Reactions of Terminal and Bridging Thiol Di-μ-methylene Dirhodium Complexes with Alkynes to Afford the Corresponding Ethenethiolate Complexes. Remarkable C−C Bond Formation between Two μ-CH_2 and Alkynes on the Bridging Ethenethiolate Complexes

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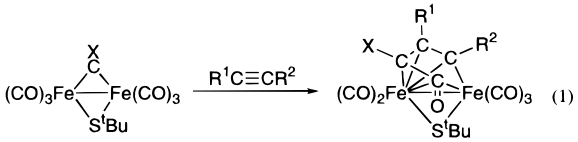
The reaction of the terminal dithiol complex *trans*-[(RhCp*)$_2$(μ-CH_2)$_2$(SH)$_2$] (**1**, Cp* = η^5-C_5Me_5) with dialkyl acetylenedicarboxylate gives the terminal bis(ethenethiolate) complex *trans*-[(RhCp*)$_2$(μ-CH_2)$_2$(SCR^1=CHR^2)$_2$] (**2a**, R^1, R^2 = COOMe; **2b**, R^1, R^2 = COOEt). Treatment of the cationic bridging thiol complex [(RhCp*)$_2$(μ-CH_2)$_2$(μ-SH)](BPh_4) (**3**) with dimethyl acetylenedicarboxylate or carbyl propiolate very easily gives the bridging ethenethiolate complex [(RhCp*)$_2$(μ-CH_2)$_2$(μ-SCR^1=CHR^2)](BPh_4) (**4a**, R^1, R^2 = COOMe; **4b**, R^1 = H, R^2 = COOPh; **4c**, R^1 = H, R^2 = COOMe). Although complex **2** is not able to react further with alkyne, complex **4** does and forms the butadiene complex [(RhCp*)$_2$(η^2:η^2-μ-CH_2=CR^3-CR^4=CH_2)(μ-SCR^1=CHR^2)](BPh_4) (**5a**, R^1, R^2, R^3, R^4 = COOMe; **5a-Et$_2$**, R^1, R^2 = COOMe, R^3, R^4 = COOEt; **5a-Et$_1$**, R^1, R^2 = COOMe, R^3 = H, R^4 = COOEt; **5b**, R^1 = H, R^2 = COOPh, R^3, R^4 = COOMe; **5c**, R^1 = H, R^2 = COOMe, R^3, R^4 = COOMe). The structures of complexes **2b**, **4a**, and **5a** have been confirmed by an X-ray diffraction study.

Introduction

Recently, several research groups have shown that the complexes containing thiol or thiolate ligands are useful for the chemical transformation of alkynes based on electrophilic reactions including Michael-type addition with thiolate and thiol ligands,[1−7] C−C bond formations with carbene- and carbyne-like ligands,[8] or oligomerization.[1g,i,6,7,9] The C−C bond formation of alkynes with carbene- or carbyne-like ligands in dinuclear complexes having a M(μ-SR)M functionality, of particular relevance to the present study, has been observed in [{$Fe(CO)_3$}$_2$(μ-CX)(μ-S^{t}Bu)] (X = CH=$CHOCH_3$ or OC_2H_5) systems, as shown in eq 1.[8c] The



(1)

X = CH=$CHOCH_3$ or OC_2H_5
R^1, R^2 = H, Me, $COCH_3$, $COOCH_3$

μ-S^{t}Bu ligand is employed in this system, but its role is not yet clear.

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We established synthetic routes to the terminal thiol complex *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$(SH)$_2$] (**1**) and the bridging thiol complex [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-SH)](BPh$_4$) (**3**), which each contain two μ-CH$_2$ groups,[10] and then we elucidated their reactivities.[11] In the course of extending our study to the organic synthesis and catalytic oligomerization of unsaturated hydrocarbons[12] by using the bis(μ-methylene)bis((pentamethylcyclopentadienyl)-rhodium) complexes,[13,14] we found that the bridging thiol and μ-CH$_2$ ligands in complex **3** are transformed stepwise by their reaction with dimethyl acetylenedicarboxylate as follows: Rh(μ-CH$_2$)$_2$(μ-SH)Rh (in **3**) → Rh(μ-CH$_2$)$_2${μ-SC(COOMe)=CH(COOMe)}Rh (in **4a**) → Rh{η^2:η^2-μ-CH$_2$=C(COOMe)C(COOMe)=CH$_2$}{μ-SC(COOMe)=CH(COOMe)}Rh (in **5a**), where the Michael-type addition and the C−C bond formation are involved as described in our recent communication.[15] In this paper, we will disclose (i) that the terminal thiol ligands in **1** also perform a Michael-type addition to the alkyne to afford a terminal bis(ethenethiolate) complex *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$(SCR^1=CHR^2)$_2$] (**2a**, R^1, R^2 = COOMe; **2b**, R^1, R^2 = COOEt) and (ii) that the bridging thiol dirhodium complex **3** is much more reactive than the terminal complex **1** toward various activated alkynes in converting the functional groups of μ-SH and μ-CH$_2$ in **3**, respectively, into the ethenethiolate and butadiene moieties in the final product of **5**, and (iii) we will describe the role of the bridging ethenethiolate ligand in **4** in the intriguing C−C bond formation through a full account of the reactions of the bridging ethenethiolate and other carbyl thiolate complexes with various alkynes.

Results and Discussion

Reaction of Thiol Complexes with Activated Alkynes. (1) Reaction of Terminal Thiol Complex 1 with Dialkyl Acetylenedicarboxylates. A characteristic reaction of organic thiols is their Michael-type addition to alkynes.[16] Several attempts to perform the corresponding addition using the terminal thiol ligands in metal complexes were unsuccessful,[4,17] except in the case of [NiCp(PBu$_3$)(SH)].[5] Unexpectedly, terminal thiol ligands in metal complexes seemed to have low reactivities toward alkynes.

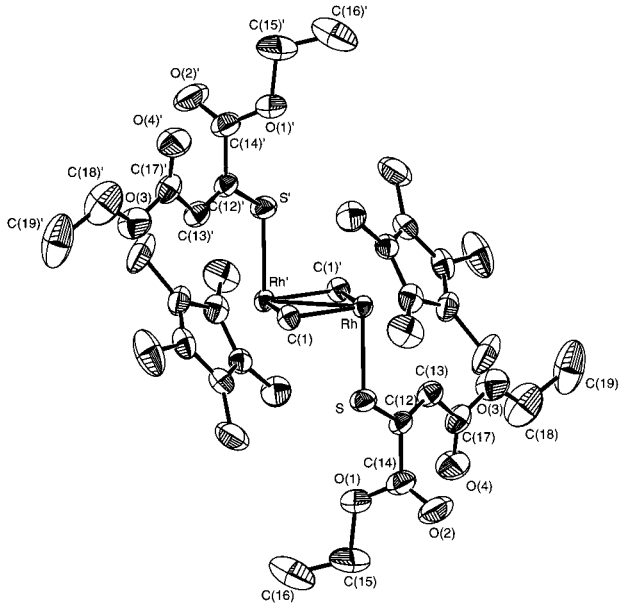
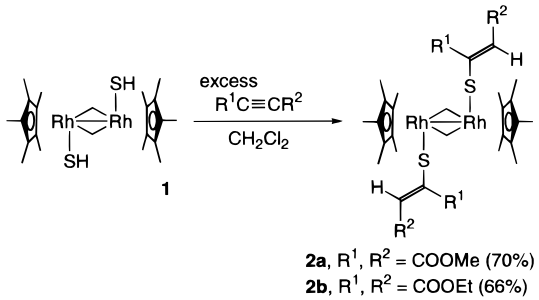


Figure 1. ORTEP drawing for **2b**. Thermal ellipsoids are shown at the 50% probability level.

When *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$(SH)$_2$] (**1**) was treated with excess dimethyl or diethyl acetylenedicarboxylate in CH$_2$Cl$_2$ at 25 °C, a terminal bis(ethenethiolate) complex *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$(SCR^1=CHR^2)$_2$] (**2a**, R^1, R^2 = COOMe; **2b**, R^1, R^2 = COOEt) was obtained in ca. 70% yield (eq 2). The reaction proceeded smoothly



(2)

without any basic promoter. The reaction was monitored by ^{1}H NMR spectroscopy, but any intermediate such as a monoethenethiolate complex was not detected at −40 °C. The high reactivitiy of **1**, compared with other terminal thiol complexes, is rather novel. The structure of **2b** was confirmed by an X-ray diffraction study as shown in Figure 1. The crystal data and the selected bond lengths and angles are summarized in Tables 1and 2. The two disubstituted ethenethiolate ligands are in a trans position to each other and have *E*-configuration due to the syn addition of the thiol ligands to the alkynes. The Rh$_2$C$_2$ ring is planar, and its structural parameters are nearly the same as those of the previously reported di-μ-CH$_2$ complexes.[14a] The characteristic structural feature of **2b** is that the Rh−S

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Table 1. Crystallographic Data, Experimental Conditions, and Refinement Details of X-ray Analysis for 2B, 4, and 5A

	2b	4a	5a
Crystal Data			
formula	$C_{38}H_{56}O_8Rh_2S_2$	$C_{52}H_{61}BO_4Rh_2S$	$C_{58}H_{67}BO_8Rh_2S$
fw	910.79	998.73	1140.84
color	red	brown	dark blue
cryst size, mm	0.25 × 0.24 × 0.20	0.50 × 0.48 × 0.20	0.30 × 0.30 × 0.20
cryst syst	monoclinic	triclinic	triclinic
space group (number)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	8.238(4)	12.509(3)	14.345(2)
b, Å	14.681(2)	11.813(3)	17.700(2)
c, Å	16.835(2)	11.902(3)	11.856(2)
α, deg		94.32(2)	102.89(1)
β, deg	94.54(2)	108.05(2)	107.45(1)
γ, deg		70.28(1)	101.46(1)
V, Å^3	2030(1)	2372(1)	2682.8(7)
Z	2	2	2
D_{calcd}, g cm^{-3}	1.490	1.398	1.412
μ(Mo Kα), cm^{-1}	9.44	7.68	6.93
F(000)	940	1032	1180
Data Collection			
diffractometer	AFC-5R	AFC-5R	AFC-5R
radiation (*λ*, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	23	23	23
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
2*θ* range, deg	2−60	2−60	2−60
range of *h*, *k*, *l*	$0 \le h \le 11$, $0 \le k \le 14$, $-23 \le l \le 23$	$0 \le h \le 17$, $-23 \le k \le 25$, $-16 \le l \le 15$	$0 \le h \le 18$, $-22 \le k \le 22$, $-15 \le l \le 14$
no. of indep reflns	5924	13840	12352
abs corr	empirical	empirical	empirical
transmission coeffs	0.966−1.000	0.815−1.000	0.907−1.000
Structure Analysis			
no. of params refined	311	786	900
no. of obsd reflns ($\|F_o\| > 3\sigma(\|F_o\|)$)	4537	9855	9621
R	0.041	0.045	0.036
R_w	0.062	0.052	0.042
S	1.87	1.50	1.58
Δ*ρ*, e Å^3	−0.82, 0.89	−1.50, 0.98	−1.19, 0.57

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2b

Bond Lengths			
Rh−S	2.341(1)	Rh−C(1)	2.034(4)
Rh−Rh′	2.6636(5)	Rh−C(1)′	2.051(4)
S−C(12)	1.722(4)	O(1)−C(14)	1.322(7)
O(2)−C(14)	1.195(7)	O(3)−C(17)	1.331(7)
O(4)−C(17)	1.213(7)	C(12)−C(13)	1.364(6)
C(12)−C(14)	1.500(7)	C(13)−C(17)	1.460(6)

Bond Angles			
S−Rh−Rh′	90.86(3)	C(1)−Rh−Rh′	49.6(1)
C(1)−Rh−C(1)′	98.6(2)	Rh−Rh′−C(1)′	49.0(1)
Rh−C(1)−Rh′	81.4(2)	Rh−S−C(12)	115.1(2)
S−C(12)−C(13)	129.1(4)	S−C(12)−C(14)	110.6(3)
C(12)−C(13)−C(17)	122.2(5)	O(1)−C(14)−C(12)	110.9(5)
O(2)−C(14)−C(12)	124.1(5)	O(3)−C(17)−C(13)	111.0(4)
O(4)−C(17)−C(13)	125.9(5)		

bond distance (2.341(1) Å) is shorter than that of the dithiol complex **1** (2.3591(8) Å).[10] The Rh, S, C(12), and C(13) atoms are coplanar (torsion angle Rh−S−C(12)−C(13), 0.0(5)°), and that of the carboxyl C═O bonds, C(17)−O(4), is nearly parallel to this plane (torsion angle C(12)−C(13)−C(17)−O(4), −11.5(8)°). On the other hand, the other C═O in the carboxyl group is perpendicular to this plane (torsion angle S−C(12)−C(14)−O(2), 95.4(5)°). Furthermore, the distance of the C(13)−C(17) single bond (1.460(6) Å) which connects the olefinic part and the carboxyl group in the same plane is significantly shorter than that of the C(12)−C(14) bond (1.500(7) Å) with the perpendicular carboxyl group. These data suggest that the ethenethiolate ligands have a long electronic conjugate system through the six atoms from Rh to O(4).

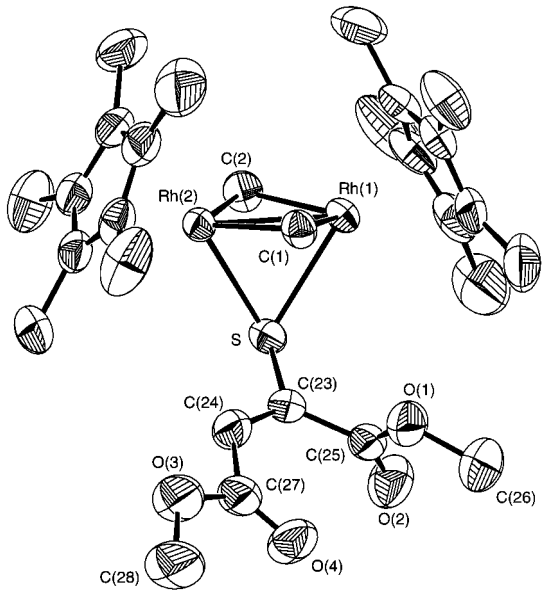


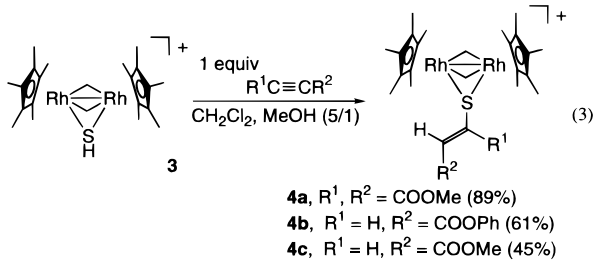
Figure 2. ORTEP drawing for the cationic part of **4a**. Thermal ellipsoids are shown at the 50% probability level.

(2) Reaction of Bridging Thiol Complex 3 with Dimethyl Acetylenedicarboxylate or Carbyl Propiolate. As early as 1975 it was indicated that the reactivity of M(*μ*-SH)M groups is different from that of M-SH groups and is low because one lone pair of

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4a

Bond Lengths			
Rh(1)−Rh(2)	2.5535(7)	Rh(1)−S	2.428(1)
Rh(1)−C(1)	2.037(3)	Rh(1)−C(2)	2.052(5)
Rh(2)−S	2.423(1)	Rh(2)−C(1)	2.055(4)
Rh(2)−C(2)	2.039(3)	S−C(23)	1.775(4)
O(1)−C(25)	1.327(6)	O(2)−C(25)	1.186(4)
O(3)−C(27)	1.336(5)	O(4)−C(27)	1.195(6)
Bond Angles			
Rh(2)−Rh(1)−S	58.14(3)	Rh(2)−Rh(1)−C(1)	51.7(1)
Rh(2)−Rh(1)−C(2)	51.14(8)	Rh(1)−Rh(2)−S	58.33(3)
Rh(1)−Rh(2)−C(1)	51.07(8)	Rh(1)−Rh(2)−C(2)	51.6(1)
Rh(1)−S−Rh(2)	63.53(3)	Rh(1)−S−C(23)	114.4(1)
Rh(2)−S−C(23)	110.0(1)	Rh(1)−C(1)−Rh(2)	77.2(1)
Rh(1)−C(2)−Rh(2)	77.3(1)	S−C(23)−C(24)	121.8(4)
S−C(23)−C(25)	115.6(2)		

electrons on the sulfur atom of μ-SH is blocked in order to coordinate to two metal atoms.[18] However, recent studies have revealed that the bridging thiol ligands in dinuclear complexes have rather high reactivities and show additions to alkynes.[2−4] The reaction of the cationic bridging thiol complex $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)](BPh_4)$ (**3**) with 1 equiv of dimethyl acetylenedicarboxylate or carbyl propiolate in a mixed solvent of CH_2Cl_2/MeOH (5:1) gave $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SCR^1{=}CHR^2)](BPh_4)$ (**4a**, R^1, R^2 = COOMe; **4b**, R^1 = H, R^2 = COOPh; **4c**, R^1 = H, R^2 = COOMe) (eq 3). For the preparation



(3)

of **4b** and **4c**, the reaction proceeded only in the presence of a stoichiometric amount of Et_3N in response to low electrophilicity of the used carbyl propiolates. The obtained Michael-type products are a single isomer with an *E*-form confirmed by X-ray analysis (for **4a**) or by ^{1}H NMR spectroscopy (for **4b** and **4c**). The structure of the cationic part of **4a** is shown in Figure 2. The crystal data and the selected bond lengths and angles are summarized in Tables 1 and 3. The insertion of the alkyne molecule into the bridging thiol proved to construct an *E*-ethenethiolate moiety, similar to what occurred in the preparation of **2b**. In contrast to **2b**, complex **4a** has a considerably long Rh−S bond distance (2.428(1) Å), which is longer than those of the starting μ-SH complex of **3** (2.400(4) Å)[10] and of the previously reported bridging thiolate complexes of $[(RhCp^*)_2(\mu\text{-}SMe)_2Cl_2]$ (2.381(2) Å)[19] and $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ (2.328(3) Å).[20] Other characteristic features of the structure of **4a** are as follows: the S, C(23), C(24), C(27), and O(4) atoms are nearly coplanar; the S−C(23) bond length, 1.775(4) Å, is considerably shorter than that of the bridging methanethiolate ligand in $[(RhCp^*)_2(\mu\text{-}SMe)_2Cl_2]$ (1.828(7) Å);[19] the C(24)−C(27) bond distance (1.468(6) Å) is relatively shorter than the common C−C single-bond distance. In this case, an electronic conjugate system in the thiolate moiety should lie in the five atoms from S to O(4). Although complex **4a** in CH_2Cl_2 or $CHCl_3$ keeps the same structure as that found in solid and does not show any observable dynamic behavior in the formation and cleavage of the bridging Rh−S bond at 25 °C, complex **4a** in $CDCl_3$-containing pyridine displays the Rh−S bond cleavage to form a pyridine adduct of $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{SC(COOMe){=}CH(COOMe)\}(py)]^+$ (vide infra).

We have compared the abilities of the bridging thiol and the terminal thiol in executing the S−H addition to alkyne by using a competition reaction system containing complexes **1** and **3** along with dimethyl acetylenedicarboxylate in CD_2Cl_2 + CD_3OD. The experimental results clearly show that the bridging thiol in **3** reacts much faster than the terminal one in **1**. The same tendency in the reactivities of the terminal and bridging thiol dinuclear complexes was observed in the Rh−Mn dinuclear systems of $[RhMn(CO)_3(\mu\text{-}H)(dppm)_2(SH)]$ and $[RhMn(CO)_4(dppm)_2(\mu\text{-}SH)]^+$.[4]

Reaction of Ethenethiolate Complexes with Activated Alkynes. (1) Reaction of Terminal Ethenethiolate Complex 2 with Dimethyl Acetylenedicarboxylate. The activated alkynes are inserted into M−S bonds in some terminal thiolate complexes such as $[MoCp(F_3CC{\equiv}CCF_3)_2(SC_6F_5)]$, $[WCp(CO)_3(SMe)]$, and $[FeCp(CO)_2(SMe)]$ to give vinyl thioether complexes.[1] However, the dithiolate complex **2** did not react further with dimethyl acetylenedicarboxylate. Complex **2** is very stable both in solution and in solid form. Each rhodium atom in **2** attains a rigid 18 outer electron configuration and is surrounded by the sterically bulky Cp* and ester groups. As mentioned before, the Rh−S bond distance (2.341(1) Å) is considerably short, and the long electronic conjugate system in the thiolate moiety reduces the nucleophilicity of the S atom.

(2) Reaction of Bridging Ethenethiolate Complex 4 with Dialkyl Acetylenedicarboxylates or Ethyl Propiolate and Adduct Formation of 4 with Pyridine. Complex **4** includes the Rh−(SR)−Rh and Rh−(CH_2)−Rh groups. Both functionalities can react with alkynes: Hidai's[7] group and other groups[1a,6] reported that alkynes perform insertions into the M−(SR)−M bonds and oligomerizations on the bridging thiolate metal complexes, and studies, albeit limited in number, on the C−C bond formation between alkynes and the μ-CH_2 ligand in dinuclear complexes have been performed.[12b,21] Seyferth has examined the reactivity of $[Fe_2(CO)_6(\mu\text{-}CCH{=}CR_2)(\mu\text{-}SR)]$, which contains the bridging carbyne ligand and the bridging thiolate ligands, toward alkynes and has found that C−C bond formation between the μ-$CCH{=}CR_2$ ligand and alkynes proceeds.[8c] Complex **4** can also react with activated

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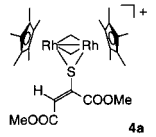
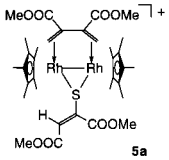
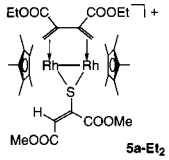
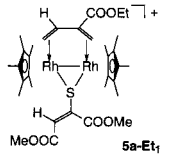
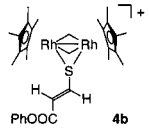
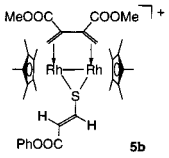
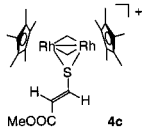
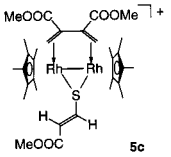
(20) Elduque, A.; Oro, L. A.; Pinillos, M. T.; Tiripicchio, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1994**, 385.

(21) (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803. (b) Adams, P. Q.; Davis, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1983**, 222. (c) Meanwell, N. J.; Smith, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1419. (d) Knox, S. A. R. *J. Organomet. Chem.* **1990**, *400*, 255. (e) Knox, S. A. R. *J. Cluster Sci.* **1992**, *3*, 385. (f) Akita, M.; Hua, R.; Nakanishi, S.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*, 5572.

Table 4. Insertion Reactions of Activated Alkynes into the Bridging Ethenethiolate Complexes[a]

starting complex	alkyne	product (yield)
 **4a**	MeOOC—≡—COOMe	 **5a** (76%)
4a	EtOOC—≡—COOEt	 **5a-Et₂** (72%)
4a	H—≡—COOEt	 **5a-Et₁** (65%)
 **4b**	MeOOC—≡—COOMe	 **5b** (40%)
 **4c**	MeOOC—≡—COOMe	 **5c** (57%)

[a] All complexes are monocationic compounds bearing one BPh_4 anion.

alkynes at the Rh−C bonding site of the two μ-CH_2 ligands to form butadiene complexes, but not at the Rh−(SR)−Rh bonding site.

Treatment of complex **4** with excess dialkyl acetylenedicarboxylates or ethyl propiolate in CH_2Cl_2 gives the disubstituted butadiene complexes $[(RhCp^*)_2(\eta^2{:}\eta^2\text{-}\mu\text{-}CH_2{=}CR^3CR^4{=}CH_2)(\mu\text{-}SCR^1{=}CHR^2)](BPh_4)$ (**5a**, R^1, R^2, R^3, R^4 = COOMe; **5a-Et₂**, R^1, R^2 = COOMe, R^3, R^4 = COOEt; **5a-Et₁**, R^1, R^2 = COOMe, R^3 = H, R^4 = COOEt; **5b**, R^1 = H, R^2 = COOPh, R^3, R^4 = COOMe; **5c**, R^1 = H, R^2 = COOMe, R^3, R^4 = COOMe). The results are summarized in Table 4. Among the reactions of **4a**, **4b**, and **4c** with dimethyl acetylenedicarboxylate, the relative rates of formation of **5** could be ordered as follows: **5b** > **5a** > **5c** (vide infra). The relative yields, however, were as follows: **5a** > **5c** > **5b**, due to the influence of the decomposition of the starting compounds and/or the intermediary species (as shown in Scheme 1, vide infra) under the reaction conditions. Among the reactions of **4a** with dimethyl and diethyl acetylenedicarboxylate and ethyl propiolate to give **5a**, **5a-Et₂**, and **5a-Et₁**, respectively, the former two reactions do not show much difference in their formation rates, while the latter is relatively slow. The bis(alkyl ester) alkynes, which have a strong ability to coordinate to soft metals, seem to be more reactive than the mono(alkyl ester) alkynes. The use of other alkynes, such as alkyl- or arylacetylene, usually resulted in the formation of complicated products, which were not isolated and characterized.

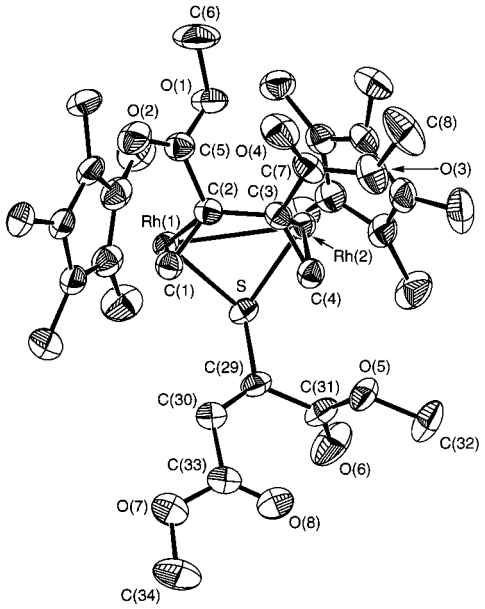


Figure 3. ORTEP drawing for the cationic part of **5a**. Thermal ellipsoids are shown at the 50% probability level.

The structure of the cationic part of **5a**, confirmed by X-ray analysis, is shown in Figure 3. The crystal data and the selected bond lengths and angles are summarized in Tables 1 and 5. The complex has an *s-cis*-$\eta^2{:}\eta^2$-μ-butadiene ligand, which is formed by incorporating one dimethyl acetylenedicarboxylate into two μ-CH_2 groups of **4a**. The Rh−Rh bond distance (2.9012(4) Å) is longer than that in the starting μ-CH_2 complex. The distance of Rh(1)−C(2) (2.308(3) Å) is longer than those of the other three Rh−butadiene bonds (2.127(3), 2.186(3), and 2.148(3) Å). The angle of S−Rh(1)−C(1) (98.95(9)°) is much larger than that of S−Rh(2)−C(4) (88.4(1)°). The bond of C(2)−C(3) in the butadiene ligand is not parallel to the Rh(1)−Rh(2) bond. The butadiene ligand twisted to avoid a steric repulsion between the bulky Cp* and the ester substituents. The

Scheme 1

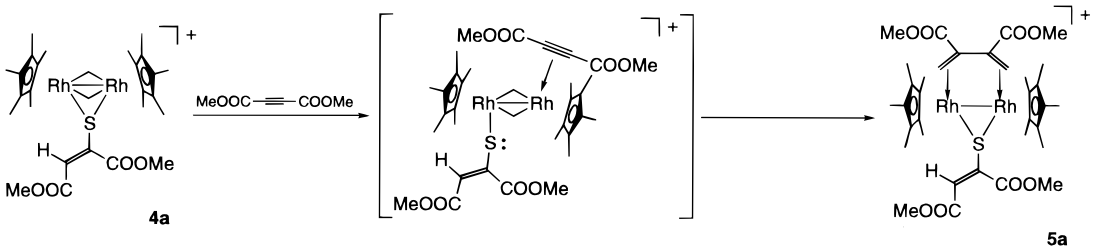


Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for 5a

Bond Lengths			
Rh(1)−Rh(2)	2.9012(4)	Rh(1)−S	2.291(1)
Rh(1)−C(1)	2.127(3)	Rh(1)−C(2)	2.308(3)
Rh(2)−S	2.320(1)	Rh(2)−C(3)	2.186(3)
Rh(2)−C(4)	2.148(3)	S−C(29)	1.780(3)
O(1)−C(5)	1.346(4)	O(2)−C(5)	1.205(5)
O(3)−C(7)	1.345(5)	O(4)−C(7)	1.202(5)
O(5)−C(31)	1.317(5)	O(6)−C(31)	1.192(5)
O(7)−C(33)	1.328(5)	O(8)−C(33)	1.191(5)
C(1)−C(2)	1.404(5)	C(2)−C(3)	1.481(5)
C(2)−C(5)	1.503(5)	C(3)−C(4)	1.414(5)
C(3)−C(7)	1.491(5)		
Bond Angles			
Rh(2)−Rh(1)−S	51.46(2)	Rh(2)−Rh(1)−C(1)	88.9(1)
Rh(2)−Rh(1)−C(2)	64.17(9)	S−Rh(1)−C(1)	98.95(9)
S−Rh(1)−C(2)	100.69(9)	Rh(1)−Rh(2)−S	50.56(2)
Rh(1)−Rh(2)−C(3)	78.19(9)	Rh(1)−Rh(2)−C(4)	91.81(9)
S−Rh(2)−C(3)	105.81(9)	S−Rh(2)−C(4)	88.4(1)
Rh(1)−S−Rh(2)	77.98(3)	Rh(1)−S−C(29)	119.2(1)
Rh(2)−S−C(29)	115.6(1)	C(1)−C(2)−C(3)	121.8(3)
C(1)−C(2)−C(5)	118.9(3)	C(3)−C(2)−C(5)	116.2(3)
C(2)−C(3)−C(4)	121.3(3)	C(2)−C(3)−C(7)	116.1(3)
C(4)−C(3)−C(7)	117.8(3)	S−C(29)−C(30)	124.6(3)
S−C(29)−C(31)	111.6(2)		

general features of the structure of the bridging thiolate moiety are nearly the same as those in complex **4a**.

Interestingly, alkane- or benzenethiolate analogues of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SR)](BPh_4)$ (R = Me, ^{t}Bu, Ph) did not react with alkynes. The starting complexes were recovered unchanged under the same reaction conditions. The difference in the reactivity between the ethenethiolate complexes and these complexes is a result of the ease of the Rh−S bond cleavage. The ease with which cleavage occurs can be roughly estimated by the values of the equilibrium constant, *K*, for the adduct formations with pyridine in solution. The alkane- and benzenethiolate analogues did not form any pyridine adduct. However, the ethenethiolate complex **4** is able to reversibly produce a 1:1 adduct with pyridine. The reversible reaction is much slower than the NMR time scale, so that the NMR signals of the pyridine adducts appear separately from those of the complex **4** and free pyridine. The ^{1}H NMR spectrum of the pyridine adduct species of **4c** showed two Cp* signals at δ 1.32 and 1.40 and two μ-CH_2 signals at δ 9.66 and 9.85, indicating that both the thiolate and pyridine act as terminal ligands coordinated to different Rh atoms and work to produce the species $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{SCH{=}CH(COOMe)\}(py)]^+$. The interaction of pyridine with the complex is also confirmed by an NOE study. Irradiation of one of the μ-CH_2 signals (δ 9.66) caused enhancement (10%) of the ortho proton signal of the pyridine ligand. Furthermore, NOEs were also detected between the other μ-CH_2 signal (δ 9.85) and the olefinic protons of the ethenethiolate ligand with 3 and 7% enhancements, confirming that the pyridine ligand is trans to the thiolate ligand as shown in Figure 4. The adduct formation ability depends on the substituents of the ethenethiolate ligand. The order of the estimated equilibrium constants, *K*, in adduct formation at 25 °C is **4b** (K = 58) > **4a** (40) > **4c** (11). This order indicates that the long conjugate system formed by electronic resonance and the substitution of electron-withdrawing groups reduces the Rh−S bond strength and increases the adduct formation. The larger the equilibrium constants that are obtained, the faster the

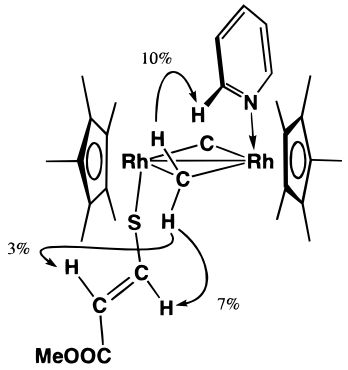


Figure 4. NOE correlations observed for complex **4c** with pyridine.

formation of complex **5**, although the precise reaction rates of the C−C bond formations could not be estimated due to the decomposition of the starting compounds and/or intermediary species (vide supra) under the reaction conditions. The findings mentioned above suggest that the ethenethiolate ligands, in particular, since they have a long conjugate system, stabilize the free lone pair electrons on the S atom and cleave one of the weak Rh−S bonds. This cleavage forms a vacant site on a rhodium atom where the alkyne is able to coordinate to couple with two μ-CH_2 groups.

Knox[21e] and Akita[21f] investigated the coupling of one μ-CH_2 group on a diruthenium complex with acetylene, which afforded a σ,π-allyl complex due to the formation of one C−C bond. The present study is the first example of a butadiene framework being constructed through the coupling of two μ-CH_2 groups with one alkyne on the dirhodium to simultaneously form two C−C bonds. The reaction sequence from **4a** to **5a** is summarized in Scheme 1. The C−C bond formation was achieved by the insertion of the alkyne into two μ-CH_2 groups to give the butadiene complex **5** through an intermediate π-alkyne complex. As mentioned above, the ethenethiolate ligand in **4** plays an important role in the formation of the π-alkyne complex that leads to the unprecedented alkyne insertion reaction. We were not able to detect the π-alkyne complex spectroscopically. This, as well as the dependence of the formation rate of complex **5** on the concentration of the alkyne, suggests that the formation of the π-alkyne complex is a rate-determining step in the formation of **5**.

Conclusion

The terminal thiol complex **1** and the bridging thiol complex **3** react with activated alkynes to give the corresponding ethenethiolate complexes **2** and **4**, respectively. The Michael-type addition of the bridging thiol in **3** to alkynes is much faster compared with that of the terminal thiol in **1**. The terminal bis(ethenethiolate) complex **2** has the rigid 18e outer electron configuration and therefore does not react further with the alkyne. On the other hand, the bridging ethenethiolate complex **4** is able to react and to give the butadiene complex **5** through the coupling of two μ-CH_2 groups with one alkyne on the dirhodium. The high reactivity of **4** is attributed to the ease of cleavage of the Rh−S bond. The long conjugated ethenethiolate ligands stabilize the free lone pair of electrons on the S atom and

cleave one of the weak Rh−S bonds to form a vacant site which is offered to alkynes for the coordination. The C−C bond formation may proceed through an intermediate of the π-alkyne complex as shown in Scheme 1. Thus, the C−C bond formation on the dirhodium depends on the characteristics of the Rh(μ-SCR^1=CHR^2)Rh group in **4**.

Experimental Section

General Procedures. Complexes *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$(SH)$_2$] (**1**) and [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-SH)](BPh$_4$) (**3**) were prepared according to a literature procedure.[10] Phenyl propiolate was prepared according to a literature procedure.[22] Other alkynes were obtained from Tokyo Kasei Kogyo Co. and degassed with Ar before using. Solvents were dried over P_2O_5 (for CH_2Cl_2) or Mg (for MeOH) and distilled immediately prior to use. All reactions with alkynes were carried out under Ar or N_2 atmosphere. Column chromatography was performed using 70−230 mesh silica gel. NMR spectra were recorded on a JEOL Λ-400 spectrometer. Chemical shifts are given in ppm from $SiMe_4$. FAB mass spectra were recorded on a SHIMADZU/KRATOS CONCEPT I S mass spectrometer. Elemental analyses were carried out with a Perkin-Elmer 2400 microanalyzer.

Preparation of *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2${SC(COOMe)=CH(COOMe)}$_2$] (2a). Dimethyl acetylenedicarboxylate (142 mg, 1.0 mmol) was added to a solution of **1** (114 mg, 0.20 mmol) in CH_2Cl_2 (10 mL), and the reaction mixture was stirred at 25 °C for 24 h. Complex **2a** precipitated readily on addition of MeOH (30 mL) to the mixture. The obtained red product was collected and washed with a small amount of MeOH and Et_2O (120 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (br s, 4H, μ-CH$_2$), 5.55 (s, 2H, olefinic), 3.82 (s, 6H, COO*Me*), 3.68 (s, 6H, COO*Me*), 1.72 (s, 30H, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9 (br, μ-CH$_2$), 169.4 (carboxyl or olefinic), 165.7 (carboxyl or olefinic), 163.8 (carboxyl or olefinic), 110.4 (olefinic), 105.1 (C_5Me_5), 52.8 (COO*Me*), 51.3 (COO*Me*), 10.1 (C_5*Me*$_5$). Anal. Calcd for $C_{34}H_{48}O_8Rh_2S_2$: C, 47.78; H, 5.66. Found: C, 47.88; H, 5.91.

***trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2${SC(COOEt)=CH(COOEt)}$_2$] (2b).** Complex **2b** was obtained from the reaction of **1** and diethyl acetylenedicarboxylate as red crystals by the method similar to that for **2a** (66% yield). Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (br s, 4H, μ-CH$_2$), 5.52 (s, 2H, olefinic), 4.25 (q, *J* = 6.8 Hz, 4H, COO*CH*$_2$CH$_3$), 4.13 (q, *J* = 6.8 Hz, 4H, COOCH$_2$*CH*$_3$), 1.70 (s, 30H, Cp*), 1.30 (t, *J* = 6.8 Hz, 6H, COOCH$_2$*CH*$_3$), 1.26 (t, *J* = 6.8 Hz, 6H, COOCH$_2$*CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.6 (br, μ-CH$_2$), 168.7 (s, carboxyl or olefinic), 165.0 (carboxyl or olefinic), 163.1 (carboxyl or olefinic), 110.6 (olefinic), 104.9 (C_5Me$_5$), 61.4 (COO*CH*$_2$CH$_3$), 59.6 (COO*CH*$_2$CH$_3$), 14.4 (COOCH$_2$*CH*$_3$), 14.0 (COOCH$_2$*CH*$_3$), 9.9 (C_5*Me*$_5$). FAB mass spectrum: *m*/*z* (%) 910 (2) $C_{38}H_{56}O_8Rh_2S_2$ M$^+$, 707 (33) $C_{38}H_{45}O_4Rh_2S_2$ (M − $C_8H_{11}O_4S$)$^+$, 441 (100) $C_{18}H_{26}O_4RhS$ [(M − C_2H_4)/2]$^+$. Anal. Calcd for $C_{38}H_{56}O_8Rh_2S_2$: C, 50.11; H, 6.20. Found: C, 49.88; H, 6.01.

Preparation of [(RhCp*)$_2$(μ-CH$_2$)$_2${μ-SC(COOMe)=CH(COOMe)}] (BPh$_4$) (4a). Dimethyl acetylenedicarboxylate (28 mg, 0.20 mmol) was added to a solution of **3** (172 mg, 0.20 mmol) in a mixed solvent (24 mL of CH_2Cl_2/MeOH = 5:1), and the reaction mixture was stirred at 25 °C for 12 h. After removing the solvent under reduced pressure, the crude product was purified by recrystallization from CH_2Cl_2/MeOH to give a pure brown product (173 mg, 89% yield). Single crystals suitable for X-ray analysis were obtained by recrystallization from THF/toluene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H, μ-CH$_2$), 8.05 (s, 1H, μ-CH$_2$), 7.97 (s, 1H, μ-CH$_2$), 7.60 (s, 1H, μ-CH$_2$), 7.42−7.40 (m, 8H, ortho protons of BPh$_4$), 7.02 (t, *J* = 7.3 Hz, 8H, meta protons of BPh$_4$), 6.87 (t, *J* = 7.3 Hz, 4H, para protons of BPh$_4$), 5.74 (s, 1H, olefinic), 3.79 (s, 3H, COO*Me*), 3.75 (s, 3H, COO*Me*), 1.71 (s, 30H, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6 (t, J_{Rh-C} = 24 Hz, μ-CH$_2$), 166.3 (t, J_{Rh-C} = 24 Hz, μ-CH$_2$), 165.9 (carboxyl), 164.2 (q, J_{B-C} = 50 Hz, BPh$_4$), 163.3 (carboxyl), 144.3 (olefinic), 136.3 (BPh$_4$), 127.9 (olefinic), 125.4 (BPh$_4$), 121.6 (BPh$_4$), 103.2 (C_5Me_5), 53.1 (COO*Me*), 52.4 (COO*Me*), 10.2 (C_5*Me*$_5$). FAB mass spectrum: *m*/*z* (%) 679 (100) $C_{28}H_{41}O_4Rh_2S$ (M − BPh$_4$)$^+$. Anal. Calcd for $C_{52}H_{61}BO_4Rh_2S$: C, 62.54; H, 6.16. Found: C, 62.20; H, 6.16.

[(RhCp*)$_2$(μ-CH$_2$)$_2${μ-SCH=CH(COOPh)}](BPh$_4$) (4b). Complex **4b** was prepared from **3** and phenyl propiolate. The reaction proceeded only in the presence of a stoichiometric amount of Et_3N. Other reaction conditions were similar to those for **4a** (61% yield). The brown crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (br s, 1H, μ-CH$_2$), 8.20 (br s, 1H, μ-CH$_2$), 7.97 (br s, 1H, μ-CH$_2$), 7.73 (br s, 1H, μ-CH$_2$), 7.42 (m, 11H, ortho protons of BPh$_4$ and meta and para protons of Ph), 7.12 (d, *J* = 14.9 Hz, 1H, olefinic), 7.11 (d, *J* = 7.5 Hz, 2H, ortho protons of Ph), 7.03 (t, *J* = 7.3 Hz, 8H, meta protons of BPh$_4$), 6.88 (t, *J* = 7.3 Hz, 4H, para protons of BPh$_4$), 6.36 (d, *J* = 14.9 Hz, 1H, olefinic), 1.73 (s, 30H, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6 (br, μ-CH$_2$), 166.7 (br, μ-CH$_2$), 164.2 (q, *J* = 49 Hz, BPh$_4$), 162.4 (carboxyl), 150.3(Ph), 144.0 (olefinic), 136.3 (BPh$_4$), 129.5 (Ph), 129.1 (olefinic), 126.2 (Ph), 125.4 (BPh$_4$), 121.5 (BPh$_4$), 121.3 (Ph), 102.6(C_5Me_5), 10.1 (C_5*Me*$_5$). Anal. Calcd for $C_{55}H_{61}BO_2Rh_2S$: C, 65.88; H, 6.13. Found: C, 65.98; H, 6.21.

[(RhCp*)$_2$(μ-CH$_2$)$_2${μ-SCH=CH(COOMe)}](BPh$_4$) (4c). Complex **4c** was prepared from **3** and methyl propiolate by the method similar to that for **4b** (45% yield). The brown crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (br s, 1H, μ-CH$_2$), 8.12 (br s, 1H, μ-CH$_2$), 7.95 (br s, 1H, μ-CH$_2$), 7.65 (br s 1H, μ-CH$_2$), 7.43−7.39 (m, 8H, ortho protons of BPh$_4$), 7.02 (t, *J* = 7.3 Hz, 8H, meta protons of BPh$_4$), 6.90 (d, *J* = 14.8 Hz, 1H, olefinic), 6.87 (t, *J* = 7.3 Hz, 4H, para protons of BPh$_4$), 6.15 (d, *J* = 14.8 Hz, 1H, olefinic), 3.74 (s, 3H, COO*Me*), 1.70 (s, 30H, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8 (br, μ-CH$_2$), 166.4, (br, μ-CH$_2$), 164.4 (carboxyl), 164.2 (q, J_{B-C} = 49 Hz, BPh$_4$), 141.2 (olefinic), 136.3 (BPh$_4$), 129.8 (olefinic), 125.4 (BPh$_4$), 121.5 (BPh$_4$), 102.5 (C_5Me_5), 52.0 (COO*Me*), 10.1 (C_5*Me*$_5$). Anal. Calcd for $C_{50}H_{59}BO_2Rh_2S$: C, 63.84; H, 6.32. Found: C, 64.02; H, 6.04.

Competition Reaction of 1 and 3 with Dimethyl Acetylenedicarboxylate. Dimethyl acetylenedicarboxylate (16 mg, 0.11 mmol) was added to a solution containing both complexes **1** (20 mg, 35 μmol) and **3** (30 mg, 35 μmol) in a mixed solvent (3 mL of CD_2Cl_2/CD_3OD = 5:1). After stirring for 2 h at 25 °C, the reaction mixture was monitored by ^{1}H NMR. The spectrum showed that the solution contained the starting materials and complexes **2a** and **4a** obtained in 21 and 72% yields, respectively. About 6 h were required to convert over 95% of **3** to **4a**. At this point, 65% of **1** remained in the reaction mixture. In addition, a small amount of **5a** (<10%) was formed by the reaction of **4a** and the alkyne. The yields were determined by the intensity of the methyl proton signals of the Cp* groups in the ^{1}H NMR spectrum.

Preparation of [(RhCp*)$_2${η^2:η^2-μ-CH$_2$=C(COOMe)C(COOMe)=CH$_2$}{μ-SC(COOMe)=CH(COOMe)}](BPh$_4$) (5a). To a solution of **4a** (200 mg, 0.20 mmol) in CH_2Cl_2 (20 mL) was added dimethyl acetylenedicarboxylate (142 mg, 1.0 mmol). The brown reaction mixture slowly turned to dark blue, and the reaction was almost completed after 2 days at 25 °C. After removing the solvent under reduced pressure, the crude product was purified by column chromatography

(22) Trahanovsky, W. S.; Emeis, S. L.; Lee, A. S. *J. Org. Chem.* **1976**, *41*, 4043.

using CH_2Cl_2 as an eluent to give a pure dark blue product (174 mg, 76% yield). Further purification was performed by recrystallization from CH_2Cl_2/Et_2O. Single crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.39 (m, 8H, ortho protons of BPh_4), 7.00 (t, J = 7.3 Hz, 8H, meta protons of BPh_4), 6.86 (t, J = 7.3 Hz, 4H, para protons of BPh_4), 5.41 (s, 1H, olefinic), 3.81 (s, 3H, COO*Me*), 3.71 (s, 6H, COO*Me*), 3.68 (s, 3H, COO*Me*), 3.18 (br s, 2H, butadiene), 1.67 (s, 30H, Cp*), 0.57 (br s, 2H, butadiene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0 (carboxyl), 164.6 (carboxyl), 164.2 (q, J_{B-C} = 50 Hz, BPh_4), 162.3 (carboxyl), 147.7 (olefinic), 136.3 (BPh_4), 126.3 (olefinic), 125.4 (BPh_4), 121.6 (BPh_4), 105.1 (d, J_{Rh-C} = 3 Hz, C_5Me_5), 67.8 (br, butadiene), 53.4 (COO*Me*), 53.1 (COO*Me*), 52.4 (COO*Me*), 47.5 (br, butadiene), 9.9 (C_5Me_5). Anal. Calcd for $C_{58}H_{67}BO_8Rh_2S$: C, 61.06; H, 5.92. Found: C, 60.89; H, 6.02.

[(RhCp*)$_2${η^2:η^2-μ-CH_2=C(COOEt)C(COOEt)=CH_2}{μ-SC(COOMe)=CH(COOMe)}](BPh$_4$) (5a-Et$_2$). Complex **5a-Et$_2$** was prepared from **4a** and diethyl acetylenedicarboxylate by a method similar to that for **5a** (72% yield). The dark blue crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.38 (m, 8H, ortho protons of BPh_4), 7.00 (t, J = 7.3 Hz, 8H, meta protons of BPh_4), 6.85 (t, J = 7.3 Hz, 4H, para protons of BPh_4), 5.42 (s, 1H, olefinic), 4.21−4.12 (m, 4H, COOCH_2CH$_3$), 3.80 (s, 3H, COO*Me*), 3.67 (s, 3H, COO*Me*), 3.15 (br s, 2H, butadiene), 1.69 (s, 30H, Cp*), 1.28 (t, J = 7.3 Hz, 6H, COOCH$_2$$CH_3$), 0.59 (br s, 2H, butadiene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6 (carboxyl), 164.6 (carboxyl), 164.1 (q, J_{B-C} = 49 Hz, BPh_4), 162.2 (carboxyl), 147.6 (olefinic), 136.3 (BPh_4), 126.3 (olefinic), 125.4 (BPh_4), 121.5 (BPh_4), 105.0 (C_5Me_5), 68.6 (br s, butadiene), 62.6 (COOCH_2CH$_3$), 53.1 (COO*Me*), 52.4 (COO*Me*), 48.0 (br s, butadiene), 14.2 (COOCH$_2$$CH_3$), 10.0 ($C_5Me_5$). Anal. Calcd for $C_{60}H_{71}BO_8Rh_2S$: C, 61.65; H, 6.12. Found: C, 61.60; H, 5.98.

[(RhCp*)$_2${η^2:η^2-μ-CH_2=C(COOEt)CH=CH_2}{μ-SC(COOMe)=CH(COOMe)}](BPh$_4$) (5a-Et$_1$). Complex **5a-Et$_1$** was prepared from **4a** and ethyl propiolate by a method similar to that for **5a** (65% yield). The red crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.38 (m, 8H, ortho protons of BPh_4), 7.00 (t, J = 7.3 Hz, 8H, meta protons of BPh_4), 6.85 (t, J = 7.3 Hz, 4H, para protons of BPh_4), 5.44 (s, 1H, olefinic), 4.34 (dd, J = 8.1, 12.9 Hz, 1H, butadiene), 4.30−4.11 (m, 2H, COOCH_2CH$_3$), 3.79 (s, 3H, COO*Me*), 3.67 (s, 3H, COO*Me*), 3.04 (br s, 1H, butadiene), 2.58 (d, J = 8.1 Hz, 1H, butadiene), 1.76 (s, 15H, Cp*), 1.66 (s, 15H, Cp*), 1.31 (t, J = 7.3 Hz, 3H, COOCH$_2$$CH_3$), 0.78 (br s, 1H, butadiene), 0.60 (d, J = 12.9 Hz, 1H, butadiene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3 (carboxyl), 164.8 (carboxyl), 164.2 (q, J_{B-C} = 49 Hz, BPh_4), 162.4 (carboxyl), 148.5 (olefinic), 136.3 (BPh_4), 125.4 (BPh_4), 125.2 (olefinic), 121.5 (BPh_4), 104.3 (d, J_{Rh-C} = 6 Hz, C_5Me_5), 102.9 (d, J_{Rh-C} = 6 Hz, C_5Me_5), 65.3 (d, J_{Rh-C} = 7 Hz, butadiene), 63.3 (d, J_{Rh-C} = 8 Hz, butadiene), 62.0 (COOCH_2CH$_3$), 53.0 (COO*Me*), 52.3 (COO*Me*), 49.8 (d, J_{Rh-C} = 11 Hz, butadiene), 43.5 (d, J_{Rh-C} = 11 Hz, butadiene), 14.4 (COOCH$_2$$CH_3$), 9.9($C_5Me_5$). Anal. Calcd for $C_{57}H_{67}BO_6Rh_2S$: C, 62.42; H, 6.16. Found: C, 62.16; H, 6.23.

[(RhCp*)$_2${η^2:η^2-μ-CH_2=C(COOMe)C(COOMe)=CH_2}{μ-SCH=CH(COOPh)}](BPh$_4$) (5b). Complex **5b** was prepared from **4b** and dimethyl acetylenedicarboxylate by a method similar to that for **5a** (40% yield). The dark blue crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.38 (t, J = 7.6 Hz, 2H, meta protons of Ph), 7.31−7.27 (m, 8H, ortho protons of BPh_4), 7.25 (t, J = 7.6 Hz, 1H, para proton of Ph), 7.04 (d, J = 7.6 Hz, 2H, ortho protons of Ph), 7.00 (t, J = 7.3 Hz, 8H, meta protons of BPh_4), 6.97 (d, J = 14.9 Hz, 1H, olefinic), 6.85 (t, J = 7.3 Hz, 4H, para protons of BPh_4), 5.92 (d, J = 14.9 Hz, 1H, olefinic), 3.71 (s, 6H, COO*Me*), 3.14 (br s, 2H, butadiene), 1.81 (s, 30H, Cp*), 0.25 (br s, 2H, butadiene). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 169.5 (carboxyl), 164.4 (q, J_{B-C} = 49 Hz, BPh_4), 162.0 (carboxyl), 150.7(Ph), 147.3 (olefinic), 136.3 (BPh_4), 129.9 (Ph), 129.1 (Ph), 126.6 (olefinic), 126.0 (BPh_4), 122.0 (BPh_4), 121.7 (Ph), 105.3 (C_5Me_5), 67.7 (d, J_{Rh-C} = 6 Hz, butadiene), 53.7 (COO*Me*), 47.0 (d, J_{Rh-C} = 13 Hz, butadiene), 10.3 (C_5Me_5). Anal. Calcd for $C_{61}H_{67}BO_6Rh_2S$: C, 64.00; H, 5.90. Found: C, 64.12; H, 6.00.

[(RhCp*)$_2${η^2:η^2-μ-CH_2=C(COOMe)C(COOMe)=CH_2}{μ-SCH=CH(COOMe)}](BPh$_4$) (5c). Complex **5c** was prepared from **4c** and dimethyl acetylenedicarboxylate by a method similar to that for **5a** (57% yield). The dark blue crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.36 (m, 8H, ortho protons of BPh_4), 7.01 (t, J = 7.3 Hz, 8H, meta protons of BPh_4), 6.86 (t, J = 7.3 Hz, 4H, para protons of BPh_4), 6.67 (d, J = 15.1 Hz, 1H, olefinic), 5.69 (d, J = 15.1 Hz, 1H, olefinic), 3.69 (s, 3H, COO*Me*), 3.68 (s, 6H, COO*Me*), 3.04 (br s, 2H, butadiene), 1.68 (s, 30H, Cp*), 0.36 (br s, 2H, butadiene). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2 (carboxyl), 164.2 (q, J_{B-C} = 49 Hz, BPh_4), 163.6 (carboxyl), 144.6 (olefinic), 136.3 (BPh_4), 129.1 (olefinic), 125.4 (BPh_4), 121.5 (BPh_4), 104.8 (C_5Me_5), 67.0 (butadiene), 53.4 (COO*Me*), 52.2 (COO*Me*), 46.4 (butadiene), 9.9 (C_5Me_5). Anal. Calcd for $C_{56}H_{65}BO_6Rh_2S$: C, 62.12; H, 6.05. Found: C, 61.98; H, 5.95.

Pyridine Adduct Formation from 4. The structures of the pyridine adducts in $CDCl_3$ and their equilibrium constants were confirmed by NMR spectroscopy. The ratio of the starting complex and the product was determined by the intensity of the methyl proton signals of the Cp* groups in the ^{1}H NMR spectrum. The typical procedure is as follows: A solution of **4a** (20 mM, 0.25 mL, 5 μmol) in $CDCl_3$ and a solution of pyridine (94 mM, 0.25 mL, 23.5 μmol) in $CDCl_3$ were combined in an NMR tube. The brown mixture was allowed to stand for 10 min at 25 °C to give a 1:1 adduct in 62% yield. The equilibrium constant, K, of the adduct formation is estimated as ca. 40 at 25 °C. Characterization of [(RhCp*)$_2$(μ-CH_2)$_2${SC(COOMe)=CH(COOMe)}(py)]$^+$ species in the solution: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (br s, 2H, μ-CH_2), 9.85 (br s, 2H, μ-CH_2), 7.62 (d, J = 7.5 Hz, 2H, ortho protons of py), 7.24 (t, J = 7.5 Hz, 1H, para proton of py), 6.74 (t, J = 7.5 Hz, 2H, meta protons of py), 5.50 (s, 1H, olefinic), 3.82 (s, 3H, COO*Me*), 3.71 (s, 3H, COO*Me*), 1.40 (s, 15H, Cp*), 1.36 (s, 15H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4 (t, J = 29 Hz, μ-CH_2), 168.6 (carboxyl), 165.1 (carboxyl), 160.6 (olefinic), 152.5 (py), 140.0 (olefinic), 127.8 (py), 110.8 (py), 105.2 (C_5Me_5), 104.7 (C_5Me_5), 52.7 (COO*Me*), 51.3 (COO*Me*), 9.5 (C_5Me_5), 9.3 (C_5Me_5). The pyridine adducts of **4b** and **4c** were generated in a manner similar to that above. Characterization of [(RhCp*)$_2$(μ-CH_2)$_2${SCH=CH(COOPh)}(py)]$^+$ species in the solution: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 2H, μ-CH_2), 9.69 (s, 2H, μ-CH_2), 7.78 (dd, J = 2.4, 14.6 Hz, 1H, olefinic), 7.63 (d, J = 5.1 Hz, 2H, ortho protons of py), 7.41−7.10 (m, 6H, Ph and para proton of py), 6.77 (dd. J = 5.1, 7.3 Hz, 2H, meta protons of py), 5.96 (d, J = 14.6 Hz, 1H, olefinic), 1.39 (s, 15H, Cp*), 1.33 (s, 15H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.8 (t, J = 26 Hz, μ-CH_2), 164.5 (carboxyl), 164.0 (olefinic), 152.4 (py), 151.2 (Ph), 139.9 (olefinic), 129.2 (Ph), 127.9 (py), 125.2 (Ph), 121.8 (Ph), 114.3 (py), 104.9 (d, J = 4 Hz, C_5Me_5), 104.2 (d, J = 5 Hz, C_5Me_5), 9.8 (C_5Me_5), 9.2 (C_5Me_5). Characterization of [(RhCp*)$_2$(μ-CH_2)$_2${SCH=CH(COOMe)}(py)]$^+$ species in the solution: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (br s, 2H, μ-CH_2), 9.66 (br s, 2H, μ-CH_2), 7.62 (d, J = 5.4 Hz, 2H, ortho protons of py), 7.56 (dd, J = 2.4, 14.9 Hz, 1H, olefinic), 7.23 (t, J = 7.8 Hz, 1H, para proton of py), 6.75 (dd, J = 5.4, 7.8 Hz, 2H, meta protons of py), 5.77 (d, J = 14.9 Hz, 1H, olefinic), 3.70 (s, 3H, COOMe), 1.40 (s, 15H, Cp*), 1.32 (s, 15H, Cp*).

X-ray Crystallographic Study. The X-ray diffraction experiments were performed at 23 °C on a Rigaku automated four-circle diffractometer AFC-5R with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The lattice constants were determined by least-squares treatment using setting

angles of 25 reflections in the $25° < 2\theta < 30°$ range. Crystallographic data for **2b**, **4a**, and **5a** are summarized in Table 1. Three standard reflections were monitored at every 150 measurements and showed no detectable decay of the crystal during the data collection. The intensities were corrected for Lorentz-polarization factors, and empirical absorption corrections[23] with a set of Ψ scan data were applied. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms, except for those bound to C(1) and C(13) of **2b** and C(1), C(2), and C(24) of **4a** which were located by Fourier-difference syntheses, were introduced at theoretical positions and refined isotropically. Complex neutral-atom scattering factors were taken from the ref 24. The function $\sum w||F_o| - |F_c||^2$ was minimized with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ by the block-diagonal least-squares method. All the calculations were carried out using *Xtal3.2* software[25] on a Fujitsu S-4/IX workstation.

(23) Watenpaugh, K.; Stewart, J. ABSCAL; Scale diffractometer intensity data in Xtal 3.2 program system (ref 25).

(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

(25) Hall, S. R.; Flack, H. D.; Stewart, J. M. *Xtal 3.2*; Program for X-ray crystal structure analysis; Universities of Western Australia, Geneva, and Maryland, 1992.

Supporting Information Available: Tables of crystal data, bond lengths and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom locations for **2b**, **4a**, and **5a** (36 pages). Ordering information is given on any current masthead page.

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