 (31)	7.8
C(39)	6210 (18)	1776 (26)	5706 (29)	10.9
C(40)	8265 (12)	2070 (13)	4940 (26)	5.0
C(41)	8723 (14)	1976 (15)	3990 (27)	5.8
C(42)	9000 (11)	2619 (15)	3635 (20)	4.9
C(43)	8699 (15)	3137 (15)	4424 (27)	6.5
C(44)	8259 (13)	2819 (15)	5181 (23)	5.7
C(45)	7997 (18)	1598 (27)	5858 (32)	12.1
C(46)	8915 (21)	1252 (20)	3531 (43)	11.6
C(47)	9574 (13)	2656 (19)	2787 (26)	7.4
C(48)	8908 (22)	3872 (18)	4558 (46)	12.4
C(49)	7922 (18)	3108 (19)	6279 (25)	8.1

[a] $B_{eq} = {}^4/_3\{\sum_i \sum_j B_{ij} \mathbf{a}_i \mathbf{a}_j\}$.

Table III. Selected Bond Distances and Angles for Complex 2a[a]

Distances, Å			
Ru(1)–Ru(2)	2.809 (3)		
Ru(1)–S(1)	2.301 (6)	Ru(2)–S(1)	2.290 (6)
Ru(1)–S(2)	2.292 (6)	Ru(2)–S(2)	2.304 (6)
Ru(1)–C(7)	2.04 (3)	Ru(2)–C(16)	2.00 (2)
Ru(1)–C(30)	2.30 (3)	Ru(2)–C(40)	2.30 (3)
Ru(1)–C(31)	2.19 (3)	Ru(2)–C(41)	2.29 (3)
Ru(1)–C(32)	2.22 (3)	Ru(2)–C(42)	2.22 (2)
Ru(1)–C(33)	2.20 (2)	Ru(2)–C(43)	2.16 (3)
Ru(1)–C(34)	2.29 (3)	Ru(2)–C(44)	2.19 (3)
C(7)–C(8)	1.16 (4)	C(16)–C(17)	1.14 (4)
Angles, deg			
Ru(1)–S(1)–Ru(2)	75.5 (2)	Ru(1)–S(2)–Ru(2)	75.4 (2)
Ru(1)–Ru(2)–S(1)	52.5 (2)	Ru(2)–Ru(1)–S(1)	52.1 (2)
Ru(1)–Ru(2)–S(2)	52.1 (2)	Ru(2)–Ru(1)–S(2)	52.5 (2)
Ru(1)–Ru(2)–C(16)	99.8 (7)	Ru(2)–Ru(1)–C(7)	99.1 (7)
Ru(1)–C(7)–C(8)	170 (2)	Ru(2)–C(16)–C(17)	173 (2)

[a] Numbers in parentheses are estimated standard deviations.

Table IV. Atomic Coordinates (×10⁴) for Complex 5a with Estimated Standard Deviations in Parentheses

	x	y	z	B_{eq},[a] Å^2
Ru(1)	92.1 (11)	6817.0 (9)	1699.5 (12)	1.8
Ru(2)	–833.4 (11)	6806.3 (10)	3480.2 (12)	1.9
S(1)	380 (4)	7374 (3)	3216 (5)	2.5
S(2)	–1109 (4)	6227 (3)	1984 (4)	2.2
C(1)	–598 (15)	7639 (13)	1267 (19)	2.9
C(2)	–1217 (15)	7894 (12)	1870 (16)	2.4
C(3)	–1412 (13)	7609 (11)	2896 (16)	1.6
C(4)	–2080 (15)	8041 (12)	3352 (19)	3.1
C(5)	–2290 (15)	8548 913)	2553 (20)	2.8
C(6)	–2836 (16)	9091 (13)	2639 (20)	2.9
C(7)	–2959 (14)	9543 (14)	1769 (19)	3.1
C(8)	–2422 (19)	9457 (15)	913 (21)	4.1
C(9)	–1891 (16)	8909 (13)	886 (19)	2.9
C(10)	–1767 (11)	8487 (11)	1739 (15)	1.4
C(11)	–2555 (23)	9955 (15)	30 (23)	4.7
C(12)	–452 (13)	7966 (11)	281 (18)	2.2
C(13)	58 (16)	8537 (11)	196 (17)	2.4
C(14)	127 (17)	8858 (11)	–789 (18)	2.7
C(15)	–284 (16)	8816 (11)	–1639 (17)	2.8
C(16)	–790 (18)	8064 (11)	–1535 (17)	3.5
C(17)	–876 (15)	7691 (13)	–611 (18)	2.7
C(18)	–138 (24)	8962 (15)	–2685 (20)	5.1
C(21)	381 (17)	8337 (11)	3207 (19)	3.4
C(22)	1213 (19)	8597 (16)	2897 (23)	4.5
C(23)	158 (19)	8533 (13)	4405 (23)	3.9
C(31)	–2023 (15)	6514 (13)	1266 (19)	3.1
C(32)	–2120 (22)	6014 (14)	291 (23)	4.9
C(33)	–2777 (16)	6420 (17)	1896 (23)	4.6
C(101)	524 (19)	5986 (13)	541 (23)	4.0
C(102)	829 (15)	5806 (12)	1548 (20)	2.9
C(103)	1389 (13)	6344 (12)	1831 (20)	2.4
C(104)	1355 (17)	6874 (14)	1054 (21)	3.9
C(105)	847 (17)	6616 (12)	275 (21)	3.7
C(106)	–36 (23)	5496 (14)	–73 (22)	5.0
C(107)	748 (25)	5122 (13)	2061 (22)	5.3
C(108)	1965 (18)	6345 (16)	2686 (26)	4.8
C(109)	1962 (17)	7449 (14)	949 (27)	4.5
C(110)	818 (21)	6902 (16)	–821 (21)	5.7
C(201)	–350 (15)	5987 (13)	4692 (19)	2.9
C(202)	–446 (15)	6660 (12)	5199 (18)	2.7
C(203)	–1314 (16)	6854 (16)	5013 (18)	3.4
C(204)	–1715 (16)	6289 (13)	4559 (19)	2.9
C(205)	–1111 (16)	5759 (13)	4313 (19)	2.9
C(206)	436 (20)	5589 (16)	4741 (20)	4.4
C(207)	181 (24)	7015 (13)	5840 (20)	5.2
C(208)	–1749 (23)	7432 (16)	5702 (20)	5.0
C(209)	–2609 (17)	6172 (13)	4521 (20)	3.2
C(210)	–1355 (16)	5125 (13)	3911 (20)	3.0
F(1)	–1514 (13)	5188 (8)	8204 (12)	5.7
F(2)	–1807 (17)	5504 (13)	6622 (17)	12.1
F(3)	–573 (15)	5676 (14)	7225 (21)	12.0
F(4)	–1517 (19)	6275 (11)	7660 (18)	11.6
B(1)	–1370 (21)	5658 (25)	7406 (34)	6.3

[a] $B_{eq} = {}^4/_3\{\sum_i \sum_j B_{ij} \mathbf{a}_i \mathbf{a}_j\}$.

Complex **6a** (Figure 3) crystallized in the space group $P2_1/n$. The typical carbon–carbon double bond distance of 1.36 (1) Å for C(3)–C(4) clearly demonstrates that deprotonation takes place at C(4) of **5a** to form the observed indene framework. The Ru_2S_2 core is almost planar and the dihedral angle between the Ru(1)–Ru(2)–S(1) plane and the Ru(1)–Ru(2)–S(2) plane is 176°. The diruthenacyclopentenoindene framework formed by the Ru(1), Ru(2), C(1)–C(9), and C(10) atoms shows a nearly planar fused-ring system.[12]

Reaction of 2 with I_2 To Eliminate 1,4-Disubstituted 1,3-Diynes. Although halogens have been reported to act as electrophiles toward mononuclear acetylides to form vinylidenes (vide supra),[1,2,15] the terminal diacetylides on the thiolate bridged diruthenium center react with I_2 in quite a different manner. When I_2 (1.2 equiv per complex)

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[12] Maximum deviation: Ru(1), 0.001; Ru(2), 0.001; C(1), –0.023; C(2), –0.008; C(3), –0.017; C(4), –0.014; C(5), 0.018; C(10), 0.024 Å.

Table V. Selected Bond Distances and Angles for Complex 5a[a]

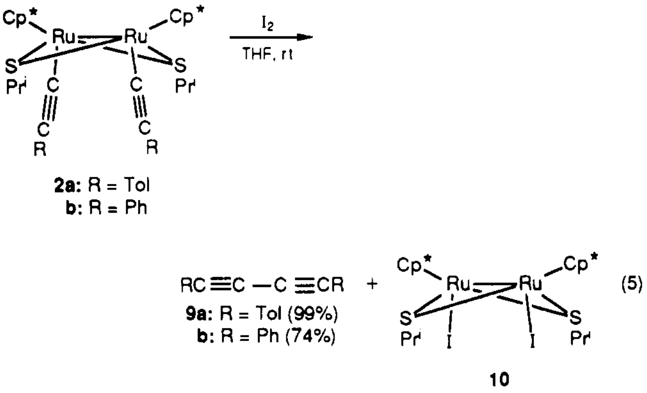
	Distances, Å		
Ru(1)–Ru(2)	2.776 (3)		
Ru(1)–S(1)	2.306 (6)	Ru(2)–S(1)	2.301 (6)
Ru(1)–S(2)	2.310 (7)	Ru(2)–S(2)	2.301 (6)
Ru(1)–C(1)	2.04 (3)	Ru(2)–C(3)	1.98 (2)
Ru(1)–C(101)	2.33 (3)	Ru(2)–C(201)	2.38 (3)
Ru(1)–C(102)	2.32 (2)	Ru(2)–C(202)	2.35 (2)
Ru(1)–C(103)	2.32 (2)	Ru(2)–C(203)	2.26 (2)
Ru(1)–C(104)	2.24 (3)	Ru(2)–C(204)	2.26 (3)
Ru(1)–C(105)	2.27 (3)	Ru(2)–C(205)	2.36 (3)
C(1)–C(2)	1.38 (3)	C(1)–C(12)	1.46 (3)
C(2)–C(3)	1.49 (3)	C(2)–C(10)	1.48 (3)
C(3)–C(4)	1.50 (3)	C(4)–C(5)	1.48 (4)
C(5)–C(10)	1.37 (3)		
	Angles, deg		
Ru(2)–Ru(1)–S(1)	52.9 (2)	Ru(1)–Ru(2)–S(1)	53.0 (2)
Ru(2)–Ru(1)–S(2)	52.9 (2)	Ru(1)–Ru(2)–S(2)	53.1 (2)
Ru(2)–Ru(1)–C(1)	86.2 (7)	Ru(1)–Ru(2)–C(3)	86.2 (6)
S(1)–Ru(1)–S(2)	105.7 (2)	S(1)–Ru(2)–S(2)	106.2 (2)
S(1)–Ru(1)–C(1)	88.9 (7)	S(1)–Ru(2)–C(3)	88.6 (6)
S(2)–Ru(1)–C(1)	87.8 (8)	S(2)–Ru(2)–C(3)	88.1 (6)
Ru(1)–C(1)–C(2)	122 (2)	Ru(2)–C(3)–C(2)	123 (2)
Ru(1)–C(1)–C(12)	120 (2)	Ru(2)–C(3)–C(4)	130 (2)
C(2)–C(1)–C(12)	118 (2)	C(2)–C(3)–C(4)	108 (2)
C(1)–C(2)–C(3)	123 (2)	C(3)–C(4)–C(5)	105 (2)
C(1)–C(2)–C(10)	132 (2)	C(4)–C(5)–C(10)	110 (2)
C(3)–C(2)–C(10)	105 (2)	C(2)–C(10)–C(5)	111 (2)

[a] Numbers in parentheses are estimated standard deviations.

Table VI. Atomic Coordinates for Complex 6a with Estimated Standard Deviations in Parentheses

	x	y	z	B_eq, Å^2
Ru(1)	0.75564 (7)	0.02881 (5)	0.81279 (4)	2.50 (4)
Ru(2)	0.81679 (7)	0.02305 (5)	0.67585 (4)	2.64 (4)
S(1)	0.6757 (2)	–0.0453 (1)	0.7241 (1)	2.8 (1)
S(2)	0.8876 (2)	0.1009 (1)	0.7615 (1)	3.0 (1)
C(1)	0.6107 (9)	0.0951 (5)	0.7747 (5)	2.7 (5)
C(2)	0.592 (1)	0.1144 (5)	0.7060 (5)	2.7 (5)
C(3)	0.6700 (9)	0.0886 (5)	0.6508 (5)	2.7 (5)
C(4)	0.623 (1)	0.1183 (6)	0.5883 (5)	4.0 (6)
C(5)	0.519 (1)	0.1638 (5)	0.5958 (6)	3.6 (6)
C(6)	0.444 (1)	0.2030 (6)	0.5476 (6)	4.6 (7)
C(7)	0.352 (1)	0.2419 (6)	0.5689 (7)	5.2 (7)
C(8)	0.328 (1)	0.2429 (6)	0.6382 (7)	4.1 (6)
C(9)	0.401 (1)	0.2027 (5)	0.6879 (6)	3.8 (6)
C(10)	0.497 (1)	0.1628 (5)	0.6676 (5)	3.1 (5)
C(11)	0.226 (1)	0.2868 (6)	0.6601 (6)	5.5 (7)
C(12)	0.524 (1)	0.1239 (5)	0.8236 (5)	2.6 (5)
C(13)	0.553 (1)	0.1847 (6)	0.8616 (6)	4.2 (6)
C(14)	0.468 (1)	0.2129 (6)	0.9018 (6)	4.6 (6)
C(15)	0.354 (1)	0.1835 (6)	0.9074 (6)	4.1 (6)
C(16)	0.327 (1)	0.1240 (6)	0.8718 (6)	5.0 (7)
C(17)	0.410 (1)	0.0938 (5)	0.8304 (6)	4.1 (6)
C(18)	0.261 (1)	0.2179 (7)	0.9479 (6)	6.8 (8)
C(21)	0.5084 (9)	–0.0408 (5)	0.6877 (5)	3.3 (5)
C(22)	0.492 (1)	–0.0726 (7)	0.6154 (6)	6.5 (8)
C(23)	0.434 (1)	–0.0811 (6)	0.7345 (6)	5.3 (7)
C(31)	0.845 (1)	0.1923 (5)	0.7458 (6)	3.5 (5)
C(32)	0.898 (1)	0.2169 (6)	0.6825 (6)	6.8 (8)
C(33)	0.989 (1)	0.2309 (6)	0.8118 (6)	6.1 (8)
C(101)	0.920 (1)	–0.0132 (6)	0.8899 (5)	3.7 (6)
C(102)	0.867 (1)	0.0451 (6)	0.9211 (5)	3.5 (6)
C(103)	0.741 (1)	0.0253 (7)	0.9305 (5)	4.0 (6)
C(104)	0.718 (1)	–0.0398 (5)	0.9020 (5)	3.1 (6)
C(105)	0.832 (1)	–0.0639 (6)	0.8790 (5)	3.4 (6)
C(106)	1.057 (1)	–0.0158 (6)	0.8801 (5)	5.0 (6)
C(107)	0.936 (1)	0.1073 (6)	0.9497 (5)	6.4 (8)
C(108)	0.657 (1)	0.0655 (6)	0.9755 (5)	5.4 (7)
C(109)	0.604 (1)	–0.0786 (6)	0.9116 (5)	5.1 (7)
C(110)	0.849 (1)	–0.1356 (6)	0.8548 (5)	4.6 (6)
C(201)	0.841 (1)	–0.0148 (6)	0.5687 (6)	3.9 (6)
C(202)	0.929 (1)	0.0386 (6)	0.5868 (6)	4.0 (6)
C(203)	1.015 (1)	0.0148 (6)	0.6457 (5)	3.2 (5)
C(204)	0.986 (1)	–0.512 (6)	0.6624 (5)	3.2 (6)
C(205)	0.877 (1)	–0.0702 (6)	0.6153 (6)	3.4 (6)
C(206)	0.748 (1)	–0.0195 (7)	0.5029 (5)	6.7 (7)
C(208)	1.131 (1)	0.0535 (6)	0.6760 (6)	5.6 (7)
C(209)	1.062 (1)	–0.0998 (6)	0.7081 (6)	5.4 (7)
C(210)	0.819 (1)	–0.1381 (6)	0.6104 (6)	5.2 (7)
C(207)	0.940 (1)	0.1025 (6)	0.5407 (6)	5.9 (7)

was added, the color of a solution of **2a** and **2b** in THF immediately turned from brown to green, and then gradually changed to brown. The 1,4-disubstituted 1,3-diynes **9** were isolated as white solid in high yield by silica gel chromatography and were spectroscopically characterized (eq 5). For example, the mass spectrum of **9a** shows a parent ion at m/z = 230.1124 (calcd m/z = 230.1096), and its ^{1}H NMR spectrum (see Experimental Section) is fully consistent with the indicated formulation. From the reaction mixture Cp*Ru(I)(μ_2-SPr^i)$_2$Ru(I)Cp* (**10**) was obtained in moderate yield and spectroscopically characterized.[13] Analogous treatment of complexes **4a–c** and **2c,d** gave complicated reaction mixtures, and the corresponding butadiynes were not isolated.



Discussion

The results reported herein demonstrate that the diruthenium-bridging thiolate complex Cp*Ru(μ_2-SPr^i)$_3$-Cp* (**1**) readily reacts with terminal alkynes to give a new series of dinuclear terminal diacetylide complexes Cp*Ru-(C≡CR)(μ_2-SPr^i)$_2$Ru(C≡CR)Cp* (**2**), which show quite unusual reactivities toward H$^+$ and I$_2$. Although a large number of studies have been carried out on acetylide ligands bound to metal clusters, multinuclear complexes with terminal acetylides are remarkably rare.[3] This is probably due to the ease with which the C≡C bond can interact with the other metals present in the cluster framework. Previously Stone and co-workers reported that treatment of Pt(C$_2$H$_4$)$_2$(PR$_3$)$_2$ with dimethyl(bisphenylethynyl)silane afforded a diplatinum complex (PR$_3$)-Pt(μ_2-SiMe$_2$)(η^1:η^2-μ_2-C≡CPh)Pt(C≡CPh)(PR$_3$), which contains both σ- and σ,π-bonded acetylide ligands on the bimetallic center.[15] It should be noted that the facile formation of complexes **2** offers an unique example of multinuclear polyacetylide compounds which possess *only terminal acetylide ligands on the bimetallic center.*

The most surprising finding in this research is the facile coupling of the terminal acetylide ligands on the diru-

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(13) This diamagnetic complex was alternatively obtained by treatment of Cp*Ru(μ_2-SPr^i)$_2$RuCp* with I$_2$ or excess MeI. Its Cl analogue Cp*Ru(Cl)(μ_2-Pr^i)$_2$Ru(Cl)Cp* was previously prepared[7c] and recently fully characterized by X-ray crystallography.[14]

(14) Matsuzaka, H.; Takagi, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. To be submitted for publication.

(15) Ciriano, M.; Howard, J. A. K.; Spencer, J.; Stone, F. G. A.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1979**, 1749.

Table VII. Selected Bond Distances and Angles for Complex 6a[a]

Distances, Å			
Ru(1)-Ru(2)	2.767 (1)		
Ru(1)-S(1)	2.305 (3)	Ru(2)-S(1)	2.298 (3)
Ru(1)-S(2)	2.301 (3)	Ru(2)-S(2)	2.287 (3)
Ru(1)-C(1)	2.08 (1)	Ru(2)-C(3)	2.042 (9)
Ru(1)-C(101)	2.30 (1)	Ru(2)-C(201)	2.214 (9)
Ru(1)-C(102)	2.270 (9)	Ru(2)-C(202)	2.224 (9)
Ru(1)-C(103)	2.265 (9)	Ru(2)-C(203)	2.29 (1)
Ru(1)-C(104)	2.238 (9)	Ru(2)-C(204)	2.37 (1)
Ru(1)-C(105)	2.30 (1)	Ru(2)-C(205)	2.29 (1)
C(1)-C(2)	1.35 (1)	C(1)-C(12)	1.50 (1)
C(2)-C(3)	1.51 (1)	C(2)-C(10)	1.51 (1)
C(3)-C(4)	1.36 (1)	C(4)-C(5)	1.45 (1)
C(5)-C(10)	1.41 (1)		
Angles, deg			
Ru(2)-Ru(1)-S(1)	52.91 (7)	Ru(1)-Ru(2)-S(1)	53.17 (7)
Ru(2)-Ru(1)-S(2)	52.66 (7)	Ru(1)-Ru(2)-S(2)	53.14 (7)
Ru(2)-Ru(1)-C(1)	87.4 (3)	Ru(1)-Ru(2)-C(3)	85.7 (3)
S(1)-Ru(1)-S(2)	105.48 (9)	S(1)-Ru(2)-S(2)	106.22 (9)
S(1)-Ru(1)-C(1)	86.7 (3)	S(1)-Ru(2)-C(3)	85.8 (3)
S(2)-Ru(1)-C(1)	87.0 (3)	S(2)-Ru(2)-C(3)	85.8 (3)
Ru(1)-C(1)-C(2)	121.6 (7)	Ru(2)-C(3)-C(2)	121.9 (7)
Ru(1)-C(1)-C(12)	120.7 (7)	Ru(2)-C(3)-C(4)	131.5 (8)
C(2)-C(1)-C(12)	117.7 (9)	C(2)-C(3)-C(4)	106.6 (8)
C(1)-C(2)-C(3)	123.4 (9)	C(3)-C(4)-C(5)	112.5 (9)
C(1)-C(2)-C(10)	130.8 (9)	C(4)-C(5)-C(10)	108 (1)
C(3)-C(2)-C(10)	105.8 (8)	C(2)-C(10)-C(5)	107.0 (9)

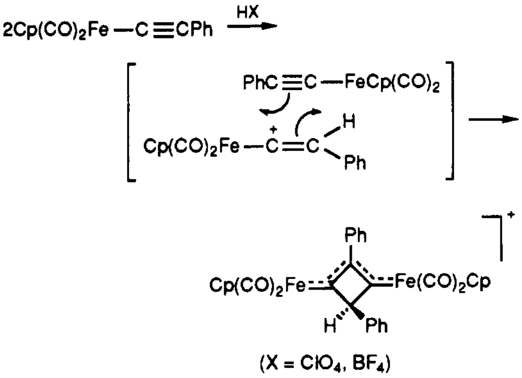
[a] Numbers in parentheses are estimated standard deviations.

thenium site accompanied by aromatic C–H bond activation to form the diruthenacyclopentadienoindane complexes **5a** and **5b** upon treatment of **2a** and **2b** with HBF_4. Since complexes **5** and **6** are readily available from **1** and alkynes, the present reactions offer a potential route to substituted indane and indene derivatives from terminal alkynes. The proposed mechanism to explain the formation of **5a** is shown in Scheme II. The initial step is believed to be proton addition to a C_β of one of the two terminal acetylides to give the dinuclear acetylide–vinylidene intermediate **11**. The cationic, coordinatively unsaturated Ru(IV) center in **11** would be a highly electrophilic metal center which could attack the tolyl ring of the vinylidene ligand to generate the intermediate **12**. Elimination of HC≡CTol from the intermediate **12** would then form the π-alkyne complex **13**, where insertion of HC≡CTol into the $Ru–C_{sp2}$ bond could occur to generate the eight-membered metallacycle **14**.

To complete the sequence of reactions in Scheme II, the metallacycle containing two Ru atoms must undergo cyclization to yield **15**, which would eliminate H^+ to form **6a**. Evidence for the formation of **6a** prior to that of **5a** comes from observation that treatment of **2a** with a catalytic amount of HBF_4 (0.1 equiv) affords **6a** in 40% yield (after 12 h). Complex **6a** would then be protonated to give **5a**. Actually, **6a** can be quantitatively (>97%) converted to **5a** when allowed to react with 1 equiv of HBF_4.

Another possible pathway to explain the formation of **5a** would involve acetylide migration to the vinylidene ligand in **11** to give an dinuclear η^1-butenynyl intermediate **16**. Recently Wakatsuki and Yamazaki et al. reported intramolecular migration of an acetylide to a vinylidene ligand on a mononuclear ruthenium center to form η^1-butenynyl complex $RuCl(CO)(PPh_3)_2\{C(C{\equiv}CBu^t){=}CHBu^t\}$.[16] The intermediate **16** could give **6a** by a cyclization reaction involving this organic substituent, facilitated by coordination of the electrophilic ruthenium center to the acetylide portion of the ligand.[17]

In contrast, the coupling reaction of a monomeric acetylide complex previously reported by two research groups proceeds in quite a different manner (eq 6).[18]



(6)

Treatment of $Cp(CO)_2Fe(C{\equiv}CPh)$ with HX (X = ClO_4, BF_4) gave the dimeric product $\{[Cp(CO)_2Fe]_2(Ph_2C_4H)\}X$, having a bridging cyclobutenylidene framework resulting from intermolecular carbon–carbon bond formation between the vinylidene intermediate and the parent acetylide complex. The unprecedented *intramolecular* coupling reaction to form diruthenacyclopentadienoindane structure described in this paper must arise from the mutual cis configuration of two acetylide ligands on the thiolate bridged diruthenium center in **2a** and **2b**.[19,20]

Another intriguing finding in this research is the formation of 1,4-disubstituted 1,3-butadiynes **9a** and **9b** when **2a** and **2b** were allowed to react with I_2. Halogens have been known to add to the C_β in several acetylide ligands to form the corresponding vinylidenes. Bruce and co-workers reported that reactions of halogens with $Cp(PPh_3)_2Ru(C{\equiv}CPh)$ afforded a halovinylidene complex $[Cp(PPh_3)_2Ru({=}C{=}CXPh)]X_3$ (X = Cl, Br, I); in some cases halogenation of the phenyl group of a C≡CPh ligand also occurred, for example, in the structurally characterized $[Cp(PPh_3)_2Ru{=}C{=}CBr(C_6H_4Br\text{-}p)]Br_3$.[21] These reac-

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[16] Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem.* **1991**, *113*, 9604.

[17] Authors express appreciation to one of the reviwers for pointing out this possibility.

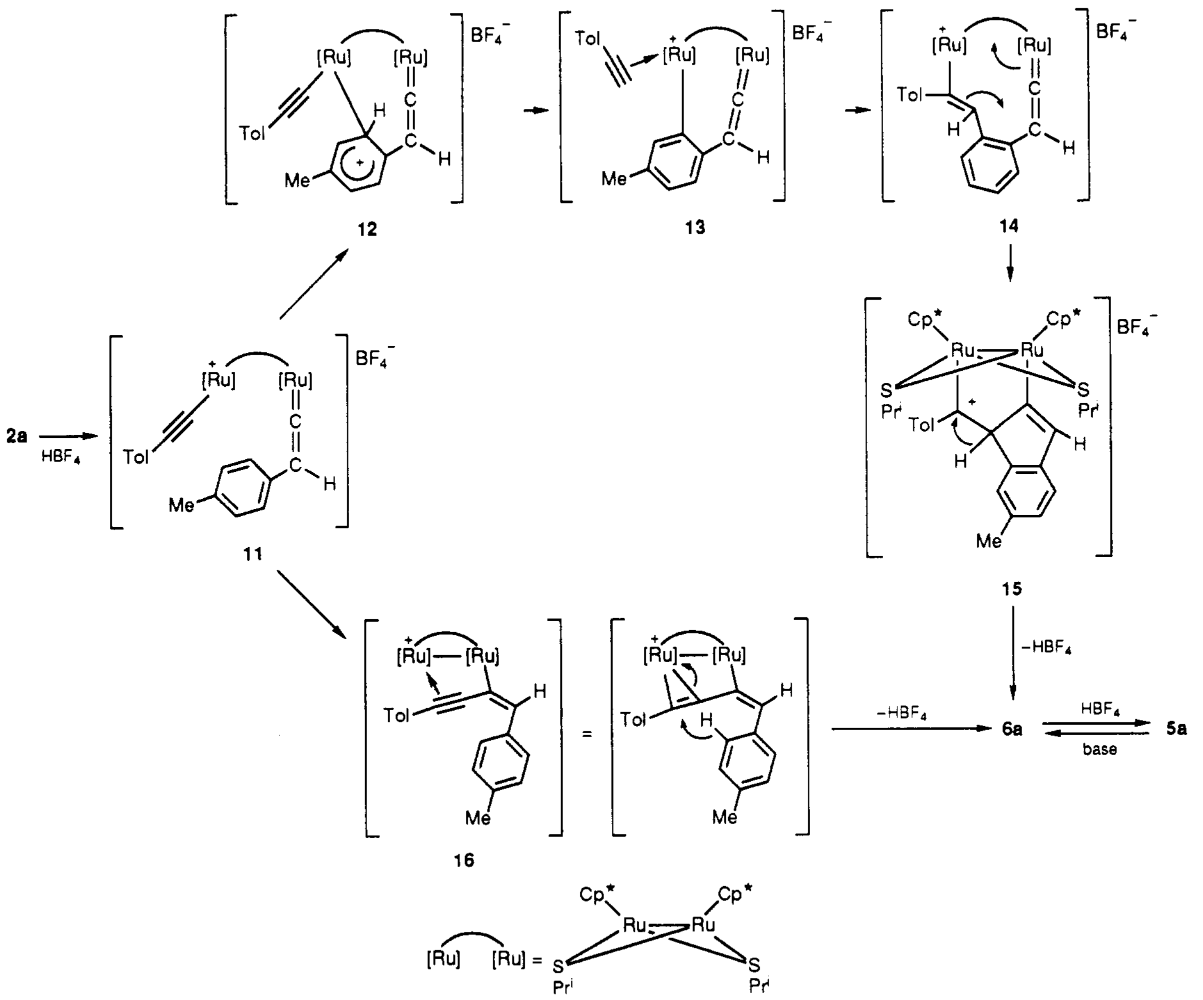
[18] (a) Davidson, A.; Solar, J. P. *J. Organomet. Chem.* **1978**, *155*, C8. (b) Kolobova, N. Ye; Skripkin, V. V.; Alexandrov, G. G.; Struchkov, Yu T. *J. Organomet. Chem.* **1979**, *169*, 293.

[19] Several coupling reactions of transition metal-centered acetylide fragments to give unsaturated C_4 ligands have recently been reported. See: (a) Bruce, M. I.; Koutsantonis, G. A.; Liddell, M. J.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *420*, 253. (b) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376. (c) Ustynyuk, N. A.; Vinogradova, V. N.; Korneva, V. N.; Kravtsov, D. N.; Andrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *277*, 285. (d) Götzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (e) Field, L. D.; Geroge, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565. (f) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M.-C. *J. Chem. Soc., Chem. Commun.* **1991**, 522. (g) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (h) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K. Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621. (i) Klein, H. F.; Beck-Hemetsbergerm, H.; Reitzel, L.; Rodenhäuser, B.; Cordier, G. *Chem. Ber.* **1989**, *122*, 43. (j) Dobson, A.; Moore, D. S.; Robinson, S. D.; Hursthouse, M. B.; New, L. *J. Organomet. Chem.* **1979**, *177*, C8. (k) Davan Kumar, P. N. V.; Jemmis, E. D. *J. Am. Chem. Soc.* **1988**, *110*, 125. (l) Müller, E.; Thomas, R.; Sauerbier, M.; Langer, E. Streichfuss, D. *Tetrahedron Lett.* **1971**, 521.

[20] Coupling reactions of non-metal-centered alkynes via promoted electrophilic attack on o-diethynyl benzene and naphthalene were also reported. Whitlock, H. W., Jr.; Sandvick, P. F. *J. Am. Chem. Soc.* **1966**, *88*, 4525.

[21] Bruce, M. I.; Koutsantoun, G. A.; Liddell, M. J. *J. Organomet. Chem.* **1987**, *320*, 217.

Scheme II



tions demonstrate the remarkable resistance of the Ru–C_{sp} bond toward cleavage by halogens. It is in sharp contrast that the Ru–C_{sp} bonds in **2a** and **2b** were so smoothly and cleanly cleaved by I_2 to give the 1,4-disubstituted 1,3-butadiynes.

The I_2-induced reaction of dinuclear terminal diacetylide complexes described herein is particularly interesting because it provides a quite rare example of the coupling of two organic moieties on the two adjacent metal atoms directly joined by a metal–metal bond. Hoffmann and Trinquier carried out qualitative molecular orbital study on the model reaction: $L_4(R)M{-}M(R)L_4 \rightarrow R_2 + L_4M{=}ML_4$ (R = H, Me) and have shown that this intramolecular dinuclear reductive elimination is symmetry forbidden and exhibits a large activation energy for a C_{2v} concerted least-motion pathway.[22] Actually, Chisholm and co-workers observed that elimination of butane does not occur from the dimolybdenum center in $(Me_2N)_2Mo(Et){\equiv}Mo(Et)(NMe_2)_2$ but instead ethylene and ethane are evolved, when treated with CO_2 or alcohol.[23] It is noteworthy that, in the present case, treatment of **2a** and **2b** with I_2 yields 1,4-disubstituted-1,3-butadiynes, although we must await further studies to elucidate the detailed reaction mechanism.

In conclusion, reactions of $Cp^*Ru(\mu_2\text{-}SPr^i)_3RuCp^*$ (**1**) with alkynes have given entry into a new type of multinuclear polyacetylide complexes possessing only terminal acetylide ligands on the diruthenium center. These novel polyacetylide complexes show quite unusual reactivities toward HBF_4 and I_2 (e.g. formation of diruthenacyclopentadienoindane structure and liberation of 1,4-disubstituted 1,3-butadiynes), which are extremely different from those observed for common mononuclear and polynuclear monoacetylide systems.

Further studies are in progress aimed at inducing additional transformations of the dinuclear terminal diacetylide complexes through their reactions with other organic and inorganic substrates.

Experimental Section

General Considerations. Complex $Cp^*Ru(\mu_2\text{-}SPr^i)_3RuCp^*$ (**1**) was prepared by the literature procedure.[8d] The alkynes $HC{\equiv}CTol$, $HC{\equiv}CPh$, $HC{\equiv}CC{=}CH(CH_2)_3CH_2$, and $HC{\equiv}CBu^t$ were obtained commercially, degassed, and stored over molecular sieve 4A. Solvents were dried by refluxing over Na/benzophenone ketyl (THF, benzene, hexane), or CaH_2 (acetonitrile) and freshly distilled prior to use. All manipulations were performed with standard Schlenk tube techniques. IR spectra were recorded on a Shimadzu DR-8000 spectrometer. NMR spectra were obtained on a JEOL GX-400 spectrometer, and mass spectra were recorded on a JEOL AX-505H spectrometer. Elemental analyses were performed at Elemental Analysis Laboratory, Department of Chemistry, The University of Tokyo.

Reaction of $Cp^*Ru(\mu_2\text{-}SPr^i)_3RuCp^*$ (1) with $HC{\equiv}CR$ To Form $Cp^*Ru(C{\equiv}CR)(\mu_2\text{-}SPr^i)_2Ru(C{\equiv}CR)Cp^*$ (2). To a green solution of complex **1** (100 mg, 0.143 mmol) in THF (10

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[22] Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370.

[23] (a) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138. (b) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075.

mL) was added 5–10 equiv of HC≡CR (**2a**, R = Tol; **2b**, R = Ph), and the reaction mixture was stirred at room temperature for 3 h. After removal of the solvent, the resulting solid was chromatographed on alumina first with hexane then with benzene–hexane (2:1). Evaporation of the solvent from a single brown band gave a dark brown solid, which was recrystallized from benzene–acetonitrile to give **2a** or **2b** as brown crystalline solid.

Data for 2a. Yield, 44%. IR (KBr): ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.36 (d, 4 H, *J* = 7.9 Hz, aryl), 6.98 (d, 4 H, *J* = 7.9 Hz, aryl), 5.03 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 2.15 (s, 6 H, C$_6$H$_4$*Me*), 1.69 (s, 30 H, Cp*), 1.66 (d, 12 H, SCH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 132.69, 131.06, 128.06 (aryl), 115.74 (C≡*C*Tol), 107.55 (*C*≡CTol), 98.59 (*C*$_5$Me$_5$), 41.01 (S*C*HMe$_2$), 24.49 (SCH*Me*$_2$), 21.16 (C$_6$H$_4$*Me*), 10.72 (C$_5$*Me*$_5$). Anal. Calcd for C$_{44}$H$_{58}$S$_2$Ru$_2$: C, 61.93; H, 6.86; S, 7.51. Found: C, 61.60; H, 6.85; S, 7.65.

Data for 2b. Yield, 41%: IR (KBr): ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.27–6.74 (d and 2t, 10 H, Ph), 4.83 (sep, 2 H, *d* = 6.4 Hz, SC*H*Me$_2$), 1.50 (s, 30 H, Cp*), 1.48 (d, 12 H, *J* = 6.4 Hz, SCH*Me*$_2$). Anal. Calcd for C$_{42}$H$_{54}$S$_2$Ru$_2$: C, 61.12; H, 6.61; S, 7.77. Found: C, 61.15; H, 6.58; S, 7.70.

As for complex **2c** (R = $\overline{\mathrm{C{=}CH(CH_2)_3C}}\mathrm{H_2}$), the reaction mixture was refluxed for 1 day. After removal of the solvent the resulting solid was recrystallized from toluene–acetonitrile to give dark brown microcrystals.

Data for 2c. Yield, 37%. IR (KBr): ν(C≡C) 2089 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, methylene protons in the cyclohexenyl groups omitted): δ 5.82 (m, 2 H, $\overline{\mathrm{C{=}}C\mathit{H}\mathrm{(CH_2)_3C}}\mathrm{H_2}$), 4.90 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 1.68 (s, 30 H, Cp*), 1.68 (d, 12 H, *J* = 6.7 Hz, SCH*Me*$_2$). Anal. Calcd for C$_{42}$H$_{62}$S$_2$Ru$_2$: C, 60.53; H, 7.51; S, 7.70. Found: C, 61.11; H, 7.30; S, 7.45.

Reaction of Cp*Ru(μ_2-SPr^i)$_3$RuCp* (1) with HC≡CBu^t To Form Cp*Ru(C≡CBu^t)(μ_2-SPr^i)$_2$Ru(SPr^i)Cp* (3). To a solution of complex 1 (1.0 g, 1.43 mmol) in THF (50 mL) was added HC≡CBu^t (0.7 mL, 5.7 mmol), and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the resulting brown solid was recrystallized from benzene–acetonitrile (10 mL–50 mL) to give **3** as brown crystalline solid (650 mg, 58%). IR (KBr): ν(C≡C) 2099 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 4.25 (sep, 2 H, *J* = 6.7 Hz, μ_2-SC*H*Me$_2$), 2.74 (sep, 1 H, *J* = 6.7 Hz, SC*H*Me$_2$), 1.75 (d, 6 H, *J* = 6.7 Hz, μ_2-SCH*Me*Me), 1.68 (s, 15 H, Cp*), 1.63 (d, 6 H, *J* = 6.7 Hz, μ_2-SCHMe*Me*), 1.57 (d, 6 H, *J* = 6.7 Hz, SCH*Me*$_2$), 1.44 (s, 15 H, Cp*), 1.35 (s, 9 H, Bu^t). Anal. Calcd for C$_{35}$H$_{60}$S$_3$Ru$_2$: C, 53.94; H, 7.78; S, 12.35. Found: C, 53.72; H, 7.63; S, 13.14.

Reaction of Cp*Ru(C≡CBu^t)(μ_2-SPr^i)$_2$Ru(SPr^i)Cp* (3) with HC≡CR To Form Cp*Ru(C≡CBu^t)(μ_2-SPr^i)$_2$Ru(C≡CR)Cp* (4) or Cp*Ru(C≡CBu^t)(μ_2-SPr^i)$_2$Ru(C≡CBu^t)Cp* (2d). A THF (15 mL) solution of complex **3** (100 mg, 0.143 mmol) and 5–10 equiv of HC≡CR were charged in a 50-mL stainless steal autoclave. The reactor was heated to 90 °C and kept at the temperature for 1 day with magnetic stirring. After the reactor was cooled to room temperature, the mixture was immediately analyzed by GLC. Then the solvent was evaporated and the resulting brown solid was recrystallized from toluene–acetonitrile to give **4** or Cp*Ru(C≡CBu^t)(μ_2-SPr^i)$_2$Ru(C≡CBu^t)Cp* (**2d**) as brown crystalline solid.

Data for 4a. Yield, 39%. IR (KBr): ν(C≡C) 2093 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.39 (d, 2 H, *J* = 7.6 Hz, aryl), 7.05 (d, 2 H, *J* = 7.6 Hz, aryl), 4.94 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 2.17 (s, 3 H, C$_6$H$_4$*Me*), 1.76 (d, 6 H, *J* = 6.7 Hz, SCH*Me*Me), 1.68 (s, 15 H, Cp*), 1.67 (s, 15 H, Cp*), 1.64 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*), 1.25 (s, 9 H, Bu^t). Anal. Calcd for C$_{38}$H$_{62}$S$_2$Ru$_2$·C$_6$H$_6$: C, 62.91; H, 7.41; S, 7.15. Found: C, 63.76; H, 7.30; S, 6.90.

Data for 4b. Yield, 37%. IR (KBr): ν(C≡C) 2110, 2091 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.5–6.9 (m, 5 H, aryl), 4.91 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 1.75 (d, 6 H, *J* = 6.7 Hz, SCH*Me*Me), 1.67 (s, 15 H, Cp*), 1.66 (s, 15 H, Cp*), 1.63 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*), 1.21 (s, 9 H, Bu^t). Anal. Calcd for C$_{40}$H$_{58}$S$_2$Ru$_2$: C, 59.66; H, 7.27; S, 7.97. Found: C, 59.41; H, 7.04; S, 8.33.

Data for 4c. Yield, 38%. IR (KBr): ν(C≡C) 2089 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, methylene protons in the cyclohexenyl group omitted): δ 5.76 (m, 1 H, vinyl), 4.85 (sep, 2 H, *J* = 6.7 Hz, SC*H* Me$_2$), 1.70 (d, 6 H, *J* = 6.7 Hz, SCH*Me* Me), 1.68 (s, 15 H, Cp*), 1.67 (s, 15 H, Cp*), 1.63 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*), 1.38 (s, 9 H, Bu^t). Anal. Calcd for C$_{40}$H$_{62}$S$_2$Ru$_2$: C, 59.36; H, 7.74; S, 7.93. Found: C, 60.06; H, 7.51; S, 7.53.

Data for 2d. Yield, 41%. IR (KBr): ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 4.65 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 1.67 (s, 30 H, Cp*), 1.63 (d, 12 H, *J* = 6.7 Hz, SCH*Me*$_2$), 1.41 (s, 18 H, Bu^t). Anal. Calcd for C$_{38}$H$_{62}$S$_2$Ru$_2$: C, 58.12; H, 7.97; S, 8.17. Found: C, 58.98; H, 7.69; S, 8.67.

Reaction of 2a with HBF$_4$ To Form 5a. To a solution of **2a** (60 mg, 0.070 mmol) in THF (10 mL) was added HBF$_4$·Et$_2$O (17 μL, 0.18 mmol). The original dark brown solution immediately turned to deep green, and the reaction mixture was stirred 30 min at room temperature. After removal of the solvent, the resulting green solid was washed with ether and recrystallized from CH$_2$Cl$_2$–ether (2 mL–5 mL) to give **5** as green columnar crystals (62 mg, 94%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.29 (d, 2 H, *J* = 7.9 Hz, aryl), 7.05 (d, 1 H, *J* = 7.6 Hz, aryl), 6.71 (d, 1 H, *J* = 7.6 Hz, aryl), 6.28 (d, 2 H, *J* = 7.9 Hz), 4.91 (s, 1 H, aryl), 3.63 (s, 2 H, CH$_2$), 3.32 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 2.44 (s, 3 H, C$_6$H$_4$*Me*), 1.89 (s, 15 H, Cp*), 1.85 (s, 3 H, C$_6$H$_4$*Me*), 1.49 (s, 15 H, Cp*), 1.43 (d, 6 H, *J* = 6.7 Hz, SCH*Me*Me), 0.88 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*). Anal. Calcd for C$_{44}$H$_{59}$BF$_4$S$_2$Ru$_2$: C, 56.15; H, 6.33; S, 6.81. Found: C, 56.17; H, 6.17; S, 7.11.

Complex **5b** was obtained by analogous treatment of **2b** with HBF$_4$. Yield 95%. ^{1}H NMR (CDCl$_3$): δ 7.47–5.15 (m, 9 H, aryl), 3.68 (s, 2 H, CH$_2$), 3.36 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 1.94 (s, 15 H, Cp*), 1.51 (s, 15 H, Cp*), 1.46 (d, 6 H, *J* = 6.7 Hz, SCH*Me*Me), 0.92 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*). Anal. Calcd for C$_{42}$H$_{55}$BF$_4$S$_2$Ru$_2$·CH$_2$Cl$_2$: C, 51.81; H, 5.72; S, 6.43. Found: C, 51.30; H, 5.85; S, 6.42.

Deprotonation of 5a To Form 6a. To a suspension of **5a** (40 mg, 0.043 mmol) in THF (10 mL) was added 1.2 equiv of LiBHEt$_3$ or NEt$_3$. The original green suspension turned to brown solution within a few minutes. After 1 h, the solvent was evaporated and the resulting brown residue was extracted with benzene (5 mL × 3). Addition of acetonitrile to the concentrated benzene solution gave deep wine red columnar crystals of **6a** (36 mg, 99%). ^{1}H NMR (C$_6$D$_6$) δ 7.31 (d, 2 H, *J* = 7.9 Hz, aryl), 7.19 (d, 1 H, *J* = 8.2 Hz, aryl), 6.88 (d, 1 H, *J* = 8.2 Hz, aryl), 6.87 (d, 2 H, *J* = 7.9 Hz, aryl), 6.65 (s, 1 H, aryl), 5.79, (s, 1 H, vinyl), 3.37 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 2.42 (s, 3 H, C$_6$H$_4$*Me*), 2.14 (s, 3 H, C$_6$H$_4$*Me*), 1.73 (s, 15 H, Cp*), 1.37 (s, 15 H, Cp*), 1.32 (d, 6 H, *J* = 6.7 Hz, SCH*Me*Me), 1.09 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*). Anal. Calcd for C$_{44}$H$_{58}$S$_2$Ru$_2$: C, 61.93; H, 6.86; S, 7.51. Found: C, 62.40; H, 6.72; S, 7.89.

Complex **6b** was obtained by analogous treatment of **5b**. Yield 98%. ^{1}H NMR (CDCl$_3$): δ 7.49–6.68 (m, 9 H, aryl), 5.86 (s, 1 H, vinyl), 3.36 (sep, 2 H, *J* = 6.7 Hz, SC*H*Me$_2$), 1.79 (s, 15 H, Cp*), 1.38 (s, 15 H, Cp*), 1.31 (d, 6 H, *J* = 6.7 Hz, SCH*Me*Me), 1.07 (d, 6 H, *J* = 6.7 Hz, SCHMe*Me*). Anal. Calcd for C$_{42}$H$_{54}$S$_2$Ru$_2$: C, 61.12; H, 6.61; S, 7.77. Found: C, 61.01; H, 7.07; S, 8.21.

Reaction of 2a with I$_2$ To Form 9a and 10. A THF (5 mL) solution of I$_2$ (15 mg, 0.056 mmol) was added to a solution of **2a** (40 mg, 0.047 mmol) in THF (10 mL). The brown solution immediately turned to green and stirring was continued for 8 h, during which time the color changed to brown. After removal of the solvent, the resulting brown solid was extracted with hexane. The hexane solution was concentrated and chromatographed on silica gel with hexane to give a single colorless band of **9a**, which was isolated as a white microcrystalline solid in 99% yield (11 mg, 0.047 mmol). On the other hand, recrystallization (CH$_2$Cl$_2$–hexane) of the residual brown solid after extraction with hexane gave complex **10** in 53% yield. Treatment of **2b** with I$_2$ was carried out analogously.

Data for 9a. MS (high resolution) calcd for C$_{18}$H$_{14}$ m/z = 230.1096 (M$^+$), found m/z = 230.1124 (M$^+$). ^{1}H NMR (CDCl$_3$):

δ 7.43 (d, 4 H, J = 8.1 Hz, aryl), 7.15 (d, 4 H, J = 8.1 Hz, aryl), 2.37 (s, 6 H, Me).

Data for 9b. MS (high resolution) calcd for $C_{16}H_{10}$ m/z = 202.0783 (M^+), found m/z = 202.0771 (M^+). ^1H NMR ($CDCl_3$): δ 7.70–7.20 (m, aryl).

Data for 10. ^1H NMR (C_6D_6): δ 5.85 (sep, 2 H, J = 6.7 Hz, SC*H*Me$_2$), 1.65 (d, 12 H, J = 6.7 Hz, SCH*Me*$_2$), 1.57 (s, 30 H, Cp*). Anal. Calcd for $C_{26}H_{44}S_2I_2Ru_2$: C, 35.62; H, 5.06. Found: C, 35.67; H, 4.98.

Crystal and Molecular Structures of Complexes 2a, 5a, and 6a. Crystallographic data are presented in Table I. Crystals suitable for diffraction were sealed in glass capillaries under Ar and mounted on a four-circle diffractometer equipped with a graphite monochrometer. The orientation matrices and unit cell parameters were derived from a least-squares fit of 25 machine-centered reflections with 2θ values between 20 and 25°. The data collection was performed at room temperature, and no significant decay was observed for three check reflections measured every 100 reflections. Intensity data were corrected for the Lorentz–polarization effect, and absorption corrections were performed.

All structures were solved by direct methods, which located the Ru atoms. The remaining non-hydrogen atoms were located through subsequent least-squares refinement and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters.[24] Hydrogen atoms in **2a** were placed at the calculated positions. Computations for **2a** and **5a** used UNIX-III program[25] and SHELX86 software[26] at the computer center of The University of Tokyo, whereas those for **6a** employed TEXSAN crystallographic software package[27] at Toho University.

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Supplementary Material Available: Anisotropic thermal parameters for **2a**, **5a**, and **6a** (3 pages). Ordering information is given on any current masthead page.

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