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Dehydration Reaction of Hydroxyl Substituted Alkenes and Alkynes on the Ru_2S_2 Complex

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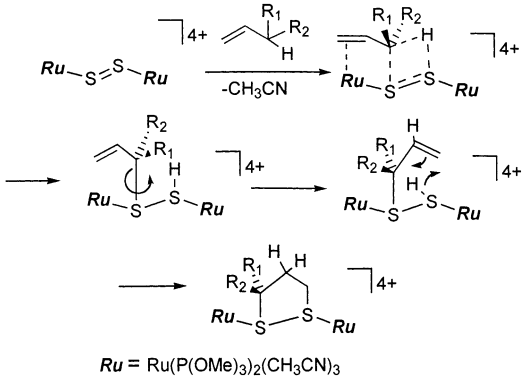
Abstract: A variety of inter- and intramolecular dehydration was found in the reactions of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_4$ (**1**) with hydroxyl substituted alkenes and alkynes. Treatment of **1** with allyl alcohol gave a C_3S_2 five-membered ring complex, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CH$_2$CH(OCH$_2$CH=CH$_2$)S}](CF$_3$SO$_3$)$_4$ (**2**), via C−S bond formation after C−H bond activation and intermolecular dehydration. On the other hand, intramolecular dehydration was observed in the reaction of **1** with 3-buten-1-ol giving a C_4S_2 six-membered ring complex, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$ {μ-SCH$_2$CH=CHCH$_2$S}](CF$_3$SO$_3$)$_4$ (**3**). Complex **1** reacts with 2-propyn-1-ol or 2-butyn-1-ol to give homocoupling products, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCR=CHCH(OCH$_2$C≡CR)S}](CF$_3$SO$_3$)$_4$ (**4**: R = H, **5**: R = CH$_3$), via intermolecular dehydration. In the reaction with 2-propyn-1-ol, the intermediate complex having a hydroxyl group, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OH)S}](CF$_3$SO$_3$)$_4$ (**6**), was isolated, which further reacted with 2-propyn-1-ol and 2-butyn-1-ol to give **4** and a cross-coupling product, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OCH$_2$C≡CCH$_3$)S}](CF$_3$SO$_3$)$_4$ (**7**), respectively. The reaction of **1** with diols, (HO)CHRC≡CCHR(OH), gave furyl complexes, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SSC=CROCR=CH}](CF$_3$SO$_3$)$_3$ (**8**: R = H, **9**: R = CH$_3$) via intramolecular elimination of a H_2O molecule and a H^+. Even though (HO)(H$_3$C)$_2$CC≡CC(CH$_3$)$_2$(OH) does not have any propargylic C−H bond, it also reacts with **1** to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$C(=CH$_2$)C(=C=C(CH$_3$)$_2$)}S](CF$_3$SO$_3$)$_4$ (**10**). In addition, the reaction of **1** with (CH$_3$O)(H$_3$C)$_2$CC≡CC(CH$_3$)$_2$(OCH$_3$) gives [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_2$}{μ-S=C(C(CH$_3$)$_2$OCH$_3$)C=CC(CH$_3$)CH$_2$S}{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}](CF$_3$SO$_3$)$_4$ (**11**), in which one molecule of CH$_3$OH is eliminated, and the S−S bond is cleaved.

Introduction

In our recent studies, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_4$ (**1**) was found to react with unsaturated organic molecules such as ketones,[1] alkenes,[2] and alkynes[3] to give the corresponding addition products, in which C−S bonds are formed on the bridging disulfide ligand via α-ketonyl, allylic, or propargylic C−H bond cleavage. In the reactions, the bridging disulfide ligand acts as the reaction center, to which the alkyl group and a hydrogen atom are bound via C−H bond activation (Scheme 1). The disulfide ligand in **1** acts like transition metals, and the C−S and H−S bond formations correspond to oxidative addition. Only a few types of C−S bond formation are known on sulfur ligands, and little attention has been paid to the transformation of the organic moiety bound to the sulfur ligand into another organic compound. The protonation of [{(C$_5$H$_5$)Mo}$_2$(μ-SCH$_2$){μ-SC(C$_6$H$_5$)=CHS}] to give [{(C$_5$H$_5$)Mo}$_2$(μ-SCH$_2$){μ-SC(C$_6$H$_5$)=CH$_2$}(μ-S)]$^+$ is one of these rare examples.[4] On the other hand, the C−S bond cleavage reactions of thiolate ligand have been widely studied,[5] with the aim to develop the efficient HDS (hydro desulfurization) reaction[6] for petroleum chemistry. For example, the C−S bond in the SC-

Scheme 1



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$(CH_3)_3$ ligand is known to be cleaved on the transition metal.[7] In the reaction, isobutane and isobutene are liberated as the organic products via the homolytic and heterolytic C−S bond cleavage, respectively. In the present study, it was attempted to transform the organic group on the disulfide bridging ligand of **1** for organic molecules carrying appropriate functional groups. There is no precedent of such transformation and liberation of organic substances on a disulfide ligand. In this report, reactions of **1** with hydroxyl substituted alkenes and alkynes are described. Transformation of the organo-disulfide ligand was observed after elimination of hydroxyl groups. Also, unusual dehydration and methanol elimination were found in the reactions of **1** with 2,5-dimethyl-3-hexyn-2,5-diol and 2,5-dimethoxy-2,5-dimethyl-3-hexyne. These reactions seem to be only a few examples of the novel inorganic sulfide reactivities and suggest profound chemistry of a disulfide ligand yet to be discovered.

Experimental Section

All of the reactions were carried out under an Ar or N_2 atmosphere by using the standard Schlenk line technique. The dry and oxygen-free solvents were purchased from Kanto Chemical Co. The acetonitrile-d_3 was dried over CaH_2 and distilled by the trap-to-trap distillation prior to use. The reagents were purchased and used without further purification. Allyl-3,3-d_2-alcohol was prepared according to the literature procedure.[8] Complex **1** was prepared according to the literature.[9] The NMR spectra were recorded on a JEOL Lambda 270 spectrometer operating at 270 MHz (^{1}H), and at 109 MHz (^{31}P). The chemical shift is reported in the δ (ppm) unit downfield from the TMS for ^{1}H, and H_3PO_4 for ^{31}P. The carbon, hydrogen, and nitrogen analysis was performed on a Perkin-Elmer PE2000 microanalyzer at the Material Characterization Central Laboratory in Waseda University.

Synthesis of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CH$_2$CH(OCH$_2$CH=CH$_2$)S}] (CF$_3$SO$_3$)$_4$ (2). To a CH_3CN (0.75 mL) solution of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-S$_2$)] (CF$_3$SO$_3$)$_4$ (**1**) (80 mg, 0.05 mmol) was added allyl alcohol (0.4 mL), and the solution was stirred at ambient temperature for 12 h. The solution was evaporated, and the residue was washed with Et_2O (6 mL) and dried in vacuo. The residue was dissolved in CH_3CN, to which DME (dimethoxyethane) was layered to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CH$_2$CH(OCH$_2$CH=CH$_2$)S}](CF$_3$SO$_3$)$_4$ (**2**) as yellow crystals in 98% yield.

Anal. Calcd for $C_{34}H_{64}F_{12}N_6O_{25}P_4Ru_2S_6$: C, 23.97; H, 3.79; N, 4.93. Found: C, 23.28; H, 3.74; N, 4.73. ^{1}H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4CH_3CN), 2.50 (s, 3H, CH_3CN), 2.51 (s, 3H, CH_3CN), 2.71 (m, 1H, SCH$_2$CHH'CH(OCH$_2$CH=CH$_2$)S), 3.03 (m, 1H, SCH$_2$CHH'CH(OCH$_2$CH=CH$_2$)S), 3.71−4.02 (m, 2H, SCH_2-CH$_2$CH(OCH$_2$CH=CH$_2$)S), 3.80−3.90 (m, 36H, P(OCH_3)$_3$), 4.10 (dd, J = 5 and 13 Hz, 1H, SCH$_2$CH$_2$CH(OCHH$'$CH=CH$_2$)S), 4.24 (dd, J = 5 and 13 Hz, 1H, SCH$_2$CH$_2$CH(OCHH$'$CH=CH$_2$)S), 5.33−5.45 (m, 2H, SCH$_2$CH$_2$CH(OCH$_2$CH=CH_2)S), 5.95−6.09 (m, 1H, SCH$_2$-CH$_2$CH(OCH$_2$CH=CH$_2$)S), 6.00 (m, 1H, SCH$_2$CH$_2$CH(OCH$_2$CH=CH$_2$)S). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz, room temperature): δ 125.1 and 125.7 (d, $^2J_{PP}$ = 78 Hz), 125.3 and 125.5 (d, $^2J_{PP}$ = 74 Hz).

Analogously, use of allyl-3,3-d_2-alcohol (0.1 mL) gave [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CHDCHD(OCD$_2$CH=CH$_2$)S}](CF$_3$SO$_3$)$_4$ (**2**-d_4) in 83% yield from **1** (290 mg, 0.18 mmol) in CH_3CN (0.5 mL).

Unless specifically described, complexes **3**−**12** were also synthesized with a similar procedure. Thus, only the elemental analysis and NMR data are shown below.

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH$_2$CH=CHCH$_2$S)](CF$_3$SO$_3$)$_4$ (3). Yield: 31%. Anal. Calcd for $C_{32}H_{60}F_{12}N_6O_{24}P_4Ru_2S_6$: C, 23.16; H, 3.64; N, 5.06. Found: C, 23.04; H, 3.51; N, 4.88. ^{1}H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4CH_3CN), 2.49 (s, 6H, 2CH_3CN), 3.74 (m, 2H, eq SCH_2), 3.87 (vt, $^3J_{PH}$ = 6 Hz, P(OCH_3)$_3$), 4.07 (m, 2H, ax SCH_2), 6.28 (d, J = 2 Hz, 2H, SCH$_2$CH). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz, room temperature): δ 125.1 (s).

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SC(CH$_3$)=CHCH(OCH$_2$C≡CCH$_3$)S}](CF$_3$SO$_3$)$_4$ (4). Yield: 57%. Anal. Calcd for $C_{38}H_{67}F_{12}N_7O_{25}P_4Ru_2S_6$ (as **4**·CH_3CN): C, 25.81; H, 3.82; N, 5.54. Found: C, 25.60; H, 3.70; N, 5.39. ^{1}H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4CH_3CN), 2.16 (s, 3H, CH_3C≡C), 2.505 (s, 3H, CH_3CN), 2.510 (s, 3H, CH_3CN), 3.86−3.90 (m, 36H, P(OCH_3)$_3$), 4.24 (dq, J = 2 and 16 Hz, 1H, SCHOCHH$'$C≡CCH$_3$), 4.34 (dq, J = 2 and 16 Hz, 1H, SCHOCHH'C≡CCH$_3$), 6.27 (d, J = 3 Hz, 1H, SC(CH$_3$)=CHCHS), 6.60 (dd, J = 3 and 1 Hz, 1H, SCHOCH$_2$C≡CCH$_3$). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz, room temperature): δ 125.1 and 125.5 (s, 2P).

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OCH$_2$C≡CH)S}](CF$_3$SO$_3$)$_4$ (5). Yield: 44% (from **1** (80 mg, 0.05 mmol) in CH_3CN (0.75 mL) and HC≡CCH$_2$OH (0.6 mL), stirred at 50 °C for 6 h). Anal. Calcd for $C_{34}H_{60}F_{12}N_6O_{25}P_4Ru_2S_6$: C, 24.03; H, 3.56; N, 4.95. Found: C, 23.91; H, 3.65; N, 4.30. ^{1}H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4CH_3CN), 2.49 (s, 6H, 2CH_3CN), 3.07 (t, J = 3 Hz, 1H, SCHOCH$_2$C≡CH), 3.81−3.91 (m, 36H, P(OCH_3)$_3$), 4.38 (d, J = 3 Hz, 2H, SCHOCH_2C≡CH), 6.45 (d, J = 3 Hz, 1H, SCHOCH$_2$C≡CH), 6.72 (d, J = 6 Hz, SCH=CHCHS), 6.84 (dd, J = 3 and 6 Hz, 1H, SCH=CHCHS). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz, room temperature): δ 124.9 (s), 125.1 and 125.5 (d, $^2J_{PP}$ = 76 Hz)

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OH)S}](CF$_3$SO$_3$)$_4$ (6). Yield: 94% (from **1** (80 mg, 0.05 mmol) in CH_3CN (1 mL) and HC≡CCH$_2$OH (0.4 mL), stirred at room temperature for 10 min). Anal. Calcd for $C_{31}H_{58}F_{12}N_6O_{25}P_4Ru_2S_6$: C, 22.41; H, 3.52; N, 5.06. Found: C, 22.38; H, 3.40; N, 4.81. ^{1}H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4CH_3CN), 2.49 (s, 6H, 2CH_3CN), 3.82−3.91 (m, 36H, P(OCH_3)$_3$), 6.61 (d, J = 6 Hz, 1H, SCH=CHCHS), 6.78 (dd, J = 3 and 6 Hz, 1H, SCH=CHCHS), 6.83 (m, 1H, SCH=CHCH(OH)S). ^{31}P{^{1}H} NMR (CD_3CN, 109 MHz, room temperature): δ 125.4 and 125.8 (d, $^2J_{PP}$ = 77 Hz), 125.7 and 126.2 (d, $^2J_{PP}$ = 76 Hz).

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OCH$_2$C≡CCH$_3$)S}](CF$_3$SO$_3$)$_4$ (7). To a CH_3CN (0.4 mL) solution of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OH)S}](CF$_3$SO$_3$)$_4$ (**6**) (160 mg, 0.1 mmol) was added 2-butyn-1-ol (0.6 mL), and the solution was stirred at 50 °C for 6 h. The solution was washed with Et_2O (6 mL) and dried in vacuo. The residue was recrystallized from CH_3CN/DME to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OCH$_2$C≡CCH$_3$)S}](CF$_3$SO$_3$)$_4$ (**7**) as yellow crystals in 20% yield. Yield: 20%. Anal. Calcd for $C_{35}H_{62}F_{12}N_6O_{25}P_4Ru_2S_6$: C, 24.54; H, 3.65; N, 4.91. Found: C, 24.29; H, 3.24; N, 4.86. ^{1}H NMR (CD_3CN, 270 MHz, room temperature): δ 1.91 (t, J = 3 Hz, 3H, SCHOCH$_2$C≡CCH_3), 1.97 (s, 12H, 4CH_3CN), 2.50 (s, 6H, 2CH_3CN), 3.85−3.91 (m, 36H, P(OCH_3)$_3$), 4.31 (m, 2H, SCHOCH_2C≡CCH$_3$), 6.44 (d, J = 3 Hz, 1H, SCHOCH$_2$C≡

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CCH_3), 6.73 (d, J = 6 Hz, SC*H*=CHCHS), 6.85 (dd, J = 3 and 6 Hz, 1H, SCH=C*H*CHS). $^{31}P\{^1H\}$ NMR (CD_3CN, 109 MHz, room temperature): δ 125.1 (s), 125.2 and 125.6 (d, $^2J_{PP}$ = 77 Hz)

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SSC=CHOCH=CH)](CF$_3$SO$_3$)$_3$ (8). Yield: 63%. Anal. Calcd for $C_{31}H_{57}F_9N_6O_{22}P_4Ru_2S_5$: C, 25.04; H, 3.74; N, 5.47. Found: C, 25.04; H, 3.83; N, 4.76. ^1H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.32 (s, 3H, C*H*$_3$CN), 2.39 (s, 3H, C*H*$_3$CN), 3.69 (vt, J = 5H, 18H, 2P(OC*H*$_3$)$_3$), 3.79 (br s, 18H, 2P(OC*H*$_3$)$_3$), 6.79 (s, 1H, SC=CHOCH=C*H*), 7.57 (t, 1H, SC=CHOC*H*=CH), 7.59 (s, 1H, SC=C*H*OCH=CH). $^{31}P\{^1H\}$ NMR (CD_3CN, 109 MHz, room temperature): δ 129.7, 130.2, 136.0, and 136.1. (According to the structure of **5**, two sets of AB quartet pattern are expected. However, only two sets of two central strong signals were observed, and the two weak side signals were not observed. Therefore, only the raw data are given here.)

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SSC=C(CH$_3$)OC(CH$_3$)=CH}](CF$_3$SO$_3$)$_3$ (9). Yield: 34%. Anal. Calcd for $C_{33}H_{61}F_9N_6O_{22}P_4Ru_2S_5$: C, 25.55; H, 3.96; N, 5.42. Found: C, 25.40; H, 3.63; N, 5.23. ^1H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4C*H*$_3$CN), 2.14 (s, 3H, OC(C*H*$_3$)), 2.28 (s, 3H, OC(C*H*$_3$)), 2.32 (s, 3H, CH3CN), 2.38 (s, 3H, C*H*$_3$CN), 3.68 (vt, $^3J_{PH}$ = 5 Hz, 18H, 2P(OC*H*$_3$)$_3$), 3.71 (vt, $^3J_{PH}$ = 5 Hz, P(OC*H*$_3$)$_3$), 3.83 (vt, $^3J_{PH}$ = 5 Hz, P(OC*H*$_3$)$_3$), 6.34 (br s, 1H, SCC*H*=C(CH$_3$)O). $^{31}P\{^1H\}$ NMR (CD_3CN, 109 MHz, room temperature): δ 130.3 (s, 2P), 135.6 and 136.2 (d, $^2J_{PP}$ = 90 Hz, 2P).

[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$C(=CH$_2$)C(=C=C(CH$_3$)$_2$)S}](CF$_3$SO$_3$)$_4$ (10). Yield: 19%. 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, 24.60; H, 3.44; N, 4.48. ^1H NMR (CD_3CN, 270 MHz, room temperature): δ 1.95 (s, 12H, 4C*H*$_3$CN), 1.97 (s, 3H, C(C*H*$_3$)(CH$'_3$)), 2.10 (s, 3H, C(CH$_3$)(C*H*$'_3$)), 2.47 (s, 6H, 2C*H*$_3$CN), 3.73−3.89 (m, 36H, P(OC*H*$_3$)$_3$), 4.21 (d, J = 17 Hz, 1H, SC*H*H$'$), 4.77 (dq, J = 17 and 2 Hz, 1H, SCH*H*$'$), 5.45 (d, J = 2 Hz, 1H, SCH$_2$C(C*H*H$'$)), 5.51 (d, J = 1 Hz, SCH$_2$C(CH*H*$'$)). $^{31}P\{^1H\}$ NMR (CD_3CN, 109 MHz, room temperature): δ 124.5, 124.8, and 124.9. (Only three signals were observed. Two of them are central strong signals of the AB quartet pattern. Therefore, the raw data are given here.)

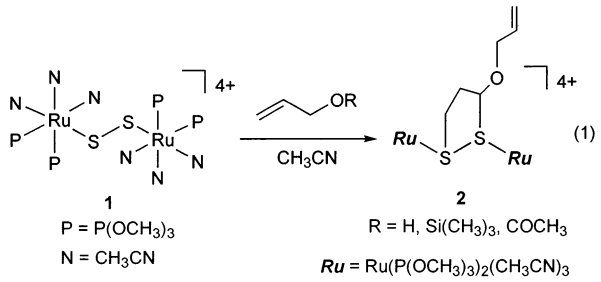
[{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_2$}{μ-S=C(C(CH$_3$)$_2$OCH$_3$)C=C(CH$_3$)CH$_2$S}{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}](CF$_3$SO$_3$)$_4$ (11). Yield: 41%. Anal. Calcd for $C_{35}H_{65}F_{12}N_5O_{25}P_4Ru_2S_6$: C, 24.69; H, 3.85; N, 4.11. Found: C, 24.35; H, 3.61; N, 4.17. ^1H NMR (CD_3CN, 270 MHz, room temperature): δ 1.53 (s, 3H, CH$_3$OC(C*H*$_3$)(CH$'_3$)C=S), 1.63 (s, 3H, CH$_3$OC(CH$_3$)(C*H*$'_3$)C=S), 1.89 (s, 3H,CC=C(C*H*$_3$)CH$_2$S), 1.95 (s, 12H, 4C*H*$_3$CN), 2.58 (s, 3H, C*H*$_3$OC(CH$_3$)$_2$C=S), 3.72−3.96 (m, 36H, P(OC*H*$_3$)$_3$), 4.15 (2H, CC=C(CH$_3$)C*H*$_2$S, overlapped with P(OCH$_3$)$_3$). $^{31}P\{^1H\}$ NMR (CD_3CN, 109 MHz, room temperature): δ 127.4 and 127.6 (d, $^2J_{PP}$ = 33 Hz), 129.2 and 129.6 (d, $^2J_{PP}$ = 78 Hz).

X-ray Diffraction Study. The diffraction data of **2**−**11** were collected on a Bruker CCD SMART 1000 area detector diffractometer with graphite-monochromated Mo Kα irradiation (λ = 0.70695 Å) of a shield tube. The intensities of the reflections were integrated by a SAINT program. The absorption correction was applied for the collected data by a SADABS program. The structure solutions were performed on a SHELXTL program package. Details of the crystallographic data are deposited as Supporting Information.

Result and Discussion

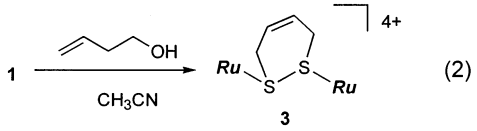
Treatment of [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-S$_2$)](CF$_3$SO$_3$)$_4$ (**1**) with an excess amount of allyl alcohol gave [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CH$_2$CH(OCH$_2$CH=CH$_2$)S}](CF$_3$SO$_3$)$_4$ (**2**) in 92% yield as yellow crystals (eq 1).

Analogously, **1** reacts with allyl alcohol-3,3-d_2 to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CHDCD(OCD$_2$CH=CH$_2$)S}](CF$_3$SO$_3$)$_4$ (**2**-d_4) in 83% yield. The ^1H NMR spectra of **2** and **2**-d_4 were compared to assign the signals of the allyloxy



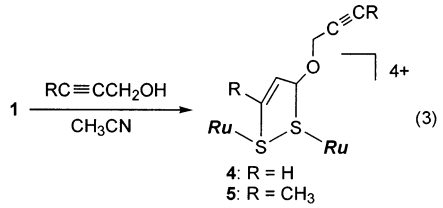
substituted C_3S_2 five-membered ring. If the reaction is analogous to the previous reactions with non-hydroxylated alkenes,[2] dithiacyclopentane complex [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CH$_2$CH(OH)S}](CF$_3$SO$_3$)$_4$ is expected (Scheme 1); however, an intermolecular coupling reaction occurred, giving **2** as the final product. The coupling reaction was also observed in the reaction of **1** with allyloxytrimethylsilane or allyl acetate, and the same product **2** was obtained.

The hydroxyl group on the carbon atom connected to the bridging sulfide seems to be activated by the electron-deficient RuSSRu core, and after one molecule of hydroxyalkene reacts with **1**, condensation with the second molecule takes place by losing a H_2O molecule. The RuSSRu core seems to act as the Lewis acid. However, the influence of the RuSSRu core is decreased, when the hydroxyl group is located far from the sulfide ligand, and condensation of two alcohol molecules becomes unfavorable, when 3-buten-1-ol is used as the substrate. In this reaction, intramolecular elimination of a water molecule occurred to give the C_4S_2 six-membered ring complex, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH$_2$CH=CHCH$_2$S}](CF$_3$SO$_3$)$_4$ (**3**), in 31% yield (eq 2). A complex of this type can also be obtained from the reaction of **1** with conjugated dienes.[10]



These reactions show that the difference of only one methylene group between the terminal C=C double bond and the hydroxyl group in the substrate leads to quite different products.

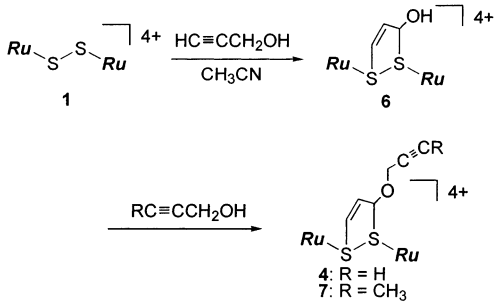
The reaction of **1** with 2-propyn-1-ol or 2-butyn-1-ol also gave the coupling products [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCR=CHCH(OCH$_2$C≡CR)S}](CF$_3$SO$_3$)$_4$ (**4**: R = H, 44%; **5**: R = CH$_3$, 57%) (eq 3).



At the early stage of the reaction with 2-propyn-1-ol, the one-molecular addition product, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2${μ-SCH=CHCH(OH)S}](CF$_3$SO$_3$)$_4$ (**6**), was confirmed by ^1H NMR spectroscopy. The isolated compound **6** was confirmed to react with 2-propyn-1-ol to give **4**, whereas a cross-coupling

(10) Sugiyama, H.; Lin, Y.-S.; Matsumoto, K. *Angew. Chem.* **2000**, *112*, 4224; *Angew. Chem., Int. Ed.* **2000**, *39*, 4058.

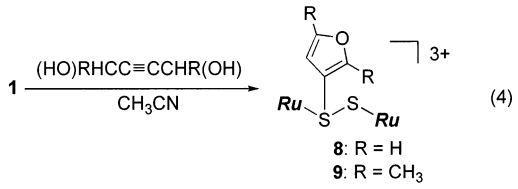
Scheme 2



product, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH═CHCH(OCH$_2$C≡CCH$_3$)S}](CF$_3$SO$_3$)$_4$ (**7**), was obtained in the reaction of **6** with 2-butyn-1-ol (Scheme 2). This shows that the coupling reactions take place after formation of the five-membered ring.

In the previous study on the reaction of **1** with unsymmetric alkyne, 2-pentyne having C−H bonds at both propargylic positions of the C≡C triple bond, the two expected products were obtained,[3] corresponding to the C−H bond activation at the two possible C−H sites. Therefore, in the present reaction with 2-butyn-1-ol, [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SC(CH$_2$OH)═CHCH$_2$S}](CF$_3$SO$_3$)$_4$ is also expected as a result of the activation. Actually, small unknown peaks were sometimes observed in the ^{1}H NMR spectrum of the crude product of **5**. However, only **5** is purely isolated and fully characterized. At least it seems that **5** is formed as the major product of the present reaction.

The reaction of dihydroxy substituted internal alkynes was also examined: treatment of **1** with (HO)RHCC≡CCHR(OH) resulted in the formation of the furyl complexes [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SSC═CROCR═CH}](CF$_3$SO$_3$)$_3$ (**8**: R = H, 63%; **9**: R = CH$_3$, 34%) via intramolecular H$_2$O elimination with the concomitant cyclization (eq 4).

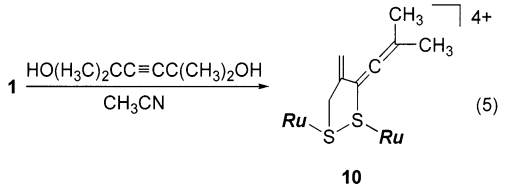


(4)

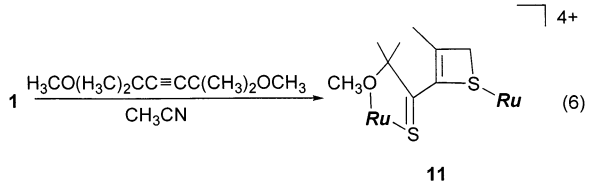
In the reaction, one hydrogen atom in addition to a water molecule is liberated as a proton. As a result, the charge of the complex cation is reduced from +4 to +3, similar to the ketonated complexes.[1]

All of the reactions described above can be understood on the basis of the allylic or propargylic C−H bond activation, similar to our previous studies on the simple alkene[2] and alkyne[3] reactions. Surprisingly, 2,5-dimethyl-3-hexyn-2,5-diol (HO(H$_3$C)$_2$CC≡CC(CH$_3$)$_2$OH), having no propargylic C−H bond, also reacts with **1** to give [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}$_2$(μ-SCH$_2$C(═CH$_2$)C(═C═C(CH$_3$)$_2$)}S](CF$_3$SO$_3$)$_4$ (**10**) in 19% yield via elimination of two H$_2$O molecules (eq 5). Close observation of the structure of **10** reveals that the topological geometry of the carbon backbone of the substrate is retained in the reaction. Seemingly, two hydrogen atoms are eliminated from the two methyl groups on the same carbon atom.

Because the reaction of **1** with another substrate having no propargylic C−H bond may give helpful information to understand the reaction of eq **5**, the reaction with 2,5-dimethoxy-2,5-dimethyl-3-hexyne was also examined, and [{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_2$}{μ-S═C(C(CH$_3$)$_2$OCH$_3$)C═C(CH$_3$)CH$_2$S}-{Ru(P(OCH$_3$)$_3$)$_2$(CH$_3$CN)$_3$}](CF$_3$SO$_3$)$_4$ (**11**) was obtained in 41% yield via elimination of a CH$_3$OH molecule (eq 6). The geometry of the carbon backbone is retained, and the remaining methoxy group is coordinated to the Ru center, to which a thioketone is also coordinated. To the other ruthenium atom is bound thiacyclobutene.



(5)



(6)

Formation of **11** is the first example of the S−S bond cleavage in this class of complexes. The seemingly unfavorable disulfide cleavage seems to be compensated thermodynamically by forming more stable S═C−C═C−C conjugation of the ligand via an allenyl intermediate. The details are described later in the discussion of the mechanism.

Proposed Mechanisms. Most of the reactions in the present study proceed via activation of the allylic or propargylic C−H bond of the substrates in the first step, except for the reactions with 2,5-dimethyl-3-hexyne-2,5-diol (HO(H$_3$C)$_2$CC≡CC(CH$_3$)$_2$-OH) and 2,5-dimethoxy-2,5-dimethyl-3-hexyne (H$_3$CO(H$_3$C)$_2$-CC≡CC(CH$_3$)$_2$OCH$_3$). The reaction patterns are discussed in the following.

In the intermolecular coupling reaction of allyl alcohol, the intermediate one-molecular addition product acts as Lewis acid, and the condensation proceeds. This means that the coupling reaction occurs after the first allyl alcohol molecule reacts with **1** to form the C−S bonds of the C$_3$S$_2$ ring, as shown in Scheme 3, and the oxygen atom in the final product **2** comes from the first alcohol molecule.

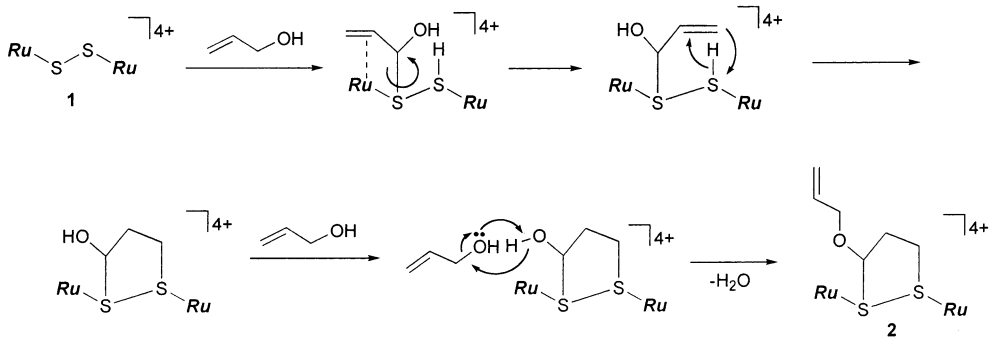
The reaction of **1** with 2-butyn-1-ol or 2-propyn-1-ol is also explained with a similar mechanism, in which activation of the propargylic C−H bond occurs in the first step.

The reaction of **1** with 3-buten-1-ol is explained as shown in Scheme 4.

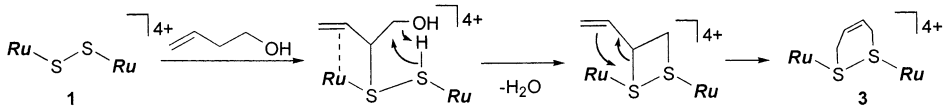
The C−H activation and the concomitant C−S bond formation, followed by the intramolecular elimination of H$_2$O, form the four-membered C$_2$S$_2$ ring. However, the strained four-membered ring is rearranged to the more stable C$_4$S$_2$ six-membered ring.

On the other hand, the reactions of **1** with dihydroxyl substituted alkynes result in the formations of the furyl complexes **8** and **9**. In the reactions, a H$_2$O molecule and a proton are eliminated. The mechanism is proposed as shown in Scheme 5. After formation of the allenyl intermediate, rearrangement of the C−S bond occurs to induce the cyclization. Similar cyclization reactions of an allenyl anion with isothio-

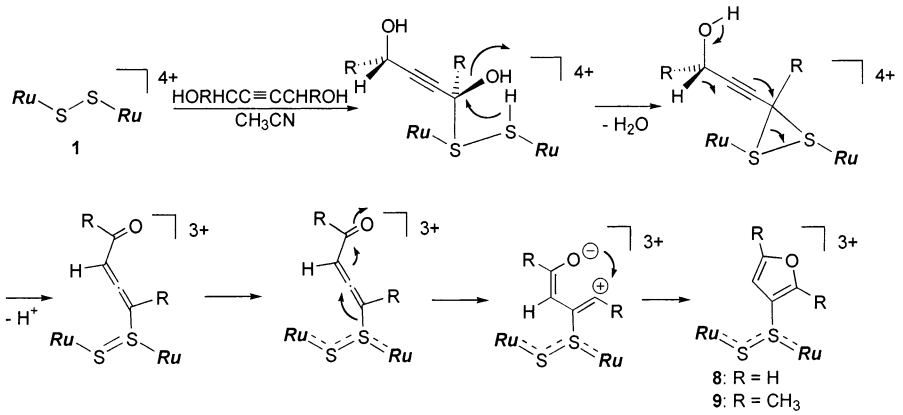
Scheme 3



Scheme 4



Scheme 5



cyanates via the allenylimmine intermediates are reported.[11] Because the reaction of **1** with furan did not give **8** or another addition product, the initial formation of furan from the dihydoroxyl-alkyne before the C−S bond formation is ruled out.

In organometallic chemistry, terminal propargyl alcohols are often used for the syntheses of allenylidene complexes.[12] Coincidentally, allenylidene ruthenium complexes are the most extensively studied ones in allenylidene-transition metal chemistry. However, it seems difficult to relate their reactions to the formation of the allenyl sulfide intermediate in Scheme 5. Both **8** and **9** are synthesized by the reaction of **1** with nonterminal propargyl alcohol, 2-butyn-1,4-diol derivatives, (HO)RHCC≡CCHR(OH) (R = H, CH_3), and it is known that terminal propargylic alcohols react in a different manner. As it is well known, terminal alkynes liberate protons leaving acetylide and facilitate elimination of the hydroxyl group on the propargylic position as H_2O. However, because 2-butyn-1,4-diol derivatives do not have terminal protons, such a dehydration process is improbable. Rather, the mechanism involving the propargylic C−H bond activation and subsequent release of the proton as in Scheme 5 seems more reasonable.

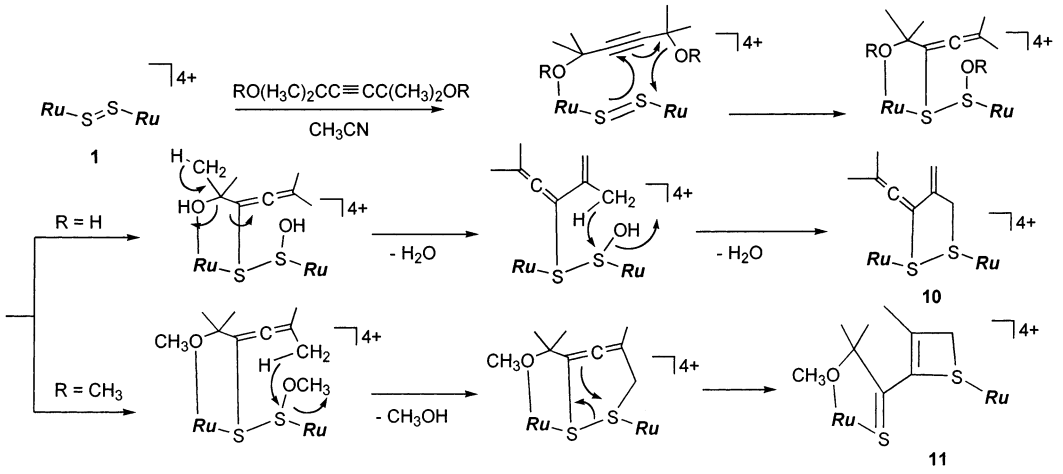
The reaction of **1** with 2,5-dimethyl-3-hexyne-2,5-diol (eq 6) and 2,5-dimethoxy-2,5-dimethyl-3-hexyne (eq 7) cannot be explained with the propargylic C−H bond cleavage observed in the previous reactions of eqs 3 and 4, because the substrates do not have a propargylic C−H bond. In both cases, the first step of the reaction may be the coordination of either the OR (R = H, CH_3) group or the C≡C triple bond of the substrates to the Ru center. Therefore, two reaction mechanisms can be considered as shown in Schemes 6 and 7.

If the reactions undergo as described in Scheme 6, the OR (R = H, CH_3) group is coordinated to the Ru center in the first step. The S=S double bond then attacked the C≡C bond to form the allenyl intermediate via rearrangement of RO^-. In the case of R = H, the C−S bond rotates, and the reaction gives the stable C_3S_2 five-membered ring. However, the rotation of the C−S axis is hindered in the case of R = OCH_3, and the sterically distorted dithiacyclohexadiene is formed, and then the S−S bond is cleaved to give the stable product [{Ru($P(OCH_3)_3$)$_2$(CH_3CN)$_2$}{μ-S=C($C(CH_3)_2OCH_3$)C=CC(CH_3)CH_2S}{Ru($P(OCH_3)_3$)$_2$(CH_3CN)$_3$}](CF_3SO_3)$_4$ (**11**).

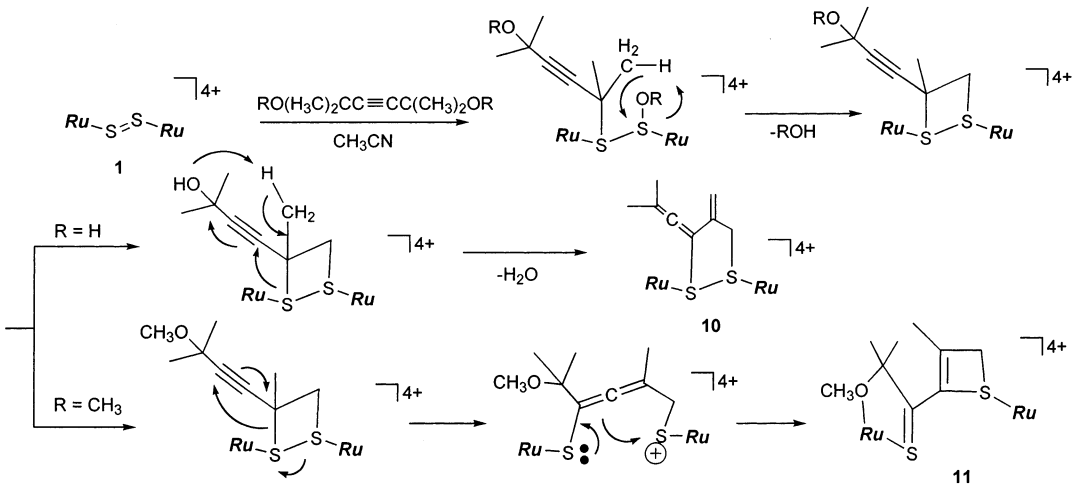
On the other hand, if the triple bond approaches the Ru center in the first step, one of the propargylic bonds, C−CH_3 and C−OR, should be activated and cleaved. Because the activation of a C−CH_3 bond is much more difficult, the C−OR bond is cleaved. In the second step, the unstable four-membered ring is formed via the elimination of ROH. When R = H, one of the S−C bonds is cleaved, and the hydroxyl group is eliminated as H_2O. The stable C_3S_2 five-membered ring complex, [{Ru($P(OCH_3)_3$)$_2$(CH_3CN)$_3$}$_2$}{μ-SCH_2C(=CH_2)C(=C=C(CH_3)$_2$)}S](CF_3SO_3)$_4$ (**10**), is then formed. Because it is more

(11) Brandsma, L.; Nedolya, N. A.; Verkruijsse, H. D.; Owen, N. L.; Li, D.; Trofimov, B. A. *Tetrahedron Lett.* **1997**, *38*, 6905.
(12) (a) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1997**, *193*−*195*, 977.

Scheme 6



Scheme 7



difficult to cleave a C−OCH_3 bond than C−OH, the ring-opening step is accompanied with the cleavage of the S−S bond, and the reaction results in the formation of **11**.

With the usual organometallic and organic reactions, the cleavage of a C−H bond in CH_3 with a hydroxyl group as in Scheme 6 cannot be explained, but it can be possible if the CH_3 is located close to the activated OH (Scheme 6) or is conjugated and facilitates the HO^- release (Scheme 7). The comparison of Schemes 6 and 7 is an interesting discussion. We reported that the S−S bond in **1** has a double bond nature, which has been shown spectroscopically[9] and by reactions with conjugated dienes.[1−3,10] Considering this fact, the first step of Scheme 6 corresponds to the ene reaction, that is, a reaction between two kinds of olefins to form another mono olefin via C−C bond formation.[13−16] By assuming ene reaction in the first step of the reaction in Scheme 6, the ensuing reaction steps become plausible. On the other hand, in Scheme 7, the elimination of H_2O or methanol needs more long-range rearrangement. The authors therefore think at this moment that Scheme 6 seems more plausible, but more careful examination of the related reactions needs to be done.

Structural Study. Complexes **2**−**11** were characterized by X-ray diffraction study as well as NMR spectroscopy. The structural features of the complexes are discussed below.

The structure of **2** was not well refined due to the disorder of the terminal sp^2 carbon atom, and the structural detail is deposited in the Supporting Information. The existence of the terminal C═C double bond of **2** has been confirmed by ^1H NMR spectroscopy.

The structure of **3** is shown in Figure 1. No significant change is observed between the structures of **3** and the previously reported $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_3\}_2\{\mu\text{-}SCH_2C(CH_3)═C(CH_3)\text{-}CH_2S\}](CF_3SO_3)_4$.[10] However, the structural feature of these C_4S_2 complexes is unusual as compared to those of other types of tetracationic complexes having C_3S_2 and other rings and is similar to those of the tricationic complexes such as the acetonyl complex $[\{Ru(P(OCH_3)_3)_2(CH_3CN)_2\}(\mu\text{-}SSCH_2COCH_3)\{Ru\text{-}(P(OCH_3)_3)_2(CH_3CN)_3\}](CF_3SO_3)_3$.[1] For instance, the relatively short S−S distances and the Ru−S−S−Ru torsion angles close to 180° are the features of the tricationic complexes.

The structure of **5** is shown in Figure 2. The **4**, **5**, and **7** complexes have similar structural features. The structural parameters of **4**, **5**, **6**, and **7** are deposited in the Supporting Information. They show clearly the unsaturated C_3S_2 ring having a C═C double bond (1.324(16), 1.318(13), and 1.25(2) Å for **4**, **5**, and **7**, respectively), and the propargyloxy groups having a C≡C triple bond (1.161(18), 1.154(16), and 1.20(2) Å). The C3−O1−C4−C5 torsion angles are almost the same in **4** and

(13) Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021.
(14) Davis, A. G.; Kinart, W. J. *J. Chem. Soc., Perkin Trans.* **1993**, 2281.
(15) Trost, B. M.; Toste, F. D. *Tetrahedron Lett.* **1999**, *40*, 7739.
(16) Clennnan, E. L.; Koola, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 3802.

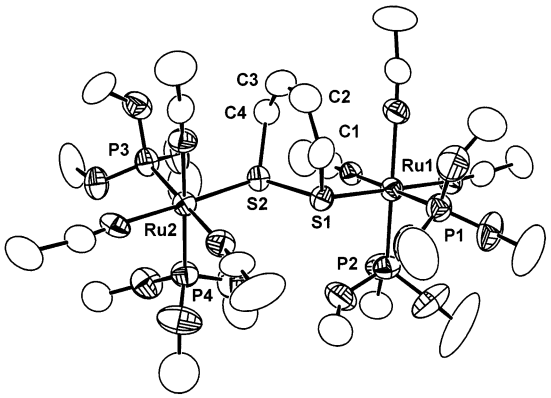


Figure 1. Structure of complex **3** (the cation part, drawn at the 50% probability level). Selected bond length [Å] and angles [deg]: Ru1−S1 2.356(2), Ru2−S2 2.365(2), Ru1−P1 2.251(3), Ru1−P2 2.244(3), Ru2−P3 2.258(3), Ru2−P4 2.249(3), S1−S2 2.097(3), S1−C1 1.816(10), S2−C4 1.835(10), C1−C2 1.513(16), C2−C3 1.276(17), C3−C4 1.494(17); C1−C2−C3 128.2(11), C2−C3−C4 129.9(10), S1−C1−C2 118.2(8), S2−C4−C3 116.0(7), S2−S1−C1 101.5(3), S1−S2−C4 100.7(3), Ru1−S1−C1 112.0(3), Ru2−S2−C4 114.3(3), Ru1−S1−S2 112.53(10), Ru2−S2−S1 111.37(10), Ru1−S1−S2−Ru2 167.66(9).

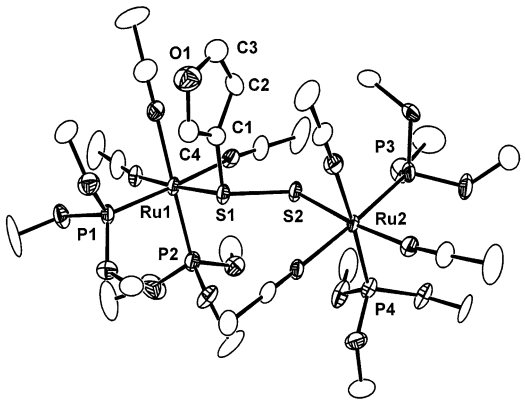


Figure 3. Structure of complex **8** (the cation part, drawn at the 50% probability level). Selected bond length [Å] and angles [deg]: Ru1−S1 2.385(3), Ru2−S2 2.371(3), Ru1−P1 2.257(3), Ru1−P2 2.243(3), Ru2−P3 2.227(3), Ru2−P4 2.233(3), S1−S2 2.070(3), S1−C1 1.756(11), C1−C2 1.453(14), C2−C3 1.325(17), O1−C3 1.395(15), O1−C4 1.336(13), C1−C4 1.347(16); S1−C1−C2 129.8(9), S1−C1−C4 123.8(8), C1−C2−C3 105.6(11), O1−C3−C2 110.6(11), C3−O1−C4 106.6(10), O1−C4−C1 110.8(10), C2−C1−C4 106.4(10), Ru1−S1−C1 106.3(3), S2−S1−C1 103.9(4), Ru1−S1−S2 107.37(13), Ru1−S1−S2−Ru2 163.62(10).

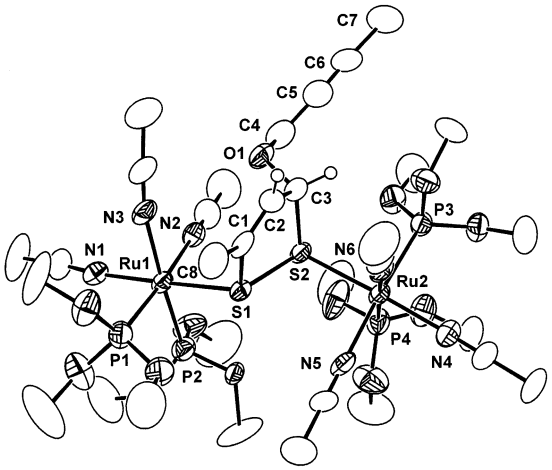


Figure 2. Structure of complex **5** (the cation part, drawn at the 50% probability level). Selected bond length [Å] and angles [deg]: Ru1−S1 2.343(2), Ru2−S2 2.356(2), Ru1−P1 2.244(3), Ru1−P2 2.254(3), Ru2−P3 2.251(3), Ru2−P4 2.268(3), S1−S2 2.123(3), S1−C1 1.808(10), S2−C3 1.884(11), C1−C2 1.318(13), C2−C3 1.481(14), C3−O1 1.413(11), O1−C4 1.397(13), C4−C5 1.468(17), C5−C6 1.154(16); S1−S2−C3 93.9-(3), S2−S1−C1 94.2(3), S2−C3−C2 107.5(7), S1−C1−C2 116.0(8), C1−C2−C3 122.4(10), Ru1−S1−C1 109.8(3), Ru2−S2−C3 110.4(3), Ru1−S1−S2 110.65(12), Ru2−S2−S1 107.77(11), Ru1−S1−S2−Ru2 152.23(10), C3−O1−C4−C5−74.0(13).

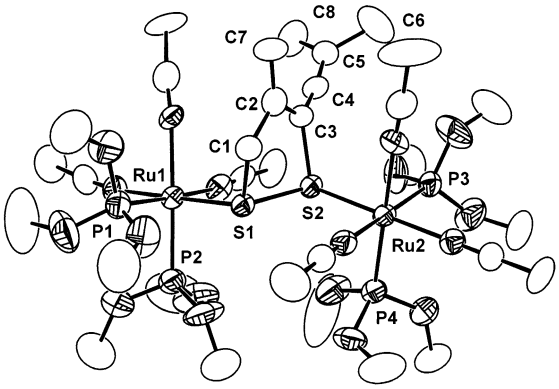


Figure 4. Structure of complex **10** (the cation part, drawn at the 50% probability level). Selected bond length [Å] and angles [deg]: Ru1−S1 2.314(3), Ru2−S2 2.322(3), Ru1−P1 2.246(5), Ru1−P2 2.249(4), Ru2−P3 2.252(4), Ru2−P4 2.250(4), S1−S2 2.131(4), S1−C1 1.781(12), S2−C3 1.838(13), C1−C2 1.504(17), C2−C3 1.47(2), C2−C7 1.362(18), C3−C4 1.266(18), C4−C5 1.279(19), C5−C6 1.55(2), C5−C8 1.49(2); S1−S2−C3 93.1(5), S2−S1−C1 92.4(4), S1−C1−C2 113.1(10), S2−C3−C2 111.6(10), C1−C2−C3 115.4(12), C1−C2−C7 121.2(15), C3−C2−C7 123.3(15), S2−C3−C4 120.5(13), C2−C3−C4 127.9(13), C3−C4−C5 168.9(17), C6−C5−C8 117.1(15), Ru1−S1−C1 110.7(4), Ru2−S2−C3 111.8(4), Ru1−S1−S2 110.16(17), Ru2−S2−S1 108.61(16), Ru1−S1−S2−Ru2 165.02(12).

7 (−164.2(10) and 178.0(17)° for **4** and **7**, respectively, whereas it is −74.0(13)° in **5**).

Figure 3 shows the structure of **8**. The C1−C2 (1.453(14) Å for **8** and 1.428(10) Å for **9**), C2−C3 (1.325(17) Å for **8** and 1.350(9) Å for **9**), and C1−C4 (1.347(16) for **8** and 1.362(10) Å for **9**) distances are assigned to a C−C single bond and two C=C double bonds. Because the sums of the angles around C3 and C4 for **9**, and C1 for both **8** and **9**, are approximately 360°, these carbon atoms are sp^2 hybridized.

Figure 4 shows the structure of the complex cation of **10**. In the structure of **10**, C2, C3, C5, and C7 are sp^2 hybridized carbon atoms, whereas C4 is the sp hybridized one. The C3−C4−C5 angle (168.9(17)°) is as close to linear as expected for the allene structure. The distances of C2−C7 (1.362(18) Å), C3−C4 (1.266(18) Å), and C4−C5 (1.279(19) Å) are assigned to C=C double bonds.

The structure of complex **11** is shown in Figure 5. The S=C bond distance of 1.631(10) Å in **11** is slightly shorter than those of the η^1-S=C complexes, such as *E*-[W(CO)$_5${S=CHC(Ph)=C(OEt)Ph}] (1.63(2) Å), *E*-[W(CO)$_5${S=C(Ph)CH=C(OEt)Ph}] (1.667(6) Å), *E*-[W(CO)$_5${S=C(SEt)C(Ph)=C(OEt)Ph}] (1.657-(8) Å),[17] and [CpRu{(*S*,*S*)-CHIRAPHOS}($SC_{19}H_{14}O$)]$^+$ (1.655-(8) Å).[18] The sum of the angles around C2 in **11** is approximately 360°, and the carbon atom is sp^2 hybridized. The distance of C3−C4 (1.335(12) Å) is assigned to a C=C double bond.

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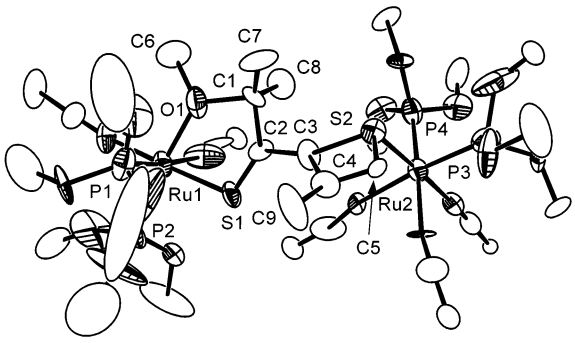

Figure 5. Structure of complex **11** (the cation part, drawn at the 50% probability level). Selected bond length [Å] and angles [deg]: Ru1−S1 2.262(3), Ru2−S2 2.354(3), Ru1−P1 2.246(3), Ru1−P2 2.210(4), Ru2−P3 2.251(3), Ru2−P4 2.249(3), Ru1−O1 2.206(7), S1−C2 1.631(10), S2−C3 1.840(10), S2−C5 1.851(10), C1−C2 1.525(13), O1−C1 1.435(12), C2−C3 1.445(12), C3−C4 1.335(12), C4−C5 1.486(14); Ru1−S1−C2 105.8(3), S1−C2−C1 123.3(7), O1−C1−C2 107.8(7), Ru1−O1−C1 122.7-(5), S1−Ru1−O1 79.80(19), Ru2−S2−C3 111.9(3), Ru2−S2−C5 110.4-(4), C3−S2−C5 73.2(4), S2−C3−C4 94.9(7), C3−C4−C5 102.4(8), S2−C5−C4 89.5(6), S1−C2−C3 116.7(7), C1−C2−C3 119.8(8), S2−C3−C2 131.4(7), C2−C3−C4, 132.1(9).

Conclusion

The present transformation reactions of the hydroxyl substituted alkenes and alkynes on the disulfide ligand show that the disulfide ligand, after forming the C−S bond, exerts a significantly strong effect on the terminal β-hydroxyl group. The elimination of water is either intermolecular (Schemes 1 and 2) or intramolecular (Scheme 3), depending on the structure of the substrate. These water elimination reactions are a typical nature of an electron-deficient group and show that the disulfide ligand in the widely conjugated RuSSRu core is electron-withdrawing. This is notable, because C−H bond activation is usually a phenomenon occurring on an electron-rich center, whereas the hydroxyl elimination as water is a feature of an electron-deficient center. These facts show the unique character of the disulfide center and must be owing to the flexible π-electron delocalization through the RuSSRu bond and the flexibility of the valence of the sulfur atoms.

The reactions in eqs 5 and 6 are really striking. In both reactions, the substrates do not have a propargylic C−H bond, and therefore the reaction must start with a step other than the propargylic C−H bond cleavage. Our previous reactions of **1** with ketones,[1] alkenes,[2] and alkynes[3] all show that the initial reaction step is the activation of the α-C−H, allylic, and propargylic C−H bonds, respectively, and these C−H bonds must be situated at a suitable orientation relative to the S−S bond for the C−H bond to be cleaved. This was achieved by the coordination of the ketonyl oxygen, the C═C bond, and the C≡C bond, respectively, to the Ru atom. The substrates in eqs 5 and 6 can similarly coordinate to the Ru atom, and the C−OR bond may be cleaved, or the OR group may coordinate to the Ru center at first. These are basic reaction steps common in Schemes 5 and 6.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **2**−**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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