# Facile Allylic C−H Bond Activation on the Bridging Disulfide Ligand in the $Ru^{III}$ Dinuclear Complex Having a Conjugated RuSSRu Core

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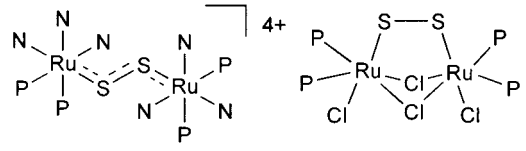
Treatment of $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_4$ (**1**), which is prepared by the reaction of $[\{RuCl(P(OCH_3)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**2**) with 4 equiv of $AgCF_3SO_3$, with terminal alkenes such as 1-pentene, allyl ethyl ether, allyl phenyl ether, 1,4-hexadiene, and 3-methyl-1-butene, resulted in the formation of complexes carrying a $C_3S_2$ five-membered ring, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2CH_2CR^1R^2S\}](CF_3SO_3)_4$ (**3**, $R^1 = CH_2CH_3$, $R^2 = H$, 40%; **4**, $R^1 = OCH_2CH_3$, $R^2 = H$, 60%; **5**, $R^1 = OC_6H_5$, $R^2 = H$, 73%; **6**, $R^1 = CH{=}CHCH_3$, $R^2 = H$, 48%; **7**, $R^1 = R^2 = CH_3$, 40%). Reaction of **1** with methylenecycloalkanes was found to give several different types of products, depending on the ring size of the substrates. A trace of $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SCH(CH_2CH_2)CH(CH_3)S\}](CF_3SO_3)_4$ (**9**) having a $C_2S_2$ four-membered ring to bridge the two Ru atoms was obtained by the reaction of **1** with methylenecyclobutane, whereas the reaction with methylenecyclohexane gave $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}S(CH_2(C{=}CHCH_2CH_2CH_2CH_2)S)\}(CF_3SO_3)_3$ (**10**) in 69% yield via C−S bond formation and elimination of a proton. Throughout these reactions with alkenes giving a variety of products, the activation of the allylic C−H bond is always the essential and initial key step.

## Introduction

Cycloaddition is a well-known reaction and has been utilized in the synthesis of a number of heterocyclic compounds. In the reactions, appropriate carbon−carbon double or triple bonds react with other components to form cyclic compounds, and among others, the reaction of conjugate dienes with dienophiles is the most well-known one. Zwitterionic "1,3-dipoles" having oxygen and/or nitrogen rather than carbon are also known to react with carbon−carbon double or triple bonds to form a five-membered ring.[1] However, analogous reactions of allylic hydrocarbon compounds are very rare. It is reported that the reaction of 2-phenylallyl anion with stilbene and the following hydrolysis gives 1,2,4-triphenylcyclopentane, where preliminarily prepared allyl anion is necessary for the reaction.[2]

In contrast, we have reported that the reaction of the disulfide-bridged $Ru^{III}$ dinuclear complex $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_4$ (**1**) (Scheme 1), prepared from $[\{RuCl(P(OCH_3)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$ (**2**),[3−10] with 1-pentene gives $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2CH_2CH(CH_2CH_3)S\}](CF_3SO_3)_4$ (**3**),[11] in which an unactivated allylic C−H bond reacts with the disulfide ligand to form a C−S bond. Neutral alkene can be used for the reaction without any preliminary treatment to prepare active species like allyl anion. This means that a C−H bond activation reaction is involved in the reaction, similar to the previously reported reactions of **1** with ketones.[12,13] As an extended study of the cycloadditions,[11,14] we have examined other types of alkenes to find unexpectedly a variety of reaction patterns, depending on the steric size of the substrate. In the present report, the reactions of **1** with terminal alkenes and methylenecycloalkanes are described.

**Scheme 1**




## Experimental Section

All experiments were carried out under nitrogen or argon, by using standard Schlenk tube techniques or a glovebox. The solvent $CD_3CN$

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(1) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403.
(2) Eidenschink, R.; Kauffman, T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 292; *Angew. Chem.* **1972**, *84*, 292.
(3) Matsumoto, T.; Matsumoto, K. *Chem Lett.* **1992**, 559.
(4) Matsumoto, K.; Matsumoto, T.; Kawano, M.; Ohnuki, H.; Shichi, Y.; Nishide, T.; Sato, T. *J. Am. Chem. Soc.* **1996**, *118*, 3597.
(5) (a) Kawano, M.; Hoshino, C.; Matsumoto, K. *Inorg. Chem.* **1992**, *31*, 5158. (b) Matsumoto, K.; Uemura, H.; Kawano, M. *Chem. Lett.* **1994**, 1215.
(6) Matsumoto, K.; Ohnuki, H.; Kawano, M. *Inorg. Chem.* **1995**, *34*, 3838.
(7) Matsumoto, K.; Sano, Y.; Kawano, M.; Uemura, H.; Matsunami, J.; Sato, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1239.
(8) Matsumoto, K.; Sano, Y. *Inorg. Chem.* **1997**, *36*, 4405.
(9) Koyama, T.; Koide, Y.; Matsumoto, K. *Inorg. Chem.* **1999**, *38*, 3241.
(10) Matsumoto, K.; Koyama, T.; Koide, Y. *J. Am. Chem. Soc*. **1999**, *121*, 10913.
(11) Hossain, Md. M.; Lin, Y.-S.; Sugiyama, H.; Matsumoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 172.
(12) Matsumoto, K.; Uemura, H.; Kawano, M. *Inorg. Chem*. **1995**, *34*, 658.
(13) Sugiyama, H.; Hossain, Md. M.; Lin, Y.-S.; Matsumoto, K. *Inorg. Chem*. **2000**, *39*, 3948.
(14) Sugiyama, H.; Lim, Y.-S.; Matsumoto, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 4058; *Angew. Chem.* **2000**, *112*, 4224.

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**Table 1.** Summary of Crystallographic Data

| | **5** | **6** | **7** | **9** | **10** |
|---|---|---|---|---|---|
| formula | $C_{43}H_{64}F_{12}N_6O_{25}P_4Ru_2S_6$ | $C_{34}H_{64}F_{12}N_6O_{24}P_4Ru_2S_6$ | $C_{33}H_{64}F_{12}N_6O_{24}P_4Ru_2S_6$ | $C_{33}H_{62}F_{12}N_6O_{24}P_4Ru_2S_6$ | $C_{34}H_{65}F_9N_6O_{21}P_4Ru_2S_5$ |
| fw | 1811.38 | 1687.29 | 1675.28 | 1673.27 | 1551.24 |
| cryst syst | monoclinic | monoclinic | triclinic | monoclinic | triclinic |
| space group | $P2_1/c$ (No. 14) | $Cc$ (No. 9) | $P1$ (No. 2) | $P2_1/c$ (No. 14) | $P1$ (No. 2) |
| $a$ (Å) | 13.267(5) | 13.3995(9) | 12.7356(10) | 12.0626(18) | 12.1799(15) |
| $b$ (Å) | 21.456(5) | 20.1101(14) | 12.7416(9) | 20.535(3) | 12.7237(16) |
| $c$ (Å) | 25.962(6) | 25.2525(16) | 20.6047(15) | 26.819(4) | 23.504(3) |
| α (deg) | | | 94.527(2) | | 79.478(2) |
| $\beta$ (deg) | 103.93(3) | 99.308(2) | 105.9470(10) | 92.039(4) | 75.505(2) |
| $\gamma$ (deg) | | | 90.173(2) | | 62.339(2) |
| $V$ (Å$^3$) | 7173(4) | 6715.1(8) | 3203.8(4) | 6639.0(18) | 3114.1(7) |
| $Z$ | 4 | 4 | 2 | 4 | 2 |
| $d_{calcd}$ (g·cm$^{-3}$) | 1.677 | 1.669 | 1.737 | 1.674 | 1.654 |
| $\mu$ (mm$^{-1}$) | 0.792 | 0.837 | 0.877 | 0.846 | 0.853 |
| diffractometer | AFC7R | SMART 1000 | SMART 1000 | SMART 1000 | SMART 1000 |
| radiation, $\lambda$ (Å) | Mo Kα, 0.71069 | Mo Kα, 0.71069 | Mo Kα, 0.71069 | Mo Kα, 0.71069 | Mo Kα, 0.71069 |
| abs corr | $\psi$ scan | SADABS | SADABS | SADABS | SADABS |
| reflns (total) | 12610 | 11488 | 14302 | 15217 | 13833 |
| reflns ($F_o^2 > 2\sigma(F_o^2)$) | 5819 | 8364 | 9982 | 4395 | 8438 |
| no of params | 702 | 679 | 804 | 806 | 756 |
| R1[a] | 0.1293 | 0.0786 | 0.0788 | 0.0806 | 0.0758 |
| wR2[b] | 0.3267 | 0.2028 | 0.1919 | 0.1972 | 0.1900 |
| GOF[c] | 1.181 | 0.989 | 0.981 | 0.844 | 0.961 |

[a] $R1 = \sum|F_o - F_c|/\sum|F_o|$ for reflections $F_o^2 > 2\sigma(F_o^2)$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $GOF = [\sum w(F_o^2 - F_c^2)^2/\sum(n - p)]^{1/2}$.

was dried over $CaH_2$ and purified by trap-to-trap distillation prior to use. Other solvents were purchased dry and used without further purification. Complexes **1**,[13] **2**,[3] and 1-pentene-3,3-$d_2$[15] were prepared as described in the literature. The NMR spectra were recorded on a JEOL Lambda 270 spectrometer, operating at 270 MHz for $^1$H and 109 MHz for $^{31}$P, or on a JEOL Lambda 500 spectrometer, operating at 202 MHz for $^{31}$P. The chemical shifts are reported in $\delta$ units (ppm) downfield from $Me_4Si$ for $^1$H and $^{13}$C, and from $H_3PO_4$ (85%, external reference) for $^{31}$P. All the carbon, hydrogen, and nitrogen analyses were carried out on a Perkin-Elmer PE 2400II elemental analyzer except for **4**, for which the analysis including sulfur was carried out at the Elemental Analysis Center at the Department of Chemistry, Faculty of Science, The University of Tokyo.

**Synthesis of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$($\mu$-SCH$_2$CH$_2$CHRS)](CF$_3$SO$_3$)$_4$ (4, R = OCH$_2$CH$_3$; 5, R = OC$_6$H$_5$; 6, R = CH=CHCH$_3$).** To a $CH_3CN$ (1 mL) solution of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$($\mu$-S$_2$)](CF$_3$SO$_3$)$_4$ (**1**) (111.3 mg, 0.075 mmol) was added allyl ethyl ether (0.1 mL, 88 mmol) via a syringe. After stirring of the mixture for 3 h, $Et_2O$ was added to form the yellow precipitate. The supernatant was removed, and the precipitate was washed with $Et_2O$. The residue was crystallized from $CH_3CN$/DME to give the analytically pure product [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${$\mu$-SCH$_2$CH$_2$CH(OCH$_2$CH$_3$)S}](CF$_3$SO$_3$)$_4$ (**4**) as yellow crystals. Yield: 70.8 mg (0.045 mmol, 60%). $^1$H NMR ($CD_3CN$, 270 MHz, room temperature (rt)): $\delta$ 1.30 (t, $J$ = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.95 (s, 12H, 4C*H*$_3$CN), 2.50 (s, 3H, C*H*$_3$CN), 2.51 (s, 3H, C*H*$_3$CN), 2.71 (m, 1H, SCH$_2$C*H*H′CHS(OCH$_2$CH$_3$)), 2.96 (m, 1H, SCH$_2$CH*H*′CH (OCH$_2$CH$_3$)S), 3.64 (m, 2H, C*H*$_2$CH$_3$), 3.86 (m, 36H + 1H, P(OC*H*$_3$)$_3$ and SC*H*H′CH$_2$CH(OCH$_2$CH$_3$)S), 3.90 (m, 1H, SCH*H*′CH$_2$CH(OCH$_2$CH$_3$)S), 6.01 (dd, $J$ = 3.4 and 1.8 Hz, 1H, SC*H*(OCH$_2$CH$_3$)). $^{31}$P{$^1$H} NMR ($CD_3CN$, 202 MHz, rt): $\delta$ 125.05 and 125.70 (d, $^3J_{PP}$ = 77 Hz), 125.29 and 125.51 (d, $^3J_{PP}$ = 63 Hz). Anal. Calcd for $C_{37}H_{64}F_{12}N_6O_{25}P_4Ru_2S_6$: C, 25.55; H, 3.71; N, 4.83; S, 11.06. Found: C, 25.26; H, 3.76; N, 4.81; S, 10.86.

Complexes **5** and **6** were also synthesized with the analogous procedure. Thus, only the analytical data are given below.

**5.** Yield: 105.1 mg (0.065 mmol, 73%) from **1** (132.9 mg, 0.090 mmol). $^1$H NMR ($CD_3CN$, 270 MHz, rt): $\delta$ 1.95 (s, 12H, 4C*H*$_3$CN), 2.50 (s, 3H, C*H*$_3$CN), 2.51 (s, 3H, C*H*$_3$CN), 2.90 (m, 1H, SCH$_2$C*H*H′CH(OC$_6$H$_5$)S), 3.30 (m, 1H, SCH$_2$CH*H*′CH(OC$_6$H$_5$)S), 3.64 (virtual t, $^3J_{PH}$ = 5.3 Hz, 9H, 1P(OC*H*$_3$)$_3$), 3.81 (virtual t, $^3J_{PH}$ = 5.3 Hz, 9H, 1P(OC*H*$_3$)$_3$), 3.85 (m, 18H, 2P(OC*H*$_3$)$_3$), 3.96 (m, 1H, SC*H*H′CH$_2$CH(OC$_6$H$_5$)S), 4.15 (m, 1H, SCH*H*′CH$_2$CH(OC$_6$H$_5$)S), 6.43 (dd, $J$ = 3.0 and 1.6 Hz, SC*H*(OC$_6$H$_5$)), 7.21−7.30 (m, 3H, C$_6$*H*$_5$), 7.52 (m, 2H, C$_6$*H*$_5$). $^{31}$P{$^1$H} NMR ($CD_3CN$, 202 MHz, rt): $\delta$ 124.76 and 124.93 (d, $^3J_{PP}$ = 77 Hz), 124.92 and 125.10 (d, $^3J_{PP}$ = 78 Hz). Anal. Calcd for $C_{33}H_{64}F_{12}N_6O_{25}P_4Ru_2S_6$: C, 23.43; H, 3.64; N, 4.97. Found: C, 23.29; H, 3.64; N, 4.90.

**6.** Yield: 40.3 mg (0.024 mmol, 48%) from **1** (80.2 mg, 0.050 mmol). $^1$H NMR ($CD_3CN$, 270 MHz, rt): $\delta$ 1.78 (dd, $J$ = 6.5 and 1.1 Hz, 3H, CH=CHC*H*$_3$), 1.95 (s, 12H, 4C*H*$_3$CN), 2.51 (s, 3H, CH$_3$CN), 2.52 (s, 3H, CH$_3$CN), 2.63 (m, 1H, SCH$_2$C*H*H′CH(CH=CHCH$_3$)S), 3.19 (m, 1H, SCH$_2$CH*H*′CH(CH=CHCH$_3$)S), 3.65 (m, SC*H*$_2$CH$_2$CH(CH=CHCH$_3$)S), 4.88 (dd, $J$ = 7.7 and 6.3 Hz, 1H, C*H*(CH=CHCH$_3$)S), 5.54 (ddq, $J$ = 15.1, 7.7 and 1.1 Hz, CH(C*H*=CHCH$_3$)S, 5.89 (dq, $J$ = 15.1 and 6.5 Hz, CH(CH=C*H*CH$_3$)). $^{31}$P{$^1$H} NMR ($CD_3CN$, 109 MHz, rt): $\delta$ 125.00 (br s, 2*P*(OCH$_3$)$_3$), 126.25 and 126.65 ($^3J_{PP}$ = 80 Hz). Anal. Calcd for $C_{34}H_{64}F_{12}N_6O_{24}P_4Ru_2S_6$: C, 24.20; H, 3.82; N, 4.98. Found: C, 24.22; H, 3.59; N, 4.86.

**Synthesis of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${$\mu$-SCH$_2$CH$_2$C(CH$_3$)$_2$S}](CF$_3$SO$_3$)$_4$ (7).** In an 80 mL Schlenk tube, complex **1** (269 mg, 0.167 mmol) in $CH_3CN$ (2 mL) was cooled in a dry ice−methanol bath. After the frozen solution was degassed with the vacuum line, 3-methyl-1-butene was introduced through a silicone rubber tube. The color of the solution gradually turned from dark blue to pale green. This reaction mixture was stirred for 3 h at room temperature, before the addition of $Et_2O$ to form a pale green gummy solid. The crude product was recrystallized from $CH_3CN$/DME to give yellow crystals of [Ru{P(OCH$_3$)$_3$}$_2$(CH$_3$CN)$_3$}$_2${$\mu$-SCH$_2$CH$_2$C(CH$_3$)$_2$S}](CF$_3$SO$_3$)$_4$ (**7**) (113 mg, 0.067 mmol, 40%). Anal. Calcd for $Ru_2S_6P_4N_6F_{12}O_{24}C_{33}H_{64}$: C, 23.66; H, 3.85; N, 5.02. Found: C, 23.58; H, 3.77; N, 4.91. $^1$H NMR (270 MHz, $CD_3CN$): $\delta$ 1.62 (s, 3H, SC(C*H*$_3$)(CH′$_3$)), 1.64 (s, 3H, SC(CH$_3$)(C*H*′$_3$)), 1.95 (s, 12H, 4C*H*$_3$CN), 2.51 (s, 3H, C*H*$_3$CN), 2.52 (s, 3H, C*H*$_3$CN), 2.62−2.67 (m, 2H, SCH$_2$C*H*$_2$C(CH$_3$)$_2$S), 3.62−3.65 (m, 2H, SC*H*$_2$CH$_2$C(CH$_3$)$_2$S), 3.81−3.90 (m, 36H, P(OC*H*$_3$)$_3$). $^{31}$P{$^1$H} NMR ($CD_3CN$, 109 MHz): $\delta$ 123.9 and 124.3 (d, $^2J_{PP}$ = 79 Hz, 2*P*(OCH$_3$)$_3$), 124.5 and 126.2 (d, $^2J_{PP}$ = 80 Hz, 2*P*(OCH$_3$)$_3$).

**Reaction of 1 with Methylenecyclobutane.** The reaction was carried out analogously to what is described above for **4** to **7**. Recrystallization of the crude product gave the Ru$^{II}$Ru$^{III}$ mixed-valence complex, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$($\mu$-S$_2$)](CF$_3$SO$_3$)$_3$ (**8**), as the major product together with a trace of yellow crystals. The single-crystal X-ray diffraction study of the minor product gave the structure of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${$\mu$-SCH(CH$_2$CH$_2$)CH(CH$_3$)S}](CF$_3$SO$_3$)$_4$ (**9**). The analytical data for **9** could not be obtained.

**Reaction of 1 with Methylenecyclohexane.** To a $CH_3CN$ (1.5 mL) solution of **1** (203 mg, 0.13 mmol) was added methylenecyclohexane (0.5 mL, 4.2 mmol), and the mixture was stirred for 3 h. Addition of $Et_2O$ (16 mL) resulted in the formation of pale green powder. After removal of the supernatant via a syringe, the residue was recrystallized from $CH_3CN$/DME to give yellow crystals of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${$\mu$-S(CH$_2$(C=CHCH$_2$CH$_2$CH$_2$CH$_2$)S)}(CF$_3$SO$_3$)$_3$ (**10**) (140 mg, 0.090 mmol, 69%). Single crystals suitable for X-ray diffraction study

(15) Kopinke, F.-D.; Zimmermann, G. *J. Prakt. Chem.* **1981**, *323*, 992.

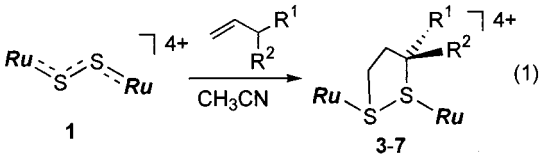
were obtained with the $CH_3CN/Et_2O$ vapor diffusion technique. $^1H$ NMR (270 MHz, $CD_3CN$, rt): $\delta$ 1.64 (m, 4H, C$H_2$), 2.06 (br s, 2H, C$H_2$), 2.36 (s, 3H, C$H_3$CN), 2.40 (s, 3H, C$H_3$CN), 3.60 (br s, 2H, C$H_2$), 3.67−3.79 (m, 36H + 4H, P(OC$H_3$)$_3$ and C$H_2$), 5.58 (br s, 1H, C═C*H*). $^{31}P\{^1H\}$ NMR (109 MHz, $CD_3CN$, rt): $\delta$ 130.4 (br s, 2*P*(OCH$_3$)$_3$), 135.7 (br s, 2*P*(OCH$_3$)$_3$). Anal. Calcd for $Ru_2S_5P_4C_{34}H_{65}N_6O_{21}F_9$: C, 26.32; H, 4.22; N, 5.42. Found: C, 25.38; H, 3.68; N, 5.32.

**Reaction of 10 with HCl.** To a $CD_3CN$ (0.5 mL) solution of **10** (15 mg) was added concentrated HCl (5 $\mu$L). An immediate color change of the solution was observed from pale blue to dark green. The $^1H$ NMR spectrum of the reaction product showed methyl and olefin proton signals at $\delta$ 1.57 and 5.37 and was practically identical to that of an authentic sample of 1-methyl-1-cyclohexene. Analogously, treatment of **10** with DCl resulted in the formation of 1-monodeuteriomethyl-1-cyclohexene, whose monodeuteriomethyl and olefin proton signals were observed at $\delta$ 1.55 ($J_{HD}$ = 2 Hz) and 5.37.

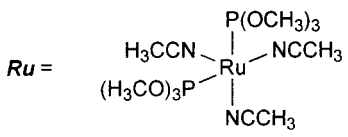
**X-ray Diffraction Studies.** The diffraction data of **5** were collected on a Rigaku AFC 7R four-circle diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). The unit cell parameters were obtained by the least-squares refinements of 25 reflections ($25° < 2\theta < 30°$). The diffraction data were corrected for Lorentz and polarization effects, and absorption corrections based on $\psi$ scans and a decay correction based on three standard reflections recorded every 150 reflections were applied. The intensity data were transformed to the SHELX format. The diffraction data for **6**, **7**, **9**, and **10** were collected on a Bruker CCD SMART 1000 diffractometer using Mo K$\alpha$ radiation. All the intensity data were processed by the SAINT-plus program package. All the structure solutions were performed with the SHELXTL software package. The details of the six crystallographic analyses are summarized in Table 1.

## Results and Discussion

**Synthesis of the Complexes.** Treatment of **1** with terminal alkenes, such as 1-pentene, allyl ethyl ether, allyl phenyl ether, and 1,4-hexadiene in $CH_3CN$ at room temperature resulted in an immediate color change of the solutions from dark blue to pale green, and the solutions were stirred for several hours. After standard workup of the reaction mixtures, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${$\mu$-SCH$_2$CH$_2$CHRS}](CF$_3$SO$_3$)$_4$ (**3**, R = $CH_2CH_3$, 40%; **4**, R = $OCH_2CH_3$, 60%; **5**, R = $OC_6H_5$, 73%; **6**, R = CH═$CHCH_3$, 48%) were obtained (eq 1).




**3**: $R^1$ = $CH_2CH_3$, $R^2$ =H, 44%
**4**: $R^1$ = $OCH_2CH_3$, $R^2$ =H, 60%
**5**: $R^1$ = $OC_6H_5$, $R^2$ =H, 73%
**6**: $R^1$ = CH=$CHCH_3$, $R^2$ =H, 48%
**7**: $R^1$ = $R^2$ = $CH_3$, 40%




In each case, the allylic carbon atom has two hydrogen atoms in the starting substrate. Complex **1** reacted also with 3-methyl-1-butene, having one hydrogen atom at the allylic carbon atom, to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${$\mu$-SCH$_2$CH$_2$C(CH$_3$)$_2$S}](CF$_3$SO$_3$)$_4$ (**7**) in 40% yield. After the reaction, the olefin proton disappeared in the $^1H$ NMR spectra, and therefore it seems that the analogous reaction occurs to 3-methyl-1-butene. Complexes **3**, **5**, **6**, and **7** have been fully characterized by X-ray crystallography to confirm the formulation of the saturated $C_3S_2$ five-membered ring bridging the two Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$ moieties. In each case, the allylic C−H bond must have been cleaved to form the first C−S bond. The liberated hydrogen atom seems to be transferred to the neighbor carbon atom, and the terminal olefinic carbon atom forms the second C−S bond to close the $C_3S_2$ ring. Several types of C−S bond formation on the sulfur ligand coordinated to a transition metal are known, where the sp$^2$- or sp-hybridized carbon atoms approach to the sulfur atom.[16−23] However, C−S bond formation via C−H bond splitting is very rare. It is reported that the $RhRu_2S_4$ cluster reacts with acetone to give $(C_5Me_5)_3RhRu_2S_3(SCH_2COCH_3)^+$.[24] It is also reported that the thermal reaction of $(C_5H_5)_2TiS_5$ gives

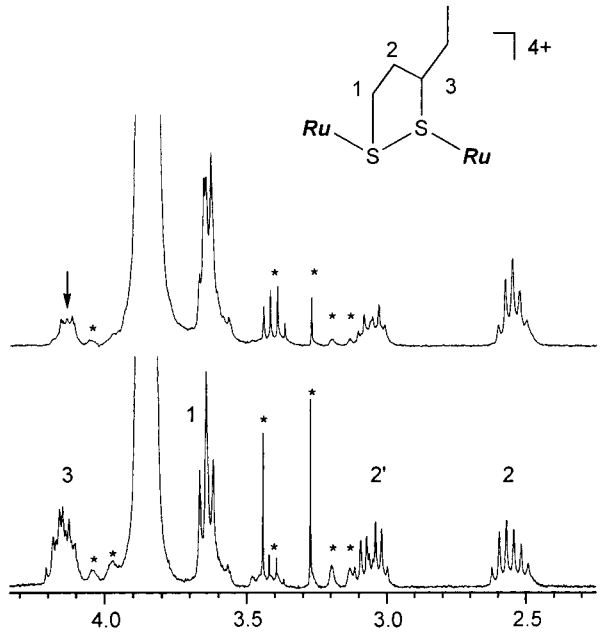
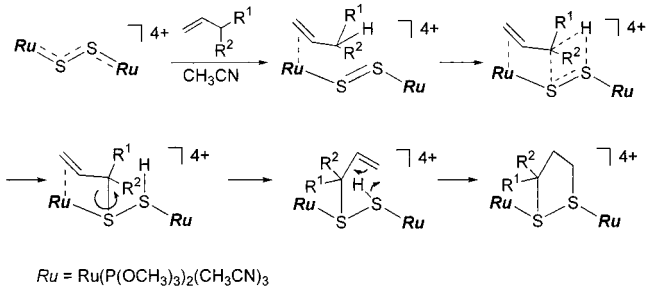



**Figure 1.** The $^1H$ NMR spectra of the products from the reactions of **1**-$d_{18}$ with 1-pentene-3,3-$d_2$ (top) and **1**-$d_{18}$ with 1-pentene (bottom). Asterisks: impurities. Arrow: $^{13}C$ satellite of P(OCH$_3$)$_3$ ligands.

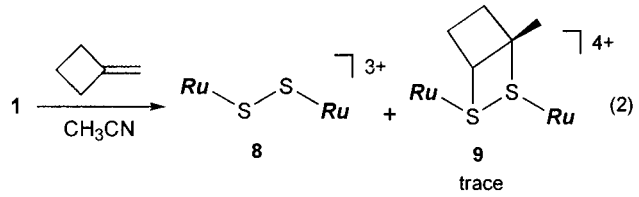
**Scheme 2**




(16) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.
(17) Goodman, J. T.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 5017.
(18) Coucouvanis, D.; Toupadakis, A.; Lane, J. D.; Koo, S. M.; Kim, C. G.; Hadjikyriacou, A. *J. Am. Chem. Soc.* **1991**, *113*, 5271.
(19) Pilato, R. S.; Eriksen, K. A.; Greaney, M. A.; Stiefel, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 9372.
(20) Inomata, S.; Hiyama, K.; Tobita, H.; Ogino, H. *Inorg. Chem.* **1994**, *33*, 5337.
(21) Kuwata, S.; Andou, M.; Hashizume, K.; Mizobe, Y.; Hidai, M. *Organometallics* **1998**, *17*, 3429.
(22) Shibahara, T.; Sakane, G.; Mochida, S. *J. Am. Chem. Soc.* **1993**, *115*, 10408.
(23) Kawaguchi, H.; Tatsumi, K. *J. Am. Chem. Soc.* **1995**, *117*, 3885.
(24) Venturelli, A.; Rauchfuss, T. B.; Verma, A. K. *Inorg. Chem.* **1997**, *36*, 1360.

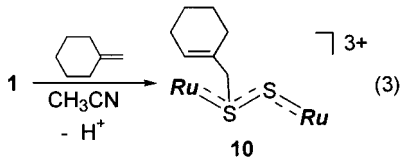
$(C_5H_5)Ti\{(S)C{=}C(S)CH_2CH_2CH(S_3)\}$, in which C−S bond formation, C−H bond rearrangement, and S−S bond cleavage take place.[25]

The reaction of **1** with geminally disubstituted olefins was also examined. The reaction of **1** with methylenecyclobutane gave a complex mixture, whose major product was dark blue crystalline $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}S_2)](CF_3SO_3)_3$ (**8**). As described in the previous report, **1** is gradually reduced to $Ru^{II}/Ru^{III}$ complex **8** in $CH_3CN$.[4] Therefore, **8** is regarded as the end product of unreacted **1**, and since methylenecyclobutane does not easily react with **1**, it is reasonable that the reaction gave a lot of **8**. However, a trace of yellow crystals was also obtained. The X-ray analysis of the yellow crystal revealed the structure of the complex carrying a $C_2S_2$ four-membered ring, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SCH(CH_2CH_2)CH(CH_3)S\}](CF_3SO_3)_4$ (**9**) (eq 2) (Figure 3).



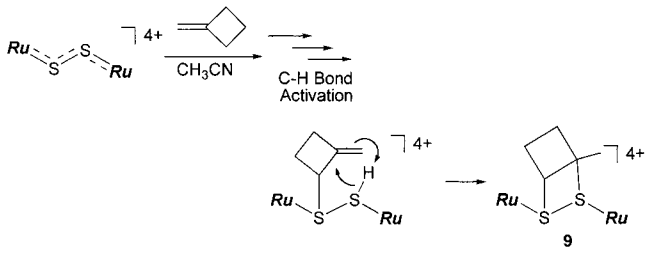

No spectroscopic and elemental analysis data was obtained for **9** because of the low yield. The formation mechanism of **9** seems to be different from that of the $C_3S_2$ five-membered ring cyclization in **3**−**7**. The possible route to **9** will be discussed later.

Unfortunately, the reaction of **1** with methylenecyclopentane did not give any noticeable product. Only the $Ru^{II}/Ru^{III}$ complex **8** was recovered. The reaction was followed by $^1H$ NMR spectroscopy; however, the observed peaks were too small to identify the product. The reaction of **1** with methylenecyclohexane is another type of reaction, giving $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}S(CH_2(C{=}CHCH_2CH_2CH_2CH_2)S)\}](CF_3SO_3)_3$ (**10**) in 69% yield (eq 3).




In the reaction, cyclization does not occur, and only one hydrogen atom is eliminated to form the C−S bond. Since the liberated proton seems to be lost as $CF_3SO_3H$, the charge of the complex cation is changed from +4 to +3, as in the previously reported ketonated complexes.[13] Formation of 1-methyl-1-cyclohexene was observed, when **10** was treated with excess HCl in an NMR tube. Formally, it is expected that **10** is obtained via the activation of the methyl C−H bond of 1-methyl-1-cyclohexene, accompanied by elimination of $H^+$. However, **10** could not be obtained in the reaction of **1** with 1-methyl-1-cyclohexene. The reaction mixture did not give any addition product, presumably because the substrate is not sterically suitable for the reaction. This fact is consistent with our observation that internal alkenes do not react with **1**. Although cyclohexene reacts with **2** in the presence of 5 equiv of $AgPF_6$, this may involve a somewhat different reaction path and would be a very rare exception.[11] Interestingly, the selenium analogue of **1**, $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2(\mu\text{-}Se_2)](CF_3SO_3)_4$ (**11**), can react with both methylenecyclopentane and internal alkenes.[26] This fact suggests that **11** has a more flexible reaction center for these substrates due to the larger steric capacity of the RuSeSeRu core. The product of the reaction of **11** with methylenecyclopentane is quite different from those of **1** with methylenecycloalkanes. The details will be reported in a separate paper.

**Scheme 3**




**Mechanistic Aspects.** In the present study, three types of alkene addition have been found to the bridging disulfide ligand in the $Ru_2S_2$ core. In the previous report, we suggested the mechanism in Scheme 2 for the $C_3S_2$ five-membered ring formation of the reaction with 1-pentene.[11]

The mechanism involves addition of an allylic C−H bond to the S−S bond to form the C−S and S−H bonds. This is an essential and common key step also in other types of reactions involving C−H bond cleavage on the disulfide bridge of the RuSSRu core. The subsequent anti-Markovnikov-type addition of the S−H to the C=C double bond gives the five-membered ring of the product. Figure 1 shows the $^1H$ NMR spectra of the $C_3S_2$ five-membered-ring region of the products for the reactions of **1**-$d_{18}$ ($CD_3CN$-substituted **1**) with 1-pentene-3,3-$d_2$ (top) and **1**-$d_{18}$ with 1-pentene (bottom), which are expected to give **3**-$d_{18}$-$d_2$ and **3**-$d_{18}$, respectively. The assignment of the signals is also shown. In the top spectrum, the intensity of 2′ is decreased to 0.46, whereas those of 1 and 2 are not changed significantly. The significant signal at the methyne position in the top spectrum is assigned to the $^{13}C$ satellites of the $P(OCH_3)_3$ ligands. The contribution of the methyne signal is negligibly small. Therefore, the cleaved allylic D atom is selectively introduced to one of the methylene positions to erase the 2′ signal. The observed intensity of 2′ in the top spectrum is due to the residual proton of 1-pentene-3,3-$d_2$ (residual proton, 8.5%). The observed intensity of 0.46 for 2′ is higher than expected and is explained by the primary kinetic isotope effect.[27] The $k_H/k_D$ value is estimated to be 9 on the basis of the intensity of 2′ and the residual proton in the substrate and is reasonably acceptable for the mechanism involving C−H (or C−D) bond cleavage. The hydrogen transfer step on the sulfur atom may also be the rate-determining step. The observed result is consistent with the mechanism shown in Scheme 2.

On the other hand, Markovnikov addition takes place in the formation of the $C_2S_2$ four-membered ring of **9**. Complex **9** is the sole example of the Markovnikov addition (Scheme 3). In contrast to the present RuSSRu core system, only Markovnikov addition is reported for the insertion of alkenes into the bridging hydrosulfide ligand in the dinuclear molybdenum complex.[28]

For the formation of a four- or five-membered ring, the C=C double bond must be located at an appropriate position after the C−S bond rotation, to receive the proton from the sulfur

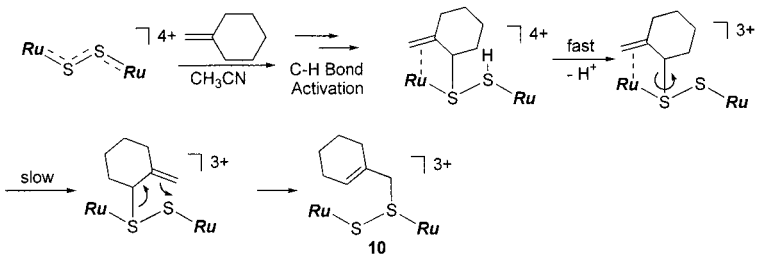
(25) Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc*. **1984**, *106*, 6455

(26) Hatemata, S.; Sugiyama, H.; Matsumoto, K. Unpublished results.

(27) Connors, K. A. *Chemical Kinetics. The study of Reaction Rates in Solution*; VCH Publishers: New York, 1990.

(28) Birnbaum, J.; Laurie, J. C. V.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 156.

**Scheme 4**



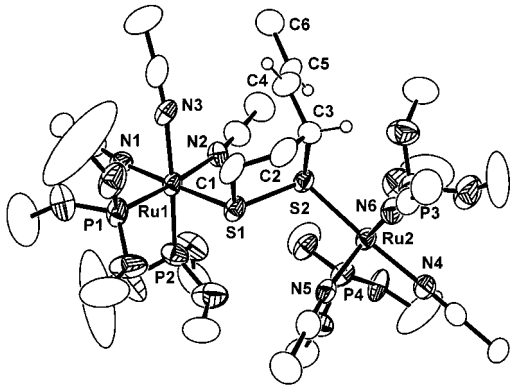




**Figure 2.** Structure of complex cation **6**. Thermal ellipsoids are drawn at the 50% probability level.

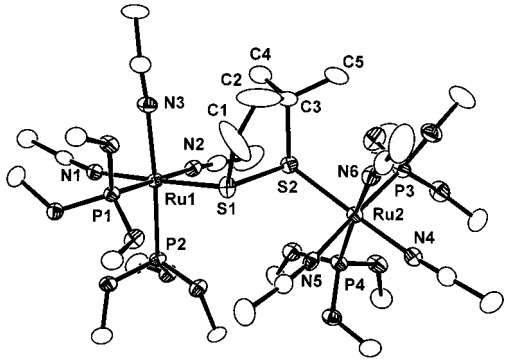



**Figure 3.** Structure of complex cation **7**. Thermal ellipsoids are drawn at the 50% probability level.

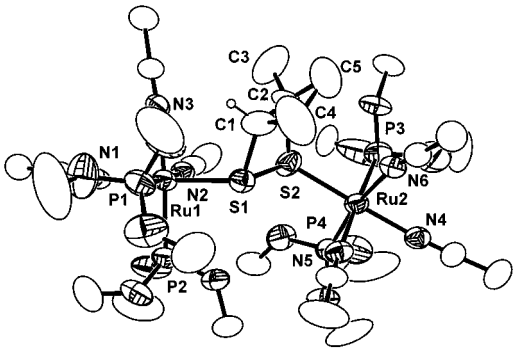



**Figure 4.** Structure of complex cation **9**. Thermal ellipsoids are drawn at the 30% probability level.

atom. However, for some bulky alkenes, the rotation is hindered, since the coordination sphere around the Ru atom is sterically crowded. This situation is observed in the reaction with methylenecyclohexane. The retarded rotation of the C−S bond may cause liberation of the hydrogen atom from the sulfur atom as proton. After the deprotonation, the steps shown in Scheme 4 take place and **10** is formed. In the previous report on the Diels−Alder type [4 + 2] cycloaddition of conjugated dienes to the $S_2$ ligand in the $Ru_2S_2$ cores of **1** and **2**,[14] double-bond character of the $S_2$ is suggested to explain the reactions.[29−31] Such S═S double bond nature must also be operating in the present cleavage of the allylic C−H bond. Since the formal oxidation state of the Ru atoms in **1** ($Ru^{III}$) is higher than the usual oxidation states of 0 or II in the Ru complexes that can activate C−H bonds, the Ru centers in **1** are ruled out as the C−H bond activation site. It should be noted that a phosphorus atom is another example of a main-group element that also cleaves C−H bonds.[32−35]

**X-ray Crystallographic Study.** The structures of **6**, **7**, and **9** are shown in Figures 2−4, respectively. The selected structural parameters of the complexes carrying the $C_3S_2$ and the $C_2S_2$ rings in **5**, **6**, **7**, and **9** are compared in Table 2 with those of the previously reported **3**. The S−S bond distances in the $C_3S_2$ ring range from 2.1102(15) to 2.164(5) Å and are longer than that found in the starting complex, **1** (1.933(11) Å).[4] The d$\pi$−p$\pi$ conjugate system of the RuSSRu core in **1** is lost in the complexes having two C−S bonds according to the Ru−S−S−Ru torsion angles (142.22(16)−157.15 (5)°), and both of the two sulfur atoms are $sp^3$ hybridized. The RuSSRu cores of **3**, **5**, **6**, **7**, and **9** are shown in Figure 5, where the *R*/*R* isomer configurations around the two sulfur atoms are drawn. Only the *R*/*R* and *S*/*S meso* isomers are in the unit cells of all the crystal structures. In the $^1$H NMR spectra, the *R*/*S* or *S*/*R rac* isomer was not found for the solutions of **3**, **5**, **6**, and **7**. In addition, the configurations around the methyne carbons of **3**, **5**, and **6** are the same. Therefore, the ring formation reaction proceeds diastereoselectively.

**Table 2.** Selected Structural Parameters of **3**, **5**, **6**, **7**, and **9**

| | **3** | **5** | **6** | **7** | **9** |
|---|---|---|---|---|---|
| Ru−P (av) | 2.253 | 2.26 | 2.25 | 2.256 | 2.25 |
| Ru1−S1 | 2.3381(11) | 2.348(4) | 2.350(3) | 2.3446(16) | 2.322(3) |
| Ru2−S2 | 2.3705(12) | 2.347(4) | 2.345(2) | 2.3875(16) | 2.326(3) |
| S1−S2 | 2.1102(15) | 2.164(5) | 2.142(4) | 2.130(2) | 2.159(4) |
| S1−C1 | 1.812(5) | 1.824(16) | 1.858(14) | 1.786(8) | 1.793(12) |
| S2−C3 | 1.886(5) | 1.890(16) | 1.822(13) | 1.922(6) | 2.128(12)[a] |
| C1−C2 | 1.493(7) | 1.50(2) | 1.455(18) | 1.396(11) | 1.547(19) |
| C2−C3 | 1.527(7) | 1.49(2) | 1.56(2) | 1.539(10) | |
| Ru1−S1−S2 | 114.19(6) | 111.20(18) | 112.41(13) | 116.20(8) | 113.31(13) |
| Ru2−S2−S1 | 107.77(6) | 112.10(18) | 111.22(12) | 107.17(8) | 115.19(13) |
| C1−C2−C3 | 115.0(4) | 110.0(12) | 108.7(11) | 120.9(6) | |
| Ru1−S1−S2−Ru2[b] | 157.15(5) | 142.22(16) | 143.38(12) | 147.34(7) | 143.25(13) |

[a] S2−C2 distance. [b] Reported without the sign.

(29) Brulet, C. R.; Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758.
(30) Elder, R. C.; Trkula, M. *Inorg. Chem.* **1977**, *16*, 1048.
(31) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3328
(32) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.
(33) Cowley, A. H.; Mehrotra, S. K. *J. Am. Chem. Soc.* **1983**, *105*, 2074.
(34) Cowley, A. H.; Kemp, R. A.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 3239.
(35) Nakazawa, H.; Buhro, W. E.; Bertrand, G.; Gladysz, J. A. *Inorg. Chem* **1984**, *23*, 3431.

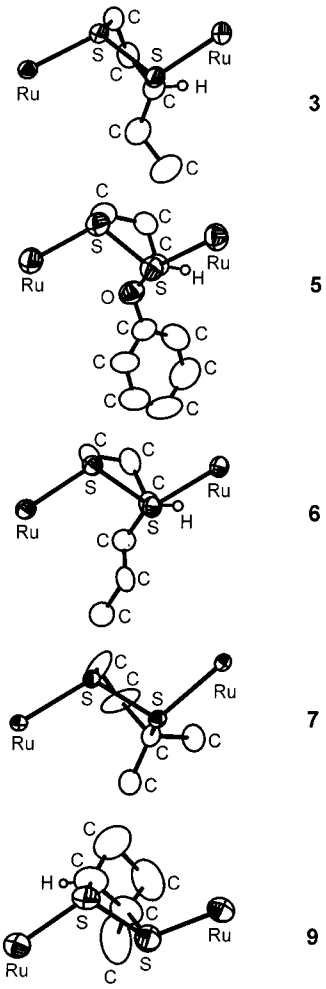



**Figure 5.** Structures around the RuSSRu cores in **3**, **5**, **6**, **7**, and **9**.

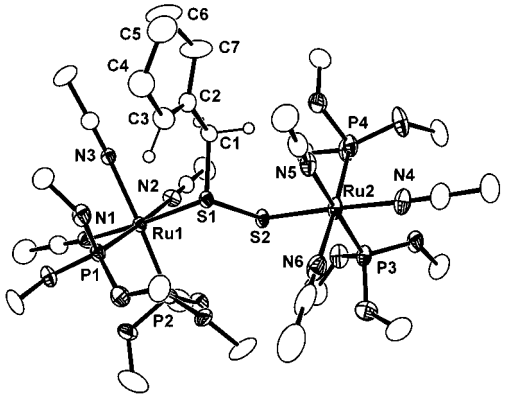



**Figure 6.** Structure of complex cation **10**. Thermal ellipsoids are drawn at the 50% probability level.

The structure and the structural parameters of **10** are shown in Figure 6 and Table 3, respectively. The S1−S2 bond distance (2.083(2) Å) of **10** is shorter than those found in the $C_3S_2$ and $C_2S_2$ rings, and it is close to those of the ketonated complexes (2.040(7)−2.069(4) Å).[13] The Ru1−S1−S2−Ru2 torsion angle of **10** (170.23(6)°) is also close to those of the ketonated complexes (167.91(9)−172.9(3)°) and **1** (168.0(3)°), rather than those in **3**, **5**, **6**, **7**, and **9**. Since one hydrogen atom is eliminated as a proton in the formation of the ketonated complexes and **10**, the remaining lone-pair electron density of the sulfur would be still in the $Ru_2S_2$ core of the complexes. The structural features of **10** suggest that the contribution of the d$\pi$−p$\pi$ conjugation is significant in **10**. The C2−C3 distance (1.311(10) Å) can be assigned as a double bond. The sum of the angles around C2 (360°) shows that the carbon atom is $sp^2$ hybridized.

**Table 3.** Selected Structural Parameters of **10**

| bond distances (Å) | | | | bond and torsion angles (deg) | |
|---|---|---|---|---|---|
| Ru1−P1 | 2.2474(16) | Ru1−P2 | 2.2532(19) | S2−S1−Ru1 | 104.23(8) |
| Ru2−P3 | 2.243(2) | Ru2−P4 | 2.2337(19) | S1−S2−Ru2 | 108.39(8) |
| Ru1−S1 | 2.3849(17) | Ru2−S2 | 2.3805(18) | C1−S1−S2 | 100.1(2) |
| S1−S2 | 2.083(2) | S1−C1 | 1.844(7) | C1−S1−Ru1 | 106.4(2) |
| C1−C2 | 1.501(9) | C2−C3 | 1.311(10) | C3−C2−C1 | 125.8(7) |
| C2−C7 | 1.502(10) | C3−C4 | 1.515(10) | C1−C2−C7 | 111.7(6) |
| C4−C5 | 1.508(12) | C5−C6 | 1.496(13) | C3−C2−C7 | 122.5(7) |
| C6−C7 | 1.523(12) | | | Ru1−S1−S2−Ru2 | 170.23(6) |
| | | | | C1−C2−C3−C4 | −178.1(8) |
| | | | | C7−C2−C3−C4 | 0.6(13) |

## Conclusion

In the present report, several types of reactions of **1** with various alkenes are shown. In all of the reactions, activation of the allylic C−H bond is the initial and essential key step. In the subsequent steps, insertion of the C═C double bond into the S−H bond takes place in two possible orientations depending on the structure and size of the substrate, to give either the Markovnikov or anti-Markovnikov addition product having a four- or five-membered ring, whereas elimination of the S−H proton occurs when the C═C double bond cannot receive the hydrogen atom. These several reaction steps after the allylic C−H bond cleavage would have given such a variety to the final products. In the above reaction mechanisms the importance of the relative stereo orientations of the S−H and C═C bonds is emphasized, which also implies that both Markovnikov and anti-Markovnikov addition reactions may be considered as metathesis processes.

The present reactions involve a very rare allylic C−H bond cleavage on a disulfide ligand. This is really rare, not only because it occurs on a disulfide ligand but also because the reaction proceeds at room temperature without any base, and the authors do not know any precedent of an allylic C−H bond activation under such mild conditions on any metal or other reaction site. The present reactions also suggest that a double bond of other main-group elements linked to a transition metal forming a $\pi$-conjugate system like the RuSSRu core may have a similar reactivity.

**Acknowledgment.** Ms. Toshiko Seki and Ms. Kimiyo Saeki of the Elemental Analysis Center at the Department of Chemistry, Faculty of Science, The University of Tokyo, are acknowledged for the analysis of **4**.

**Supporting Information Available:** X-ray crystallographic files in CIF format, for the structure determinations of **5**, **6**, **7**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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